Dedicated to my Parents
A COMPUTER-AIDED APPROACH TO THE STUDY OF ADSORBENTS

A Thesis Presented to the University of London in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Science

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Carbonaceous adsorbents have many industrial, environmental and defence applications. A general quantitative measure of the factors influencing adsorbance on the carbon surface is vital if the most suitable adsorbent for a particular application is to be selected. In addition it would be useful to increase our understanding of the role of pore size and pore size distribution in the adsorption process, particularly its role in influencing adsorption under humid conditions.

A microtechnique which combines Inverse Gas Chromatography (IGC) and computer analysis has been developed. The technique provides a convenient way of obtaining adsorbent partition data at infinite dilution for a range of adsorbates. The application of multiple linear regression, (MLR), and known adsorbate parameters to both this data and data obtained from the literature has provided characteristic descriptive equations for several carbon adsorbents. The partition data and the descriptive equations have been used to compare the carbonaceous adsorbents and have allowed the important factors influencing adsorption to be elucidated. The microtechnique has been used under humid conditions thus allowing the important influence of water on adsorption to be examined. Comparison of the descriptive equations under dry and humid conditions has revealed a possible mechanism for water adsorption and has also shown the overall effect of humidity on the factors influencing adsorption.

Comparisons of the performances of the adsorbents under humid conditions have shown quite large differences that are not present when the adsorbents are compared under dry conditions. These differences in performance may have important implications for the application of these adsorbents in the future.
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CHAPTER I
INTRODUCTION TO ADSORBENTS

INTRODUCTION

An understanding of the forces that attract the various substances of our universe together has been sought by man since antiquity. Long before the studies of the Greek philosophers ancient Sanskrit texts referred to the elemental force, jala, as that which binds substances together. In modern times perhaps the most obvious example of these attractive forces are those found in the nuclei of atoms, that have been harnessed to give us nuclear power. On an atomic level these forces can cause the chemical combinations of atoms that result in the seemingly infinite number of molecular species.

Molecules also attract each other without chemical combination, leading to various intermolecular interactions. These intermolecular interactions are the cause of a phenomena of great interest; the adsorption of gases on carbon surfaces. In the adsorptive process the solid upon which adsorption takes place is referred to as the adsorbent and the gas that is adsorbed is referred to as the adsorbate.

 ADSORBENTS

The adsorption of gases on carbon surfaces has been utilised in many fields for commercial, environmental and defence purposes. One of the earliest applications was the use of activated carbons for protection of the allied troops from the chlorine gas used by the German army in the 1914–1918 war. There was little development until the 1960’s when synthesis of carbonaceous adsorbents began. Since then it has become increasingly possible to customise adsorbent properties by physical and chemical modification of the surface. A variety of materials containing different pore sizes, pore size distributions and chemical surfaces are now available. The advent of one type of synthesised adsorbent,
carbonised polystyrene-divinylbenzene copolymers, may replace the well established activated carbons by being superior in their adsorptive strength, capacity and selectivity.

CLASSIFICATION OF ADSORBENTS

Perhaps the most commonly used means of classifying adsorbents is that used by Kiselev et al.[1]. They classify adsorbents by their chemical structure and by their pore structure.

Chemical Structure

Kiselev et al.[1] divided adsorbents into three types.

Type I - These are non-specific adsorbents which do not have any functional groups on the surface and are not capable of specific interactions with adsorbates. An example of this type of adsorbent is graphitised thermal carbon black (GTCB).

Type II - These are specific adsorbents exhibiting positive charges localised on the surface. These adsorbents are capable of specific interactions with negatively charged centres in the adsorbate. An example of this type of adsorbent is a hydroxylated silica gel with functional groups of protonated acids.

Type III - These are specific adsorbents with centres of high electron density on the surface, and capable of specific interactions with positive centres on the adsorbate. Granular activated carbons would fall into this category.

Kiselev also classified adsorbates into four types by a similar description of non-specific and specific effects. The above type of adsorbent/adsorbate classification is only qualitative and as such is limited in its usefulness for making the right choice of
adsorbent for a particular application or in understanding the processes that govern adsorption. As a wide variety of adsorbents with a range of adsorptive strengths and specificities are available, a quantitative measure of an adsorbent's ability to adsorb a challenge adsorbate is needed.

Pore Structure
Kiselev also classified adsorbents into four types of pore structure.

Type I - Non-porous adsorbents having a smooth surface. An example would be GTCB.

Type II - Homogeneous meso/macroporous adsorbents, with pore diameters of 10–200nm. An example would be silica gel.

Type III - Homogeneous mesoporous adsorbents, with pore diameters of approximately 10nm. An example would be carbon molecular sieves.

Type IV - Inhomogeneous porous adsorbents, with pore distribution 2–20nm and macropores greater than 200nm. An example would be activated charcoal or carbonised copolymers.

CARBONACEOUS ADSORBENTS
The main theme of this work will be the study of carbonaceous adsorbents. Many of the carbonaceous adsorbents are microporous in structure and contain a relatively small proportion of mesopores and macropores. The microporous structure of carbons consists of a complex matrix of flawed carbon layered sheets in which micropores are the spaces between the layered sheets. The micropores of carbon adsorbents are comparable in size to the molecules being adsorbed. High resolution electron microscopy has shown that the
micropore apertures are probably slit shaped and flat rather than circular. They are thus characterised by their width as the length and depth of the cracks or slits will be variable. The classification of pores according to their width is; micropores $< 2\text{nm} <$ mesopores $< 50\text{nm} <$ macropores. It is considered that the enhancement of the adsorption potentials of opposing slit walls by overlap of force fields leads to elevated dispersion forces in micropores leading to preferential adsorption there.
CHAPTER II
PREVIOUS WORK IN ADSORBENT CHARACTERISATION

INTRODUCTION

The types of intermolecular forces can be generally divided into two categories; non-specific and specific forces. Non-specific forces are a result of the inherent attraction of the nuclear force in a molecular species for the electron cloud of other molecular species and vice-versa, they operate over the whole molecular species and are not specific to any part of it. Specific forces are also a result of the inherent attraction of the nuclear forces in a molecule for the electron cloud of other molecular species but here one of the molecular species or both possesses due to a non-uniform nuclear distribution a corresponding non-uniform electron cloud, commonly named a dipole. Dipoles cause the intermolecular forces to be strongest at specific parts of the molecule. These forces are usually named dipole-induced dipole or dipole-dipole attractions.

A particular type of dipole caused by an electronegative element such as oxygen, nitrogen or fluorine being bonded to hydrogen causes such strong dipole-dipole interactions as to warrant a separate classification, namely hydrogen bonding.

Another type of specific force arises when the electron cloud is intrinsically non-uniform, regardless of any nuclear uniformity, as in unsaturated molecules like the alkenes and aromatics. The π clouds characteristic of this unsaturation are electron rich centres and can act in the same manner as dipoles, leading to specific interactions with electron acceptor sites on the stationary phase.

Thus, to summarise, there are several interactions that can cause adsorbance on a stationary phase and these can be broadly divided into; dispersion, dipole-induced dipole, dipole-dipole and hydrogen bonding interactions.

The intermolecular forces that cause the adsorbance of a molecular probe on a solid
surface can be investigated by the use of inverse gas chromatography (IGC), as will be discussed in Chapter IV. The fundamental measurement of overall (non-specific and specific) intermolecular attraction in IGC is the elution volume \( V_a \). \( V_a \) can be defined as the volume of carrier gas required to effect elution of the adsorbate peak. At infinite dilution \( V_a \) is independent of the concentration of adsorbate. In finite studies however \( V_a \) is concentration dependent due to multilayering on the solid surface, and it is necessary to use the partition coefficient, \( K \), obtained from the elution boundary of the adsorbate peak, (Chapter V). \( V_a \) can be related to the standard free energy of adsorption, \( \Delta G^o \), by the equation:

\[
\Delta G^o = -RT \ln V_a + C 
\]  

(2.1)

where \( R \) and \( T \) are the gas constant and temperature and \( C \) is a constant which can be given by the formula;

\[
C = \ln \frac{B}{Sm} 
\]

(2.2)

where \( B \) is related to the standard states of gas and adsorbed phases, \( m \) is the mass and \( S \) the surface area of the adsorbent.

PREVIOUS WORK

In order to discover which types of interactions govern adsorbance on a solid surface it is useful to first look at the simple case of \( n \)-alkanes which are known to only undergo non-specific dispersive interactions. It is well known that the relationship between carbon number, \( n \), and \( \Delta G^o \) for \( n \)-alkanes is linear [1]. The difference in \( \Delta G^o \) for two consecutive members of an \( n \)-alkane series, \( \Delta G^o_{CH_2} \), should therefore be constant and this can be
expressed by the formula;

\[
\Delta G_{\text{CH}_2} = \Delta G^0_{\text{C(a)H}(2a+2)} - \Delta G^0_{\text{C(a-1)H}(2a)}
\]  

(2.3)

or in terms of retention volume as;

\[
\Delta G_{\text{CH}_2} = -RT \ln \left( \frac{V_{\text{C(a)H}(2a+2)}}{V_{\text{C(a-1)H}(2a)}} \right)
\]  

(2.4)

which simplifies to;

\[
\Delta G_{\text{CH}_2} = -RT \ln V_{\text{CH}_2}
\]  

(2.5)

where \( V_{\text{CH}_2} \) is the relative retention volume for two consecutive members of an \( n \)-alkane series. The quantity \( V_{\text{CH}_2} \) should be independent of alkane chain length and any reference states. Thus, \( V_{\text{CH}_2} \) is an intrinsic property of the adsorbent and is a measure of its dispersive interaction with a \( \text{CH}_2 \) group. A measure of dispersion that uses this relationship is Gray's \( \gamma^0 \) value [2]. This is derived from \( \Delta G_{\text{CH}_2} \) and the relationship is expressed by:

\[
\gamma^0 = \left( \frac{1}{V_{\text{CH}_2}} \right) \left( \frac{\Delta G_{\text{CH}_2}}{(a_{\text{CH}_2} \cdot 2N)} \right)
\]  

(2.6)

where \( N \) is Avogadro's number, \( a_{\text{CH}_2} \) is the surface area of a \( \text{CH}_2 \) group and \( \gamma_{\text{CH}_2} \) is the surface tension of a hypothetical surface made up of \( \text{CH}_2 \) groups only as for instance in polyethylene. \( \gamma_{\text{CH}_2} \) is obtained by extrapolation of the surface tension of the low molecular weight \( n \)-alkanes to infinite chain length [3]. According to Gray, [4], \( a_{\text{CH}_2} \) is assigned a value of 0.06nm\(^2\) and \( \gamma_{\text{CH}_2} \) is assigned a value of 34.7mN.m\(^{-1}\) at 20°C. Gray’s method is very useful for quantifying dispersion forces on a solid surface but does not
account for specific forces such as dipole–dipole or dipole-induced dipole interactions.

Several attempts have been made to provide a measure of the specific forces operating on a solid surface, in order to provide a fuller understanding of the processes occurring during adsorption [5–8]. If one assumes that specific and non–specific forces are additive then it follows that:

\[ \Delta G^o = \Delta G_D + \Delta G_{SP} \]  

(2.7)

where \( \Delta G_D \) is the free energy of adsorption due to non–specific or dispersion forces and \( \Delta G_{SP} \) is the free energy of adsorption for specific forces. In the special case of n–alkanes which interact by dispersion forces then \( \Delta G_{SP} \) approximates to 0 and equation (2.7) becomes;

\[ \Delta G^o = \Delta G_D \]  

(2.8)

Thus \( \Delta G_D \) can be easily found for n–alkanes by the use of equation (2.1). A plot of \( \Delta G^o \) against some physicochemical property or against carbon number would yield a slope that measures the change in dispersion with the particular n–alkane property. If this particular n–alkane property is named P, and P is plotted against \( \Delta G^o \), then a slope as shown in figure 2.1, results.

It follows that if P is known for a polar probe then the deviation of the free energy of adsorption from the n–alkane line is equivalent to the specific contribution to free energy, \( \Delta G_{SP} \). In order for the technique to work the P value for the polar probe must be free from any specific contribution.

Schultz et al., [6], attempted the technique using the P parameter, \( a(b_D L)^{1/2} \), so that;

\[ P = a(b_D L)^{1/2} \]  

(2.9)
where $a$ is the surface area of the molecular probe and $\delta_{DL}$ is its liquid surface energy. It is somewhat questionable whether $\delta_{DL}$ is applicable to dispersion on a solid surface.

FIGURE 2.1. A theoretical plot of $\Delta G^\circ_\text{alkanes}$ vs $P$ (any n-alkane parameter)

Dominga - García et al., [9], found that $\nu^{D_g}$, the dispersion component of the adsorbent, obtained from the slope of the plot of $a(\delta_{DL})^{1/2}$ against $\Delta G^\circ$, varied with increasing chain length of the n-alkane. The property $\delta_{DL}$ is derived from the surface tension of the liquid probe and its use in characterising intermolecular dispersion forces assumes that adsorbate-adsorbate liquid interactions are equivalent to adsorbate-adsorbent gaseous interactions. The application of a bulk liquid measurement to adsorption of a gas on a solid surface may account for the variation in $\nu^{D_g}$ found by Dominga - García et al..
In addition, the liquid surface energy, \( \delta_{PL} \), would contain, in the case of polar probes, some dipole–dipole or even hydrogen bonding contribution (e.g. alcohols). This would lead to errors in the \( \Delta G_{SP} \) values obtained, as the \( \delta_{PL} \) value used to plot the polar probe would be higher than it would have been if purely a measure of dispersion. Thus, \( \Delta G_{SP} \) would be artificially lowered. Indeed Dong et al., [7], have shown that \( \Delta G_{SP} \) on graphite obtained by the Schultz method is actually negative. The negative value on graphite is almost certainly due to \( \delta_{PL} \) being more than a purely dispersive measure of interaction. Therefore for carbon adsorbents where polar effects can be negligible compared with large dispersion interactions the use of \( \delta_{PL} \) for predictions of relatively small specific interactions can lead to negative values due to the inherent polar contribution to surface tension in the liquid.

Similarly, Flour & Papirer, [5], attempted to find \( \Delta G_{SP} \) using the formula;

\[
P = P_0
\]

(2.10)

where \( P_0 \) is the saturated vapour pressure of the probe. Their results on glass–fibers gave a linear fit for the n–alkanes and chemically sensible \( \Delta G_{SP} \) values for polar probes. However, Dong et al., [7], showed that the technique gave negative values of \( \Delta G_{SP} \) for graphite. This is unsurprising as polar/dipolar effects would cause a lowering of vapour pressure compared with that of a non–polar molecule of similar dispersive strength and this error would be highlighted on graphite as discussed above. Dong et al. proposes the use of another parameter such that;

\[
P = P_D
\]

(2.11)

where \( P_D \) is the molar deformation polarisability. They claim to obtain chemically sensible results on graphite and indeed their values for \( \Delta G_{SP} \) are positive.
They define $P_D$ by the formula;

$$P_D = (n^2-1)/(n^2+2)(M/p)$$

(2.12)

where $n$ is the refractive index of the probe, $M$ is the molar mass and $\rho$ is the molar density in cm$^3$g$^{-1}$. The variation in $P_D$ is predominantly due to the volume term $M/\rho$ as $n$ only varies slightly in different liquids. It appears that the technique suffers from the same problem as the ones previously discussed. The molar volume term $M/\rho$ would be lower in a polar liquid than that due to dispersion forces only and hence $P_D$ would be artificially lowered. Therefore $\Delta G_{SP}$ would appear higher than its true value. This would explain why the authors obtained positive values for $\Delta G_{SP}$ on graphite which has a non-polar solid surface and probably should give $\Delta G_{SP}$ values close to zero.

Jagiello et al., [8], tried to alleviate the problems associated with bulk liquid measurements by plotting $\Delta G^\circ$ against carbon number, $n$, for $n$-alkanes and finding the deviation of $n$-alkenes of the same carbon number from the $n$-alkane line. He used the equation;

$$-\varepsilon = \Delta G(n)_{\text{alkene}} - \Delta G(n)_{\text{alkane}}$$

(2.13)

where $-\varepsilon$ is a measure of the specific effect of the $\pi$-electrons in the alkene double bond interacting with electron acceptor sites on the solid surface. The technique gave positive values on silica indicating the presence of electron acceptor sites on the acidic surface but on graphitised carbon black a small negative value was obtained. Presumably, the negative value for $-\varepsilon$ on graphite is a result of the assumption that $n$-alkanes and $n$-alkenes differ only in respect of a double bond. In fact an $n$-alkene has a slightly smaller dispersion interaction than the corresponding $n$-alkane owing to its smaller size. It is quite possible that the slightly negative value on graphitised carbon black is actually as a result of assigning the same dispersive interaction to the alkene as the alkane.
It is clear that there is still a need to find a satisfactory measure of non-specific interactions that is wholly independent of specific interactions so that the contribution of specific interactions to adsorbance can be quantified.

There have been few attempts to explain the $\Delta G_{gp}$ term beyond describing it as a general specific effect. Saint-Flour and Papirer, [10], used the acceptor numbers (AN) and donor numbers (DN) of Gutmann, [11]. They preferred them as the amphoteric nature of some molecules is respected; they being given both AN and DN values.

They defined $\Delta G_{gp}$ by the formula;

$$\Delta G_{gp} = (AN).C + (DN).C'$$  \hspace{1cm} (2.14)

where $C$ and $C'$ are constants. Despite the drawbacks of the method described previously the technique appears to be one of the best available.

A far more advanced approach characterisation of solid surfaces appears to be that of McGill et al., [12,13]. They successfully applied the Abraham, Kamlet, Taft (AKT) parameters, which had been in use for several years characterising liquid phases, for characterisation of carbon surfaces. McGill also reviews the history of the AKT parameters up to 1988. A discussion of the use of the AKT parameters in characterisation of carbons is the theme of the next chapter and will not be discussed any further here.

THEORY OF VOLUME FILLING OF MICROPORES (TVFM)

There is another approach to characterisation when one is investigating porous carbonaceous adsorbents. Carbonaceous adsorbents are usually microporous in structure, and contain a relatively small proportion of mesopores and macropores. The classification of pores according to their width is; micropores $< 2\text{nm} <$ mesopores $< 50\text{nm} <$ macropores [14]. It is considered that the enhancement of the adsorption potentials of
opposing slit walls by overlap of force fields leads to elevated dispersion forces in micropores leading to preferential adsorption there. The preferential adsorption in the micropores leads to volume filling of micropores (TVFM) first, not layer by layer adsorption over the whole micro-, meso- and macroporous surface [15].

Dubinin recently reviewed the work on TVFM and also showed how it has recently been applied to heterogeneous adsorbents [16]. In the simplest case of a homogeneous adsorbent the equation that Dubinin uses to describe TVFM has the formula;

$$W = W_0 \exp\left[-\left(A/\beta E_0\right)^2\right] \tag{2.15}$$

where $A$ is the negative free energy of adsorption and is related to the partial pressure of the adsorbate by the formula;

$$A = RT \ln\left(P/P_0\right) = -\Delta G \tag{2.16}$$

$\beta$ is an affinity coefficient that describes the difference in adsorption affinity between the vapour of interest and a standard vapour (usually benzene). $E_0$ is the standard’s adsorption energy. $W$ and $W_0$ are the uptake at any time and the maximum uptake of vapour possible, respectively, in units of volume. Dubinin has also related the standard energy of adsorption to the half width of the micropores, $x_*$ by the formula;

$$E_0 = k/x_* \tag{2.17}$$

where $k$ is the energy characteristic of the adsorbent if the micropores are of a constant width, i.e. the adsorbent is homogeneous. The isotherm plots of $A^2$ against $\log W$ will yield the micropore volume $W_*$, from the intercept. The slope will give information about the micropore size and characteristic adsorption energy of the standard.
A more complex set of equations takes into account non-uniform micropore size and is thus claimed to be able to predict the parameters $W_0$ and $x_0$ on heterogeneous adsorbents using the isotherm plot of the standard vapour. Further predictions of the effect of temperature on adsorption can be made. Dubinin and other workers also obtain isotherms for other adsorbates and relate them with the standard isotherm using the correction factor $\beta$ [16-18]. The use of a vapour $\beta$ value, obtained experimentally by comparison with a standard isotherm, or obtained by theoretical calculations based on parachors, relative polarities, or the theory of dispersion, is thus proffered as a means of predicting adsorption isotherms of a given vapour on any adsorbent from only the standard isotherm.

Unfortunately, the various techniques only take into account dispersion forces and all have only been applied to carbonaceous adsorbents of similar nature, surface areas and microporous content. Thus, one can only conclude that carbonaceous adsorbents with similar properties have similar adsorbance characteristics. It is unclear how applicable the Dubinin equation is to predictions where microporous content, surface area or the nature of the surface is variable. Indeed, Tsunoda [17], has claimed that the TVFM theory does not fully explain the adsorption of methanol, a polar adsorbate, on PCB active carbons. He proposes a secondary mechanism involving hydrogen bonding with electron pair donator sites on the solid surface and subsequent self association of the methanol around this site. The said mechanism competing with TVFM adsorption. However, he bases his explanation on differences between methanol and three adsorbates; benzene, cyclohexane and tetrachloromethane which all have far greater dispersive strength than methanol. It is thus unclear whether the differences he observes are actually due to hydrogen bonding or simply the weaker dispersive strength found in methanol. Nevertheless, his findings underline the limitations of using the single adsorbate parameter, $\beta$, to describe both specific and non-specific interaction potential. Thus, more than one parameter is necessary to explain differences between adsorbates, especially when there may be polar
sites on the solid surface and the subsequent possibility of several adsorption interactions. Reucroft et al. [19], have tested the predictive ability of the Dubinin–Polanyi equation for the adsorption of polar adsorbates on activated carbon. They used various methods for calculating $\beta$ values and compared them with those obtained experimentally by comparison of the adsorbate isotherms with the standard adsorbate isotherms. They concluded that the electronic polarisability term (equation (2.12)), gave the closest approximation to experimentally determined values of $\beta$. However, significant deviations in $\beta$ still existed, especially where there were large polarity differences between the standard and adsorbate. Thus, they adopted a limited predictive technique based on placing adsorbates in a group with a standard of similar polarity. The technique thus falls short of a method of general application to both polar and non-polar adsorbents.

STUDIES ON THE EFFECT OF HUMIDITY

The effects of water vapour on the adsorption of adsorbates is of increasing interest as the number of wet applications of carbonaceous adsorbents increases. Gray et al. observed that the effect of humidity on the adsorption of $n$-alkanes on cellulose paper was to lower the amount of $n$-alkane adsorbed. They showed that water vapour adsorbed on the cellulose surface lowered the available BET surface area for alkane adsorption. They were then able to correlate available BET surface area with specific retention volumes of the $n$-alkanes.

Werner [20], challenged small beds of activated charcoal to various concentrations of trichloroethylene at relative humidities of 5% – 85%. He found that the lower the concentration of adsorbate the stronger the effect of relative humidity in lowering adsorption. Underhill [21], applied the Dubinin and Radushkevich (D–R) model [22], to Werner's data. They extended the equation to include two new constants $k_1$ and $k_2$ which take account of the maximum effect of water vapour and the effect of variations in the level of water vapour respectively, on the adsorption of a water immiscible compound.
The constants are determined by trial and error. The constants $k_1$ and $k_2$ are a measure of the effect of water on the availability of adsorption sites for an immiscible compound. It is, however, unclear how the equation would apply to water miscible or partially miscible compounds which can interact with water quite strongly through specific interactions in addition to having non-specific interactions with the adsorbent. Certainly, it is clear that the affinity coefficient, $\beta$, a measure of relative dispersion forces in the D–R equation (2.15), would not be sufficient to account for specific interactions. In order to apply the D–R equation to adsorption under humid conditions a measure of specific forces in the adsorbate and in the adsorbent is needed.

Abe et al. [23], examined the adsorbability of isomers of butanol and pentanol from aqueous solution onto activated carbon. They found a good correlation between adsorption constants and a connectivity index relative to the parent isomer. The technique is, however, only applicable to predictions of an isomers adsorption onto an adsorbent for which the parent isomers adsorbance has been determined by experiment. Abe et al [24], have collected partition data for 93 compounds from aqueous solution on activated carbon. They found correlations with several physical constants including: molecular weight, molar volume, carbon number, water solubility, a modified organicity/inorganicity value (O/IO), the partition coefficient in octanol–water systems, the dielectric constant, the molar refraction and the parachor. The best correlations were found using aliphatic monofunctional values only and excluding aromatics. Among the correlations, the most successful were for water solubility ($r = 0.962$), O/IO values ($r = 0.944$) and molecular weight ($r = 0.943$). Abraham, Kamlet, Taft and coworkers correlated the same data, [25], using solute volume ($V_2$), a solute dipolarity/polarisability term ($\pi_2^*$), and a solute hydrogen bond basicity term ($\beta_2$). They found an improved correlation of $r = 0.974$ for the aliphatic monofunctional compounds only. The characteristic equation was also useful in explaining the adsorption properties of various solutes. They found that increasing $V_2$ and decreasing $\beta_2$, which lead to lower solubility in water, lead to increased
adsorption on carbon, but that increasing $\pi^2$, which leads to increased adsorbance in water also gives increased adsorbance on carbon. The work of Abraham et al. is discussed more fully in the next chapter as it is the method of choice for characterisations in this thesis.

Other workers [26,27] have shown reductions in peak tailing of gas chromatographic peaks in the presence of humid carrier gas.

Janak et al. [28], compare adsorbance with and without water of six adsorbates on Tenax-GC and concluded that the effect of water vapour could be considered insignificant for applications in concentration tubes. However, five of the six adsorbates were polar compounds and it may be that decreased adsorbate-adsorbent dispersion forces on wet Tenax-GC are counteracted by adsorbate-adsorbent specific interactions with polar water molecules on the adsorbent surface.

Mandrov & Rudenko [29], studied the effect of water vapour on the adsorption of some nitrogen containing compounds on a polar phase and concluded that water vapour prevents adsorption of polar sorbates on the interfaces.

Similarly, Scott [30], found decreases in adsorption of ethene relative to propane on alumina if increasingly humid carrier gas is used but then noted that at higher humidities the trend was reversed implying that the polarity of the adsorbent had begun to increase again.

Adams et al. [31], looked at the effect of humid oxidation on activated carbons and showed that the adsorption characteristics of carbon surfaces were altered by accelerated ageing. Interestingly, they used both polar (methanol) and non-polar (hexane) probes to determine the change in specific and non-specific sites respectively.
This thesis is confined to a comparative study of recently developed carbonised copolymers, better known activated carbons. Activated carbons and carbonised copolymers, generally referred to as carbonaceous adsorbents are found in many commercial and academic applications. Their uses include: analysis and trapping of trace elements; analytical separations; waste water treatment; spillage clean up; ground water monitoring; treatment of damaging air emissions; control of odours; protective clothing and respirators; ultra-pure water production and catalysis and solid supports.

In order to choose an adsorbent for any particular application several adsorbents may have to be tested. The choice of adsorbents to be tested will be based on previous experience, manufacturers recommendations, availability and cost. The final choice will typically depend on the results of an adsorption isotherm comparison or just simply a best estimate from the manufacturers information. In a competitive market where rapid results are required and costs are to be minimised it would be highly useful to be able to predict the most appropriate adsorbent for a particular application using sound quantitative methods and not to leave the final choice to chance.

This work attempts to characterise a range of carbonaceous adsorbents in terms of characteristic chemical parameters. This should enable them to be compared with each other so that estimates of their suitability for particular applications can be made.

There is much interest in establishing the effects of humid air streams on adsorbate-adsorbent affinity; as water vapour is commonly present in contaminated vapours and may influence contaminant adsorption. There is also much interest in the use of adsorbents for ground water remediation and other water purification processes and greater understanding of the effects of water on adsorption would be helpful in these applications.

In many of the applications listed above the presence of water will interfere with the adsorption process. In order to more fully understand the effect of water on adsorption
and to examine any variability in its effect on different adsorbents a series of commercial
carbons will be characterised under both dry and humid conditions.
Adsorption of a series of adsorbates of varying chemical nature is necessary in order to
obtain a complete picture of the nature of the adsorbent surface. This is especially
applicable under humid conditions where the polar nature of adsorbed water molecules
may render the non-polar adsorbent surface acidic or basic in character.
Adsorption on both types of carbons can be considered to be affected by their
microporous, mesoporous and macroporous structure as well as their chemical nature and
surface area. As previously mentioned, activated carbons frequently have little or no
mesoporous or macroporous content, however, the carbonised copolymers have all three
types of structure. It will thus be interesting to compare the effects if any of the
mesopores and macropores on adsorption.
CHAPTER III
LINEAR SOLVATION ENERGY RELATIONSHIPS (LSER)

INTRODUCTION

Empirical models rather than theoretical postulates have always been used by organic chemists. This is due to the complexity of organic systems being beyond the scope of even the most advanced atomic–molecular mathematical treatments.

The organic chemist has then two options open to him. The first is to take the current theoretical molecular treatments and use a series of approximations to build up a picture of the system under study so that predictions and explanations of observed behaviour can be obtained. The technique contains the inherent hazard of departing so far from the original theory as to bear no resemblance to it and in addition it may not successfully explain what is actually observed on a macroscopic level.

The second approach is to develop a successful model based on macroscopic observations and then try to relate this to available microscopic knowledge of the species under study so that the predictions can be explained in terms of accepted chemical concepts. The second approach has usually been the choice of organic chemists who most commonly find themselves researching systems for which theoretical explanations will not be available for many years to come.

In organic chemistry a number of empirical models for quantitative descriptions of experimentally observed macroscopic effects have been formulated. Perhaps the most obvious are those that describe the relationship between structure and reactivity of which linear free energy relationships (LFER), particularly those of Hammett, [32], are probably the most popular and intensively investigated, [33].

The term LFER is derived from its use in the correlations of changes in free energy in reaction series. In actual fact it can be used to describe relationships for all kinds of chemical interactions. In this work the term LSER (linear solvation energy relationships),
is used to describe the relationship between chemical structure and various adsorption related processes where LSER is simply a particular application of LFER.

Essentially, LSER's take observations on one system and relate them to observations on another similar system. Thus, in LSER it is reasonable, by analogy, to assume that solubility of a molecule on hexadecane can be related to the solubility of the same molecule in any alkane. Hammett expresses the idea well; "From its beginning the science of organic chemistry has depended on the empirical and qualitative rule that like substances react similarly and that similar changes in structure produce similar changes in reactivity." "Linear free energy relationships constitute the quantitative specialisation of this fundamental principle." [34,35]

The first step in developing a LSER that can be used to describe solvation relationships is to construct empirical scales that represent known fundamental chemical concepts.

The approach that has been adopted is to create a system wherein the variability can only be governed by one of our conceptual properties. For example, in order to derive a scale for dispersion type interactions one might observe the solubility of a series of n-alkanes on hexadecane. It would be reasonable to assume that the variability in measured solubility was due to changes in cavity size and dispersive strength only as one progressed through the homologues, since hexadecane can not accommodate dipole–dipole or acid–base interactions. This methodology has been adopted by several workers, but perhaps the most influential, and those used in this thesis, are those of Abraham, Kamlet and Taft [36,37]. The origin of these fundamental parameters will now be discussed.
SECTION I

BRIEF OUTLINE OF THE ORIGIN OF THE LSER

Abraham, Kamlet, and Taft, [36,37] have developed a methodology over the past few
years for modelling the process of solution. (The parameters used in this work are dealt
with fully in section II). Initially, they used classic parameters such as solute volume and
the Hildebrand cohesive energy density to account for cavity formation, and
solvatochromic parameters to account for dipolar effects, hydrogen bond basicity and
hydrogen bond acidity [25]. Kamlet et al. [38,39], used a convenient measure of cavity
size formation with the term,

\[(8^2_H)_{1}V_2 \quad (3.1)\]

where \(8^2_H\) is the Hildebrand cohesive energy density, which accounts for solvent-solvent
forces, and the solute size is given by the solute molar volume, \(V_2\).

The specific intermolecular forces can be accounted for by the polarisability and dipolar
terms for both solute and solvent. If the solvent or solute are polarisable or dipolar then
dipole – induced dipole or dipole – dipole interactions may be set up in the solution
represented by the product \(\pi^*_1 \pi^*_2\), where \(\pi^*_1\) is the solvent contribution and \(\pi^*_2\)
is the solute contribution based on the solvatochromic parameter \(\pi^*\), that scales
dipolarity/polarisability [40–42]. Special account is taken of hydrogen bonding, which is
an extreme form of dipole – dipole interaction. To account for hydrogen bond
interactions in the solution two terms \(\alpha_1 \beta_2\) and \(\beta_1 \alpha_2\), are required, where \(\alpha_1\) and \(\alpha_2\)
are the scaled hydrogen bond acidity of the solvent and solute respectively, and where \(\beta_1\) and
\(\beta_2\) are the hydrogen bond basicity for the solvent and solute respectively. Both terms
were mainly obtained from the solvatochromic data that scale hydrogen bond acidity and

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basicty, α and β. The terms can now be placed in a general equation, giving;

\[ \log S = S_0 + (\delta^2_0)V_2 + \pi^*_1\pi^*_2 + \alpha_1^*\beta_2 + \beta_1^*\alpha_2 \] (3.2).

Where \( S \) is some solubility related property. For situations where the solvent is not varied the terms \( \pi^*_1, \alpha_1 \) and \( \beta_1 \) are all characteristic solvent constants and can be determined by multiple linear regression analysis (MLRA) of \( S \) values for a variety of solutes, if the corresponding solute properties \( \pi^*_2, \alpha_2 \) and \( \beta_2 \) are known. It is convenient to express these solvent parameters as constants to give the simplified equation;

\[ \log S = S_0 + mV_2 + s\pi^*_2 + a\alpha_2 + b\beta_2 \] (3.3).

where \( m, s, a \) and \( b \) are characteristic constants for the solvent in question. By this means a general equation can now be formulated;

\[ \log SP = SP_0 + mV_2 + s\pi^*_2 + a\alpha_2 + b\beta_2 \] (3.4)

where \( SP_0 \) is a constant that depends upon the particular solubility process and \( SP \) is a solubility related process for a series of solutes.

Finally, there is a term which gives improved correlations from MLRA for a series of solutes on a given stationary phase (or solvent). When aromatic or polyhalogenated compounds were used as solutes, a polarisability correction term \( d\delta_2 \) was incorporated into equation 3.4. The \( \delta_2 \) was only an approximation for polarisability and consisted of 0.0 for all non-polyhalogenated aliphatics, 0.5 for polyhalogenated aliphatics, and 1.0 for all aromatics. The general equation for solutes was therefore;

\[ \log SP = SP_0 + d\delta_2 + s\pi^*_2 + a\alpha_2 + b\beta_2 + mV_2 \] (3.5).
Kamlet et al [34], have taken the cavity term for a series of solutes in the same solvent as being proportional to either the intrinsic volume, V_i, of Leahy [43], or the characteristic volume, V_x, of McGowan [44]. Equation 3.5 works very well when applied to processes in condensed phases, for example when SP is a liquid–liquid partition coefficient. This is because there is very little change in dispersion interactions moving from one liquid to another. But for processes of the type gas → condensed phase, it is clear that equation 3.5 is deficient in that there is no explicit term to describe the net gain of dispersion interaction moving from unassociated gas to the condensed phase. A solute parameter, denoted log L_{16}, was therefore devised, where L_{16} is the Ostwald solubility coefficient on n-hexadecane at 298.15K [45]. The term in solute volume is then replaced for gas–condensed phase systems to give;

\[
\log SP = SP_0 + d_2 \delta_2 + s_2 \pi_2 + a_2 \alpha_2 + b_2 \beta_2 + \log L_{16} \quad (3.6)
\]

The variety of solute properties that give rise to interaction terms are now included in this equation (solute dipolarity, hydrogen–bond acidity and basicity, and a solute size/dispersion term).

The term d_2 \delta_2 has now been replaced by the more versatile rR^2, where R^2 is a polarisability parameter that reflects the ability of a solute to interact with a solvent through \pi and n electron pairs [46]. Similarly, new hydrogen bond acidity (α_H^2), hydrogen bond basicity (β_H^2) and dipolarity/polarisability (π_H^2) scales have been developed by Abraham et al. [47,48,49], to give the new general solvation equation that will be used throughout this work.

\[
\log SP = SP_0 + rR^2 + s_H^2 \alpha_H^2 + a_H^2 + b_H^2 \quad (3.7)
\]

The origin of each term in equation 3.7 will now be discussed in greater detail in section II.
SECTION II

SOLUTE AND ADSORBENT PARAMETERS

Abraham and coworkers have used equations of the type 3.7 to correlate retention data on stationary phases, [49–51]. They have shown that the six terms or less of equation 3.7 gave good correlations in most cases. In this section the origin of each term in the LSER will be briefly discussed and set in its historical context. Over the years there has been a variation in the type of terms used, presently the terms are;

\[ \text{Log } L_{2*}^{16} - \] (Normally written as \( \log L_{1*} \), the subscript 2 referring to solute is assumed as there is no comparable solvent parameter). \( \log L_{1*} \) is the log of the solute Ostwald solubility coefficient [52], \( L \), on n-hexadecane at 298.15 K [45,53].

\[ \pi_2^{H} - \] This is the solute dipolarity/polarisability parameter as determined by Abraham et al. [49], by regression analysis and back calculation on the large data sets of McReynolds and Laffort [54,55].

\[ \alpha_{H}^{2} - \] Solute hydrogen bond acidity parameter as developed by Abraham et al [47], from log K values for hydrogen bond complexation.

\[ \beta_{H}^{2} - \] Solute hydrogen bond basicity parameter as developed by Abraham et al [48], from log K values for hydrogen bond complexation.

\[ R_{2} - \] This is a polarisability parameter that reflects the ability of a solute to interact with a solvent through \( \pi \) and \( n \) electron pairs. It is actually the excess solute molar refraction (MR\( _{2} \)) over an alkane with the same characteristic volume (\( V_{4} \)) [46].
THE SOLUTE CAVITY SIZE/DISPERSION PARAMETER

When a liquid solute molecule is dissolved in a liquid solvent the change in dispersion interactions can be assumed to be negligible [56]. The reason for this is quite clear, the solute is surrounded by other species in both cases, so the dispersion forces around the solute in the solute liquid can be taken as equal to the dispersion forces around the solute in the solvent. Therefore there is little change in dispersion forces in moving from solute liquid to solvent. The important determining factor will be the cavity formation in the solvent. For cavity formation work has to be done against solvent–solvent interactions and this can be expressed by the term;

\[(\delta_2^3 H)_1 \cdot V_2 \]  \hspace{1cm} (3.1)

where \(\delta_2^3 H\) is the Hildebrand cohesive energy density, which accounts for solvent–solvent forces, and the solute size is given by the solute molar volume \(V_2\) [56,57].

The cavity size can be taken as being proportional to the solute molar volume, \(V_2\) at 298 K. This is calculated as the bulk molar volume – the ratio of the solute molecular weight divided by the solute density. The product is then divided by 100 merely to scale the value off into the same sort of range as the polarity and hydrogen bonding parameters. 10 cm³mol⁻¹ was added to \(V_2\) for aromatic and acyclic compounds, leading to \(V_{2\text{adj}}\). These two cavity size parameters are not strictly solute parameters as they are measured as bulk solvent properties. For instance, for amphiprotic compounds which are self–associated they will not only reflect the intrinsic solute molecular volume of the monomer solute, but also the bulk structure. These two parameters are also inconvenient when considering solid solutes.

The computer–calculated intrinsic volume of Leahy [43], is therefore preferable. It is measured from specific solute conformations as derived from x–ray structures, and can be measured for any solute. It also leads to improved MLRA correlations when used as the
cavity term instead of $V_2$ or $V_{2adj}$ [43,58]. McGowan [59-61], has developed another method of calculating solute intrinsic molar volumes by the addition of characteristic atomic volumes for the constituent elements of the solute molecule, and subtracting 6.56 cm$^3$mol$^{-1}$ for each bond. The same constant term is subtracted for any bond whether it is single, double or triple etc. There is a very good correlation between $V_I$ and $V_X$ [44], (both in cm$^3$mol$^{-1}$);

$$V_I = 0.597 + 0.628V_X$$

$R = 0.9988$  S.D. = 1.24  $N = 209$

Use of either term as a cavity term in the general LSER used should give completely interchangeable results. However, as $V_X$ is so trivially calculable, this is usually the cavity size parameter employed.

$V_X$, (or $V_I$) is the preferred parameter for LSER to quantify the solubility properties of liquid solutes within condensed phases, where the net dispersion forces will be small, or at least by no means as important a consideration as for the dissolution of a gaseous solute in a solvent [56]. A typical condensed phase process is the partition of solutes between octanol and water, the log $P_{OCT}$ values measured being important for the modeling of biological membranes.

In the gaseous state, there will be no dispersion interaction of solute molecules with each other. Upon dissolution into a solvent, dispersion interactions, (or van der Waals interactions), will be set up between the solute and solvent, and there will be no net tendency for a cancelling out effect, as has been previously described for condensed phases. The log $L^{16}$ parameter was formulated to provide a parameter that was a measure of cavity size and solute-solvent dispersion interactions. Log $L^{16}$ is the log of the Ostwald solubility coefficient [52], $L$, on n-hexadecane at 298.15 K [45,53]. As it is a parameter directly measured from the dissolution of a gaseous solute into a solvent (n-hexadecane),
it will automatically be a measure of cavity size and dispersion interactions. For all LSR not concerned with processes in condensed phases, (ie. gas–liquid partition coefficients), log $L^{16}$ is preferred to $V_X$ or $V_I$, as it gives consistently better results from MLRA. Coefficients generated for log $L^{16}$ for the process gaseous solute $\rightarrow$ solute (in solution), are invariably positive, indicating that energy released from dispersion interactions between the solute and solvent is greater than that required in cavity formation. As a comparison, the log $L^{16}$ coefficient from an MLRA analysis of solutes on n–hexadecane itself would be unity, so other solubility processes can be quantified by reference to this. Abrahams and Fuchs [53], have used the log $L^{16}$ parameter itself as the study of a MLRA to try to unravel its constituent properties with the equation;

$$\log L^{16} = \text{SPo} + b.V + c.MR + d.\mu^2 \quad (3.8)$$

Log $L^{16}$ is the solubility process, SPo is the equation constant, V is $V_{2adj}$, $V_I$, or $V_X$. MR is the solute molar refraction, $\mu$ is the solute dipole moment, and b, c, and d are the coefficients produced by the MLRA. The endoergic work of creating a cavity is given by the term $b.V$, and the exoergic solute–hexadecane interactions are given by $c.MR$ (dispersion interactions) and $d.\mu^2$ (dipole–induced dipole interactions). Using $V_{2adj}$ as the cavity term, the following MLRA equation was obtained.

$$\log L^{16} = 0.293 - 0.026.V_{2adj} + 0.198.MR + 0.045.\mu^2$$

$$R = 0.986 \quad \text{S.D.} = 0.185 \quad N = 84$$

(Confidence levels for all parameters $> 99.9999\%$)

This analysis shows the log $L^{16}$ term is made up of two contributory terms, a cavity term ($b.V_{2adj}$), and a dispersion or van der Waals interaction term ($c.MR$). The term $d.\mu^2$ if calculated as a check for several solutes is comparatively very small compared to the
other two contributory terms in equation 3.8, and can for all practical purposes be ignored. The contributions to the log \( L^{16} \) term from equation 3.8 using the coefficients generated by the MLRA are shown in Table 3.1 for several important and representative solutes.

Table 3.1
Contributions to log \( L^{16} \) from Cavity Formation, Dispersion Interactions and Dipole–Induced Dipole Interactions for selected compounds using equation 3.8 [14].

<table>
<thead>
<tr>
<th>Solute</th>
<th>( b \cdot V_{2adj} )</th>
<th>c.MR</th>
<th>( d \cdot \mu^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>-3.43</td>
<td>5.90</td>
<td>0.00</td>
</tr>
<tr>
<td>Propanone</td>
<td>-1.93</td>
<td>3.20</td>
<td>0.37</td>
</tr>
<tr>
<td>2-Heptanone</td>
<td>-3.70</td>
<td>6.87</td>
<td>0.31</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>-2.57</td>
<td>4.39</td>
<td>0.14</td>
</tr>
<tr>
<td>Methanol</td>
<td>-1.07</td>
<td>1.63</td>
<td>0.13</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>-4.14</td>
<td>8.03</td>
<td>0.13</td>
</tr>
<tr>
<td>Nitropropane</td>
<td>-2.35</td>
<td>4.29</td>
<td>0.60</td>
</tr>
</tbody>
</table>

The signs of the terms also show that cavity formation opposes solute dissolution in n–hexadecane, and dispersion forces favour it, the dispersion term always being of a greater magnitude than the cavity formation term.
HYDROGEN BOND SCALES

Abraham et al [47,48], developed two new empirical solute scales for hydrogen bond acidity ($\alpha^H_2$), and hydrogen bond basicity ($\beta^H_2$). The two new scales were constructed purely on a thermodynamic basis. The scale of hydrogen bond acidity [47], was formulated using log $K$ equilibrium constants for the 1:1 complexation for a series of monomeric acids with a series of reference bases, both at low concentration to avoid association, in tetrachloromethane solvent at 298 K.

\[ \text{A} - \text{H} + \text{BASE} \rightarrow \text{A-H--BASE} \]

When log $K$ values for a series of acids (hydrogen bond donors) against a reference base are plotted versus log $K$ values for the acid series against any other reference base, there results a set of lines that intersect at a point where log $K = -1.1$ (equilibrium constants expressed in molar concentration units). It is then possible to obtain an average hydrogen bond acidity (with some exceptions) for solutes in CCl$_4$, denoted as log $K^H_A$. These values are then simply transformed into a solute hydrogen bond acidity scale via equation 3.9.

\[ \alpha^H_2 = (\log K^H_A + 1.1)/4.636 \quad (3.9) \]

It can be similarly shown [48], than when log $K$ values for a series of bases against a given reference acid are plotted versus log $K$ values for the base series against any other reference acid, a set of lines is obtained that also intersect at a point where log $K = -1.1$. Similarly to the case above, it is possible to obtain an average hydrogen bond basicity for solutes in CCl$_4$, denoted as log $K^H_B$, and then to transform them into a basicity scale using equation 3.9, where the factor 4.636 is chosen to initialise the scale so that $\beta^H_2$ is equal to 1.0 for the base hexamethylphosphortriamide. The factor has no physical
significance other than yielding a convenient working range of $\alpha_{H_2}$ and $\beta_{H_2}$ values.

\[ \beta_{H_2} = (\log K_{H_2} + 1.1)/4.636 \]  

(3.10)

The $\alpha_{H_2}$ and $\beta_{H_2}$ values so obtained (referring specifically to solute hydrogen bond complexation in $\text{CCl}_4$ at 298 K), can be combined in a general equation that can be used to predict a vast number of Log K values [62]. From the original matrix of 89 primary $\alpha_{H_2}$ and 215 primary $\beta_{H_2}$, (containing 1312 experimental log K values), many more $\alpha_{H_2}$ and $\beta_{H_2}$ values can be calculated from;

\[ \log K = (7.354 +/-.0.019)\alpha_{H_2}\beta_{H_2} - (1.094 +/-.0.007) \]  

(3.11)

\[ R = 0.9956 \quad \text{S.D.} = 0.093 \quad N = 1312 \]

This equation has been used to considerably extend the database for $\alpha_{H_2}$ and $\beta_{H_2}$ parameters. Equations 3.9 - 3.11 are not completely general, in that some particular acid–base combinations are excluded, specifically weak acids such as pyrrole, etc. with bases such as pyridine, amines and ethers [63]. These hydrogen bond acids give rise to a different electrostatic:covalent ratio in their complexes, with a Maria–Gal, [64], $\theta$ value larger than about 75°. The combination of these acids with other bases is however included.

Unfortunately, as Whiting points out, the above method of calculating $\alpha_{H_2}$ and $\beta_{H_2}$ values is limited to monomeric adds and cannot be used for polyfunctional solutes [65]. He gives two reasons for this; firstly complexation constants for multifunctional compounds cannot be practically obtained and secondly, multiple hydrogen bonding with several solvent species is possible for multifunctional compounds giving a higher $\alpha_{H_2}$ or $\beta_{H_2}$ value than could be obtained from a complexation constant. Indeed, the same may be true of even monofunctional compounds if for some reason their hydrogen bond acidity
or basicity was enhanced in the solvent.

This may indeed be the case as complexation constants are obtained with acid and base at low concentrations with little possibility of association whereas in the bulk solvent the solute may be able to form multiple hydrogen bond interactions with surrounding solvent molecules. It has been indicated that such compounds may include; aromatic ethers, phenols and aromatic amines, all of which can have activated aromatic portions that may interact with the bulk solvent.

Whiting was able to back calculate new $\beta^{H_2}$ values from HPLC data. This was termed the 'effective' hydrogen bond basicity $\Sigma \beta^{H_2}$, it was usually the averaged value from more than one result.

The $\alpha^{H_2}$ scale is clearly analogous to the $\beta^{H_2}$ scale in that there will also be problems with multifunctional and activateable monofunctional compounds in a bulk solvent where multiple hydrogen bond type interactions are possible. The problem was dealt with in a slightly different manner.

When the new $\pi_2^H$ parameter was developed by Abraham et al. [49], they included $\alpha^{H_2}$ in their calculations and similarly developed a summation scale, $\Sigma \alpha^{H_2}$, for hydrogen bond acidity of the solute. They found that it differed only slightly from the original complexation based scale. It is this new scale, based mainly on the McReynolds and Laffort [54,55], data sets, that is used in this work although many of the values are identical with the ones obtained by the complexation method outlined above. As the old and new scales are almost identical, for cases when the summation value is not known the authors recommend substituting one of the older $\alpha^{H_2}$ or $\beta^{H_2}$ values into the regression equation.
THE IMPORTANCE OF HYDROGEN BONDING PARAMETERS

A quantitative measure of the relative strength of a 'traditional' acid is its degree of
dissociation, measured in aqueous solution [66]. Similarly, the relative strength of a base
can be measured [66] by either its $pK_a$ value, or the $pK_b$ value of its conjugate acid. The
generally accepted alternative to the proton-transfer theory is that proposed by Lewis
[67], based on electron pair acceptance (acids), or electron pair donation (bases).
However, for many chemical structures and processes, including all the ones studied in
this work, a proton-transfer approach is not relevant or applicable. A large number of
processes, such as the solubility of non-electrolytes in water or organic solvents, or the
distribution of non-electrolytes between two solvent phases, do not depend upon the
actual transfer of protons, rather the ability of the solute to take part in hydrogen
bonding processes. Thus, a hydrogen bond acid will not actually donate a proton (or
accept an electron pair), it will donate a hydrogen bond, and a hydrogen bond base will
in the same way receive a hydrogen bond. These processes are of the upmost importance
in nature; the three-dimensional structure of water is based on hydrogen bond networks,
the secondary structure of proteins are held in place by hydrogen bonds of the type
$>\text{N}^\cdot\text{H}<---\text{O}\cdot\text{C}<$. Typical hydrogen bond acids and bases are given below in Table 3.2.

<table>
<thead>
<tr>
<th>Hydrogen bond bases</th>
<th>Hydrogen bond acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Me}_2\text{C}=\text{O}&lt;---$</td>
<td>$&lt;---\text{H}\cdot\text{OMe}$</td>
</tr>
<tr>
<td>$\text{Et}_2\text{O}&lt;---$</td>
<td>$&lt;---\text{H}\cdot\text{CH}_2\text{CN}$</td>
</tr>
<tr>
<td>$\text{Et}_3\text{N}&lt;---$</td>
<td>$&lt;---\text{H}\cdot\text{CH}_2\text{NO}_2$</td>
</tr>
<tr>
<td>$\text{H}—\text{O}&lt;---$</td>
<td>$&lt;---\text{H}\cdot\text{CCl}_3$</td>
</tr>
</tbody>
</table>

Table 3.2 HYDROGEN BOND ACIDS AND BASES
INTERACTIONS BETWEEN $\pi$ AND $\sigma$ ELECTRON PAIRS

The polarisability correction term $\delta_2$, has now been replaced by a more quantitative measure of polarisability $R_2$, [46]. The $\delta_2$ parameter was actually limited to one of three values; 1.0 for aromatic compounds, 0.5 for polyhalogenated aliphatics and 0.0 for all other compounds, and a more flexible measure of polarisability was needed. Polarisability can be modeled by the solute molar refraction, $MR_s$, and the solute polarisability, both were investigated by Abraham et al [46], but neither were found satisfactory when used in combination with other parameters. The solute molar refraction, for convenience, was defined in terms of the characteristic volume:

$$MR_s = 10. (n^2-1)V_x/(n^2+2) - 10\Delta(n)\cdot V_x \quad (3.12)$$

where:

$$\Delta(n) = (n^2-1)/(n^2+2) \quad (3.13)$$

With $V_x$ in units of $$(\text{cm}^3 \cdot \text{mol}^{-1})/100$$, equation 3.12 will yield $MR_s$ in the more convenient units of $$(\text{cm}^3 \cdot \text{mol}^{-1})/10$$. Note that $n$ is taken at 293K with the sodium-D line. Unlike $\Delta(n)$ itself, the molar refraction has the interesting property of being the same (within a few per cent) for a given solute in the gas phase and in solution. Hence although $\Delta(n)$ is most conveniently measured on bulk liquids, $MR_s$ (and $MR_2$) can be taken as a property of an isolated molecule∗.

In order to remove the dispersive part already incorporated in $log L^{16}$, the value of $MR_s$ for an alkane of the same characteristic volume can be subtracted out;

$$R_2 = MR_s(\text{observed}) - MR_s(\text{alkane of same } V_x) \quad (3.14)$$

∗ Abraham et al have reported that $MR$ is essentially the same in the gas phase and bulk liquid even for associated compounds such as water and alcohols. The one exception they have noted is acetic acid, which they assign to the extensive dimerisation that takes place in the gas phase [46].
The latter quantity is easily obtained through a very good regression:

\[
\text{MR}_x(\text{alkane}) = -0.52553 + 2.83195V_x
\]  \hspace{1cm} (3.15)

\[R = 0.99999, \text{SD} = 0.0078 \text{ N} = 13\]

Hence knowing \(\Delta(n)\) and \(V_x\) for any solute, \(\text{MR}_x\) and then \(R_2\) can be calculated via equations 3.12-3.15. For convenience \(R_2\) is tabulated in units of \(\text{cm}^3/10\). Note that by definition \(R_2 = 0\) for all \(n\)-alkanes, and by calculation \(R_2\) is also zero for branched chain alkanes and for the rare gases as well. The linear regression equation now becomes:

\[
\text{Log SP} = SP_0 + rR_2 + s\pi^+ + a\alpha^H + b\beta^H + l\log L^{16}
\]  \hspace{1cm} (3.16)

From the method of determination of \(R_2\), as well as from inspection of \(R_2\) values, it follows that the \(rR_2\) term in equation 3.16 is a quantitative measure of the ability of a solute to interact with the solvent through solute \(\pi\) (mainly) – or \(n\)-electron pairs.
THE NEW GENERAL SCALES FOR $\pi_2^E$.

Previous work was mainly concerned with LSER of the type represented by the general equations 3.16, specifically studying a series of solutes on one stationary phase or solvent. Initially $\pi_2^*$ as a first approximation was taken to be identical to the corresponding solvent parameters, as no solute parameter was available. This may be true for simple non-associating compounds, such as aliphatic ethers, but there is an underlying difficulty in that these solute parameters will not be equal to the solvent parameters where the solute is amphiprotic and/or self-associated.

A problem with the $\pi_1^*$ parameter is that it is only directly experimentally measurable for compounds that are liquid at 298K, thus $\pi_1^*$ has to be estimated for compounds that are solid at this temperature. Assuming that $\pi_1^*$ and $\pi_2^*$ are identical then values of $\pi_2^*$ can be obtained from such experimental measurements but the problem of compounds being solid at 298K renders the same restriction to $\pi_1^*$ as $\pi_2^*$.

It was possible to alleviate this problem by correlations of $\pi_1^*$ with measurable quantities. Kamlet et al [41,68] have related the $\pi_1^*$ parameter to such fundamental physical properties of solvent as the dipole moment and the reaction field function [69], when the solvent set is limited to non-hydrogen bonding, aliphatic liquids, which have only one dominant bond dipole, such as ethers, sulphoxides, and aldehydes. Carr and Brady [70] have also carried out similar correlations. Thus, assuming, for these compounds, that $\pi_1^*$ was identical to $\pi_2^*$, the correlations could be used to obtain further $\pi_1^*$ values and consequently $\pi_2^*$ values.

However, it is unlikely that such back calculated values of $\pi_2^*$ are always accurate due to association in the solvent contributing to $\pi_1^*$ but not to $\pi_2^*$. The problem is compounded in the case of self-associated compounds such as the alcohols which can be expected to exhibit definite differences when bulk solute and solute–solvent properties are compared.

Finally, even for non-associated compounds there is some doubt as to whether $\pi_1^*$ and $\pi_2^*$ are equivalent. The Kamlet-Taft solvatochromic solvent basicity parameter $\beta_1$ is not
exactly equivalent to the solute parameter $\beta^2$ even for non-associated compounds [71], and it is possible that the same problem may exist for $\pi_1^*$ and $\pi_2^*$.

A new solute dipolarity/polarisability scale has been set up by Abraham et al [49], by use of the LSER;

$$\log V_G^o = c + rv_2 + s_2\pi^* + a_2A_2 + b_2B_2 + l \log L_{16}$$  \hspace{1cm} (3.17)

where $V_G^o$, the specific retention volume, has been determined by McReynolds [54], for up to 376 solutes on 77 stationary phases. Abraham et al. determined LSER of the type shown above for each of the phases and found that for 75 of the 77 there was no hydrogen bond acidity at all. They could thus simplify equation 3.17 to;

$$\log V_G^o = c + rv_2 + s_2\pi^* + a_2A_2 + l \log L_{16}$$  \hspace{1cm} (3.18)

In addition as the $v_2$ term can be calculated for any solute and $r$ has already been determined by the MLRA, we can subsume $rv_2$ and the constant $c$ into the dependent variable to give;

$$V' = s_2\pi^* + a_2A_2 + l \log L_{16}$$  \hspace{1cm} (3.19)

Thus we now have a series of equations for each solute in terms of a dependent variable $V'$ and three explanatory variables; $s_2$, $a_2$ and $l$. We can now re-determine $\pi_2^*$, $A_2^H$ and $L_{16}$ by use of MLRA for each solute. As all the known data in the MLR is related to the solute the term $\pi_2^*$ is replaced by $\pi_2^H$.

$$V' = s_2\pi_2^H + a_2A_2^H + l \log L_{16}$$  \hspace{1cm} (3.20)
The new values for \( \pi_2^H \), \( \alpha_2^H \), and \( \log L^{16} \) were found to be close to the known values when these were available (table 3.3). The procedure employed above for the determination of solvation parameters can be regarded as the averages for a whole range of stationary phases (usually 30–75).

Table 3.3.

SOME CALCULATED PARAMETERS USING EQUATION 3.20.

<table>
<thead>
<tr>
<th>Solute</th>
<th>( \pi_2^H )</th>
<th>( \alpha_2^H )</th>
<th>( \log L^{16} )</th>
<th>n</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pent-l-ene</td>
<td>0.09</td>
<td>0.00</td>
<td>2.040</td>
<td>36</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>a0.08</td>
<td>0.00</td>
<td>2.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>0.47</td>
<td>-0.01</td>
<td>3.327</td>
<td>73</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>a0.55</td>
<td>0.00</td>
<td>3.344</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>0.27</td>
<td>-0.02</td>
<td>1.975</td>
<td>71</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>a0.27</td>
<td>0.00</td>
<td>2.061</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butanone</td>
<td>0.69</td>
<td>0.00</td>
<td>2.282</td>
<td>71</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>a0.67</td>
<td>0.00</td>
<td>2.287</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Propylacetate</td>
<td>0.61</td>
<td>0.00</td>
<td>2.847</td>
<td>73</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>a0.55</td>
<td>0.00</td>
<td>2.878</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propan-1-ol</td>
<td>0.41</td>
<td>0.37</td>
<td>2.060</td>
<td>72</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>a0.40</td>
<td>0.33</td>
<td>2.097</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Previous values, see ref. [46].

In the same paper, Abraham et al. also determined \( \pi_2^H \) values using the Laffort [55], data set of 240 solutes on 5 phases. They determined five regression equations, one for each phase (eqn 3.21);

\[
\log L' = c + rR_2 + s.\pi_2^H + a.\alpha_2^H + l.\log L^{16}
\]  

(3.21)

where \( \log L' = \log L - \log L_{(decane)} \).
They used the technique of back calculation using known values of $R_2$, $\alpha^H_2$ and $\log L^{16}$ to obtain five values of $\pi_2^H$ for each solute and then calculated the average. They were also able to characterise some of the Laffort solute parameters in terms of $\pi_2^H$ and $R_2$, and thus knowing $R_2$, calculated $\pi_2^H$ values. Using mainly the "inversely" calculated values from the McReynolds and the back calculated and averaged values from the Laffort together with a few calculations from the work of others [72–76], for polyhalogenated and aromatic compounds not found in the Laffort or McReynolds data, they have developed a new $\pi_2^H$ scale which is more closely related to a solute parameter for polarisability than $\pi_2^*$. The general equation 3.16 now becomes;

$$\log SP = SP_0 + r R_2 + s \pi^H_2 + a \alpha^H_2 + b \beta^H_2 + 1 \log L^{16}$$ (3.7).

Abraham et al. have recently shown that the new solvation equation, 3.7, described here can be used to characterise gas–liquid stationary phases [50,51], ionic salts [50], candidate phases for piezo–electric chemical sensors [77], and polymers [78].
MULTIPLE LINEAR REGRESSION ANALYSIS (MLRA).

MLRA is a heavily used statistical method and its applications extend to many different areas. However, care must be taken in the use of MLRA as it can have a number of pitfalls for the unwary user. The technique used in MLRA, which is an application of the least squares technique to multivariate analysis, is not very complex and can be found in most general statistical texts. It is not necessary to discuss it here but some of the ways in which errors are possible will be mentioned.

One of the more obvious traps in MLRA is the initial assumptions that are made regarding the relationship under investigation. It is necessary to make this assumption before one begins and then see if the data fits. There is obviously an inherent danger in making assumptions on which our statistical studies are based. An incorrect assumption can lead to many wasted hours especially if by some quirk, the data fits the model. It is important that the model is not an unreasonable one, and that there is general agreement regarding its validity.

In this study as in all applications of linear regressions the assumption made is that there is a linear relationship between the dependent variable, log SP, and the multiple parameters describing intermolecular interactions. This assumption is a reasonable one as there is good reason to believe that the overall interaction between two species is the sum of all the different types of specific and non specific interactions present.

A common difficulty that arises in MLRA is multicollinearity between the explanatory variables. Multicollinearity is the term given to linear relationships between two or more of the explanatory variables. The result is often problems of interpretation of the final equation and difficulties in deciding whether or not to exclude one or other of the 'offending' variables.

Another problem can be that of outliers in the regression. It is often the case that an
outlier is simply a poor measurement but it may be indicative of a secondary process. Outliers then, can usually be omitted from a regression with the proviso that the final equation may not be a full explanation of the process studied. Indeed, for many years and even today, groups such as alcohols are often left out of regressions on stationary phases even though it seems absurd to consider them all as outliers. The reason is usually to make the data fit a particular model that does not take hydrogen bonding or other polar effects into account.

Finally, there is the difficulty of obtaining a reasonable number of data points. If there are too few data points the regression may not be reliable but the problem is not merely one of quantity. The important point is that the set of solutes used to give the data points provide a range of parameter values for each parameter. They should also not overlap each other too much which would lead to problems of multicolinearity of parameters. Bearing these factors in mind one can choose the number of compounds to study. Generally the number of compounds depends upon the number of degrees of freedom in the statistical analysis. Thus, for 5 variables we require 25 compounds but for two variables ten compounds would suffice. The minimum number of compounds is five per variable although it is preferable to have more.
SECTION IV

MLRA AND LSER IN THIS WORK

The LSER that currently gives the best correlations for gas $\rightarrow$ condensed phase systems is equation 3.7, shown below.

\[
\log SP = SP_0 + r_2 R_2 + s_2 \pi_2^H + a_2 \alpha_2^H + b_2 \beta_2^H + l_2 \log L_2^{16}
\]  

The subscript 2 refers to the solute and will do so throughout this work. Each term in the equation represents the product of a particular property of the solute and the corresponding constant for the condensed phase, which will now be considered as an adsorbent.

The characteristic constants $SP_0$, $r$, $s$, $a$, $b$, and $l$ of the adsorbents are determined by MLRA of the logged retention data of various solute probes for which the solute parameters, $R_2$, $\pi_2^H$, $\alpha_2^H$, $\beta_2^H$, and $\log L_2^{16}$, are known. The characteristic constants are a quantitative description of interaction strength with the particular solute property being described.

The characteristic constants do not always represent what they seem to. For instance, $a$, the characteristic constant for $\alpha_2^H$, represents adsorbent basicity not acidity, since solutes that are hydrogen bond acids interact with hydrogen bond base sites on the adsorbent surface. Similarly, $b$, describes the adsorbent acidity as, it is the acidic sites that will interact with hydrogen bond base solutes. However, the $r$, $s$ and $l$ constants are chemically equivalent to the corresponding terms of $R_2$, $\pi_2^H$ and $\log L_2^{16}$, for the solute, i.e. $r$ is a measure of condensed phase excess polarisability, $s$ is a measure of condensed phase dipolarity and $l$ is a measure of condensed phase dispersion strength.

The characteristic constants provide a quantitative and descriptive profile of the adsorbent surface. For instance, an adsorbent that had some polarisable active sites set in a matrix
of non-specific dispersive sites could be expected to have significant terms in \( r \) and/or \( s \), and \( l \) but not in \( a \) and \( b \). The terms in \( a \) and \( b \) would probably be statistically insignificant.

Useful information can be gleaned by comparing the LSER for different adsorbents. The primary information is the adsorbent surface chemical profile that the equation quantitatively reveals. For example, we can see at a glance the adsorbents nature; acidity, basicity, dispersive strength etc. In addition, the size of the constants reveals the dominance or triviality of a particular property. Large constants are of interest as they may indicate the adsorbents potential for separating substances. For example a large \( b \) value implies that the adsorbent may be usefully employed to separate solutes according to their acidity. Alternatively, a large \( l \) value implies that separations of solutes according to their dispersive strength could be affected. On the other hand a large \( l \) value may be prohibitive in that solutes take far too long to elute. Caution must be observed when making comparisons between adsorbates, only retention data obtained under identical experimental conditions should be compared. Only isothermal conditions should be compared as temperature can have a large influence on adsorbent properties. Similarly, as will be discussed later, detector sensitivity can have a large effect on measurements made at apparent infinite dilution.

Another important factor to remember when deciding what terms contribute to the overall retention equation is the range of possible values. The log \( L^{16} \) parameter in practice varies from \(-0.5\) to \(+3.0\), whereas the other parameters are generally in the range of \( 0 \) to \( 1 \). Small \( l \) constant terms for the log \( L^{16} \) parameter do not necessarily mean that the term itself is a small contributor to retention.

Once the retention equation for a particular adsorbent is known it can be used to predict retention data for compounds for which experimental data are difficult or inconvenient to obtain. An example would be the retention data for toxic compounds which can be predicted if their parameters are known, without the need of exposure of personnel to
hazardous substances.

The retention equation is obtained by the use of retention data for about 25 compounds obtained isothermally, known solute parameters, and the MLRA program. The method has some distinct advantages: it is relatively easy to apply, and with over 2000 compounds for which parameters are available it usually requires only a knowledge of relative retention data; the constants obtained relate to specific adsorbent properties that can be comprehended by any chemist; because the method can be applied to any liquid phase, including organic solvents, adsorbent constants can be related to the sets of constants that can be obtained for common solvents; the method is very general and can cover GLC stationary phases, capillary columns, ordinary solvents as well as adsorbents.

As an example of the type of data that the MLRA gives the results obtained for Ambersorb 572 carbonaceous adsorbent at 80% humidity are shown below.

Table 3.4

<table>
<thead>
<tr>
<th>CORRELATION COEFFS BETWEEN VARIABLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_2$</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>0.730</td>
</tr>
<tr>
<td>$\alpha_2^H$</td>
</tr>
<tr>
<td>$\beta^H_2$</td>
</tr>
<tr>
<td>log$L_{16}$</td>
</tr>
<tr>
<td>Yobs</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>REGRESSION OUTPUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r$</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>Coeffs</td>
</tr>
<tr>
<td>St Dev</td>
</tr>
<tr>
<td>TTest</td>
</tr>
</tbody>
</table>

Overall cor coeff, R 0.9808
$Y_{obs}-Y_{calc}$ S.D. 0.246
Number of data points 21

LSER Equation (rounded to one decimal place)

$log K_e = -1.0 - 2.5 R_2 - (0.4 \pi_2^H) + (0.7 \alpha^H_2) + 2.8 \beta^H_2 + 2.2 \log L_{16}$
The results of the MLRA in table 3.4 are not untypical of regressions on the carbonaceous adsorbents that have been studied. The first thing to note is the low number of data points, 21, this is due to the twofold difficulty in obtaining a high number of data points on the adsorbents studied. The first difficulty is the inordinate length of time taken for full elution of even small compounds from adsorbents at the ambient temperatures required in this work. The second difficulty is a shortage of compounds that will elute in a reasonable time, often the largest compounds that would elute in a reasonable time (30 hours*) were compounds like ethanol or dichloromethane. There is not a lot of scope for a range of compounds between methane and ethanol that have the required variation in parameter size.

The analysis also informs us of the correlation coefficient between variables. The value of \( R \) between \( R_2 \) and \( \pi_2^H \), 0.730, shows that the two parameters are to some extent overlapping each other. Similarly, \( \log L^{14} \) and \( R_3 \), 0.703, and \( \log L^{14} \) and \( \pi_3^H \), 0.605, are both high cross correlations. When such correlations exist caution should be exercised in interpreting the results and the regression should be run several times dropping out each of the variables in turn to determine which are independently affecting the log SP and which if any are merely well correlated with a determining variable.

The coefficients of the characteristic constants are shown together with their standard deviation and the TTest values. Neither \( \pi_2^H \) or \( \sigma_2^H \) are statistically significant, having TTests of 0.779 and 0.862 respectively. Characteristic constants for which the TTests are less than 0.950, that is below the 95% confidence level, are bracketed throughout this work.

* Elution times in excess of 30 hours were not only tedious to obtain but very difficult to determine as the elution boundary becomes very broad after that length of time and consequently its endpoint is somewhat obscure. (See Chapter V)
The LSER equation for the adsorbent is shown with the coefficients rounded to one
decimal place. As we will see later the error in determining the elution endpoints of the
chromatographic peaks does not allow for greater accuracy than this.

We can run the regression again against fewer parameters. In this particular case it is
easy to decide which variables to keep as \( \pi_2^H \) produces a negative value of -0.379 for \( s \).
This is clearly an impossibility as it implies that the adsorbent has a negative polarity. For
the LSER equation to be meaningful, chemically sensible coefficients must be generated
for each variable. Exoergic processes should give positive coefficients, and endoergic
processes negative coefficients. If they are significant, coefficients for solute polarity,
hydrogen–bond acidity and basicity must be positive, although the coefficient for the
solute size/ dispersion parameter may be positive or negative, depending on the energy
required to form a cavity in the solute, and the energy released from solute/solvent
dispersion interactions. Thus the negative value for solute polarity/polarisability (\( \pi_2^H \))
can be regarded as an artifact of the regression analysis. The coefficient for \( \alpha_{H_2} \) is
statistically insignificant and will also be removed from the second regression. The
analysis results for the regression without \( \pi_2^H \) and \( \alpha_{H_2} \) are shown below in table 3.5, it
can be seen that judging by the small drop in the correlation coefficient, \( R \), of 0.0058,
neither added any significant improvement to the regression.

The four term LSER equation shown below differs only slightly from the six term
equation shown earlier. The \( R_2 \) and \( \log I^{16} \) parameters are still highly cross correlated but
dropping \( R_2 \) from the regression causes a drop in the overall correlation coefficient of
about 0.05, to 0.925. This implies that \( R_2 \) has some small influence on adsorption and for
this reason it is left in the final equation.
Table 3.5

CORRELATION COEFFS BETWEEN VARIABLES

<table>
<thead>
<tr>
<th></th>
<th>$R_2$</th>
<th>$\beta R_2$</th>
<th>$\log L^{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta H_2$</td>
<td>0.449</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\log L^{16}$</td>
<td>0.703</td>
<td>0.076</td>
<td></td>
</tr>
<tr>
<td>$Y_{obs}$</td>
<td>0.573</td>
<td>0.435</td>
<td>0.832</td>
</tr>
</tbody>
</table>

REGRESSION OUTPUT

<table>
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<tr>
<th>Coeffs</th>
<th>$r$</th>
<th>$b$</th>
<th>$I$</th>
<th>$SP_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coeffs</td>
<td>-2.759</td>
<td>2.757</td>
<td>2.073</td>
<td>-0.905</td>
</tr>
<tr>
<td>St Dev</td>
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<td>0.314</td>
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<td>0.184</td>
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<td>TTest</td>
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<td>1.00000</td>
<td>1.00000</td>
<td>0.99987</td>
</tr>
</tbody>
</table>

Overall cor coeff, $R$ 0.9750
$Y_{obs} - Y_{calc}$ S.D. 0.264
Number of data points 21

LSER Equation (rounded to one decimal place)

$log K_e = -0.9 - 2.8.R_2 + 2.8.\beta H_2 + 2.1.\log L^{16}$

The technique of dropping a variable from the regression and observing the effect on the correlation coefficient is an useful one in determining the importance of particular variables. There is a pitfall to this technique however, when a variable is highly cross correlated with another. In this case both variables should be deleted in turn, and the overall correlation coefficient and the remaining variables characteristic constant and TTest noted, so that the effect of the variables on each other and their effect on the overall LSER can be taken into account.

The above example was furnished in order to display some of the factors which need to be taken into account when determining the final LSER equation. It should be remembered that MLRA is only a tool of the chemist and it is vital to use sound chemical reasoning at every step. In the case of small data sets, all combinations of parameter variables should be tried in order to find the best fitting equation and caution should be exercised when variables are highly cross correlated. If these precautions are
taken then some useful information from the LSER about the adsorbent surfaces chemical nature can be obtained.
CHAPTER IV
GAS CHROMATOGRAPHY AND THE DETERMINATION OF PARTITION CONSTANTS

INVERSE GAS CHROMATOGRAPHY

The investigation of the molecular interactions that govern adsorbance on a solid surface have been increasingly carried out by inverse gas chromatography (IGC). The first mention of the technique is that of Kiselev in 1967 [1]. The recent growth of the method can be judged by the number of publications. Schreiber [79] has written that in the ten years between 1968–1977 only 3% of chromatographic publications referred to the IGC technique whereas in the years 1978–1987 approximately 30% mention it.

The IGC technique involves the characterisation of an unknown stationary phase in the chromatographic column by injection of known molecular probes. Thus whereas in analytical gas chromatography the properties of the analyte are under investigation in IGC the properties of the analyte are known and the stationary phase is under investigation, hence the name "inverse GC". The interaction of several probes with carefully chosen properties and the stationary phase may reveal the types of interactions that occur on the stationary phase. IGC has been applied to a variety of solid and liquid coated stationary phases and a recent review provides an useful overview of the wide applicability of the technique [80].

Specifically, surface characterisations by chromatography have been treated in several reviews [79,80].

The usual method of characterisation in IGC is by use of the retention volume of the peak, \( V_R \), of the adsorbate probe. However, for \( V_R \) to be independent of the concentration of the probe, the probe must be at infinite dilution. The characteristic Gaussian peak shape for a sample in equilibrium at infinite dilution is shown in figure 4.1a.
However, for the adsorbents used in this work adsorbance is so strong that the vast majority of adsorbates give tailing peaks characteristic of non-linear adsorption isotherms (fig 4.1b). Another characteristic of the tailing peaks in this work is that in order for the peak to be observed a relatively high concentration of sample should be used. It is therefore necessary to perform finite studies as oppose to infinite dilution studies in order for the peak to be clearly seen.

In carrying out finite studies the concentration of adsorbate is sufficiently high to enter the non-linear region of the isotherm. The reason for non-linear behaviour is the increasing saturation of the most active sites on the adsorbent surface causing a decrease in the amount of adsorbate adsorbed relative to the concentration at equilibrium. This relationship is shown in fig 4.2. and is the cause of the curvature in the plot of $C_e$ against $C_i$. 
The equilibrium relationship of a solid adsorbent and a gaseous adsorbate is classically described by the adsorption isotherm. The adsorption isotherm describes the relationship between the adsorbed amount and the gaseous amount of adsorbate at equilibrium and at constant temperature. The adsorbed amount is designated by the concentration in the solid phase, $C_w$, and the free amount by the concentration in the gas phase, $C_g$.

Plots of $C_w$ versus $C_g$ obtained at constant temperature and of $C_w$ vs $P_2$ are shown in figures 4.2 and 4.3, where $P_2$ is the partial pressure of adsorbate gas in the vapour phase. Langmuir [81], developed the unimolecular layer theory to describe the adsorption process. Essentially this theory views the adsorption equilibration at increasing concentrations as consisting of a process of gradual covering of the adsorbent surface. By this means, a layer one molecule in thickness is finally formed over the whole of the adsorbent surface. The limiting concentration as the monolayer reaches saturation results
in the characteristic flattening of the isotherm at higher $C_g$ or $P_j$ values.

FIGURE 4.2 Isotherm Shape Showing Linear Region

*The isotherm is taken from Axton 22 on Ambersorb 572 at 0% humidity and 298.15K

The Langmuir isotherm allows one to find the surface area of the adsorbent by the formula:

$$C_s = \frac{C_m.K.C_g}{(1 + K.C_g)}$$

(4.1)

where $C_m$ is the concentration of the gas required for a unimolecular layer to cover the solid surface and $K$ is the adsorption or partition constant. The slope of the isotherm $dC_s/dC_g$ is the equilibrium constant of the adsorption process and is a measure of the
affinity of the adsorbate gas for the adsorbent. This affinity will depend on the nature of
the adsorbent and upon the nature of the adsorbate and at the limit as adsorbate
centration approaches zero, known as infinite dilution, \( C_g \to 0 \) and equation 4.1
becomes;
\[
C_g = C_w \cdot K \cdot C_g - K' \cdot C_g
\]
where \( K' \) is a constant and is a measure of the adsorbate adsorbent affinities at infinite
dilution and is independent of concentration in this range.

**FIGURE 4.3**

Isotherm Plot of \( P_2 \) vs \( C_\gamma \) for Arcton 22 on Ambersorb 572 at 0% Humidity and 298.15K

The unimolecular layer theory actually only applies to adsorption of an ideal gas on an
homogeneous smooth surface. For solid carbon surfaces the theory has been superseded
by the theory of volume filling of micropores (TVFM) of Dubinin (refer Chap 2).
According to TVFM the steep linear portion of the isotherm represents the filling of micropores whilst the change of slope represents the completion of this process. The gently sloping plateau region of the isotherm represents the filling of larger pores such as mesopores and macropores. The isotherms shown in figure 4.2 and 4.3 show only the micropore portion of the isotherm, this is because the partial pressures used in this work do not extend into the mesopore or macropore regions. It is interesting to note that the micropore portion of the isotherm is curved and not linear. The curvature in the isotherm is only slight and may not be observed with the less sensitive methods. Nevertheless, the curvature is indicative of the heterogeneity of the micropore structure, showing a range of sites of varying adsorptive power.
The measurement of physicochemical constants can be carried out by static and dynamic techniques. The static methods although able to provide absolute measurements are laborious and lengthy and require very pure samples. It is also difficult to observe very low adsorbate concentrations using static methods such as gravimetric or volumetric. The dynamic methods are more easily carried out and are usually considerably quicker than the static methods.

There are several types of dynamic methods such as frontal analysis (FA), frontal analysis by characteristic point (FACP) and elution by characteristic point (ECP). FA and FACP both involve analysis of the frontal boundary or breakthrough curve. Briefly, the analysis involves equilibration of a packed column, containing the adsorbate with pure carrier gas at constant velocity. The inlet gas stream is then changed to a stream containing the sample gas at a known partial pressure. As the breakthrough curve appears the sample stream is switched off so that the inlet gas becomes pure carrier gas once more. By analysis of the breakthrough curve at different sample concentrations (FA), or analysis of a single breakthrough curve (FACP), one can obtain points on the adsorption isotherm.

THE ECP TECHNIQUE

Elution by characteristic point (ECP), involves analysis of the elution boundary of chromatographic peak. It is more convenient than FACP as it does not involve switching gas streams or attempting to obtain a constant concentration of sample gas. Like the FACP technique, ECP allows the isotherm to be obtained from a single run. Thus in ECP the isotherm can be obtained from a single chromatographic peak and it is this technique that is adopted in this work to obtain the isotherm and/or the partition coefficient at infinite dilution. Full descriptions of all these techniques are given by Condor and Young [82], Laub and Pecsok [83], Parchers [84], and Condor and Purnell [85].

The ECP method adopted in this work involves the injection of a sample into a carrier
gas stream which is passing through the adsorbent column. The chromatographic peak can then be analysed to give the adsorption isotherm and the partition constant, $K'$, from the linear, infinite dilution region of the isotherm. ECP and FACP do suffer the disadvantage that results can be significantly affected by non-ideal effects due mainly to the random nature of diffusion. Conder and Purnell [85] showed that band spreading leads to isotherms with more curvature than that measured by static techniques. So, when band spreading due to diffusion is observed it is necessary to correct the peak to eliminate such an effect before the isotherm is calculated.

CORRECTION OF ELUTION PEAK FOR DIFFUSION AND CALCULATION OF THE ISOTHERM BY ECP

In ECP the solute is injected into the GC column (and preferably vaporised, if liquid, by a heated injector) and passed through the column of adsorbent, the resulting chromatogram is shown in Fig 4.4a. The frontal boundary of the peak is self-sharpening, the elution boundary is diffuse and used to calculate the adsorption isotherm. If the peak is as shown in Fig 4.4b and the first boundary is now also slightly diffuse, this is due to non-ideal band spreading effects and requires correcting for, to produce the self sharpening boundary as in Fig 4.4a. Bachman et al [86], have devised two empirical procedures to correct for non-ideality, described below.
FIGURE 4.4a Self Sharpening Peak
CORRECTION FOR DIFFUSION

The simplest assumption is that the rate of broadening by diffusion is equal on both sides of the peak. Then the corrected curve lies halfway between the front and rear sides of the peak, as shown below in Fig 4.5a.

Another possibility is to subtract the distance between the maximum retention time and the front side, from the rear side (Fig 4.5b); by this manipulation one obtains values lying between the first method and the measured rear side. This correction gives the exact values for the two limiting cases; symmetrical peaks (e.g. linear isotherm) and asymmetrical peaks with vertical front sides (e.g. steep curved convex isotherm and negligible diffusion). The assumption that the rate of elution of the maximum of the peak is not influenced by diffusion, and that equilibrium is established on the front side as well as on the rear side is made for both corrections. By making the second correction (Fig
4.5b), Bachmann et al [86], showed that this is the method of choice, producing results within 5% of the values determined by static methods. Knozinger and Spannheimer [87], have criticised the use of this method to correct for diffusion, and point out that it can only be strictly correct if the rate of broadening at the front and back of the peak are identical. However for the moderate accuracy required in the present work the correction is valid and used in this work together with the ECP method to calculate adsorption isotherms.

Knozinger and Spannheimer [87], suggest that the approach of Huber and Keulemans [88], be followed, who recommended using long columns to reduce the relative contribution of non-ideality and choosing the flow rate in the region of minimum plate height. The former is limited by the time the operator is prepared to wait for the solute/adsorbate of interest to elute, which can be inordinately high for some adsorbates, especially when studied at ambient temperatures, as in this work. (a maximum elution time of 30 hours was considered acceptable).
PEAK CORRECTIONS FOR DIFFUSION

FIGURE 4.5a SYMMETRICAL DIFFUSION CORRECTION
DETERMINATION OF PARTITION CONSTANTS, $K'_e$ and $K_p$.

The partition constant at infinite dilution $K'_e$, is found by measuring the slope of the plot of $C_e$ against $P_2$ (adsorption isotherm) as $P_2 \rightarrow 0$ and is designated $K_p$ or the partition constant can be found by plotting $C_e$ against $C_g$ as $C_g \rightarrow 0$ and is thus designated $K_e$. The two terms are interchangeable by an adsorbate constant term but do actually represent different quantities, characterising the adsorbent in terms of concentration or in terms of partial pressure of adsorbate.

For adsorption on a homogeneous surface at sufficiently low concentrations, such that all adsorbate molecules are isolated from each other, the equilibrium relationship between gas phase and adsorbent is constant over a range of concentrations, known as the "Henry's region". This linear relationship between $P_2$ or $C_g$ and $C_e$ is known as Henry's
law, by analogy with the limiting behaviour of the solubility of gases in liquids. The constant of proportionality is referred to as the partition constant. We have therefore, the equations:

\[(C_v/P_2)_{P_2\to0} = K_p = 1/K_H^p \quad (4.3)\]

\[(C_v/C_p)_{C_p\to0} = K_e = 1/K_H^e \quad (4.4)\]

where the partition constant is the reciprocal of the Henry's constant.

Eqn. 4.1 can be rearranged to give eqn. 4.5;

\[\frac{C_v}{C_e} = \frac{1}{C_mK} + \frac{C_g}{C_m} \quad (4.5)\]

so that a plot of \(C_v/C_e\) against \(C_g\) will have a slope of \(1/C_mK\) and an intercept of \(1/C_mK\). In principle, values of the slope and intercept may be combined to give the parameter \(K\), but in practice it is not very accurate to use the intercept of this plot to obtain \(C_mK\) (\(K_e\) or \(K_p\)). A better method is to use a plot of \(C_v\) against \(C_g\) at low partial pressure to obtain \(K_e\), and to combine the value of \(C_mK\) thus found with the value of \(C_m\) from the \(C_v/C_e\) against \(C_g\) plot, to obtain \(K\). It should be noted that although \(C_m\) and \(K\) are interesting parameters, it is the combined parameter \(C_mK\), or \(K_p\), that reflects the adsorbance of the solute gas or vapour at low concentrations or similarly \(K_p\) at low partial pressures. \(P_2\) and \(C_g\) are related by equation 4.6;

\[P_2 = \frac{C_g \cdot R \cdot T}{M_2} \quad (4.6)\]
where \( R \) is the gas constant, \( T \) is the temperature in degrees Kelvin and \( M_j \) is the molecular weight of the adsorbate being studied in grams.

The work presented here uses the elution by characteristic point method (ECP), sometimes known as the peak profile method [82–86], to calculate adsorption isotherms. The chromatographic peak observed on injection of a solute sample is corrected for diffusion and baseline drift to give a new peak as shown in Fig 4.6. Then an area, \( A^h \), corresponding to the recorder pen deflection, \( h \), can be obtained (see Fig 4.7a). In this manner a series of areas can be constructed from the corresponding \( h \) value as shown in fig. 4.7b. \( C_g \) is calculated from the area on the chart recorder, \( A^h \), and \( C_g \), from the recorder pen deflection, \( h \), using known equations. The area, \( A^h \), is proportional to the volume of carrier gas required to elute the adsorbate (at the point on the elution curve at height, \( h \), this is the so called characteristic point), which is in turn proportional to the time spent in the adsorbent, i.e. the concentration in the adsorbent, \( C_g \). The pen deflection, \( h \), is proportional to the number of adsorbate molecules passing through the detector at that particular moment (assuming detector linearity with the concentrations studied), which is proportional to the concentration in the gas phase, \( C_g \), or the partial pressure, \( P_j \). \( C_g \) and \( C_g \) are given by;

\[
C_g = \frac{A^h}{S \cdot W_1} \quad (4.7)
\]

\[
C_g = \frac{h \cdot Q}{F \cdot S} \quad (4.8)
\]

where, \( S \) is the sensitivity, defined as the area under the uncorrected peak divided by the amount of sample injected, \( W_1 \) is the active weight of adsorbent (i.e. the dry weight after purging), \( Q \) is the chart recorder speed, and \( F \) is the carrier gas flow rate (\( \text{ls}^{-1} \)) at column temperature, \( T \) (K). The isotherm is calculated using eqns 4.7 & 4.8 above, from points on the appropriate boundary (i.e. the diffusion corrected elution boundary.
From the ratios of $A^h/h$, values of $C_g/P_2$ or $C_g/C_g$ are calculated via known eqns 4.9 and 4.10 respectively. Where, $P_2$, is the solute partial pressure (atm), $M_2$, is the solute molecular weight (g), and $R$, is the gas constant taken as $8.2056 \times 10^{-2}$ atm mol$^{-1}$ deg$^{-1}$.

(Note eqns 4.9 and 4.10 are simply related by eqn 4.6).

\[
\frac{C_g}{P_2} = \frac{A^h.F.M_2}{h.W_1.Q.R.T} \tag{4.9}
\]

\[
\frac{C_g}{C_g} = \frac{A^h.F}{h.W_1.Q.R.T} \tag{4.10}
\]
Data is collected using an on-line personal computer and an analog digital converter. A program specifically written to recalculate the chromatographic peak data into $C_g$, $C_{g^*}$ and $P_2$ values can be used to plot isotherms if required. The program also obtains the limiting values of $K_e$ and $K_p$ which are characteristic constants for each adsorbate on the adsorbent studied. Isotherms are plotted as $C_g$ vs $P_2$, $C_g$ vs $C_{g^*}$, and $C_g/C_{g^*}$ vs $C_g$, see Fig 4.3, 4.2 and 4.8. The limiting values of $C_g/P_2$ and $C_g/C_{g^*}$ can be obtained from the corresponding slopes as $P_2 \rightarrow 0$ and $C_g \rightarrow 0$, which define the partition constants, given by eqns. 4.3 and 4.4 respectively. However, it is found to be more accurate to find the limiting value from the intercept of the $C_g/C_g^*$ vs $C_g$ plot.
In order to calculate the partition constants measured at infinite dilution, the measured flow rate, $F_{m}$, is corrected to the actual flow rate, $F_{e}$, using eqn. 4.12,

$$F_{e} = F_{m} \cdot C$$

where $C$ is a system constant that depends upon carrier gas and column properties such as temperature, pressure drop and humidity in the gas stream. The pressure drop across the column is the pressure difference between the inlet and outlet of the column. The full correction is given by eqn 4.13, where $J_{23}$ is given by eqn 4.12. $J_{23}$ is the pressure correction factor required to correct for the pressure drop across the column, where $P_i$ and $P_o$ are the inlet and outlet pressures.
Further corrections are made for the differences between the temperatures of the flowmeter ($T_f$) and the column ($T_c$), for the vapour pressure of water above the soap solution in the flow meter ($P_{w^*}$), and for the average vapour pressure of water in the G.C. column, $P_{w^e}$ (for humidity measurements). The water vapour correction reduces to the more usual form $(P_0-P_{w^*})/P_0$, when the carrier gas passing through the GC column is dry, i.e. $P_{w^e}=0$.

Adsorption measurements made at different levels of relative humidity, require the correction given in eqn 4.14 to be applied to the retention volume. This equation was derived from first principles by McGill [89].

$$\frac{(P_0-P_{w^e})}{P_0} \cdot \frac{P_i}{(P_i-P_{w^e})} \cdot \frac{T_c}{T_f}$$

= water vapour correction (4.14)
FIGURE 4.8a PLOT OF $C_\text{g}/C_h$ against $C_h$ for Ethane on Ambersorb 572 at 0% Humidity and 298.15K
FIGURE 4.8b PLOT OF $C_t/C_0$ against $C_t$ for Arcton 22 on Ambersorb 572 at 0% Humidity and 298.15K.
AIMS OF THE ADSORPTION WORK

The search for a suitable adsorbent is generally the first step in the development of an adsorption, separation process (Chapter II, Adsorbents in this Work). The adsorption isotherm describes the uptake of adsorbate and from this isotherm the partition constant can be obtained. Preliminary selection of a suitable adsorbent can be made when the partition constants are known. More often than not these parameters (or others) are not known, and it is necessary to screen a range of adsorbents in order to obtain by experiment some particular function of the adsorption process. This can be time consuming and may not necessarily select the best adsorbent suitable for the process.

Recently McGill [14,90] and coworkers developed a new general method of characterising adsorbents based on a general solvation equation developed by Abraham which could successfully predict carbonaceous adsorbent–adsorbate interactions for various classes of solute and under various conditions, such as humidity.

As discussed previously, Abraham has since developed the improved solvation equation based on new hydrogen bond acidity/basicity, dipolarity, polarisability and cavity size–dispersion scales.

$$\log SP = SP_0 + rR_2 + s\pi^2 + a\alpha^2 + b\beta^2 + l\log I^{16} \quad (3.7).$$

The main aim of the present work is to attempt to characterise carbonaceous adsorbents with this equation. As a preliminary study, an attempt will be made to characterise several carbonaceous adsorbents for which retention data is available by use of equation 3.7. This will test the feasibility of characterising carbonaceous adsorbents using the equation. It should also provide an insight into the nature of many common commercial adsorbents and allow us to make comparisons between our method of characterisation and those used by other workers.

If this proves successful we will attempt to characterise several interesting adsorbents for
which retention data are not presently available and subsequently elucidate the factors contributing to adsorption. Hence it will be possible to predict the interactions between adsorbate and adsorbent for compounds where the relevant parameters are known. This is important for any application of the adsorbent to solutes for which the adsorption retention data has not been measured. For example, it would be of considerable value if the adsorption properties of toxic compounds, which are difficult or hazardous to handle, could be predicted. This would significantly reduce the exposure of personnel to the hazardous substances.

An understanding of the adsorption process is advantageous to meeting industries need to cope with the growing environmentally related demands of governments' new legislation. The legislation, which usually requires a lowering of levels of harmful chemicals, such as pesticides and herbicides in air and water effluents, is placing an increasing financial and moral burden on industry. What is required is a cheap and efficient means of controlling and disposing of industrial waste. The use of activated charcoal is known to be very effective in the removal of undesirable by-products and waste materials, but little is known about the adsorption process and what modifications can be made in order to improve the effectiveness of activated charcoal for a particular clean up process.

It is known that water has a detrimental effect on adsorption and it would be useful to research this further and to try and identify any means by which the interfering effect of water can be reduced. Partition constants for a variety of adsorbents at different relative humidities will be sought. Analysis of the measured adsorption data, using multiple linear regression analysis, will be carried out to allow the factors influencing uptake to be elucidated. Conclusions can then be reached as to whether or not the particular adsorbent is a selective, hydrophobic or hydrophilic adsorbent.

Nearly all previous work has centred on the characterisation of one particular adsorbent of interest and quite often with a limited data set, not covering a wide enough range of
solute types to be considered complete. In the work of McGill however, adsorption measurements were carried out on eight different adsorbents, four of which were studied at different relative humidities. The number and type of solutes were claimed to be chosen to provide a full range of possible adsorbent–adsorbate interactions and a sufficient variety to satisfy any statistical requirements for regression analysis. Examination of the constants in the obtained regression equations were then used to yield information to enable the adsorbent to be characterised in terms of solute or adsorbate–adsorbent interactions.

The work of McGill focussed on the effect of functionality with some work on humidity at 31 & 53%, this work will continue the work on the effect of humidity extending it to higher levels of around 80% but instead of focussing on functionality we have chosen resins for their differing pore sizes and distributions. It will be interesting to see what effect this may have on the nature of the adsorbents.

The project will focus on five adsorbents to determine the effect of pore size, pore distribution and humidity on adsorption.

DEFENCE APPLICATIONS

A current method of characterisation of adsorbents that is commonly used involves the exposure of packed beds to challenge vapour streams at constant concentration. The breakthrough time and desorption curve can then be used to compare the adsorption of different adsorbates of interest. The gas chromatographic microtechnique technique used in this work is an attempt to provide a cheaper alternative to the packed bed technique.

The microtechnique has several advantages over the packed bed technique. Firstly, the microtechnique uses less adsorbent material. Due to the smaller samples used the desorption curve can be fully eluted allowing the column to be reused for the next sample. This is not possible with the packed bed technique which uses far too much material too allow full elution to take place. The sample must be replaced with more material which is
expensive and time consuming. The packed bed technique requires a detector system to be installed at the end of the column whereas modern gas chromatographs are already equipped with a sensitive detector and there is no further adaptation necessary. The packed bed technique uses an continuous adsorbate vapour stream in the carrier gas, this has the twofold disadvantage of being subject to fluctuations and using large amounts of adsorbate. The microtechnique uses discreet sampling which avoids these two disadvantages. The large amounts of adsorbate sample necessary in the fixed bed technique are also undesirable in military applications where the adsorbate may be a nerve gas or other toxic substance. The use of the fixed bed technique in military applications has prompted this study of a microtechnique which may ultimately save on time, cost and hazards.

Perhaps the most obvious military application of adsorbents is their use in respirator cartridges. Investigations into the adsorption properties of possible cartridge materials should provide important information on the most appropriate material for cartridges. The choice of cartridge material will be influenced by the climatic conditions where troops are to be deployed. Troops using respirators in desert regions or other regions of low humidity may require a different adsorbent cartridge than troops in humid regions, where the humidity of the air will affect respirator efficiency. The situation is not quite so simple, however. Personnel wearing full protective suits will rapidly build up internal humidity levels due to perspiration and this may affect the adsorption properties of the adsorbent which is impregnated into the suit lining.

The exposure of personnel to hazardous substances is unlikely to be for long periods of time. In the typical scenario there would be an exposure to the chemical, possibly at high concentration, for a short period of time. The adsorption properties of the cartridge adsorbent are important at this stage. As the gas disperses the air concentration will usually fall rapidly to safe levels. At this stage the critical factor becomes desorption of the gas adsorbed in the cartridge. In gas chromatography a plug of adsorbate is
adsorbed onto the column and the desorption process is then observed by use of the
detector. This process mimics the mechanism of adsorption and desorption of adsorbate
in warfare quite well and the gas chromatographic technique is a useful first indicator of
respirator efficiency.
CHAPTER V

METHODOLOGY

THE ADSORPTION PROGRAM

The initial aim of the project was to write a program that could collect the peak data and process it on a PC in order to generate partition constants in terms of concentration and partial pressure. An analog digital converter and a commercial package, Unkelscope, was used to transfer the data into the PC's memory in the form of an ascii file. The next step was to write a Quickbasic program to process the collected adsorption data in order to obtain values for the partition constants Log K_p and Log K_e.

QUICKBASIC PROCESSING PROGRAM

Unkelscope stores the adsorbate peak in an ascii file. For this work it is then necessary to perform various corrections and calculations on this data and this is done by using a program written mainly in Quickbasic (see appendix) although it was also necessary to write some parts of it in the more professional 'C' language due to its greater speed.

Routines were written to implement the following processes.

a) To read and write into an array the Unkelscope.ascii file.

b) To correct the values in the array for baseline drift, a common problem when adsorbates have long retention times.

c) To find the peak retention time and consequently the retention volume.

d) To correct the values in c) above for pressure drop across the column, gas hold up time, variations in atmospheric pressure, flow rate, flow meter variations, active weight of
adsorbent, and humidity in the column, in order to obtain a value for the specific retention volume \((V_g)\) and hence \(\log V_g\).

e) To correct the values in the array for diffusion.

f) To calculate pairs of values for \(C_p, C_g\) and for \(C_p, P_2\). \(C_p\) being based on the areas under the elution boundary and \(P_2\) or \(C_g\) being based on the corresponding point on that boundary.

g) To use the values in f) to calculate, via a least squares straight line plot, the values of \(\log K_p\) and \(\log K_g\).

h) Finally to store the values in a file for later use.

The calculations necessary to perform most of these functions have been given earlier and the program simply carries out these calculations sequentially. However, the techniques by which corrections for diffusion, corrections for baseline drift and calculation of the isotherm points are made required unique solutions and these are given below in the explanation of the Quickbasic program entitled “Input.Bas”

EXPLANATION OF INPUTTEST.BAS

The main program reads in the data from the Unkelscope ascii file containing the data on the adsorbate peak. An option is given to read in one, two, or four peaks depending on how many peaks were read into the ascii file (usually one or two). After the data has been read into an array, the array can be processed, this is mainly done by the series of subprograms outlined above. Some explanation will now be given of two of those subprograms, BCorr and Corrdiff.
In this work, where adsorbates can, depending on the nature of the adsorbent, length of column and any other conditions, have very lengthy retention times in excess of twelve hours, the baseline usually 'drifts' from its original value. The occurrence of this phenomenon requires some correction so that points on the elution boundary are derived from a constant 'background' voltage or baseline. BCorr corrects for baseline drift by generating a new baseline, relative to zero and then correcting the points on the peak so that they are relative to this new baseline.

Firstly, the start and end of the peak are determined using cursors within Unkelscope, so that only the actual peak is stored in the ascii file (this is a time saving method whereby only the peak is processed and not the whole chromatographic run). A little of the baseline at the end is needed so that the end of the peak can be determined. Secondly, the subprogram determines the average baseline voltage before elution of the adsorbate, this value is subtracted from all the values in the peak data array so that all voltages are relative to an initial baseline of 0 volts, i.e. all the points on the peak are now absolute values. Thirdly, the end of the peak is found. Fourthly, the tangent of the angle between the start of the run and this point is found. The opposite side of this tangent at any time t, is equal to the extent of baseline drift at that point. Accordingly the value of the opposite to the tangent at time t, is subtracted from each data point c, collected at time t, (fig. 5.1).
FIGURE 5.1 Baseline Correction Algorithm shown Diagrammatically

KEY: Tangent of angle POQ  

\[-\tan(\theta) = \frac{PQ}{OQ}\]

Baseline drift at Time(t)  

\[-P_tQ_t = \tan(\theta) \times OQ_t\]

CORRDIFF

Due to normal band spreading processes the front profile of the peak will not be sharp but diffuse, this diffusion needs to be corrected for and this is done by subtracting the diffusion at the frontal boundary from the elution boundary.

This is done by a series of condition checks and subsequent subtractions which are a modification of an original technique of Buist [91] (fig. 5.2).
KEY:  
Peak Height  
(A)  $P_{\text{left}}$  
(B)  $P_{\text{right}}$  
(C)  $L_{\text{data}}$  

$-P$  
$-P_{\text{left}} + 1$  
$P_{\text{right}} + 1$  
$-(\text{Conc}(P_{\text{left}}) + \text{Conc}(P_{\text{left}} + 1))/2$

(A) Steps down the frontal boundary.  
(B) Steps down the elution boundary.  
(C) Averages the present and previous points on the frontal boundary.

In the subprogram if $\text{Conc}(P_{\text{right}})$ is greater than $L_{\text{data}}$ then it is unaffected. If however it is smaller than $L_{\text{data}}$ it is removed from the array. This removal generates a space in the array; to fill this space all the points succeeding $\text{Conc}(P_{\text{right}})$ are 'nudged' back one space with respect to time. This 'nudging' has the effect of assigning the previous time to each $\text{Conc}(P_{\text{right}})$ value. The $P_{\text{left}}$ value is then lowered to the previous point in the array (i.e. it steps down the frontal boundary) and the whole process is repeated. The overall effect is to subtract from each $\text{Conc}(P_{\text{right}})$ value the number of time units that $\text{Conc}(P_{\text{left}})$ has
diffused, at the voltage when \( \text{Conc}(P_{\text{right}}) \) is equal to \( \text{Conc}(P_{\text{left}}) \). After the correction the elution boundary can give us the ascii points for the adsorption isotherm.

As expected parts of the program were found to be too slow in Quickbasic and the main programming loop which calculates partition constants from the corrected peak is now written in the faster language TurboC. The main function of the Correction program is simply to correct for diffusion and baseline drift.

THE ADSORPTION PROGRAM WRITTEN IN TURBO C

This program calculates the partition constants from the corrected peak curve and the experimental variables. The method used to calculate partition constants from peak data is an application of the Langmuir adsorption isotherm (see earlier). The calculation of the area under a characteristic point on the elution boundary is divided into two algorithms, the first is the area of the rectangle preceding any given point on the elution boundary and is given in equation 5.1;

\[
A^r = h \times t \quad (5.1)
\]

where \( A^r \) is the area of the rectangle in voltsecs.

\( h \) is the height of the characteristic point in volts.

\( t \) is the elution time of the characteristic point in secs.

the second is the area under the elution boundary that lies after any given characteristic point and is given in equation 5.2

\[
A^e_1 = (h_1 \times t_d) + (h_2 \times t_d) + (h_3 \times t_d) + \ldots (h_{i-1} \times t_d) \quad (5.2)
\]

where \( A^e_1 \) is the area under the elution boundary after point i.
i is the position of the point on the elution boundary from 1 \( \rightarrow \) n.

n is the position of the final point on the boundary.

h_1 is the current point on the boundary.

td is the time gap between values of h, where td is taken as a constant interval.

Equation 5.3 follows from equation 5.2 if one takes the sum of all h values between i=x and i=n.

\[
A_{e1}^e = td \times \sum_{i=1}^{n} h_i
\]  

(5.3)

All values of \( A_{e1}^e \) are calculated for values of i from 1 to n, where \( A_{e1}^e \) is the area under the peak after the first corrected data value in volts.secs and \( A_{en}^e \) is the area under the peak after the last corrected data value. \( A_{e1}^e \) represents the area after the apex of the peak trace and \( A_{en}^e \) represents the area after the last point on the elution boundary, fig 5.3. Note that n is usually between 500 and 5000.

Now it follows from equation 5.3 that,

\[
A_{e1}^e = td \times \sum_{i=1}^{n} h_i
\]

and that,

\[
A_{e2}^e = td \times \sum_{i=2}^{n} h_i
\]

therefore,

\[
A_{e2}^e = A_{e1}^e - h_1
\]
similarly,

\[ A_{e3} = A_{e2} - h_2 \]

therefore we have equation 5.4;

\[ A_{e1} = A_{e1} - h_{t-1} \quad (5.4) \]

Thus once we have calculated the first area we can calculate the rest in sequence by simply subtracting the proceeding \( h \) value from the previous area. By this method we can calculate a series of areas and by adding these to the corresponding rectangle area we have a series of \( A_b \) values, where \( A_b \) is the total area under the characteristic point. The \( A_b \) values and their corresponding \( h \) values can then be substituted into equation (4.10), to give a series of partition constant \( K_e \) values. These \( K_e \) values are then plotted against the corresponding \( C_g \) values, see eqn. 4.8 for how to obtain \( C_g \), the intercept of the straight line region with the \( K_e \) axis is the partition constant where \( C_g = 0 \), Fig 4.11. \( K_p \) can then easily be calculated by substitution into equation 4.19

\[ K_p = K_e \times \left( \frac{M_2}{R \times T} \right) \quad (5.5) \]

where \( R \) is the gas constant taken as \( 8.2056 \times 10^{-2} \text{ atm mol}^{-1} \text{ deg}^{-1} \).

\( T \) is the temperature in degrees Kelvin.

\( M_2 \) is the adsorbate molecular weight in g mol\(^{-1}\).

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FIGURE 5.3 Calculation of $A^r A^e_i$ and thus $A_h$ to $h$ ratios
LONG ELUTION TIMES - METHODOLOGICAL MODIFICATIONS

Due to the long elution times of adsorbates such as tetrachloromethane and dichloromethane it was necessary to modify the methodology in two ways.

a) Modification of QBas program Input.Bas

The program had to be adapted in order to collect elution times in excess of 65,536 seconds, which is the upper limit of 'Single Integers' in QBas. The modification changes all variables associated with elution time to 'Long Integers' with a new upper limit of $4.2 \times 10^9$ seconds.

USE OF CHART RECORDER.

Contrary to common belief it was found that chart recorders increased the precision of elution time measurements made with the data acquisition software. The reason for this is the slower response time of chart recorders. The slower response time of chart recorders compared with modern on-line computers has been found to be advantageous when determining elution times. All signals are subject to mains and other electrical interferences. The 'mains' noise doesn't affect the chart recorder as it is designed to record changes in overall signal received, rapid periodic oscillations such as 'mains' noise causing no overall change are thus not recorded. The on-line computer is however, capable of recording all these oscillations and consequently the signal is noisier and elution times are more difficult to observe.

Thus elution peaks are now recorded with the on-line computer but the elution time is obtained from a chart recorder monitoring the same signal. The source code for both programs can be found in the appendices.
DETERMINATION OF OPTIMUM COLUMN SIZE
The optimum column size is that column size which gives correct partition constants for a range of adsorbates in the shortest possible time. If the column is too short the adsorbate is not equilibrated and the partition constants will not be correct. If the column is too long the elution time will be too long and results will be only slowly obtained. The situation is further complicated by a long column. Long columns give broad elution boundaries, as these approach the partition region they can be very close to the baseline and thus the signal:noise is lowered introducing larger errors. The error introduced by a very broad elution boundary is more likely to occur as the homologues series is ascended and adsorbance becomes stronger.

With the Ambersorb adsorbents it has been found that adsorbance increases very sharply as the adsorbates size is increased, so that unacceptable waiting times for adsorbates are very quickly reached,(up to 30 hours is regarded as acceptable). For these reasons it was necessary to have at least two columns, a short column of about 0.1g for the more highly retained adsorbates and a long column of about 0.2g for the less retained adsorbates such as the chlorofluorocarbons (CFCs).

DETERMINATION OF OPTIMUM FLOW RATE
Various flow rates were attempted to determine Height equivalent to a Theoretical Plate (HETP); it was found that flow rates between 40–65 cm³/min had acceptable plate heights and for optimum speed around 60cm³/min was used in practice.

INJECTION TEMPERATURE
In order to determine the effect if any of injection temperature an experiment was carried
out in which injection temperatures were varied between 20°C and 100°C, it was found that this had no observable effect on retention of CFC 21. Thus an injection temperature of 80°C was chosen so as to volatilize the organic sample.

** ADSORBATE STANDARD **

For comparisons of both short and long columns and also as a measure of column deterioration it was decided to use a standard. Therefore ethanol was used to check that short and long columns which contain differing amounts of adsorbent give the same partition constant for ethanol per gram of adsorbent, thus indicating that there are no secondary processes due to the use of short columns which affects adsorption. In addition the ethanol standard was used to check that any one column gives the same partition constant as the column is aged. The partition constants for ethanol are given in table 5.1.

**Table 5.1**

<table>
<thead>
<tr>
<th></th>
<th>New Column</th>
<th>After injection of five other adsorbates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>logKₑ</td>
<td>logKₑ</td>
</tr>
<tr>
<td>Long Column</td>
<td>2.10</td>
<td>2.07</td>
</tr>
<tr>
<td>(0.2139 grams)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short Column</td>
<td>2.15</td>
<td>2.12</td>
</tr>
<tr>
<td>(0.1055 grams)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The long column gives a marginally smaller partition constant than the short column in both cases, and it seems likely that one can rule out a slight contribution to desorption resulting from the shortness of the column as this would have the effect of giving smaller
partition constants for short columns not higher ones. The 0.05 log unit difference can be more reasonably assigned to experimental error. The columns may be showing some slight deterioration with time but the accuracy of the technique is only +/−0.1 log units. So this is an acceptable error as long as the effect does not exceed the +/−0.1 range.

OBSERVATIONS RELATED TO THE PEAK SHAPE.

The peak shape is a very telling factor in determining what interactions have taken place on the column, between the adsorbate and adsorbent. The peak shapes can be divided into three main categories.

a) Non equilibrated peak curve

This peak curve characterized by a sharp frontal boundary appearing immediately after injection and an elution boundary almost as sharp with little or no tailing implies that the adsorbate did not reach equilibrium with the adsorbent and a longer column should be used for this adsorbate. The simple solution to use a longer column is so obvious and in keeping with common sense that little research has been done on non equilibrated peaks. In this work however, it was necessary, due to the constraint of working at 25°C, to use the shortest column possible that was still commensurate with adsorbate adsorbent equilibrium. In the process of finding the shortest column an interesting effect was observed. The peak shape in some instances shows immediate elution as in the semi equilibrated case but thereafter displays an equilibrated elution boundary. The peak shape is shown in figure 5.5 together with the limits of non equilibrium and equilibrium fig 5.4 and fig 5.6.
FIGURE 5.4 Non Equilibrated Peak Shape on Adsorbents
FIGURE 5.5 Semi-Equilibrated Peak Shape on Adsorbents
FIGURE 5.6 Equilibrated Peak Shape on Adsorbents
It is interesting to note that although clearly non-equilibrated pathways have been found through the column in fig 5.5, the majority of molecules have attained equilibrium as displayed by the diffuse elution boundary. The observation could be explained by some mass transfer limitation. The mass transfer of molecules into the micropores may take too long for all the molecules of a sample if the column is sufficiently short. We are probably operating at the limit where mass transfer into micropores is equivalent to adsorbent exposure time of a gas molecule.

b) Equilibrated peak curve

This peak curve is characterized by a mildly diffuse frontal boundary eluting some time (>2 mins) after injection and having a very diffuse elution boundary coming out for up to 30 hrs. This peak has reached equilibrium, that is complete mass transfer into micropores has been effected, and would be saved and processed, fig 5.6.

c) Long peak curve

This peak curve has a very diffuse frontal boundary eluting some hours after injection and an almost imperceptible elution boundary over many hours (in excess of 30). The error introduced by the proximity of the elution boundary to the baseline renders this peak unprocessable to any degree of accuracy. The solution is to increase the amount injected or use a shorter column.

Apart from the three elution curves discussed above there is a fourth situation where no peak appears to be eluted at all when using a TCD detector. The problem disappears when one uses an FID detector and the reasons will be discussed below.

d) No Apparent Peak

It has been observed that when carbon tetrachloride (CCl₄) is injected onto the column for the first time it is not eluted. This lack of elution is observed after several repeat
injections but after a given amount has been injected the CCl₄ does finally elute on each injection as expected. It is possible that CCl₄ and perhaps other compounds are being effectively trapped on the column by narrow pores. The Ambersorb resins do contain a large proportion of 4.3–6Å pores as well as a larger proportion of 35–300Å pores and it may be that the spherical CCl₄ molecule, of radius 2.73Å [92], is becoming trapped in the smaller pores and effectively blocking some of the active sites off. Indeed there is experimental evidence that shows that adsorbance of ethanol on Ambersorb 572 is reduced significantly after injection of CCl₄ onto the column (table 5.2).

Table 5.2

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>logKₑ of ethanol before CCl₄ injection</td>
<td>2.12</td>
</tr>
<tr>
<td>logKₑ of ethanol after single CCl₄ injection</td>
<td>1.96</td>
</tr>
<tr>
<td>logKₑ of ethanol after repeated CCl₄ injections</td>
<td>1.69</td>
</tr>
</tbody>
</table>

The possibility that not all the sites are now active could explain the reduced adsorbance of ethanol after CCl₄ has been injected. The fact that there are a large proportion of 35–300Å pores would explain why CCl₄ does eventually elute as normal. Presumably once all possible trapping sites are blocked off the CCl₄ is able to be eluted, after adsorption as normal on the remaining non-blocked sites, giving an isotherm for the non-blocked portion of the column. But the adsorption isotherm would not now be representative of the whole adsorbent sample, it would only represent adsorption on active sites of the non-blocked areas of the column.

The explanation given above would be in line with the TVFM theory, whereby the CCl₄ molecules are initially filling the high potential micropores before being adsorbed onto the less active mesopores.
If the hypothesis is correct values for adsorbate partition constants need to be checked and in each case it is important to be sure no previously injected compound is still occupying active sites, in which case any subsequent partition constant may not be representative of all the active sites of the adsorbent.

Attempts were made to find a method of releasing the trapped gases, in order to restore the columns to their full activity. When using FID detectors, injecting a water sample was useful as a check for trapped gases as this forced some of the gas from the column. However, the technique was not sufficient to flush the column completely and the only technique that would restore the column to its original condition was to recondition at 110°C for 24 hours.

Although this method greatly slowed progress and the gathering of data it was deemed the only sure way of obtaining reproducible and reliable partition data on these adsorbents.
HUMIDITY STUDIES

i) HUMIDITY EFFECTS

The work carried out using dry helium as carrier gas was useful to quantify the potential adsorptivity of the adsorbent studied. The dry helium was passed through the column for 24 hours at 110°C in order to purge it of any contaminants and then the adsorbate was injected into the column. The resulting elution peak could be used to calculate partition constants and under dry conditions this is a reflection of adsorbate–adsorbent affinity only. As detailed in chapter three a whole series of adsorbate partition constants allow us to characterise the adsorbent by LSER and MLR.

Some work has been carried out by McGill [93], at 31% humidity on several adsorbents and at 53% on one adsorbent, Amberlite 393 at 298.2K, but at 31% and to some extent at 53% the water adsorption on carbon adsorbents is known to be quite low (fig.5.7). As can be seen from figure 5.7 it is at humidities above 60% that high water uptake is observed and as these humidities are not uncommon in many real applications it would be interesting to study the effect of higher levels of humidity on adsorption. It is expected that once equilibrium is attained a high percentage of active sites will be occupied by water molecules on the adsorbent surface and that adsorption of challenge adsorbate will be greatly altered. The degree of hydrophilicity of the adsorbent and the level of humidity in the gas stream will determine how much the column adsorption capacity is affected. Work has been carried out at around 80.7% humidity using a potassium bromide salt solution, to humidify the helium gas stream.

ii) HUMIDITY CONTROL ON THE TCD SYSTEM

A range of humidities can be conveniently obtained by use of the differing water vapour pressures above saturated salt solutions. For example saturated potassium bromide at 298.15K has a relative humidity of 80.7% and sodium nitrate has a humidity of 73.8%.
When a stream of dry gas is bubbled through a saturated salt solution the resulting level of humidity in the gas stream, given that the gas is allowed to reach equilibrium with the solution, will be equal to that above the saturated solution. The required level of humidity is thus attained by bubbling a stream of dry helium through a Dreschel bottle that contains the required saturated salt solution prior to passing the vapour over the adsorbent. As discussed earlier a level of humidity that causes relatively high water adsorption is necessary to see the effects on adsorption of high adsorbate water intake and also to reproduce common field conditions.
FIGURE 5.7 WATER ADSORPTION ISOTHERMS

![Graph showing water adsorption isotherms for different materials.]

- AMBERSORB 563
- AMBERSORB 564
- AMBERSORB 572
- CALGON BPL
It is found that at high levels of humidity, above 50%, strict temperature control is necessary. Variations in the level of humidity had to be negligible during the course of the experiment for two reasons; firstly, a constant level of humidity on the column gave reproducible adsorbate-adsorbent isotherms; and secondly, variations in humidity not only affected adsorbate-adsorbent equilibrium but gave a varying baseline (as the TCD detector used is sensitive to water), rendering the elution boundary and subsequent partition constants inaccurate. The effects on the baseline of variations in the level of humidity were unacceptable when the deviations were high enough to affect the curvature of the elution boundary and consequently partition values.

The causes of variations in the level of humidity were several. These variations together with changes in detector temperature and flow rate could all affect the output signal, from which isotherms were obtained. During the normal course of an experiment, detector temperature variations were usually small, +/-0.1°C, and this did not significantly affect the response to the eluting gas.

Flow rate variations not usually found at 0% humidity can be present at higher humidities. The variation in flow were caused by the slow deposition of salt on the inlet tube of the Dreschel bottle. The dry gas coming through the inlet tube takes up water vapour from the surrounding saturated solution this causes local supersaturation and hence crystallisation of the salt which was deposited on the walls of the inlet tube. Consequently, the inlet tube became narrower and this affected flow rate. In time the inlet tube became blocked completely, arresting gas flow. A safety cut-out switch protected the TCD detector filaments from the damage that would occur upon cessation of helium flow. The cut-out switch consisted of a mercury capillary manometer with platinum contact points. A significant drop in line pressure, perhaps due to a blocked Dreschel head, caused a contact to be made which cut the power to the TCD.

A significant increase in line pressure, perhaps due to a blocked column after the manometer, also caused a cut in power to the TCD. In both the cases outlined above
helium flow to the TCD detector filament is arrested or greatly reduced and this effect which would cause the filaments to be damaged or destroyed was thus protected against. The solution was to use a specially widened tube in the Dreschel head so that the rate of change of flow was retarded and the lifetime of continuous flow was lengthened considerably. This alleviated the problem of tube blockage occurring and a satisfactorily constant flow was obtained throughout adsorbate elution.

Line temperature fluctuations, where the line is any point between Dreschel humidity bottle inlet and detector inlet, were now found to be the main cause of deviations in the level of humidity. Only small changes caused relatively large deviations in the TCD baseline rendering elution boundaries inaccurate. Local variations in line temperature have been observed to be of three types: firstly, the humidity bottle head is exposed to the air unlike the rest of the bottle which is underneath the surface of a thermostatted water bath. If the temperature of the air above the bath varies significantly from the temperature of the bath the water/water vapour equilibrium will be affected. In addition evaporation of bath water where it meets the outside of the bottle causes local cooling of the glass and this in turn may affect the water/water vapour equilibrium inside the bottle, these changes will be somewhat re-equilibrated by post bottle diffusion and are seen as low amplitude baseline fluctuations, fig 5.8; secondly, evaporation on the outside of the column at the bath surface can cause local cooling within the column and condensation, in this case due to proximity to the detector the variation is seen as a sharp fluctuation followed by a slow return to the baseline, fig 5.9; thirdly, if the temperature of any part of the line falls below that temperature where the relative humidity rises to 100% then condensation takes place within the line and depending on proximity to the detector can cause high or low amplitude baseline fluctuations. As the humidity level of study approaches 100% an increasing amount of difficulty in avoiding condensation is experienced. In addition at higher humidities any relative change has a larger magnitude than the same relative change at a lower humidity and there is consequently a limit to the
level of humidity at which it is possible to carry out work in a non thermostatted laboratory using a TCD. Nevertheless it is preferable to go as high as is possible in order to observe the full effect on adsorption, and initially, not lower than 50% where due to low water adsorption the effect of humidity is expected to be slight.

Both Dreschel bottle and column were both submerged in a thermostatted bath at 25°C and the laboratory temperature was kept above that at which condensation would occur. The gas line was lagged to prevent sharp variations in temperature.
FIGURE 5.8 LOW AMPLITUDE BASELINE FLUCTUATIONS
FIGURE 5.9 HIGH AMPLITUDE BASELINE FLUCTUATIONS
iii) HUMIDITY MEASUREMENT TECHNIQUES ON THE TCD AND FID SYSTEMS.

An attempt was made to measure water vapour levels by comparing a sample of unknown humidity with one of known humidity. A sample was taken from the injection port of the humidity line and injected into a second column where the carrier gas is dry helium. The standard used was saturated water vapour at a known temperature for which the partial pressure was known. Comparison of the peak areas for water in each case after correcting for differences in temperature and sample size should have given the relative humidity (equations 5.6–5.9).

Assuming ideal behaviour for any vapour

\[ P_1 V_1 = n_1 R T_1. \] (5.6)

where;

- \( P_1 \) = Water vapour pressure at temperature \( T_1 \)
- \( V_1 \) = volume of gas
- \( n_1 \) = number of moles of gas
- \( R \) = the gas constant
- \( T_1 \) = temperature of the vapour

for two vapours 1 and 2,

\[ \frac{P_1}{n_1 R T_1} = \frac{P_2}{n_2 R T_2}. \] (5.7)

when \( V_1 = V_2 \) which is the case when equal sample sizes are injected.
Simplifying:

\[ \frac{n_2}{n_1} = \frac{P_2}{P_1} \]  

(5.8)

when both samples are taken at the same temperature.

If \( P_2 \) is the partial pressure of sample and \( P_1 \) is the partial pressure of the standard then;

\[ A_2 = H_R A_1 \]  

(5.9)

where:

\[ A_1 = \text{Area in volt.seconds of standard water vapour peak and is proportional to } P_1. \]

\[ A_2 = \text{Area in volt.seconds of sample water vapour peak which is assumed to be proportional to } P_2. \]

\[ H_R = \text{Relative humidity expressed as a fraction.} \]

Therefore the relative humidity can be calculated using the relative areas of a sample and standard peak if sample size\( (V) \) and temperature of sample\( (T) \) are equivalent. Humidity studies were begun and although as previously described certain difficulties were encountered with the thermal conductivity chromatographs (TCD) the use of a flame ionisation detector (FID) provided a much better system. Calibrations of the results on the FID system with those obtained previously on the TCD were attempted and are discussed later.

The disadvantage of the FID is that it does not respond to water and the humidity level would have to be measured by taking samples of inlet gas periodically and measuring the water level on a TCD. However its disadvantage is at once its advantage. The FID unlike the TCD has no response to water and small variations in humidity which would not
significantly affect adsorbance but would affect the TCD baseline have no effect on the FID baseline. Carrier gas flow rate is more difficult to measure on the FID due to interference from the flame gases but can be obtained by temporarily suspending the flame gases.

As mentioned previously an attempt was made to measure humidity by the use of GSC utilizing the TCD's sensitivity to water. A headspace sample of water vapour was used as a standard. The humidity was tested at intervals by removing samples of humid carrier gas from the GC injector port and injecting it onto a second GC column which was water retentive and measuring the area of the resulting water peak. The second GC was fitted with a water sensitive TCD. The column material was Ambersorb 572 which although relatively hydrophobic gave better results than a hydrophilic column such as Ambersorb 511. Presumably, the greater dispersive strength of 572 outweighs the basicity of 511 to attract water molecules. The sample peak area was compared with a standard headspace sample which was saturated in water vapour at the same temperature as the column. The headspace vapour was effectively at 100% relative humidity. The relative humidity of the carrier gas could thus be ascertained by comparison. It was found that variations in measurements, due to condensation in the syringe and fluctuations in the humidity channel lead to variations of up to 20% in measurements.

A more successful method of measuring humidity was found to be gravimetric analysis. Three U-tubes, each containing 50g of calcium chloride mixed with molecular sieves in a 1:1 ratio were dried overnight at 110°C in a vacuum oven and brought to room temperature in a vacuum desiccator. The weight of the cooled U-tubes was recorded. The tubes were placed in series at the outlet of the humidity line, which had been allowed to reach equilibrium overnight. The use of a mixture of calcium chloride and molecular sieve gave only a slight pressure drop of a few millimetres compared with that of calcium chloride alone. The calcium chloride also tends to form a crust increasing pressure drop but if mixed with molecular sieve the crust was sufficiently broken so as
not to affect pressure drop. The humidity stream was allowed to pass through the tubes for a period in excess of 5 hours. The tubes were then capped and reweighed separately. The weight of the third tube in the series should remain constant, showing that no water has escaped. In practice all water was trapped by the first tube. By finding the amount of water in the tube and knowing the flow rate and the temperature the partial pressure of water and hence the humidity of the carrier gas stream could be calculated.

The method is shown below in equations 5.10–5.13.

According to Boyle's Law;

\[ P_w V_e = n_w R T \]  \hspace{1cm} (5.10)

Where;
- \( P_w \) is the partial vapour pressure of water in atmospheres.
- \( V_e \) is the volume of humid carrier gas in dm\(^3\).
- \( n_w \) is the number of moles of water in the carrier gas.
- \( R \) is the gas constant, 0.08205 dm\(^3\).Atm.K\(^{-1}\).Mol\(^{-1}\).
- \( T \) is the temperature of the column in degrees Kelvin.

The measured volume of carrier gas passing through the column in a given time is;

\[ V_m = F_m t \]  \hspace{1cm} (5.11)

where;
- \( F_m \) is the observed flow rate in dm\(^3\) sec\(^{-1}\).
- \( t \) is the time taken in secs.

The actual volume of humid carrier gas can then be given as;

\[ V_e = F_c t \]  \hspace{1cm} (5.12)

Where;
- \( F_c \) is the corrected flow rate taking pressure drop and humidity into account such that;
\[ F = F_m \cdot J^2 \cdot (P_o - P_w^f) / P_o \cdot P_f / (P_f - P_w^c) \] (5.13)

Where;
- \( P_o \) is the outlet pressure (i.e. the atmospheric pressure).
- \( P_f \) is the inlet pressure (i.e. the atmospheric pressure plus the pressure drop across the column).
- \( P_w^f \) is the water vapour pressure in the flow meter.
- \( P_w^c \) is the contribution to measured inlet pressure of the pressure of water vapour in the column.
- \( J^2 \) is the pressure correction factor required to correct for the pressure gradient across the column.

This equation and its various modifications will be derived toward the end of the chapter.

Using \( V_e \) as defined and Boyle's Law the vapour pressure of water, \( P_w \), can be calculated and the actual relative humidity obtained using Eqn 5.14.

\[
\text{RH} = \frac{P_w}{P_{VP}} \quad (5.14)
\]

where;
- \( \text{RH} \) is the relative humidity.
- \( P_w \) is the water vapour pressure in the column.
- \( P_{VP} \) is the vapour pressure of water at the temperature of the column.

The \( \text{RH} \) thus calculated can be compared with that expected by use of Eqn 5.15.

\[
\overline{P_w^c} = \frac{P_w^c \cdot P_o / P_f \cdot J^2}{(5.15)}
\]

where;
- \( \overline{P_w^c} \) is the predicted average humidity across the column.
- \( P_w^c \) is the assumed humidity above the salt solution at the operating temperature and atmospheric pressure.
Equation 5.15 takes account of the humidity change across the column due to the pressure gradient.

In the present study potassium bromide salt solution was used. Potassium bromide gives a theoretical humidity of 80.7%. Due to variation in the relative humidity with pressure drop in practice it is nearer to 70%. It is important to try and keep the pressure drop to a minimum so as not to have large variations in relative humidity on different columns. Thus valid comparisons of the effect of humidity can be made on different columns.

IMPROVED METHODOLOGY USING FID SYSTEMS

The incorporation of the FID to replace the TCD was carried out, as discussed previously, in order to facilitate the collection of peak data at high relative humidity. Such collection had previously been found to be too difficult with the TCD due to its sensitivity to small changes in the humid air stream.

However, partition constants for several adsorbents at 0% humidity had already been obtained on the TCD system. It was important to know if these constants could be compared with constants obtained under humid conditions on the FID system. In order for these comparisons to be valid both detection systems should give the same partition constants if conditions were identical. Thus before any data could be collected on the FID system at high humidity it was necessary to obtain data at 0% humidity for a few standard adsorbate/adsorbent partitions and compare the partition constants so obtained with those previously obtained on the TCD system at 0% humidity. If the standard compounds gave equivalent constants on the two systems then constants obtained under humid conditions using the FID could be compared with those obtained under dry conditions on the TCD. This would render any further characterization at 0% humidity on the FID unnecessary and would save considerable time and effort.

Three compounds were compared under identical conditions of 298.15K and 0% humidity and the averaged partition constants are shown below in table 5.3.
Table 5.3

Preliminary Partition Coefficients* on Ambersorb 572 at 0% Humidity & 298.15K

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>FID</th>
<th>TCD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Log K&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Log K&lt;sub&gt;p&lt;/sub&gt;</td>
</tr>
<tr>
<td>Chlorodifluoromethane</td>
<td>1.86(1.84)</td>
<td>2.40(2.38)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.91</td>
<td>3.18</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>1.87</td>
<td>2.18</td>
</tr>
</tbody>
</table>

* The partition coefficients were obtained on a column that is too short to give accurate partition coefficients but is nevertheless still useful for FID/TCD comparisons as values are repeatable.

Where; Log K<sub>c</sub> is the Log partition constant with respect to concentration.

Log K<sub>p</sub> is the Log partition constant with respect to partial pressure.

It is quite clear from the table that the FID gives larger partition coefficients than the TCD. The figures in parenthesis are the observed partition coefficients for a second sample of adsorbate injected immediately after the first sample appeared to have eluted. The lowered values for the partition coefficients on the TCD indicate that the first sample has not been fully eluted despite the detector showing full elution. This effect is not as marked with the FID which gives reproducible values for short adsorbates although with longer adsorbates reconditioning is necessary for good reproducibility. The plot in figure 5.10 of the values in table 5.4 shows a comparison of partition coefficients obtained for the same adsorbates on the TCD & FID systems.
<table>
<thead>
<tr>
<th>Compound Name</th>
<th>( K_x ) (TCD) ( \text{dm}^3\text{g}^{-1} )</th>
<th>( K_x ) (FID) ( \text{dm}^3\text{g}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>4.4</td>
<td>11</td>
</tr>
<tr>
<td>Propane</td>
<td>72.4</td>
<td>497</td>
</tr>
<tr>
<td>Dichlorodifluoromethane</td>
<td>95.5</td>
<td>674</td>
</tr>
<tr>
<td>Dichlorofluoromethane</td>
<td>213.8</td>
<td>1,477</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>288.4</td>
<td>2,156</td>
</tr>
<tr>
<td>Ethanol</td>
<td>245.4</td>
<td>954</td>
</tr>
</tbody>
</table>

It can be seen that a general linear relationship exists but that the FID system exhibits more rapidly increasing constants as stronger adsorbates are introduced onto the column.

**EFFECT OF SENSITIVITY OF SYSTEM**

The larger partition values when one uses the FID system were due in part to the method of calculation of partition constants that was used in this work. Partition constants, \( K_x \) and \( K_p \), were obtained by finding the relative concentration between the solid and gas phases \( C_x / C_g \) as the concentration in the gas approached infinite dilution. The starting point for calculations is the choice of the elution boundary endpoint. The endpoint of a chromatographic peak can be said to be that point at which the peak elution boundary becomes indistinguishable from the succeeding baseline and for accurate calculations this point should be close to the actual endpoint (i.e. the point at which zero surface coverage is restored). The signal response to the eluting gas is dependent upon the sensitivity of the detector and this response is lower for a thermal conductivity detector \( (1 \times 10^{-6} \text{g}) \) than it is for a flame ionization detector \( (1 \times 10^{-8} \text{g}) \).
This affected the calculated partition constants by influencing the choice of endpoint.

FIGURE 5.10 Comparisons of TCD & FID Partition Coefficients (K) on Ambersorb 572 at 0% Humidity and 298.15K

As the sensitivity of the detector varies the point at which the elution boundary becomes indistinguishable from the succeeding baseline also varies. The extent to which endpoint was affected depended on the sharpness of the distinction between the elution boundary and the baseline. When this distinction was sharp the area for error was only slight (Figure 5.11,5.12) but when the distinction was broad the area for error could be very large (Figure 5.13). In practice this meant that good agreement was observed between TCD’s and FID’s for compounds with small partition values but large differences were
found for compounds with larger values (table 5.4). As the partition constants on the FID were higher than those of the TCD, it was deemed unsatisfactory to lower the sensitivity of the FID in order to be able to correlate results obtained on the two systems, as the FID values obtained at high sensitivity were necessarily the most accurate being closer to the point at which zero surface coverage was restored.

One of the practical consequences of using a TCD is that when the longer compounds with larger partition values are detected their observed endpoint is so much less than the true endpoint that a significant amount of adsorbate material may still be on the column, this effect was discussed earlier with respect to the so-called trapping of CCl\textsubscript{4}. The material may still be on the column when the next injection occurs and could so affect the nature of the column as to render any subsequent partition coefficient obtained, incorrect and unreproducible. This indeed was the case with the TCD and some difficulty was experienced in obtaining reproducible partition coefficients. However, as yet no difficulty of this kind has been found with the FID, although this does not preclude the possibility that it could happen if the broadness of the adsorbate elution boundary was sufficiently great as to keep the boundary beyond the limit of detection for a significant proportion of its true elution time.

The peaks succeeding baseline should have the same signal response as the peaks preceding baseline given that any external variables such as pressure and temperature have remained constant during the period of elution. In practice these external variables do not remain constant and in most cases the endpoint is an averaged value from several peaks in order to minimize errors due to temperature and pressure variations.
FIGURE 5.11 Comparisons of Peaks Obtained on FID & TCD for Chloromethane on
Ambersorb 572 at 0% Humidity and 298.15K

VARIATION OF FLOW RATE

The effect upon the partition coefficient of variations in flow rate was studied between $1 \times 10^{-4}$ dm$^3$s$^{-1}$ and $2.5 \times 10^{-5}$ dm$^3$s$^{-1}$ and found to vary between $+/-.05$ log units. There is no apparent change in partition coefficient as flow is increased and this implies that equilibrium has been achieved between these ranges. Due to the high adsorbance and long elution times in this work the flow was kept at about $1 \times 10^{-4}$ dm$^3$s$^{-1}$ in order achieve rapid results without being so high as to lead to non-equilibration of adsorbate.

MODIFIED FLOW RATE CORRECTION

The measured flow rate, $F_m$, at the outlet of the bubble meter differs from the true flow
rate in the column due to pressure and temperature differences in the flow meter, column and the connecting tubing. Thus corrections to the measured flow rate are required in order to ascertain the true flow rate in the column when the experiment was running.

One of the main causes of differences in measured and actual flow rate is the pressure drop as the sample vapour progresses down the column causing it to expand.

FIGURE 5.12 Effect of Detector type on Observed Peak for Chlorodifluoromethane on Ambersorb 572 at 0% Humidity and 298.15K

Consequently, the flow rate at the column inlet, \( F_{1e} \), is lower than the flow rate at the column outlet, \( F_{0e} \). The pressure gradient in the column means that the flow rate, \( F_{n,e} \), at any point \( n \), in the column is dependent upon the pressure at that point.
For measurement purposes it is convenient to calculate the average flow rate in the column given as \( \bar{F}_e \) where:

\[
\bar{F}_e = F_c J^2_3
\]  

(5.16)

and where \( J^2_3 \) is the pressure drop correction factor for obtaining the average flow in the column and is given as:

\[
J^2_3 = 3/2 \cdot \frac{[(P_i/P_o)^2 - 1] / [(P_i/P_o)^3 - 1]}
\]  

(5.17)

where \( P_i \) is the column inlet pressure and \( P_o \) is the column outlet pressure.
The relationship between the flow rate at the column outlet, \( F^{\circ}_c \), and the measured flow rate, \( F_m \), depends upon the experimental conditions of flow meter temperature, water vapour pressure in the flow meter, the humidity of the gas stream and post column pressure drops not assignable to the column but to tubing and connections. Corrections for each of these conditions will be considered in turn. In each case we need to find \( F^{\circ}_c \) in terms of measurable quantities in order to determine the average flow rate in the column.

CASE 1: Flow without bubble meter.

This is the simplest case and is shown by figure 5.14. It can readily be seen that in this case \( F_m \) at point M would be equal to \( F^{\circ}_c \), which is thus directly determinable by measuring \( F_m \).

\[
F^{\circ}_c = F_m \quad (5.18)
\]

\[
P'_t = P'_o + P_d \quad (5.19)
\]

where \( P_d \) is the pressure drop across the column.

CASE 2: Correction for Bubble Meter.

It is however necessary to attach a bubble meter at point C in order to measure the flow rate at that point. Consequently, the water vapour in the bubble meter causes a drop in the effective atmospheric pressure at C by contributing to the eluent gas pressure, making it easier for gas to elute. This is shown in figure 5.14.

\( P'_o \) is the outlet pressure of the column while the flow rate is being measured and is related to \( P_o \) by equation 5.20.

\[
P'_o = P_o - P^{f}_w \quad (5.20)
\]
where $P^f_w$ is the saturated water vapour pressure at the temperature of the flow meter, $T_f$.

Assuming that the gas in the bubble meter is saturated with water.

Now assuming conservation of mass;

$$P'_o \cdot F_m = P_o \cdot F^o_c$$  \hspace{1cm} (5.21)$$

and eqn 5.18 now becomes;

$$F^o_c = F_m \cdot [(P_o - P^f_w) / P_o] \cdot T_c / T_f$$  \hspace{1cm} (5.22)$$

where $T_c / T_f$ is a correction for temperature differences in the column and flow meter.

Thus the overall correction to flow rate for measurement made with a flow bubble meter can be obtained by substitution into equation 5.16 and becomes;

$$F_t = F^o_c \cdot [(P_o - P^f_w) / P_o] \cdot T_c / T_f$$  \hspace{1cm} (5.23)$$

Case 1 and 2 apply for dry carrier gas. The situation is more complex for wet carrier gas.

CASE 3: Flow rate correction for a humid carrier gas

The situation is analogous to that for case 2 except there is now have an intrinsic water vapour pressure in the carrier gas, $P^*_{w}$. The components of pressures can be given as;

$$P_1 = P_{He} + P^*_{w}$$  \hspace{1cm} (5.24)$$

$$P'_o = P'_{He} + P'_{w}$$  \hspace{1cm} (5.25)$$

$$P_o = P'_{He} + P^*_{w}$$  \hspace{1cm} (5.26)$$

Thus as the pressure of water in the flow meter can only increase the water vapour in the
gas stream by the amount by which it exceeds the pressure of water already in the gas stream, equation 5.20 becomes;

\[ P_o' = P_o' + P_{fw} - P'_w \]  

(5.27)

\( P'_w \) is difficult to determine but assuming ideality;

\[ \frac{P_{He}}{P'_He} - \frac{P_w}{P'_w} \]  

(5.28)

as the pressure drop must be equivalent on both components of the gas stream.

Substituting from equations 5.24 and 5.26 we obtain;

\[ P_w' = P_w \cdot \frac{(P_o - P_{fw})}{(P_f - P_{fw})} \]  

(5.29)

Substituting equation 5.29 into equation 5.27 we obtain \( P'_o \) in terms of measurable quantities and by rearrangement and use of the relationship in equation 5.21, equation 5.22 becomes;

\[ \frac{P_o}{F_m} = \frac{[P_o - P_{fw}]}{P_o} \cdot \frac{P_f}{P_f - P_{fw}} \cdot \frac{T_e}{T_f} \]  

(5.30)

and thus we obtain the corrected average flow rate in the column;

\[ \frac{F_e}{F_m} = \frac{[P_o - P_{fw}]}{P_o} \cdot \frac{P_f}{P_f - P_{fw}} \cdot J_{c3} \cdot \frac{T_e}{T_f} \]  

(5.31)

In the fourth case below we consider post column pressure drops.
CASE 4: Post Column Pressure Drops

Post column pressure drops are usually caused by constrictions in the connecting tubing between the end of the column and the detector. If a post column pressure drop is present it will contribute to the observed column pressure drop and in that case corrections need to be performed so that the true pressure drop of the column can be ascertained and subsequently the corrected average flow rate in the column.

The situation is shown in fig 5.14. The situation after the constriction is analogous to case 3, so that the true flow rate after the constriction, \( F^t \), can be given as;

\[
F^t = F_m \cdot \frac{([P_o-P^{w}_{f}]/P_o)}{[P_f/P_f-P^{w}_{f}]} \cdot \frac{T_c}{T_f} \tag{5.32}
\]

Now by the conservation of mass;

\[
P_o \cdot F^t = P'_o \cdot F^p \tag{5.33}
\]

The value \( P'_o \) can be obtained by comparison of the pressure drop when an empty column is connected and disconnected from the detector, the difference is the post column pressure drop, \( P_{pc} \). \( P'_o \) can be obtained from the relationship;

\[
P'_o = P_o + P_{pc} \tag{5.34}
\]

Thus the corrected flow at the column end when a constriction is present can be given as;

\[
F^c = F_m \cdot [(P_o-P^{w}_{f})/P_o] \cdot [P_f/P_f-P^{w}_{f}] \cdot \frac{T_c}{T_f} \cdot \frac{P_o}{(P_o + P_{pc})} \tag{5.35}
\]

and the average column flow rate in this case would be;

\[
\bar{F}_c = F_m \cdot [(P_o-P^{w}_{f})/P_o] \cdot [P_f/P_f-P^{w}_{f}] \cdot \frac{T_c}{T_f} \cdot \frac{P_o}{(P_o + P_{pc})} \tag{5.36}
\]
This is the final Case 4 correction and it can be readily seen that each of the correction terms simplifies to unity in the limit when $P_{fw}$, $P_{cw}$, or $P_{pc}$ are equal to zero. The term $J'_{3}$ is a modified version of eqn. 5.17 so that $P_{o}$ and $P_{i}$ the measured inlet and outlet pressures become $P'_{o}$ and $P'_{i}$ the true inlet and outlet pressures of the column. This correction could also be used for cases 2 and 3, although in practice the small pressures would make little difference to the final calculation. This is not the case with the pressures associated with constrictions which can be quite large and a correction here is necessary. There is one other correction which is necessary if there is a pre column pressure drop. The situation at the end of the column is analogous to case 4 and can be described by eqn. 5.34 whether $P_{pc}$ is equal to zero or not. However, the measured inlet pressure, $P_{i}$, is no longer the true inlet pressure but the pressure before the pre-column constriction, so that;

$$P_{i} = P'_{i} + P'_{pc} \quad (5.37)$$

where $P'_{pc}$ is the pressure drop across the constriction and $P'_{i}$ is the true inlet pressure. The pressure associated with the initial humidity stream is still $P_{i}$ so the case 3 correction remains unchanged it is only the value for $P_{i}$ in the $J'_{3}$ which now becomes the $P'_{i}$ in the $J'_{3}$ term that changes.

Thus equation 5.36 is a universal flow rate correction where $J'_{3}$ is given as;

$$J'_{3} = 3/2 \cdot [(P'_{i}/P'_{o})^{2} - 1] / [(P'_{i}/P'_{o})^{3} - 1] \quad (5.38)$$

where $P'_{i}$ and $P'_{o}$ are the actual pressures at the inlet and outlet to the column.

Equation 5.36 is the flow rate correction used in this work where each of the terms in the equation may drop out if they are not needed, ie where $P_{fw}$, $P_{cw}$ or $P_{pc}$ are equal to zero and the corresponding term simplifies to unity.
Figure 5.14 Flow Rate Measurement Corrections

CASE 1

CASE 2 AND 3

CASE 4

- $F_o$ measured directly at $M$
- $F_o$ measured indirectly at $C$
- $F_o$ measured with post column pressure drop
VARIATION OF ADSORBATE CONCENTRATION AND NON-IDEALITY

It is convenient to discuss non-ideality at this point in order to understand fully the effects of concentration on peak shape. Non-ideality describes those processes operating on a peak which cause band spreading. There could be said to be two types of band spreading, normal and abnormal.

Normal band spreading processes are those effects that we would expect to find on any chromatographic column such as adsorbate diffusion, resistance to mass transfer causing non-equilibrium and spreading due to non-equivalent flow paths in a packed bed. Abnormal processes are less general in nature and are more often concerned with the particular column involved. Abnormal processes include slow desorption from high energy sites, reactions involving the adsorbate and occurring on the column, and very slow diffusion-controlled mass transfer between phases. The last process differs only in degree from the normal process.

The effect of sample size on the elution curve and hence the partition coefficient should be negligible if non-linear adsorption far outweighs non-ideality [94]. Concentration does affect partition coefficients outside the infinite dilution range due to the sorption and thermal effects [95], but these effects are not significant in the concentration range of this study. However, when considering isotherm curvature outside the infinite dilution range the sorption effect and to a lesser extent the thermal effect need to be taken into account.

The test to determine if non-linearity is predominant is to vary concentration. If non-ideality is large compared with non-linearity elution boundaries at different concentrations will not coincide but the higher concentration will overlap the lower one (fig 5.15). If non-ideality is small compared with non-linearity the elution boundaries of peaks of varying concentration should coincide (fig 5.16, 5.17). For non-linearity to far outweigh non-ideality columns should be of 2–3 metres length according to Conder & Young [96], while Huber and Keulemans [88], suggest at least one metre.
FIGURE 5.15 Effect of Concentration on Peak Shape for Ethene on Sutcliffe Speakman 207A at 0% Humidity and 298.15K.
FIGURE 5.16 Effect of Concentration on Peak Shape for Difluorodichloromethane on Sutcliffe Speakman 207A at 0% Humidity and 298.15K.
As discussed in previous reports, due to the high adsorptive strength of the adsorbents studied, columns of this 'normal length' would be impractical due to the very long elution times required.

In addition, the non-ideality, normally expected on a short column to outweigh non-linearity, is not always found with the carbons studied to be sufficient to cause significant deviations in partition coefficients.

We have found that for adsorbents with high dispersive strength non-ideality does not always outweigh non-linearity when the column is less than Conder & Young’s and even Huber & Keulemans minimum prescribed length [96,88], see Fig 5.16 where the peak data is from a 35mm column.
Diffusion is probably the major contributor to non-ideality and affects the choice of elution endpoint. Diffusion varies with size of injected sample and if the adsorption is sufficiently weak then it may have a significant effect on elution time. The calculated partition coefficient, values for ethane, a weak adsorbate, on Ambersorb 572 have been found to vary between $K_e = 5 \text{ dm}^3\text{g}^{-1} - 12.5 \text{ dm}^3\text{g}^{-1}$ (dm$^3$ of carrier gas to fully elute adsorbate per gram of adsorbent), depending upon the concentration of adsorbate as well as length and width of the column. Nevertheless, weakly adsorbed species, such as methane, ethene and ethane, are found to give reproducible results on columns of around only 10cm in length in some cases. For strongly adsorbed species where diffusion of the adsorbate is negligible when compared with desorption rate, non-linear effects are found to predominate down to column lengths as low as 3cm.

In order to get reproducible values it is necessary to make columns of sufficient length to minimize non-ideality and allow non-linearity to be observed. Due to large differences in adsorbate retention however the column length needed for non-linearity to predominate depends upon the adsorbates. For strong adsorbates a short column (>3cm) is required in order for elution to take place in a reasonable time. On the other hand, weak adsorbates need a long column (>10cm) in order to keep non-ideality to a minimum. For the characterization of most adsorbents two or three columns are found to be necessary in order to give a range of adsorbate partition coefficients which are independent of the adsorbate concentration, indicating non-ideality is negligible.

**SHORT COLUMNS (LOW NO. OF THEORETICAL PLATES)**

In this work, in order to reproduce field conditions, the temperature of the columns are usually 25°C. If at all possible extrapolations from higher temperatures are avoided as they may not be reliable predictions if other factors in addition to temperature effects are present.

As temperature increases are not desirable, some other means is needed to speed up the
elution of adsorbates from what would otherwise be very long adsorption processes. In order to facilitate reasonably rapid elution times ( < 48 hours) it is necessary to operate at maximum flow rate and to use a column with the minimum number of plates necessary for elution. Unfortunately, reducing the theoretical number of plates increases non-ideal effects such as band spreading.

The minimum column length depends on the minimum number of theoretical plates for equilibration and in turn this depends on the surface area of the adsorbent.

For Ambersorb 572 with a surface area of 1100 m$^2$ g$^{-1}$ the minimum weight of material necessary to equilibrate a methane sample was found to be 0.2 grams on a 3mm i.d. column (table 5.5).

However, this amount of material was much too large for the collection of elution times of longer adsorbates such as dichloromethane and tetrachloromethane which would take too long on these columns. In order to minimize the amount of material in the column, without losing equilibration and accuracy, narrower columns were made. The narrow column had an internal diameter of 1.8mm. It was found that significant reductions in the amount of adsorbate used were possible, without loss of equilibration (table 5.5).

There are some problems associated with narrow columns however. The internal diameter of a column should be at least eight times the diameter of the adsorbent particles [97], to avoid the effect of channeling at the column wall increasing plate height. The diameter of even the smallest particles in the columns, 30 mesh (500 microns), give a prescribed minimum column diameter of 4000 microns. Obviously, the 1800 micron column is well below the minimum recommended column width. However, any increase in plate height, which should lead to band spreading and other non-ideal effects appeared negligible compared with the improved equilibration resulting from the increased number of theoretical plates on a longer column. The inference is that for adsorbents with a high surface area the general rules of minimum column width may not apply.
Table 5.5  Minimum Column Weights for Different i.d. Columns

<table>
<thead>
<tr>
<th>Adsorbent Material</th>
<th>Surface Area</th>
<th>3mm i.d.</th>
<th>1.8mm i.d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambersorb 572</td>
<td>1100 m² g⁻¹</td>
<td>0.2 g</td>
<td>0.04 g</td>
</tr>
<tr>
<td>Ambersorb 564</td>
<td>550 m² g⁻¹</td>
<td>0.4 g</td>
<td>0.08 g</td>
</tr>
</tbody>
</table>
CHAPTER VI
ANALYSIS OF LITERATURE DATA

INTRODUCTION

Abraham et al have recently shown that the new solvation equation, 3.7, described in chapter III, can be used to characterise gas-liquid stationary phases [50,51], ionic salts [50], candidate phases for piezo-electric chemical sensors [77], and polymers [78]. SP can be the partition constant, \( K \); or the specific retention volume, \( V_g \); or the adjusted relative retention time, \( t^r \).

\[
\log \text{SP} = \text{SP}_0 + r \cdot R_2 + s \cdot n^H_2 + a \cdot \alpha^H_2 + b \cdot p^H_2 + 1 \cdot \log L^{16} \tag{3.7}
\]

The solute parameters used as descriptors or explanatory variables in eqn 3.7 have been described in chapter III.

There have been a considerable number of studies on carbonaceous adsorbents using one adsorbate probe but an ever decreasing number of studies as one seeks a greater number of adsorbates. Unfortunately, in order to characterise adsorbents by MLRA one needs at least five data points per parameter in eqn. 3.7. If we assume that carbonaceous adsorbents may contain little or no acidity, basicity or dipolarity, leaving only two variable terms \( R_2 \) and \( \log L^{16} \) in the regression equation, we would still need ten data points for a reasonable regression; and even these ten should be carefully chosen to avoid any cross-correlation. Consequently, we have only selected data that contains ten or more data points and this significantly reduces the number of studies available. Nevertheless, we have found several sets of data and these are analysed in this chapter.
PANKOW DATA ON CARBOTRAP

Pankow [98], attempted to correlate log \( V_g \) values for 38 solutes on the graphitised material Carbotrap, with vapour pressure (as log\( P \) in torr at 293K) and with normal boiling point (as \( bp \) in K). Although Pankow obtained some correlations of log \( V_g \) by rather arbitrarily selecting four different regression lines in each case, there was little overall correlation of log \( V_g \) with either log\( P \) or with \( bp \).

The log \( V_g \) values at 203K, together with vapour pressures as log\( P \) with \( P \) in torr at 293K, and normal boiling points were all taken from Pankow [98] except that we include two extra log\( P \) values for hexylbenzene and octylbenzene to complete the set. These are all given in table 6.1, together with values of \( R_g \) and log\( L_{16} \) which prove significant as we shall see below. Application of the full eqn 3.7 to the 38 log \( V_g \) values showed that most of the explanatory variables were not statistically significant, as judged by the students \( t \)-test, and we were left with truncated equations 6.1 and 6.2.

\[
\log V_g = 4.74 - 2.21 R_g + 2.65 \log L_{16} \\
(6.1)
\]

\[
\log V_g = 4.83 + 2.42 \log L_{16} \\
(6.2)
\]

These may be compared with the corresponding equations in \( bp/K \) or in log\( P \), again for all 38 solutes;

\[
\log V_g = -12.64 + 0.040 bp/K \\
(6.3)
\]

\[
\log V_g = 5.14 - 2.00 \log P \\
(6.4)
\]
where \( n \) is the number of solutes, \( r \) is the overall correlation coefficient, and \( sd \) is the standard deviation in \( \log V_g \). It is clear that \( \log L^{16} \) is a very much better descriptor than either \( bp/K \) or \( \log P \); this is shown rather well in Figs. 6.1–6.3. Pankow [98], pointed out that some of the \( \log V_g \) values at 293K had been obtained by extrapolation from higher temperatures, and this probably accounts for the rather large \( sd \) values in eqns. 6.1 – 6.4. Nevertheless, either eqn 6.1 or eqn. 6.2 could be used to estimate \( \log V_g \) values for any solute from either \( R_2 \) and \( \log L^{16} \) or simply \( \log L^{16} \). Both of the parameters are easily obtainable as detailed in chapter III.

Although the \( sd \) value in eqn. 6.1 is 0.88 log units, it should be remembered that the spread in the experimental \( \log V_g \) values covers over 15 log units. The rather large \( sd \) value is unlikely to originate from errors in the \( R_2 \) or \( \log L^{16} \) parameters, at least to any extent, because even for the \( n \)-alkanes (for which there are very reliable parameters) application of eqn. 6.2 leads to an \( sd \) of 0.94 log units.

The improved correlation with the \( R_2 \) parameter, which is a measure of \( \pi \) and \( n \) electron pair interactions, is an interesting finding. It may be an artifact of the regression, but if it is not then the implication is that Carbotrap not only interacts through dispersion forces but also to a small degree it repulses specific \( \pi \) and \( n \) electron pairs. This observation would lead one to classify Carbotrap as a weak type III adsorbent according to Kiselev [1], (refer chapter I). This is not what was expected as it is usually classified, as are all graphitised carbon blacks, as a type I adsorbent. Further work would be necessary to determine if Carbotrap is a weak type III adsorbent or not.
Figure 6.1

Log $V_g$ vs Log $L^{16}$ for Compounds on Carbotrap at 293K
Figure 6.2

Log $V_\text{g}$ vs $-\log P$ for Compounds on Carbotrap at 293K
Figure 6.3

Log $V_g$ vs $T_b$ (K) for Compounds on Carbotrap at 293K
CAO DATA ON CARBOSIEVE AND CHARCOAL CLOTH

The general equation was also tested against the data of Cao [99], who obtained $V_g$ values for a variety of hydrocarbons on three microporous carbons, viz. Carbosieve B (Carb B), (a weak type III adsorbent), and two charcoal cloths, CC1 and CC2. The log $V_g$ values recorded by Cao at 293K, together with the corresponding solute $R_2$ and log$L_{16}$ values, are in table 6.2. With no data exclusion at all, we can construct the following equations:

\[
\log V_g (\text{Carb B}) = -0.41 - 4.45 R_2 + 2.82 \log L_{16} \quad (6.5)
\]
\[n = 14, \quad r = 0.9836, \quad sd = 0.58\]

\[
\log V_g (\text{Carb B}) = -0.40 + 2.59 \log L_{16} \quad (6.6)
\]
\[n = 14, \quad r = 0.9525, \quad sd = 0.94\]

\[
\log V_g (\text{CC1}) = -1.05 - 3.35 R_2 + 3.06 \log L_{16} \quad (6.7)
\]
\[n = 17, \quad r = 0.9868, \quad sd = 0.66\]

\[
\log V_g (\text{CC1}) = -1.17 + 3.00 \log L_{16} \quad (6.8)
\]
\[n = 17, \quad r = 0.9769, \quad sd = 0.84\]

\[
\log V_g (\text{CC2}) = -0.71 - 2.23 R_2 + 2.48 \log L_{16} \quad (6.9)
\]
\[n = 15, \quad r = 0.9897, \quad sd = 0.40\]

\[
\log V_g (\text{CC2}) = -0.70 + 2.38 \log L_{16} \quad (6.10)
\]
\[n = 15, \quad r = 0.9800, \quad sd = 0.53\]

Bearing in mind the spread of data, some 14 log units for CC1, eqns 6.5–6.10, especially the double regressions in $R_2$ and log$L_{16}$, do provide a useful means of estimating further
log $V_g$ values.

In addition, eqns 6.5–6.10 are especially valuable in the characterisation of adsorbents. Plots according to eqns. 6.6, 6.8 and 6.10 are shown in fig. 6.4 and illustrate how difficult it is to define what is the “best” adsorbent, even for $n$-alkanes. For rather small compounds, i.e. those with low log$L_{16}$ values, Carbosieve B is the best adsorbent, but for larger compounds CC1 is the best. For the $n$-alkanes shown in fig.6.4 the cross over point is between ethane and propane for CC1 and CC2 and between hexane and heptane for CC1 and Carbosieve B.

We can also compare Carbotrap with Carbosieve B, through eqns. 6.2–6.6. It is now clear that $V_g$ values on Carbosieve B are always greater than on Carbotrap by factors upwards of $10^4$, no matter what the size of the solute is, i.e. no matter what is the solute log$L_{16}$ value.
Figure 6.4

Log $V_g$ vs Log $L^{16}$ for Compounds on Carbosieve B, CC1 and CC2 at 293K
TABLE 6.1

SPECIFIC RETENTION VOLUME ($V_{g,293}$, dm$^3$g$^{-1}$) ON CARBOTRAP AT 293K, AND COMPOUND PARAMETERS FOR REGRESSIONS ON THE DATA OF PANKOW [98].

<table>
<thead>
<tr>
<th>Compound</th>
<th>log $p_{293}$ (torr)</th>
<th>log $V_{g,293}$ (l/g)</th>
<th>B.P. (°C)</th>
<th>$R^2$</th>
<th>log$L^{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>4.47</td>
<td>-1.76</td>
<td>-88</td>
<td>0.000</td>
<td>0.492</td>
</tr>
<tr>
<td>Propane</td>
<td>3.81</td>
<td>-1.26</td>
<td>-42</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>n-Butane</td>
<td>3.18</td>
<td>-0.39</td>
<td>-1</td>
<td>0.000</td>
<td>1.615</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>2.63</td>
<td>0.77</td>
<td>36</td>
<td>0.000</td>
<td>2.162</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>2.08</td>
<td>1.90</td>
<td>69</td>
<td>0.000</td>
<td>2.668</td>
</tr>
<tr>
<td>n-Octane</td>
<td>1.04</td>
<td>4.21</td>
<td>126</td>
<td>0.000</td>
<td>3.677</td>
</tr>
<tr>
<td>n-Decane</td>
<td>0.43</td>
<td>6.68</td>
<td>174</td>
<td>0.000</td>
<td>4.686</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>-0.52</td>
<td>11.21</td>
<td>216</td>
<td>0.000</td>
<td>5.696</td>
</tr>
<tr>
<td>n-Tetradecane</td>
<td>-1.57</td>
<td>13.92</td>
<td>252</td>
<td>0.000</td>
<td>6.705</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>1.78</td>
<td>0.29</td>
<td>84</td>
<td>0.416</td>
<td>2.573</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>1.78</td>
<td>1.10</td>
<td>87</td>
<td>0.369</td>
<td>2.733</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>1.28</td>
<td>1.39</td>
<td>114</td>
<td>0.499</td>
<td>3.290</td>
</tr>
<tr>
<td>Butanone</td>
<td>1.88</td>
<td>0.58</td>
<td>80</td>
<td>0.166</td>
<td>2.287</td>
</tr>
<tr>
<td>Heptan-4-one</td>
<td>-0.08</td>
<td>3.39</td>
<td>149</td>
<td>0.113</td>
<td>3.705</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>0.60</td>
<td>3.31</td>
<td>157</td>
<td>0.403</td>
<td>3.792</td>
</tr>
<tr>
<td>n-Butylamine</td>
<td>1.86</td>
<td>3.32</td>
<td>78</td>
<td>0.224</td>
<td>2.618</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>1.07</td>
<td>-0.15</td>
<td>118</td>
<td>0.265</td>
<td>1.750</td>
</tr>
<tr>
<td>Propanoic Acid</td>
<td>0.46</td>
<td>0.22</td>
<td>141</td>
<td>0.233</td>
<td>2.290</td>
</tr>
<tr>
<td>Pentanoic Acid</td>
<td>-0.82</td>
<td>2.63</td>
<td>187</td>
<td>0.205</td>
<td>3.380</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.64</td>
<td>-0.31</td>
<td>78</td>
<td>0.246</td>
<td>1.485</td>
</tr>
<tr>
<td>Butan-1-ol</td>
<td>0.64</td>
<td>1.28</td>
<td>118</td>
<td>0.224</td>
<td>2.601</td>
</tr>
</tbody>
</table>
TABLE 6.1 CONT.

SPECIFIC RETENTION VOLUME \( (V_{293}, \text{ dm}^3\text{g}^{-1}) \) ON CARBOTRAP AT 293K, AND COMPOUND PARAMETERS FOR REGRESSIONS ON THE DATA OF PANKOW [98].

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \log p^{293} ) (torr)</th>
<th>( \log V_{293} ) (l/g)</th>
<th>B.P. (°C)</th>
<th>( R^2 )</th>
<th>( \log L^{16} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>4.47</td>
<td>-1.76</td>
<td>-88</td>
<td>0.000</td>
<td>0.492</td>
</tr>
<tr>
<td>2-Methylpropan-2-ol</td>
<td>1.49</td>
<td>0.81</td>
<td>83</td>
<td>0.180</td>
<td>1.963</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.88</td>
<td>1.07</td>
<td>80</td>
<td>0.610</td>
<td>2.786</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.34</td>
<td>2.81</td>
<td>111</td>
<td>0.601</td>
<td>3.325</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.85</td>
<td>4.31</td>
<td>136</td>
<td>0.613</td>
<td>3.778</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.81</td>
<td>4.63</td>
<td>138</td>
<td>0.613</td>
<td>3.839</td>
</tr>
<tr>
<td>n-Propylbenzene</td>
<td>0.40</td>
<td>6.24</td>
<td>159</td>
<td>0.604</td>
<td>4.230</td>
</tr>
<tr>
<td>Isopropylbenzene</td>
<td>0.51</td>
<td>5.23</td>
<td>153</td>
<td>0.602</td>
<td>4.084</td>
</tr>
<tr>
<td>n-Butylbenzene</td>
<td>-0.05</td>
<td>6.77</td>
<td>183</td>
<td>0.600</td>
<td>4.730</td>
</tr>
<tr>
<td>n-Hexylbenzene</td>
<td>-1.16</td>
<td>9.85</td>
<td>226</td>
<td>0.591</td>
<td>5.720</td>
</tr>
<tr>
<td>n-Octylbenzene</td>
<td>-2.15</td>
<td>12.12</td>
<td>262</td>
<td>0.579</td>
<td>6.714</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>-1.41</td>
<td>9.57</td>
<td>258</td>
<td>1.360</td>
<td>6.063</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.94</td>
<td>3.20</td>
<td>132</td>
<td>0.718</td>
<td>3.640</td>
</tr>
<tr>
<td>1,4-Dichlorobenzene</td>
<td>-0.22</td>
<td>4.13</td>
<td>173</td>
<td>0.825</td>
<td>4.446</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>-0.46</td>
<td>4.81</td>
<td>202</td>
<td>0.818</td>
<td>4.483</td>
</tr>
<tr>
<td>Benzyamine</td>
<td>-0.24</td>
<td>4.35</td>
<td>184</td>
<td>0.829</td>
<td>4.319</td>
</tr>
<tr>
<td>Phenol</td>
<td>-0.70</td>
<td>2.79</td>
<td>182</td>
<td>0.805</td>
<td>3.897</td>
</tr>
<tr>
<td>p-Cresol</td>
<td>-1.40</td>
<td>4.31</td>
<td>202</td>
<td>0.820</td>
<td>4.307</td>
</tr>
</tbody>
</table>
### TABLE 6.2

SPECIFIC RETENTION VOLUMES ($V_{293}$, dm$^3$g$^{-1}$) OF VARIOUS ADSORBENTS AT 293K, AND COMPOUND PARAMETERS FOR REGRESSIONS ON THE DATA OF CAO, [99].

<table>
<thead>
<tr>
<th>Compound</th>
<th>log $V_{293}$ (dm$^3$g$^{-1}$)</th>
<th>$R_2$</th>
<th>log$L^16$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbosieve B</td>
<td>CC1</td>
<td>CC2</td>
</tr>
<tr>
<td>Methane</td>
<td>-0.92</td>
<td>-0.89</td>
<td>-1.30</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.76</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>Propane</td>
<td>2.52</td>
<td>1.70</td>
<td>1.72</td>
</tr>
<tr>
<td>n-Butane</td>
<td>4.28</td>
<td>3.71</td>
<td>3.26</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>5.70</td>
<td>5.23</td>
<td>4.45</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td>5.36</td>
<td>4.57</td>
<td>4.62</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>6.88</td>
<td>6.79</td>
<td>6.08</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>6.45</td>
<td>6.52</td>
<td>5.41</td>
</tr>
<tr>
<td>2,2-Dimethylpentane</td>
<td>-</td>
<td>6.34</td>
<td>5.20</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>9.60</td>
<td>8.59</td>
<td>7.62</td>
</tr>
<tr>
<td>n-Octane</td>
<td>-</td>
<td>10.26</td>
<td>-</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>-</td>
<td>13.18</td>
<td>-</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>5.41</td>
<td>6.00</td>
<td>5.08</td>
</tr>
<tr>
<td>Ethene</td>
<td>-0.10</td>
<td>-0.17</td>
<td>-0.21</td>
</tr>
<tr>
<td>Propene</td>
<td>1.65</td>
<td>1.52</td>
<td>1.53</td>
</tr>
<tr>
<td>But-1-ene</td>
<td>3.08</td>
<td>3.04</td>
<td>3.00</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.45</td>
<td>5.96</td>
<td>5.30</td>
</tr>
</tbody>
</table>
In a recent paper by Betz and Supina [100] specific retention volumes for a series of adsorbates on four carbonaceous adsorbents, three type I thermally modified carbon blacks and one weak type III carbon molecular sieve, were obtained using gas chromatography. The results were carried out at four elevated temperatures and extrapolated to give the specific retention volumes at 20°C. In the paper the specific retention volumes at 20°C were plotted on a least squares straight line plot using polarisability ($\rho$) and molecular connectivity ($\chi$) as the input value $x$ in the equation $y=mx+c$. The straight line equation was then used to predict unknown adsorbate specific retention volumes. It is useful to regress these results against our parameters, particularly against $\log L_{16}$ and compare the regressions obtained for the different adsorbents and to compare the regressions with the results of Betz and Supina.

The physical properties of the adsorbents studied are shown in table 6.3a and the parameters and retention volumes for each compound is given in table 6.3b. The four sets of retention data were regressed, in the first instance, against five parameters $\pi_2^R$, $\alpha_2^R$, $\beta_2^R$, $R_2$ and $\log L_{16}$. In the case of the type I adsorbents it was found that only the $\log L_{16}$ parameter was significant, with no significant parameter for the molecular sieve Carboxen-569. Any specific retention volumes with an error of greater than two standard deviation units were omitted. The results of the final regressions are shown below in table 6.4.

The compounds which were left out of the regression, due to their retention volumes causing too large an error, were frequently erroneous on more than one adsorbent and were usually long chain hydrocarbons in excess of C$_{18}$. 
<table>
<thead>
<tr>
<th>Particle</th>
<th>Particle Size</th>
<th>Density (g/ml)</th>
<th>Surface Area (m²/gram)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbotrap B</td>
<td>20/40</td>
<td>0.38</td>
<td>98.3</td>
<td>Type I, gcb*</td>
</tr>
<tr>
<td>Carbotrap C</td>
<td>20/40</td>
<td>0.72</td>
<td>10.1</td>
<td>Type I, gcb*</td>
</tr>
<tr>
<td>Carbopack F</td>
<td>60/80</td>
<td>0.60</td>
<td>5.1</td>
<td>Type I, gcb*</td>
</tr>
<tr>
<td>Carboxen-569</td>
<td>20/45</td>
<td>0.58</td>
<td>490.0</td>
<td>Weak Type III cms*</td>
</tr>
</tbody>
</table>

*(gcb) Graphitized carbon black
*(cms) Carbon molecular sieve
TABLE 6.3b

SPECIFIC RETENTION VOLUMES \( V_{L,293} \, (\text{dm}^3 \text{g}^{-1}) \) OF VARIOUS ADSORBENTS AT 293K, AND COMPOUND PARAMETERS FOR REGRESSIONS ON THE DATA OF BETZ AND SUPINA, [100].

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \log V_{L,293} ) ( (\text{dm}^3 \text{g}^{-1}) )</th>
<th>R²</th>
<th>( \log L^{16} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbo-trap B</td>
<td>Carbo-trap C</td>
<td>Carbo-pack F</td>
</tr>
<tr>
<td>Methane</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ethane</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Propane</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>n-Butane</td>
<td>-0.65</td>
<td>-1.42</td>
<td>-1.52</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>-0.08</td>
<td>-1.08</td>
<td>-1.18</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.48</td>
<td>-0.49</td>
<td>-0.92</td>
</tr>
<tr>
<td>n-Octane</td>
<td>1.75</td>
<td>0.14</td>
<td>-0.04</td>
</tr>
<tr>
<td>n-Decane</td>
<td>4.46</td>
<td>1.11</td>
<td>1.15</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>9.69</td>
<td>3.52</td>
<td>1.76</td>
</tr>
<tr>
<td>n-Tetradecane</td>
<td>-</td>
<td>-</td>
<td>4.32</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>-0.03</td>
<td>-1.14</td>
<td>-1.22</td>
</tr>
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<td>Propanone</td>
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<td>-0.27</td>
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TABLE 6.4 REGRESSION RESULTS ON THERMALLY MODIFIED CARBON BLACK FROM THE DATA OF BETZ AND SUPINA[100].

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<tr>
<th>Adsorbent</th>
<th>SP,</th>
<th>(\log L^{16})</th>
<th>n</th>
<th>r</th>
<th>sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbotrap B</td>
<td>(\log V_g)</td>
<td>-2.28</td>
<td>1.03</td>
<td>15</td>
<td>.9740</td>
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<td>Carbotrap C</td>
<td>(\log V_g)</td>
<td>-2.24</td>
<td>0.67</td>
<td>15</td>
<td>.9098</td>
</tr>
<tr>
<td>Carbopack F</td>
<td>(\log V_g)</td>
<td>-2.57</td>
<td>0.68</td>
<td>19</td>
<td>.9301</td>
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<tr>
<td>Carboxen-569</td>
<td>(\log V_g)</td>
<td>0.41</td>
<td>0.37</td>
<td>9</td>
<td>.5395</td>
</tr>
</tbody>
</table>

*The values of \(V_g\) are taken in dm\(^3\)g\(^{-1}\).*

The results in table 6.4 show that the first three adsorbents interact with any given adsorbate using general dispersion forces, reflected by the \(\log L^{16}\) term. The absence of any significant terms in \(R_3, \pi_2^H, \alpha_2^H\) or \(\beta_2^H\) show that the adsorbents probably have no acidic, basic or polar sites. This is the expected behaviour of a type I adsorbent. The poor correlation for Carboxen 549 is due to the sieving of molecules above a certain size. Molecular sieving cannot be taken into account by the LSER parameters and thus gives a poor correlation.

Comparing the three graphitized carbon black adsorbents, Carbotrap B, Carbotrap C and Carbopack F, we find the \(\log L^{16}\) parameter varies with surface area of adsorbent. The parameter is approximately twice as large for Carbotrap B c.f. the other two. This is a reflection of Carbotrap B’s greater surface area 98.3 m\(^2\)/g c.f. 10.0 and 5.1 m\(^2\)/g for Carbotrap C and F respectively. This was expected as a greater surface area provides more sites for general dispersion interactions with an adsorbate. Based on surface area alone we would expect Carbopack F to have a lower 'T' value than Carbotrap C but they are very similar. However, it is likely that the lower surface area of Carbopack F is reflected in its larger negative constant value.

In the case of Type I adsorbents the correlations are quite good and approach the correlations for the straight line found by Betz and Supina. This implies that their straight
line can mainly be attributed to factors contained within the log$L^{16}$ parameter i.e. cavity formation and dispersion forces. The term ‘cavity formation’ is used very loosely and it is not altogether clear what ‘cavity formation’ means for a solid adsorbent. However, there are almost certainly overlapping force fields on opposing micropore walls. These may attract each other in some way in the absence of any other species, causing a ‘pseudo cavity formation’ on introduction of an adsorbate.
STUDIES ON TENAX RETENTION DATA

It has been possible to obtain several regressions from published retention data on Tenax, an adsorbent of considerable interest. Tenax has been studied as a possible sorbent for use in environmental, industrial, biological and trace analysis [101-107]. Due to this, four series of retention values have been obtained from the literature [102-105], and regressed against the solute parameters $\log L$, $R_2$, $\pi_2^H$, $\alpha_2^H$ and $\beta_2^H$. Two series of results are on Tenax TA and two are on Tenax GC. For more detailed information on the properties and applications of Tenax GC, from which Tenax TA differs only in that it has reduced column bleeding [106], refer to Nunez et al.,[107].

Tenax-TA is a polymer of 2,6-diphenyl-p-phenylene oxide and has the general structural formula;
Maier et al [102], attempted to characterise Tenax TA using a range of solutes, giving breakthrough, retention and peak end volumes, at a series of temperatures (130, 100, 80, 60, 45, & 30°C). However due to a lack of data at the lower temperatures it has only been possible to regress the results obtained at 130, 100, & 80°C (table 6.5a). The parameters for the compounds for which Maier et al. collected retention data are given in table 6.5b. The results of the regressions are shown in table 6.6. The regressions of specific retention volume against all five parameters are found to contain unacceptably high cross correlations between $\pi$ and $R_3$ (0.58–0.65), between $\pi$ and $\beta$ (0.71–0.79), and between $\alpha$ and $\beta$ (0.35–0.46). As one can expect Tenax to have some polarity term (s.$\pi$), due to the benzene rings, some possible hydrogen bond base sites (a.$\alpha$), due to the ether oxygen links, but no acid term (b.$\beta$), due to an absence of hydrogen bond acid sites, the b.$\beta$ term was dropped from all regressions. The loss of $\beta$ resolved the problem of high cross correlations between $\pi$ and $R_3$, and between $\alpha$ and $\beta$. The results of the regressions with significant (i.e. t-test > 0.95) sorbent parameters in table 6.6 for Tenax TA, it is quite clear that the dominant sorbent property in all cases is dispersion, expressed as $L^6$. The values of $I$ (0.577–1.009) show that Tenax is a strong dispersion interactor. The results show that $I$ is temperature dependent, increasing with decreasing temperature as is expected. The $\pi$ coefficient, however, seems to less dependent on temperature. This may be due to the delocalised electrons in the benzene rings being more polarisable at higher temperatures. The $\alpha$ term, although significant does not very much increase the correlation coefficient or alter the coefficients for $s$ and $I$ and is thus left out of the table. The compounds used by Maier and Fieber did not have a wide range of $\alpha$ values and it may be that Tenax can act as a hydrogen bond base with appropriate hydrogen bond acids; further work would be necessary to show this. The values of $s$, (0.283–0.862) show significant polarity on Tenax-TA. Removal of $\pi$ from the
regression causes the correlation coefficient, $r$, to fall considerably, so the possibility of adsorption being governed by dispersion ($\log L^{16}$), only, is ruled out.

The properties of Tenax-TA can be discussed in terms of its structure. The high dispersion properties of Tenax-TA can be assigned to the backbone of the polymer provided by the etheric benzene chain and perhaps more importantly to the benzene side chains, the delocalised electrons in the ring giving Tenax its significant polarity. Weak basicity is expected due to the ether oxygens present in the benzene backbone providing sites for hydrogen bond formation with solute acids, although these sites may be partially masked by the bulky side chains. Unfortunately, due to a poor and limited selection of hydrogen bond acids in the data set it is unclear whether Tenax-TA can act as a hydrogen bond base or not.
TABLE 6.5a

LOG OF BREAKTHROUGH(Vb), RETENTION(Vg), AND PEAK END(Ve) VOLUMES IN ML/G ON TENAX TA USING RESULTS OF MAIER & FIEBER [102].

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<td>Ve</td>
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<td>Ethane</td>
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<td>0.70</td>
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<td>1.30</td>
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### TABLE 6.5a CONT

**LOG OF BREAKTHROUGH (Vb), RETENTION (Vg), AND PEAK END (Ve) VOLUMES IN ML/G ON TENAX TA USING RESULTS OF MAIER & FIEBER [102].**

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Table 6.5b

Parameters used in the Regressions on the data of Maier and Fieber [102].

<table>
<thead>
<tr>
<th>#</th>
<th>Compound</th>
<th>$\pi^H_2$</th>
<th>log$L_{16}$</th>
</tr>
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<tbody>
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<tr>
<td>19</td>
<td>Nitrogen dioxide</td>
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<td>Methane</td>
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<td>Propane</td>
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<td>Diethylether</td>
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<tr>
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<td>Propionaldehyde</td>
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Table 6.5b Cont.

Parameters used in the Regressions on the data of Maier and Fieber [102].

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<th>$\log L^{16}$</th>
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<td>Furan</td>
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Regression Results on Tenax-TA from Maier et al. [102]

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<th>n</th>
<th>r</th>
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<td>130</td>
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<td>0.086</td>
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<tr>
<td>130</td>
<td>log V_g</td>
<td>-0.051</td>
<td>0.536</td>
<td>0.680</td>
<td>56</td>
<td>0.9892</td>
<td>0.082</td>
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<tr>
<td>130</td>
<td>log V_r</td>
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<td>0.283</td>
<td>0.577</td>
<td>56</td>
<td>0.9754</td>
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<td>0.812</td>
<td>49</td>
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<td>0.9849</td>
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<tr>
<td>100</td>
<td>log V_r</td>
<td>0.594</td>
<td>0.325</td>
<td>0.725</td>
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<td>0.9757</td>
<td>0.127</td>
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<tr>
<td>80</td>
<td>log V_b</td>
<td>0.001</td>
<td>0.862</td>
<td>1.009</td>
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<td>0.9388</td>
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<tr>
<td>80</td>
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<td>0.608</td>
<td>0.973</td>
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<td>0.9785</td>
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<tr>
<td>80</td>
<td>log V_r</td>
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<td>0.309</td>
<td>0.829</td>
<td>35</td>
<td>0.9719</td>
<td>0.140</td>
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</table>

All characteristic constants have > 0.95 Ttest

Azarova and Sukhorukov [103], have studied the adsorption of n–alkanes and aromatic hydrocarbons on Tenax-TA. The study involved obtaining the retention volume per gram of adsorbent $V_g$, for 13 compounds at different temperatures. The linear dependence of the logarithm of the retention volume, log $V_g$, on the reciprocal of the absolute temperature, $(1/T)$, was then used to extrapolate the results to 20°C. The retention data together with the regression results are shown in table 6.7 and equations 6.11 and 6.12 for the extrapolated log $V_g$ values at 20°C are below.

$$\log V_g \text{ (Tenax TA)} = -0.04 - 0.01 \cdot n^{1/2} + 1.58 \cdot \log L_{16}$$  \hspace{1cm} (6.11)

$n = 13$, $r = 0.9952$, $sd = 0.09$

$$\log V_g \text{ (Tenax TA)} = -0.04 + 1.58 \cdot \log L_{16}$$  \hspace{1cm} (6.12)

$n = 13$, $r = 0.9952$, $sd = 0.09$
Table 6.7

LOG OF EXTRAPOLATED SPECIFIC RETENTION VOLUMES \( (V_g) \) IN ML/G FROM A CHROMATOGRAPHIC STUDY OF THE ADSORPTION OF N-ALKANES AND AROMATIC HYDROCARBONS ON TENAX-TA POLYMERIC SORBENT AT 20°C, [103].

<table>
<thead>
<tr>
<th>#</th>
<th>Compound</th>
<th>( \log V_g \cdot \pi^H_2 )</th>
<th>( \log L^{16} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>109</td>
<td>n-Hexane</td>
<td>4.00 0.000</td>
<td>2.668</td>
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<td>5.02 0.000</td>
<td>3.173</td>
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<td>n-Octane</td>
<td>5.87 0.000</td>
<td>3.677</td>
</tr>
<tr>
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<td>n-Nonane</td>
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<td>10001</td>
<td>Benzene</td>
<td>4.48 0.520</td>
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<tr>
<td>10002</td>
<td>Toluene</td>
<td>5.25 0.520</td>
<td>3.325</td>
</tr>
<tr>
<td>10004</td>
<td>o-Xylene</td>
<td>6.10 0.560</td>
<td>3.939</td>
</tr>
<tr>
<td>10005</td>
<td>m-Xylene</td>
<td>6.05 0.520</td>
<td>3.839</td>
</tr>
<tr>
<td>10006</td>
<td>p-Xylene</td>
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<td>3.839</td>
</tr>
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<td>10003</td>
<td>Ethylbenzene</td>
<td>5.97 0.510</td>
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<tr>
<td>10011</td>
<td>Mesitylene</td>
<td>6.77 0.520</td>
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<tr>
<td>10008</td>
<td>Isopropylbenzene</td>
<td>6.46 0.490</td>
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<tr>
<td>10007</td>
<td>Propylbenzene</td>
<td>6.62 0.500</td>
<td>4.230</td>
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</table>

The regression results show a good correlation between \( \log V_g \) and \( \log L^{16} \) of 0.9952. The value of 1.58 shows that Tenax TA has strong dispersive forces. However, unlike the results of Maier and Fieber [102], discussed earlier, there is no significant term in \( \pi^H_2 \). There may be several reasons for this, the most likely is that there is no significant variation in \( \pi^H_2 \) (0.49-0.56), for the compounds that have a \( \pi^H_2 \) parameter. More work, with a better choice of compounds possessing varying degrees of dipolarity is needed before any conclusions can be drawn regarding the dipolarity of Tenax TA at ambient temperatures.
The behaviour of Tenax GC has been studied by Brown & Purcell [105], and by Gallant et al [104]. Both papers provide retention data at 20°C, however the data of Brown and Purcell is extrapolated from higher temperatures.

The results are shown in tables 6.8–6.12; in both cases the coefficient, \( I \) (1.37–1.42 and 1.27–1.29 respectively in the final regression), is the largest and most correlated parameter coefficient. The regressions also find the \( \pi^H_2 \) coefficient \( g \) (0.68 and 0.86), to be correlated as well as \( I \). The removal of the dipolarity term from the regression still leaves a reasonably good regression in both cases. The combined regression of both sets of data is also shown and provides a correlation of Tenax–GC for a large data set.

All the regressions imply that Tenax GC is a strong dispersion interactor. This is in agreement with the regressions obtained on Tenax TA, and the values of \( I \) obtained at this temperature (20°C) are approximately what we would expect from the results on Tenax TA at the lower temperature of 20°C. The significance of the \( \pi^H_2 \) coefficient \( g \) in the regressions on Tenax GC is also in agreement with the work on Tenax TA. However the continued absence of any significance for the \( \alpha^H_2 \) term \( a \) may be simply that the hydrogen bond basicity of the ether linkage is either very weak or sterically hindered by the benzene side chains. Further experimental work with solutes that are greater hydrogen bond acids would confirm this.

Brown and Purcell plotted retention volume against boiling point and obtained a straight line for some compounds but noted that there were important exceptions, viz., alcohols, acids, anhydrides, higher amines and chlorobenzene. It is interesting to compare a plot of \( \log V_g \) vs different parameters. Below are the equations of \( \log V_g \) against the negative logarithm of vapour pressure (\(-\log P\)), boiling point in Kelvin (bp/K), and \( \log L_{146} \).
Table 6.8
SPECIFIC RETENTION VOLUMES ($V_{g298}, \text{dm}^3\text{g}^{-1}$) FOR VARIOUS ADSORBENTS AT 298K, AND COMPOUND PARAMETERS FOR REGRESSIONS ON DATA OF BROWN AND PURCELL,[105].

<table>
<thead>
<tr>
<th>#</th>
<th>Compound</th>
<th>log $V_g$</th>
<th>$\pi^*_2$</th>
<th>log$L^{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>106</td>
<td>n-Pentane</td>
<td>0.66</td>
<td>0.000</td>
<td>2.162</td>
</tr>
<tr>
<td>109</td>
<td>n-Hexane</td>
<td>1.52</td>
<td>0.000</td>
<td>2.668</td>
</tr>
<tr>
<td>114</td>
<td>n-Heptane</td>
<td>2.25</td>
<td>0.000</td>
<td>3.173</td>
</tr>
<tr>
<td>126</td>
<td>n-Octane</td>
<td>2.89</td>
<td>0.000</td>
<td>3.677</td>
</tr>
<tr>
<td>1150</td>
<td>Buta-1,3-diene</td>
<td>0.09</td>
<td>0.230</td>
<td>1.543</td>
</tr>
<tr>
<td>2501</td>
<td>Chloromethane</td>
<td>-1.11</td>
<td>0.430</td>
<td>1.163</td>
</tr>
<tr>
<td>2502</td>
<td>Dichloromethane</td>
<td>0.60</td>
<td>0.570</td>
<td>2.019</td>
</tr>
<tr>
<td>2503</td>
<td>Trichloromethane</td>
<td>1.28</td>
<td>0.490</td>
<td>2.480</td>
</tr>
<tr>
<td>2504</td>
<td>Tetrachloromethane</td>
<td>1.79</td>
<td>0.380</td>
<td>2.823</td>
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<td>Chloroethane</td>
<td>-0.11</td>
<td>0.400</td>
<td>1.678</td>
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<tr>
<td>2506</td>
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<td>2507</td>
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<td>2.733</td>
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<tr>
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<td>1,1,2-Trichloroethane</td>
<td>2.54</td>
<td>0.680</td>
<td>3.290</td>
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<td>2510</td>
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<td>3.23</td>
<td>0.760</td>
<td>3.803</td>
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<tr>
<td>2511</td>
<td>1,1,1,2-Tetrachloroethane</td>
<td>2.89</td>
<td>0.630</td>
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<tr>
<td>2800</td>
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<td>-</td>
<td>-</td>
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<tr>
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<td>0.340</td>
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<tr>
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<td>cis-1,2-Dichloroethene</td>
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<td>0.610</td>
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</tr>
<tr>
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<td>Tetrachloroethene</td>
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<tr>
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<td>Bromomethane</td>
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<td>1.630</td>
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<tr>
<td>4050</td>
<td>Fluorotrichloromethane</td>
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<td>1.930</td>
</tr>
<tr>
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<td>0.380</td>
<td>2.177</td>
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<tr>
<td>4304</td>
<td>1,1,2-Trifluorotrichloroethane</td>
<td>-0.64</td>
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<tr>
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<td>Acetaldehyde</td>
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<td>0.670</td>
<td>1.230</td>
</tr>
<tr>
<td>5401</td>
<td>Propenal</td>
<td>0.68</td>
<td>0.740</td>
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<td>5501</td>
<td>Propanone</td>
<td>0.73</td>
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<td>0.700</td>
<td>2.287</td>
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<tr>
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<td>0.650</td>
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<td>Isopropyl Acetate</td>
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<td>2.546</td>
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<td>n-Butyl Acetate</td>
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<td>0.600</td>
<td>3.353</td>
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<td>Acetonitrile</td>
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<td>-</td>
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<tr>
<td>6801</td>
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<td>1.300</td>
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<tr>
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<td>Ethylamine</td>
<td>0.43</td>
<td>0.350</td>
<td>1.677</td>
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</table>
TABLE 6.8 cont.
SPECIFIC RETENTION VOLUMES ($V_{e298}$, dm³g⁻¹) FOR VARIOUS ADSORBENTS AT 298K,
AND COMPOUND PARAMETERS FOR REGRESSIONS ON DATA OF BROWN AND PURCELL,[105].

<table>
<thead>
<tr>
<th>#</th>
<th>Compound</th>
<th>log $V_e$</th>
<th>$\pi^H_2$</th>
<th>log$L^{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6803</td>
<td>n-Propylamine</td>
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<td>0.350</td>
<td>2.141</td>
</tr>
<tr>
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<td>Acetic Acid</td>
<td>0.89</td>
<td>0.650</td>
<td>1.750</td>
</tr>
<tr>
<td>7701</td>
<td>Acetic Anhydride</td>
<td>0.89</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8001</td>
<td>Methanol</td>
<td>-0.51</td>
<td>0.440</td>
<td>0.970</td>
</tr>
<tr>
<td>8002</td>
<td>Ethanol</td>
<td>-0.27</td>
<td>0.420</td>
<td>1.485</td>
</tr>
<tr>
<td>8003</td>
<td>Propan-1-ol</td>
<td>0.93</td>
<td>0.420</td>
<td>2.031</td>
</tr>
<tr>
<td>8004</td>
<td>Propan-2-ol</td>
<td>0.63</td>
<td>0.360</td>
<td>1.764</td>
</tr>
<tr>
<td>8005</td>
<td>Butan-1-ol</td>
<td>1.71</td>
<td>0.420</td>
<td>2.601</td>
</tr>
<tr>
<td>8006</td>
<td>2-Methylpropan-1-ol</td>
<td>1.45</td>
<td>0.390</td>
<td>2.413</td>
</tr>
<tr>
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<td>1.33</td>
<td>0.360</td>
<td>2.338</td>
</tr>
<tr>
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<td>Octan-1-ol</td>
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<td>4.619</td>
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<td>Prop-2-en-1-ol</td>
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<td>1.951</td>
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<td>0.350</td>
<td>2.173</td>
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<tr>
<td>10001</td>
<td>Benzene</td>
<td>1.79</td>
<td>0.520</td>
<td>2.786</td>
</tr>
<tr>
<td>10002</td>
<td>Toluene</td>
<td>2.59</td>
<td>0.520</td>
<td>3.325</td>
</tr>
<tr>
<td>10004</td>
<td>o-Xylene</td>
<td>3.49</td>
<td>0.560</td>
<td>3.939</td>
</tr>
<tr>
<td>10005</td>
<td>m-Xylene</td>
<td>3.49</td>
<td>0.520</td>
<td>3.839</td>
</tr>
<tr>
<td>10006</td>
<td>p-Xylene</td>
<td>3.49</td>
<td>0.520</td>
<td>3.839</td>
</tr>
<tr>
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<td>Isopropylbenzene</td>
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<td>1,2,3-Trimethylbenzene</td>
<td>4.14</td>
<td>0.610</td>
<td>4.565</td>
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<tr>
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<td>1,2,4-Trimethylbenzene</td>
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<td>4.441</td>
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<tr>
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<td>Chlorobenzene</td>
<td>2.42</td>
<td>0.670</td>
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<td>Aniline</td>
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<td>0.960</td>
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<tr>
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<td>Nitrobenzene</td>
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<td>1.100</td>
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<tr>
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<td>Pyridine</td>
<td>1.89</td>
<td>0.820</td>
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Table 6.9
SPECIFIC RETENTION VOLUMES ($V_{298}$, dm$^3$g$^{-1}$) FOR VARIOUS ADSORBENTS AT
298K, AND COMPOUND PARAMETERS FOR REGRESSIONS ON DATA OF
GALLANT ET AL.[104].

<table>
<thead>
<tr>
<th>#</th>
<th>Compound</th>
<th>log $V_g$</th>
<th>$\pi_H^2$</th>
<th>log$L^{16}$</th>
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</thead>
<tbody>
<tr>
<td>109</td>
<td>n-Hexane</td>
<td>1.41</td>
<td>0.000</td>
<td>2.668</td>
</tr>
<tr>
<td>126</td>
<td>n-Octane</td>
<td>2.28</td>
<td>0.000</td>
<td>3.677</td>
</tr>
<tr>
<td>180</td>
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<td>0.000</td>
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<tr>
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<td>2-Dichloroethane</td>
<td>1.37</td>
<td>0.640</td>
<td>2.573</td>
</tr>
<tr>
<td>2804</td>
<td>Trichloroethene</td>
<td>1.95</td>
<td>0.400</td>
<td>2.997</td>
</tr>
<tr>
<td>5502</td>
<td>Butanone</td>
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<td>0.700</td>
<td>2.287</td>
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<td>0.51</td>
<td>0.650</td>
<td>1.750</td>
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<td>0.670</td>
<td>3.640</td>
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<td>3.20</td>
<td>0.800</td>
<td>4.319</td>
</tr>
<tr>
<td>16501</td>
<td>Phenol</td>
<td>3.39</td>
<td>0.880</td>
<td>3.897</td>
</tr>
<tr>
<td>16502</td>
<td>o-Cresol</td>
<td>4.00</td>
<td>0.860</td>
<td>4.242</td>
</tr>
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<td>m-Cresol</td>
<td>4.07</td>
<td>0.870</td>
<td>4.329</td>
</tr>
<tr>
<td>16504</td>
<td>p-Cresol</td>
<td>4.15</td>
<td>0.870</td>
<td>4.307</td>
</tr>
</tbody>
</table>
Table 6.10

Regression Results on Tenax-GC from Brown and Purcell, (B & P), Gallant et al., (G), and both data sets combined, (COMB),[104,105]

<table>
<thead>
<tr>
<th>Source</th>
<th>SP</th>
<th>SP_0</th>
<th>s.R^2</th>
<th>-1.LogL^16</th>
<th>n</th>
<th>r</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B &amp; P</td>
<td>log Vg</td>
<td>-2.29</td>
<td>0.68</td>
<td>1.37</td>
<td>67</td>
<td>0.9795</td>
<td>0.28</td>
</tr>
<tr>
<td>B &amp; P</td>
<td>log Vg</td>
<td>-2.14</td>
<td>-</td>
<td>1.42</td>
<td>69</td>
<td>0.9624</td>
<td>0.39</td>
</tr>
<tr>
<td>G</td>
<td>log Vg</td>
<td>-2.18</td>
<td>0.86</td>
<td>1.27</td>
<td>40</td>
<td>0.9727</td>
<td>0.30</td>
</tr>
<tr>
<td>G</td>
<td>log Vg</td>
<td>-1.81</td>
<td>-</td>
<td>1.29</td>
<td>40</td>
<td>0.9575</td>
<td>0.37</td>
</tr>
<tr>
<td>COMB</td>
<td>log Vg</td>
<td>-2.23</td>
<td>0.77</td>
<td>1.31</td>
<td>107</td>
<td>0.9779</td>
<td>0.29</td>
</tr>
<tr>
<td>COMB</td>
<td>log Vg</td>
<td>-1.91</td>
<td>-</td>
<td>1.34</td>
<td>107</td>
<td>0.9701</td>
<td>0.34</td>
</tr>
</tbody>
</table>

\[
\log V_g = -2.14 + 1.42 \log L_{16} \\
\text{where } n = 69, \quad r = 0.9624, \quad \text{sd} = 0.386
\]

\[
\log V_g = -7.54 + 0.025 \text{bp/K} \\
\text{where } n = 69, \quad r = 0.9244, \quad \text{sd} = 0.543
\]

\[
\log V_g = 3.69 - 1.23 \log P \\
\text{where } n = 68, \quad r = 0.8424, \quad \text{sd} = 0.768
\]

where \( n \) is the number of solutes, \( r \) is the overall correlation coefficient, and \( \text{sd} \) is the standard deviation in \( \log V_g \). It is clear that \( \log L_{16} \) is a very much better descriptor than either \( \text{bp/K} \) or \( \log P \); this is shown rather well in Figs. 6.5–6.7.

From the data of Maier and Fieber [102], at high temperatures, determination of the \( l \) constant at ambient temperatures has been carried out. Using the linear relationship between \( \log L_{16} \) and the reciprocal of the absolute temperature \( 1/K \), the \( l \) constant for
Tenax TA at 293.15K is found by extrapolation to be $l = 1.45$. This value compares well with those obtained on Tenax GC of $l = 1.42$ and $l = 1.29$ for Brown and Purcell and Gallant et al. respectively, at 293.15K (table 6.10). It also compares well with that obtained on Tenax TA at 293.15K of $l = 1.58$ (eqn. 6.12). All the $l$ values for the four different data sets on Tenax are within 0.3 log units of each other and although this may seem large it should be remembered that the data are from four different sets of workers and that in some cases the compounds studied covered a range of $V_g$ values of over six log units. In addition most of the ambient log $V_g$ values have been extrapolated from higher temperatures which will introduce an unknown variance into the results.

FIGURE 6.5 Plot of Log $V_g$ vs Boiling Point (K) from Tenax GC Data of Brown and Purcell at 298.15K.
FIGURE 6.6

Plot of Log $V_g$ vs $-\log P$ from Tenax GC Data of Brown and Purcell at 298.15K
FIGURE 6.7

Plot of Log $V_g$ vs Log $L^{16}$ from Tenax GC Data of Brown and Purcell

at 298.15K
This study has shown that retention behaviour on a range of solids can be described by an LSER using only a few parameters. It has also been shown that the relationship of retention behaviour and the parameters of the adsorbates, is better correlated than the classical techniques of solid characterisation using vapour pressure or boiling point. Retention volumes could now be predicted on various adsorbents using the known parameter values for the adsorbate and the determined LSER equation for the carbon. This would be particularly useful where the experimental value is difficult to obtain, for example, if the adsorbate was highly toxic. However, the main advantage of predicting ambient adsorption on carbonaceous or other 'trapping' solids such as Tenax is the inordinate length of time that is usually necessary for elution of the adsorbate at ambient temperatures. After all, the purpose of many of these adsorbents is to remove chemicals from air and water media at ambient temperatures. It is therefore natural that retention data at ambient temperatures are difficult to obtain, simply due to the high residence times encountered.

As environmental concerns come increasingly to the fore, so too will the development of solids for the adsorption of unwanted chemicals. It is important that a means of classification for adsorbents is developed in tandem with their proliferation. In this manner specific adsorbents can be utilised for specific applications without the need for repeated testing of every possible adsorbent available, at the outset of every project.
CHAPTER VII
RESULTS AND DISCUSSION OF COMMERCIAL ADSORBENTS

GENERAL INTRODUCTION

The main aim of this work was to determine the surface nature of several adsorbents in terms of characteristic constants. The adsorbents could then be compared with each other and meaningful conclusions could be drawn regarding the relative adsorptive strength of a series of adsorbents. The work was carried out under both dry and humid conditions in order to determine the effect of water vapour on the adsorption process.

The adsorbents studied were chosen for their high adsorptive strength and/or their hydrophobicity. Unlike the sample-trap adsorbents discussed in the previous chapter, whose characteristics must usually allow for ease of liberation of the adsorbate from the adsorbent for sampling and analysis purposes, the adsorbents in this chapter are chosen so as to be able to adsorb the adsorbates strongly and do not necessarily allow for ease of liberation. They are commonly used in water and air purification applications. These include; respirator cartridges, waste water treatment, waste gas treatment, ground water remediation, protective suit linings, domestic and industrial water filtration, spillage clean up and odour control.

The manufacturers of the adsorbents frequently claim that their adsorbents have particular chemical affinities for example for halogenated compounds, or they may claim that a particular adsorbent is hydrophobic so that it performs almost as well when wet as when dry. However, no simple method of ascertaining the chemical nature of the adsorbent surface is in use. In this work the chemical nature of each adsorbent surface, under both dry and wet conditions, has been ascertained by obtaining the characteristic constants of the adsorbent. From these constants an overall equation which is an unique descriptor of any particular adsorbent has been constructed. Comparison of these equations for different adsorbents has allowed quantitative inferences to be made as to
the nature of each adsorbent surface. In this manner it has been possible to show, for example, which adsorbent is the most hydrophobic and which has the highest affinity for halogenated compounds. In addition, the adsorptive process has been considered in terms of adsorbent pore structure and pore size distribution. Knowledge of each adsorbents strengths and weaknesses should allow future workers to choose the most appropriate adsorbent for a particular application. In addition, specific quantitative knowledge of each adsorbent should allow manufacturers of adsorbents to hone their production methods to produce specific adsorptive qualities, such as hyrophobicity, in their adsorbents.

PHYSICAL PROPERTIES OF THE ADSORBENTS

This study has characterised seven adsorbents and the singlepoint BET surface area values of these and their pore size distributions are given in table 7.1.

TABLE 7.1 Physical Properties of Adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Lot</th>
<th>BET Surface Area (m²g⁻¹)</th>
<th>Micropore Volume (cm³g⁻¹)</th>
<th>Mesopore Volume (cm³g⁻¹)</th>
<th>Macropore Volume (cm³g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambersorb 88/007 564</td>
<td>486(606)</td>
<td>0.25</td>
<td>0.16</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>Ambersorb 89/2147 572</td>
<td>738(917)</td>
<td>0.38</td>
<td>0.21</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>ASC Whetlerite</td>
<td>708(856)</td>
<td>0.36</td>
<td>0.04</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Sutcliffe-Speakman 207A</td>
<td>796(923)</td>
<td>0.40</td>
<td>0.03</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>SAR-O SGM1701-1</td>
<td>914(1131)</td>
<td>0.46</td>
<td>0.03</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Ambersorb¹ 563</td>
<td>550</td>
<td>0.24</td>
<td>0.24</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Chem-VironTE10102A SCI</td>
<td>1253</td>
<td>0.51</td>
<td>0.01</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

¹ All adsorbents are 20/30 mesh. ² Manufacturers Estimate Only. Data obtained from Rohm and Haas Ltd, USA. Figures in parenthesis are BET multipoint values.
PARTITION CONSTANTS ON ADSORBENTS

For each adsorbent, partition constants at infinite dilution for a range of adsorbates have been determined by the chromatographic technique described in chapter IV. These are shown in tables 7.2-7.6. The values at 0% humidity are somewhat less numerous than those at 80% humidity due to the long duration of experiments on dry adsorbents at 298.15K.

TABLE 7.2
Partition Constants for Ambersorb 564 at 0% and 80% Humidity

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Compound</th>
<th>0% Humidity</th>
<th>80% Humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Log $K_e$</td>
<td>Log $K_p$</td>
</tr>
<tr>
<td>101</td>
<td>Methane</td>
<td>1.34</td>
<td>1.15</td>
</tr>
<tr>
<td>102</td>
<td>Ethane</td>
<td>1.57</td>
<td>1.66</td>
</tr>
<tr>
<td>103</td>
<td>Propane</td>
<td>1.66</td>
<td>1.92</td>
</tr>
<tr>
<td>104</td>
<td>n-Butane</td>
<td>2.88</td>
<td>3.25</td>
</tr>
<tr>
<td>1001</td>
<td>Ethene</td>
<td>0.26</td>
<td>0.32</td>
</tr>
<tr>
<td>1002</td>
<td>Propene</td>
<td>1.67</td>
<td>1.90</td>
</tr>
<tr>
<td>2153</td>
<td>1,1,1,2-Tetrafluoroethane</td>
<td>0.18</td>
<td>0.80</td>
</tr>
<tr>
<td>2154</td>
<td>1,1,2,2-Tetrafluoroethane</td>
<td>0.67</td>
<td>1.29</td>
</tr>
<tr>
<td>2501</td>
<td>Chloromethane</td>
<td>1.48</td>
<td>1.80</td>
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<tr>
<td>2502</td>
<td>Dichloromethane</td>
<td>3.71</td>
<td>4.25</td>
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<td>2.90</td>
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<td>4026</td>
<td>Difluorochloromethane</td>
<td>1.10</td>
<td>1.64</td>
</tr>
<tr>
<td>4051</td>
<td>Difluorodichloromethane</td>
<td>2.40</td>
<td>3.10</td>
</tr>
<tr>
<td>4206</td>
<td>Arcton 133A*</td>
<td>1.79</td>
<td>2.48</td>
</tr>
<tr>
<td>5302</td>
<td>Acetaldehyde</td>
<td>2.37</td>
<td>2.62</td>
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<tr>
<td>6001</td>
<td>Methyl Formate</td>
<td>2.76</td>
<td>3.15</td>
</tr>
<tr>
<td>6801</td>
<td>Methylamine</td>
<td>2.88</td>
<td>2.98</td>
</tr>
<tr>
<td>8001</td>
<td>Methanol</td>
<td>2.46</td>
<td>2.57</td>
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<td>8002</td>
<td>Ethanol</td>
<td>3.06</td>
<td>3.34</td>
</tr>
<tr>
<td>8303</td>
<td>2,2,2-Trifluoroethanol</td>
<td>2.76</td>
<td>3.37</td>
</tr>
</tbody>
</table>

* 1,1,1-Trifluoro-2-chloroethane
TABLE 7.3

Partition Constants for Ambersorb 572 at 0% and 80% Humidity and 298.15K

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Compound</th>
<th>0% Humidity</th>
<th>80% Humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Log (K_e)</td>
<td>Log (K_p)</td>
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<tr>
<td>101</td>
<td>Methane</td>
<td>0.85</td>
<td>0.67</td>
</tr>
<tr>
<td>102</td>
<td>Ethane</td>
<td>1.05</td>
<td>1.13</td>
</tr>
<tr>
<td>103</td>
<td>Propane</td>
<td>2.70</td>
<td>2.95</td>
</tr>
<tr>
<td>104</td>
<td>n-Butane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>106</td>
<td>n-Pentane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>109</td>
<td>n-Hexane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1001</td>
<td>Ethene</td>
<td>0.98</td>
<td>1.03</td>
</tr>
<tr>
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<td>Propene</td>
<td>2.41</td>
<td>2.65</td>
</tr>
<tr>
<td>2153</td>
<td>1,1,1,2-Tetrafluoroethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2154</td>
<td>1,1,2,2-Tetrafluoroethane</td>
<td></td>
<td></td>
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<tr>
<td>2501</td>
<td>Chloromethane</td>
<td>2.08</td>
<td>2.40</td>
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<td>Dichloromethane</td>
<td>3.33</td>
<td>3.87</td>
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<td>4.67</td>
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<td>4206</td>
<td>Arcton 133A*</td>
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</tr>
<tr>
<td>4220</td>
<td>Arcton 123 *</td>
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<td></td>
</tr>
<tr>
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<td>Diethylether</td>
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</tr>
<tr>
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<td>Propanone</td>
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<td>Ethanol</td>
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</tr>
</tbody>
</table>

* 1,1,1-Trifluoro-2-chloroethane
+ 1,1,1-Trifluoro-2,2-dichloroethane
### TABLE 7.4
Partition Constants for Ambersorb 563 at 0% and 80% Humidity and 298.15K

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Compound</th>
<th>0% Humidity</th>
<th>80% Humidity</th>
<th>0% Humidity</th>
<th>80% Humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Log $K_e$</td>
<td>Log $K_p$</td>
<td>Log $K_e$</td>
<td>Log $K_p$</td>
</tr>
<tr>
<td>101</td>
<td>Methane</td>
<td>-0.50</td>
<td>-0.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>Ethane</td>
<td>0.97</td>
<td>1.06</td>
<td>0.59</td>
<td>0.67</td>
</tr>
<tr>
<td>103</td>
<td>Propane</td>
<td>2.80</td>
<td>3.06</td>
<td>2.07</td>
<td>2.33</td>
</tr>
<tr>
<td>104</td>
<td>n-Butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>106</td>
<td>n-Pentane</td>
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<tr>
<td>109</td>
<td>Hexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1001</td>
<td>Ethene</td>
<td>0.81</td>
<td>0.87</td>
<td>0.46</td>
<td>0.52</td>
</tr>
<tr>
<td>1002</td>
<td>Propene</td>
<td>2.68</td>
<td>2.92</td>
<td>1.95</td>
<td>2.19</td>
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<td>2153</td>
<td>1,1,1,2-Tetrafluoroethane</td>
<td>2.29</td>
<td>2.91</td>
<td>1.33</td>
<td>1.95</td>
</tr>
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<td>1,1,2,2-Tetrafluoroethane</td>
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<td>1.42</td>
<td>2.04</td>
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<td>2501</td>
<td>Chloromethane</td>
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<td></td>
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<td>Dichloromethane</td>
<td>3.59</td>
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<td>3.68</td>
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<td>2503</td>
<td>Trichloromethane</td>
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<td>Tetrachloromethane</td>
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<td></td>
<td>3.58</td>
<td>4.38</td>
</tr>
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<td>4025</td>
<td>Fluorodichloromethane</td>
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<td>4.01</td>
<td>3.11</td>
<td>3.74</td>
</tr>
<tr>
<td>4026</td>
<td>Difluorochloromethane</td>
<td>2.30</td>
<td>2.85</td>
<td>1.71</td>
<td>2.26</td>
</tr>
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<td>Difluorodichloromethane</td>
<td>2.80</td>
<td>3.50</td>
<td>2.67</td>
<td>3.36</td>
</tr>
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<td>1-fluoro-1,1-dichloroethane</td>
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<td></td>
</tr>
<tr>
<td>4206</td>
<td>Arcton 133A*</td>
<td></td>
<td></td>
<td>3.00</td>
<td>3.69</td>
</tr>
<tr>
<td>4220</td>
<td>Arcton 123*</td>
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<tr>
<td>4502</td>
<td>Diethylether</td>
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<tr>
<td>5302</td>
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<td>3.03</td>
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<td>Acetonitrile</td>
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<td></td>
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<td>Propan-2-ol</td>
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TABLE 7.5
Partition Constants for Sutcliffe-Speakman 207A at 0% and 80% Humidity and 298.15K

<table>
<thead>
<tr>
<th>Compound Compound No.</th>
<th>0% Humidity</th>
<th>80% Humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Log $K_e$</td>
<td>Log $K_p$</td>
</tr>
<tr>
<td>101 Methane</td>
<td>0.24</td>
<td>0.33</td>
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<tr>
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<td>2.10</td>
<td>2.36</td>
</tr>
<tr>
<td>103 Propane</td>
<td>3.20</td>
<td>3.42</td>
</tr>
<tr>
<td>104 n-Butane</td>
<td>2.18</td>
<td>2.65</td>
</tr>
<tr>
<td>106 n-Pentane</td>
<td>2.31</td>
<td>2.86</td>
</tr>
<tr>
<td>109 Hexane</td>
<td>0.17</td>
<td>0.23</td>
</tr>
<tr>
<td>1001 Ethene</td>
<td>2.02</td>
<td>2.26</td>
</tr>
<tr>
<td>2153 1,1,1,2-Tetrafluoroethane</td>
<td>1.95</td>
<td>2.58</td>
</tr>
<tr>
<td>2154 1,1,2,2-Tetrafluoroethane</td>
<td>2.32</td>
<td>2.94</td>
</tr>
<tr>
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<tr>
<td>2504 Tetrachloromethane</td>
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<td>2.39</td>
</tr>
<tr>
<td>4025 Fluorodichloromethane</td>
<td>2.33</td>
<td>3.02</td>
</tr>
<tr>
<td>4026 Difluorochloromethane</td>
<td>3.15</td>
<td>3.83</td>
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<tr>
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<td>2.96</td>
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<tr>
<td>4206 Arcton 133A*</td>
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<tr>
<td>4220 Arcton 123*</td>
<td>2.40</td>
<td>2.65</td>
</tr>
<tr>
<td>4502 Diethylether</td>
<td>2.57</td>
<td>2.96</td>
</tr>
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<td>5302 Acetaldehyde</td>
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<td>3.25</td>
</tr>
<tr>
<td>6800 Ammonia</td>
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<td>2.65</td>
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<tr>
<td>6801 Methyl Formate</td>
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<td>3.86</td>
</tr>
<tr>
<td>6803 n-Propylamine</td>
<td>3.33</td>
<td>3.55</td>
</tr>
</tbody>
</table>

* 1,1,1-Trifluoro-2-chloroethane
+ 1,1,1-Trifluoro-2,2-dichloroethane
TABLE 7.6
Partition Constants for ASC Whetlerite at 0% and 80% Humidity and 298.15K

<table>
<thead>
<tr>
<th>Compound Compound No.</th>
<th>0% Humidity</th>
<th>80% Humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Log K_e</td>
<td>Log K_p</td>
</tr>
<tr>
<td>101 Methane</td>
<td>0.85</td>
<td>0.67</td>
</tr>
<tr>
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<td>0.96</td>
<td>1.04</td>
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<tr>
<td>103 Propane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>104 n-Butane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>106 n-Pentane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>109 Hexane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1001 Ethene</td>
<td>0.94</td>
<td>1.00</td>
</tr>
<tr>
<td>1002 Propene</td>
<td>2.48</td>
<td>2.71</td>
</tr>
<tr>
<td>2153 1,1,1,2-Tetrafluoroethane</td>
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<td>2.82</td>
</tr>
<tr>
<td>2154 1,1,2,2-Tetrafluoroethane</td>
<td>2.36</td>
<td>2.98</td>
</tr>
<tr>
<td>2501 Chloromethane</td>
<td>1.71</td>
<td>2.03</td>
</tr>
<tr>
<td>2502 Dichloromethane</td>
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<td></td>
</tr>
<tr>
<td>2504 Tetrachloromethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4025 Fluorodichloromethane</td>
<td>3.22</td>
<td>3.84</td>
</tr>
<tr>
<td>4026 Difluorochloromethane</td>
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<tr>
<td>4051 Difluorodichloromethane</td>
<td>2.53</td>
<td>3.22</td>
</tr>
<tr>
<td>4154 1-fluoro-1,1-dichloroethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4206 Arcton 133A*</td>
<td>3.19</td>
<td>3.87</td>
</tr>
<tr>
<td>4220 Arcton 123 *</td>
<td>2.36</td>
<td>3.16</td>
</tr>
<tr>
<td>4502 Diethylether</td>
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<td></td>
</tr>
<tr>
<td>5302 Acetaldehyde</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6001 Methyl Formate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6051 Methyl Acetate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6601 Acetonitrile</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6800 Ammonia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6801 Methylamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6803 n-Propylamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6851 Dimethylamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8000 Water</td>
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<td></td>
</tr>
<tr>
<td>8001 Methanol</td>
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<td>2.64</td>
</tr>
<tr>
<td>8002 Ethanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8003 Propan-1-ol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8004 Propan-2-ol</td>
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</tr>
<tr>
<td>8303 2,2,2-Trifluoroethanol</td>
<td>2.42</td>
<td>3.04</td>
</tr>
<tr>
<td>8323 1,1,1,3,3,3-Hexafluoropropanol</td>
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<td></td>
</tr>
</tbody>
</table>

* 1,1,1-Trifluoro-2-chloroethane
* 1,1,1-Trifluoro-2,2-dichloroethane
SUTCLIFFE SPEAKMAN 207A

Sutcliffe Speakman 207A is a coal based carbon adsorbent. It is mainly microporous with a high surface area and high capacity for the larger types of molecules. It is used as a benchmark in this work for comparison with the Ambersorb, polymer derived, carbons. The partition constants for various adsorbates on Sutcliffe Speakman 207A at both 0% and 80% humidity are shown in table 7.5. Regression analysis of each data set gives characteristic equations for \( \log K_e \) and \( \log K_p \) at 0% and 80% humidity.

The parameters, \( R_3, \pi^H_2, \alpha^H_2, \beta^H_2 \) and \( \log L^{16} \) for each adsorbate studied are shown in table 7.7 for the adsorbates studied at 0% and table 7.8 for the adsorbates studied at 80% humidity.

The regression equation for \( \log K_e \) at 0% humidity is shown in equation 7.1.

\[
\log K_e = -3.77R_3 + 1.75\pi^H_2 + 1.85\alpha^H_2 + 1.94\beta^H_2 + 0.04 (7.1)
\]

\[R = 0.960 \quad \text{S.D.} = 0.299 \quad N = 20\]

where \( R \) is the correlation coefficient, S.D. is the standard deviation and \( N \) is the number of adsorbates studied.

The \( \log L^{16} \) constant (\( \beta = 1.94 \)) is high and is the main contributor to adsorbance in most cases. The microporous surface of activated carbons is the cause of such high dispersion constants. The micropores are known to be narrow enough to interact with incoming molecules from two sides simultaneously. This enhancement in the adsorption is not a specific interaction but a non-specific dispersion interaction and is what causes adsorption on carbons to be mainly governed by dispersion forces.

The regression equation at 0% humidity reveals that there is significant acidity, \( \beta = 1.85 \), and basicity, \( \alpha = 1.75 \), on the carbon surface.

170
<table>
<thead>
<tr>
<th>Set</th>
<th>C.N. Adsorbate Name</th>
<th>$R_2$</th>
<th>$\pi_{r_2}$</th>
<th>$\alpha_{r_2}$</th>
<th>$\beta_{r_2}$</th>
<th>logL$^{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>102 Ethane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.492</td>
</tr>
<tr>
<td>2</td>
<td>103 Propane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>3</td>
<td>104 n-Butane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.615</td>
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<td>4</td>
<td>1001 Ethene</td>
<td>0.107</td>
<td>0.100</td>
<td>0.000</td>
<td>0.070</td>
<td>0.289</td>
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<tr>
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<td>1002 Propene</td>
<td>0.103</td>
<td>0.080</td>
<td>0.000</td>
<td>0.070</td>
<td>0.946</td>
</tr>
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<td>2153 1,1,1,2-Tetrafluoroethane(134a)</td>
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<td>-0.300</td>
<td>0.200</td>
<td>0.000</td>
<td>0.226</td>
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<tr>
<td>7</td>
<td>2154 1,1,2,2-Tetrafluoroethane(134)</td>
<td>-0.280</td>
<td>-0.300</td>
<td>0.300</td>
<td>0.000</td>
<td>0.289</td>
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<tr>
<td>8</td>
<td>2501 Chloromethane</td>
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<td>0.430</td>
<td>0.000</td>
<td>0.080</td>
<td>1.163</td>
</tr>
<tr>
<td>9</td>
<td>2502 Dichloromethane</td>
<td>0.387</td>
<td>0.570</td>
<td>0.100</td>
<td>0.050</td>
<td>2.019</td>
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<tr>
<td>10</td>
<td>2504 Tetrachloromethane</td>
<td>0.458</td>
<td>0.380</td>
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<td>0.000</td>
<td>2.823</td>
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<td>11</td>
<td>4025 Fluorodichloromethane(21)</td>
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<td>0.400</td>
<td>0.200</td>
<td>0.000</td>
<td>1.614</td>
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<tr>
<td>12</td>
<td>4026 Difluorochloromethane(22)</td>
<td>0.000</td>
<td>0.250</td>
<td>0.200</td>
<td>0.000</td>
<td>0.690</td>
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<td>13</td>
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<td>0.140</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
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<td>0.000</td>
<td>0.000</td>
<td>1.932</td>
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<td>0.000</td>
<td>0.450</td>
<td>1.230</td>
</tr>
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<td>6001 Methyl formate</td>
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<td>0.000</td>
<td>0.380</td>
<td>1.285</td>
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<td>0.090</td>
<td>0.300</td>
<td>1.739</td>
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<tr>
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<td>0.370</td>
<td>0.480</td>
<td>1.485</td>
</tr>
<tr>
<td>20</td>
<td>8303 2,2,2-Trifluoroethanol</td>
<td>0.015</td>
<td>0.600</td>
<td>0.570</td>
<td>0.150</td>
<td>1.224</td>
</tr>
</tbody>
</table>

() CFC identification number.

The large and negative $R_2$ constant, ($r = -3.77$), was an interesting finding. The $R_2$ scale is a polarisability scale relative to alkanes of equal size, thus a negative $r$ constant for an adsorbent implies that the adsorbent has a lower polarisability than alkanes in contact with it. The carbon surface, it is generally agreed, consists of interlocking sheets of graphite monolayers. The absence of hydrogen atoms in this structure compared with alkanes presumably contributes to its lower polarisability. It can be concluded that the tightly held electrons around carbon present a non polarisable surface to adsorbates. $\pi_{r_2}$ was not found to be statistically significant under the conditions of this study and is thus left out of the regression equation. This was found to be the case at both 0% and 80% humidity.
The regression equation for log \( K_p \) at 0% humidity is shown in equation 7.2.

\[
\log K_p = -4.29R_j + 1.85\alpha H_2 + (1.38)\beta H_2 + 2.18\log L^{16} + 0.25
\]

\( R = 0.934 \) \( \text{S.D.} = 0.420 \) \( N = 20 \)  

The equation in \( \log K_p \) is similar to that in \( \log K_e \), the coefficient in \( \beta H_2 \) drops a little, however, and is not quite statistically significant with a confidence level of only 93.6%. This actually sheds some doubt on the significance of \( \beta H_2 \) at all, and further studies would be needed to verify the possible hydrogen bond acidity of the carbon. There is agreement in the two equations over the significance of the other constants. The high dispersion constant \( l = 2.18 \) and large negative \( R_2 \) constant \( (r = -4.29) \) are in the same region as the equation in \( \log K_e \), and this is not surprising for a carbon as discussed for the \( \log K_e \) results earlier. What may seem surprising however is the confirmation that this carbon has some hydrogen bond basicity \( (\alpha = 1.85) \). The phenomenon, however, may be explained by the presence of oxygen groups on the carbon surface. These may take the form of carbonyl or ether links and are probably a result of oxidation during the activation step in the manufacture of the adsorbent. The results are in agreement with those of McGill [108], who also studied this adsorbent and found that it had a significant hydrogen bond basicity for \( \log K_e \) values at 0% humidity. McGill did not find the \( \alpha H_2 \) constant significant in \( \log K_p \) but this may have been due to an absence of strong hydrogen bond acids in the selection of adsorbates used. McGill’s finding is now supported by the confirmation in this work of the presence of significant hydrogen bond basicity on 207A regardless of whether one is considering \( \log K_e \) or \( \log K_p \). A useful test for the statistical significance of a constant is to remove it from the regression and observe the effect on the overall correlation coefficient, \( R \). The removal of \( \alpha H_2 \) from the analysis, results in a significant reduction in the correlation coefficient. The correlation coefficient, \( R \), for regressions of \( \log K_e \) and \( \log K_p \) against the parameters \( R_2 \) and \( \log L^{16} \) only, are \( R = 0.8056 \) and \( R = 0.8298 \) respectively. Thus the evidence is quite strong that
207A has significant hydrogen bond basicity at 0% humidity.

The regression equation for log $K_e$ at 80% humidity is shown in equation 7.3.

$$\log K_e = -1.31R_2 + 1.49\alpha_{H_2}^0 + 1.66\beta_{H_2}^0 + 1.37\log L^{16} - 0.87 \quad (7.3)$$

$$R = 0.948 \text{ S.D.} = 0.268 \text{ N} = 20$$

The most important term is the dispersion constant for $\log L^{16} (q = 1.37)$, this may not appear immediately obvious as it is not the largest constant in the equation, both $\alpha_{H_2}^0 (a = 1.49)$ and $\beta_{H_2}^0 (b = 1.66)$, being larger. However, in order to decide on the relative importance of the terms in the equation one should not consider the particular constants in isolation but the product of the constant and its parameter. The $\log L^{16}$ parameter is by far the largest for most adsorbates. Thus the other characteristic constants must have a considerably greater magnitude than the $l$ constant in the regression equation in order to supersede the $l\log L^{16}$ term in importance.

The $\log L^{16}$ constant for 207A at 80% humidity is less than its value at 0% humidity ($l = 1.94$). The reduction in the $\log L^{16}$ constant shows that the active sites on the adsorbent surface have lower dispersion interaction strength when wet than when dry. The presence of water lowers the large negative $r$ value from $-3.77$ to $-1.31$. The effect of water molecules present on the surface would give the surface more polarity than that of the dry carbon. This would have the effect of increasing the overall polarisability of the adsorbent and would cause the $R_2$ constant to increase. An alternative explanation may be found by considering the composition of the carrier gas. The $R_2$ value of water is 0.0, which actually makes it considerably more polarisable than the dry carbon surface with its large negative value. Thus, the possibility exists of water in the carrier gas attracting other polarisable molecules off the carbon surface. However, for this to be valid the polarisability of the dry carrier gas, helium, must be less than the polarisability of the wet carrier gas. In actual fact they are exactly the same, the $R_2$ value of helium being 0.0.
### TABLE 7.8
Parameters for the Adsorbates Studied at 80% Humidity on Sutcliffe Speakman 207A at 298.15K

<table>
<thead>
<tr>
<th>Set</th>
<th>C.N. Adsorbate Name</th>
<th>( R_1 )</th>
<th>( \pi^H_2 )</th>
<th>( \alpha^H_2 )</th>
<th>( \beta^H_2 )</th>
<th>( \log L_2^{16} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>103 Propane</td>
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<tr>
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<td>104 n-Butane</td>
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<td>0.000</td>
<td>0.000</td>
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<td>3</td>
<td>106 n-Pentane</td>
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<td>0.000</td>
<td>0.000</td>
<td>2.162</td>
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<td>0.000</td>
<td>0.000</td>
<td>2.668</td>
</tr>
<tr>
<td>5</td>
<td>1002 Propene</td>
<td>0.103</td>
<td>0.080</td>
<td>0.000</td>
<td>0.070</td>
<td>0.946</td>
</tr>
<tr>
<td>6</td>
<td>2154 1,1,2,2-Tetrafluoroethane(134)</td>
<td>-0.280</td>
<td>-0.300</td>
<td>0.300</td>
<td>0.000</td>
<td>0.289</td>
</tr>
<tr>
<td>7</td>
<td>2502 Dichloromethane</td>
<td>0.387</td>
<td>0.570</td>
<td>0.100</td>
<td>0.050</td>
<td>2.019</td>
</tr>
<tr>
<td>8</td>
<td>2503 Trichloromethane</td>
<td>0.425</td>
<td>0.490</td>
<td>0.150</td>
<td>0.020</td>
<td>2.480</td>
</tr>
<tr>
<td>9</td>
<td>2504 Tetrachloromethane</td>
<td>0.458</td>
<td>0.380</td>
<td>0.000</td>
<td>0.000</td>
<td>2.823</td>
</tr>
<tr>
<td>10</td>
<td>4025 Fluorodichloromethane (21)</td>
<td>0.206</td>
<td>0.400</td>
<td>0.200</td>
<td>0.000</td>
<td>1.614</td>
</tr>
<tr>
<td>11</td>
<td>4026 Difluorochloromethane (22)</td>
<td>0.000</td>
<td>0.250</td>
<td>0.200</td>
<td>0.000</td>
<td>0.690</td>
</tr>
<tr>
<td>12</td>
<td>4051 Difluorodichloromethane (12)</td>
<td>0.001</td>
<td>0.140</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>13</td>
<td>4154 1-fluoro-1,1-dichloroethene(141b)</td>
<td>0.160</td>
<td>0.400</td>
<td>0.000</td>
<td>0.000</td>
<td>1.932</td>
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<tr>
<td>14</td>
<td>4206 1,1,1-Trifluoro-2-chloroethane(133a)</td>
<td>0.010</td>
<td>0.400</td>
<td>0.150</td>
<td>0.000</td>
<td>1.168</td>
</tr>
<tr>
<td>15</td>
<td>5302 Acetaldehyde</td>
<td>0.208</td>
<td>0.670</td>
<td>0.000</td>
<td>0.450</td>
<td>1.230</td>
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<td>16</td>
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<td>17</td>
<td>6001 Methyl formate</td>
<td>0.192</td>
<td>0.680</td>
<td>0.000</td>
<td>0.380</td>
<td>1.285</td>
</tr>
<tr>
<td>18</td>
<td>6601 Acetonitrile</td>
<td>0.237</td>
<td>0.900</td>
<td>0.090</td>
<td>0.300</td>
<td>1.739</td>
</tr>
<tr>
<td>19</td>
<td>8001 Methanol</td>
<td>0.278</td>
<td>0.440</td>
<td>0.430</td>
<td>0.470</td>
<td>0.970</td>
</tr>
<tr>
<td>20</td>
<td>8002 Ethanol</td>
<td>0.246</td>
<td>0.420</td>
<td>0.370</td>
<td>0.480</td>
<td>1.485</td>
</tr>
<tr>
<td>21</td>
<td>8303 2,2,2-Trifluoroethanol</td>
<td>0.015</td>
<td>0.600</td>
<td>0.570</td>
<td>0.150</td>
<td>1.224</td>
</tr>
</tbody>
</table>

() CFC identification number.

This fact allows us to draw some interesting conclusions. The increase of \( R_2 \) on the wet column is not due to the competing attraction of the humid carrier gas and must therefore be due to an increased polarisability on the carbon surface. This can only be explained by the presence of water in adsorbance sites and therefore some adsorbate molecules must be adsorbing on water as oppose to carbon. In reality it is likely that water and adsorbate are intermingled in the micropores and that the adsorbate is undergoing both the attraction of the carbon surface and the attraction of surrounding water molecules that are themselves adsorbed on the carbon or onto other water or adsorbate molecules.

The hydrogen bond base constant \( (a = 1.49) \) is lowered as is the hydrogen bond acid constant \( (b = 1.66) \) on wet 207A. This result was unexpected as the presence of water
molecules would be expected to increase the acidity and basicity of the surface. However, the $\alpha_H^2$ parameter for water, (0.82), and the $\beta_H^2$ parameter, (0.35), are both less than the respective $\alpha_H^2$ (1.75) and $\beta_H^2$ (1.85) constants found on dry 207A. It is not surprising then that the net effect of water molecules on the surface of 207A is to lower the $\alpha_H^2$ and $\beta_H^2$ constants. The final point to note about equation 7.3 is the constant term, -0.87 c.f. +0.04 on the dry surface. This probably reflects a decrease in surface area available for adsorbates and can be explained by the condensation of water in the micropores actually filling and blocking access to some micropores. This reduction in the constant term is actually the biggest effect of introducing water vapour into the gas stream, accounting for a decrease in adsorbance of 0.91 log units for every adsorbate.

It is now possible to comprehend the effect of water vapour as consisting of two processes. Firstly, the water vapour adsorbs into the micropores effectively reducing the surface area available for adsorbance, and may eventually condense. Secondly, the water vapour competes with any other adsorbate for active sites on the adsorbent surface. The latter effect will take place at any level of humidity. But the whole of the former step may only be possible at the particular level of humidity in the gas stream that is high enough for water condensation to occur. The condensation on the carbon surface is likely to occur on both polar and eventually, at higher levels of humidity, non-polar sites. In either case, the attraction of the carbon surface for the water molecules, albeit weak in the case of non-polar sites, will be enough to cause condensation before 100% humidity is reached. This would explain the lowering of surface area available for adsorption at 80% humidity.

The surface onto which the adsorbates are adsorbing is interesting to consider. Two mechanisms are possible, the first follows the TVFM theory of Dubinin [15], where the water would be expected to adsorb in the micropore from the narrowest possible point and steadily fill the micropore as it became wider until the whole micropore contained water. Adsorbance in this instance would be on the walls of the micropore which the
water had not yet filled. The interaction in this case is still that between adsorbate and carbon. Such an interaction could be expected to be comparable with that on a dry carbon although it would be lowered by competition from water molecules in the carrier gas and by the fact that the most active sites will be already occupied by water molecules.

The second possible mechanism for adsorption under humid conditions follows the theory of Langmuir [4.3]. According to the adsorption-by-monolayer theory of Langmuir, the water would adsorb onto the micropore walls, filling the most active sites first, until a monolayer was formed on the surface. The process would then be repeated to form bilayers etc. If this were the case it would be expected that an incoming adsorbate would be adsorbed on a water covered surface, provided enough water has been adsorbed to cover a monolayer. The log$L^*_{16}$ constant for the adsorbent under such circumstances could be expected to be akin to the log$L^*_{16}$ for water itself. The log$L^*_{16}$ value for water is 0.260, which is considerably smaller than that found on the wet carbon. The log$L^*_{16}$ constant, $I$, on the wet carbon, (1.37), is much closer to that on the dry carbon, (1.94), than that of water. The implication is that the carbon surface is still playing an important part in the adsorption process. The TVFM seems to be the most likely mechanism for adsorption on wet carbon surfaces. The adsorbates are adsorbed onto carbon walls in micropores where the most active sites are already occupied by water molecules. The water adsorbed is probably condensing to form pools in the micropore effectively blocking off these most active sites and lowering the surface area of the adsorbent available for adsorption. To say that the Langmuir theory of adsorption by monolayer does not apply on carbons is something of a moot point. The theory assumes that adsorption is taking place on a flat surface so that once the most active sites are filled the remainder of the surface steadily fills up. In the case of activated carbons the most active sites are indeed filled up first, but there is no longer a flat surface, rather a series of slit shaped micropores. The monolayer theory may still hold true if the micropores are regarded as making up a very large flat surface with another very large flat surface
opposite and lying parallel to it. The parallel surfaces are so proximate that they actually enhance adsorption potential between them as Dubinin [15], has proposed. In this case the TVFM theory is only an application of the Langmuir theory to microporous surfaces. The reason that the I constant is not close to water is simply that the micropores are not fully occupied and a monolayer in the Langmuir sense has not been fully formed so that the carbon surface with its high adsorption potential is still partially available for adsorbate interaction.

The proximity of the walls of the micropores and or basic or acidic sites is probably what causes the condensation of water. The adsorption of one water molecule would act as a nucleus for other water molecules to adsorb around and in the narrow micropores this would probably lead to condensation of water. It is in this respect that the TVFM and the monolayer theory truly differ, the monolayer theory does not account for the possibility of condensation of adsorbate in the micropore.

The regression of log $K_p$ at 80% humidity is shown below.

$$
\log K_p = -1.25R^2 + 1.68\alpha H_2 + 0.93\beta H_2 + 1.43\log L_{w} - 0.39 \quad (7.4)
$$

$$
R = 0.939 \text{ S.D.} = 0.303 \text{ N} = 20
$$

The results are in agreement with the equation in log $K_*$ at 80% humidity. The $I$ constant has diminished from 2.18 to 1.43. The $R_2$ constant rises from -4.29 to -1.25. The $\alpha H_2$ and $\beta H_2$ constants both decrease ($a = 1.85$ to $a = 1.68$ and $b = 1.38$ to $b = 0.93$), as does the constant term 0.25 to -0.39. Changes of this kind have already been discussed for the corresponding results for log $K_*$ at 0% and 80% humidity and need not be repeated here.
ASC-WHETLERITE.

ASC-Whetlerite is an impregnated carbon derived from BPL activated carbon. It is used in breathing apparatus to adsorb toxic agents. It is particularly effective against a range of toxic agents whose small molecular size does not allow for physical adsorption. The range includes; hydrogen cyanide, phosgene and arsine which are neutralised by chemical reaction with the metal impregnants, copper, silver and chromium. It also adsorbs larger molecules by the usual physical adsorption. The characterisation of this carbon together with the elucidation of the effect of a humid gas stream on its adsorption capabilities may provide valuable insights into the scope of future applications of the impregnated carbon in war gas defence systems.

The parameters, $R_2$, $\alpha^H_2$, $\beta^H_2$ and $\log L^{16}$ for each adsorbate studied are shown in table 7.9 for the adsorbates studied at 0% and table 7.10 for the adsorbates studied at 80% humidity.

### TABLE 7.9

Parameters for the Adsorbates Studied at 0% Humidity on ASC-Whetlerite at 298.15K

<table>
<thead>
<tr>
<th>Set</th>
<th>C.N. Adsorbate Name</th>
<th>$R_2$</th>
<th>$\pi^H_2$</th>
<th>$\alpha^H_2$</th>
<th>$\beta^H_2$</th>
<th>$\log L^{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>101 Methane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
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<td>0.000</td>
<td>0.000</td>
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<tr>
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<td>0.100</td>
<td>0.000</td>
<td>0.070</td>
<td>0.289</td>
</tr>
<tr>
<td>4</td>
<td>1002 Propene</td>
<td>0.103</td>
<td>0.080</td>
<td>0.000</td>
<td>0.070</td>
<td>0.946</td>
</tr>
<tr>
<td>5</td>
<td>2153 1,1,1,2-Tetrafluoroethane(134a)</td>
<td>-0.280</td>
<td>-0.300</td>
<td>0.200</td>
<td>0.000</td>
<td>0.226</td>
</tr>
<tr>
<td>6</td>
<td>2154 1,1,2,2-Tetrafluoroethane(134)</td>
<td>-0.280</td>
<td>-0.300</td>
<td>0.300</td>
<td>0.000</td>
<td>0.289</td>
</tr>
<tr>
<td>7</td>
<td>2501 Chloromethane</td>
<td>0.249</td>
<td>0.430</td>
<td>0.000</td>
<td>0.080</td>
<td>1.163</td>
</tr>
<tr>
<td>8</td>
<td>2502 Dichloromethane</td>
<td>0.387</td>
<td>0.570</td>
<td>0.100</td>
<td>0.050</td>
<td>2.019</td>
</tr>
<tr>
<td>9</td>
<td>2504 Tetrachloromethane</td>
<td>0.458</td>
<td>0.380</td>
<td>0.000</td>
<td>0.000</td>
<td>2.823</td>
</tr>
<tr>
<td>10</td>
<td>4025 Fluorodichloromethane(21)</td>
<td>0.206</td>
<td>0.400</td>
<td>0.200</td>
<td>0.000</td>
<td>1.614</td>
</tr>
<tr>
<td>11</td>
<td>4026 Difluorochloromethane(22)</td>
<td>0.000</td>
<td>0.250</td>
<td>0.200</td>
<td>0.000</td>
<td>0.690</td>
</tr>
<tr>
<td>12</td>
<td>4051 Difluorodichloromethane(12)</td>
<td>0.001</td>
<td>0.140</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>13</td>
<td>4206 1,1,1-Trifluoro-2-chloroethane(133a)</td>
<td>0.010</td>
<td>0.400</td>
<td>0.150</td>
<td>0.000</td>
<td>1.168</td>
</tr>
<tr>
<td>14</td>
<td>8001 Methanol</td>
<td>0.278</td>
<td>0.440</td>
<td>0.430</td>
<td>0.470</td>
<td>0.970</td>
</tr>
</tbody>
</table>
### Table 7.10

Parameters for the Adsorbates Studied at 80% Humidity on ASC-Whetlerite at 298.15K

<table>
<thead>
<tr>
<th>Set</th>
<th>C.N. Adsorbate Name</th>
<th>$R_2$</th>
<th>$\pi^H_2$</th>
<th>$\alpha^H_2$</th>
<th>$\beta^R_2$</th>
<th>$\log L^{16}$</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>103 Propane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>2</td>
<td>104 n-Butane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.615</td>
</tr>
<tr>
<td>3</td>
<td>106 n-Pentane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>2.162</td>
</tr>
<tr>
<td>4</td>
<td>1002 Propene</td>
<td>0.103</td>
<td>0.080</td>
<td>0.000</td>
<td>0.070</td>
<td>0.946</td>
</tr>
<tr>
<td>5</td>
<td>2501 Chloromethane</td>
<td>0.249</td>
<td>0.430</td>
<td>0.000</td>
<td>0.080</td>
<td>1.163</td>
</tr>
<tr>
<td>6</td>
<td>2502 Dichloromethane</td>
<td>0.387</td>
<td>0.570</td>
<td>0.100</td>
<td>0.050</td>
<td>2.019</td>
</tr>
<tr>
<td>7</td>
<td>2503 Trichloromethane</td>
<td>0.425</td>
<td>0.490</td>
<td>0.150</td>
<td>0.020</td>
<td>2.480</td>
</tr>
<tr>
<td>8</td>
<td>2504 Tetrachloromethane</td>
<td>0.458</td>
<td>0.380</td>
<td>0.000</td>
<td>0.000</td>
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<tr>
<td>9</td>
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<td>0.000</td>
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<td>1.050</td>
</tr>
<tr>
<td>12</td>
<td>4154 1-fluoro-1,1-dichloroethane(141b)</td>
<td>0.160</td>
<td>0.400</td>
<td>0.000</td>
<td>0.000</td>
<td>1.932</td>
</tr>
<tr>
<td>13</td>
<td>4206 1,1,1-Trifluoro-2-chloroethane(133a)</td>
<td>0.010</td>
<td>0.400</td>
<td>0.150</td>
<td>0.000</td>
<td>1.168</td>
</tr>
<tr>
<td>14</td>
<td>4220 1,1,1-Trifluoro-2,2-dichloroethane(123)</td>
<td>-0.160</td>
<td>0.400</td>
<td>0.220</td>
<td>0.000</td>
<td>1.746</td>
</tr>
<tr>
<td>15</td>
<td>5302 Acetaldehyde</td>
<td>0.208</td>
<td>0.670</td>
<td>0.000</td>
<td>0.450</td>
<td>1.230</td>
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<td>6001 Methyl formate</td>
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<td>0.380</td>
<td>1.285</td>
</tr>
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<td>17</td>
<td>6601 Acetonitrile</td>
<td>0.237</td>
<td>0.900</td>
<td>0.090</td>
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<td>1.739</td>
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<tr>
<td>18</td>
<td>8001 Methanol</td>
<td>0.278</td>
<td>0.440</td>
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<td>0.970</td>
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<td>19</td>
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<td>0.246</td>
<td>0.420</td>
<td>0.370</td>
<td>0.480</td>
<td>1.485</td>
</tr>
<tr>
<td>20</td>
<td>8303 2,2,2-Trifluoroethanol</td>
<td>0.015</td>
<td>0.600</td>
<td>0.570</td>
<td>0.150</td>
<td>1.224</td>
</tr>
</tbody>
</table>

The regression equations for log $K_e$ and log $K_p$ values at 0% humidity are shown below.

\[
\begin{align*}
\log K_e &= -2.08R_2 + 2.04\alpha^H_2 + 1.36\log L^{16} + 0.93 \\
R &= 0.940 \ S.D. = 0.347 \ N = 14
\end{align*}
\]

\[
\begin{align*}
\log K_p &= -3.69R_2 + 2.23\alpha^H_2 + 1.92\log L^{16} + 0.93 \\
R &= 0.958 \ S.D. = 0.376 \ N = 14
\end{align*}
\]

The regression equations both show that the $R_2$, $\alpha^H_2$ and $\log L^{16}$ constants, $r$, $a$ and $I$ are all significant at 0% humidity. The $\beta^R_2$ and $\pi^H_2$ constants are both statistically insignificant and are not shown. The dominant term is the dispersion constant $I$. Although there is a high negative $R_2$ constant in both cases. The high negative values for $r$ (-2.08 and -3.69), are indicative of a low polarisability as discussed for 207A. The values are higher than those for 207A implying that the carbon is more polarisable. The $\alpha^H_2$ constant, $a$, of 2.04 for log $K_e$ and 2.23 for log $K_p$ is indicative of basic sites on the carbon and these are probably a result of oxidation in the activation step during the
manufacture of ASC Whetlerite. The $a$ constants are higher than those for 207A and indicate that this carbon has a more basic surface. The $l$ constants are lower than those for the standard adsorbent 207A and indicate that ASC Whetlerite is a weaker dispersion interactor.

The regression equations for log $K_e$ and log $K_p$ values at 80% humidity are shown below.

\begin{align*}
\log K_e &= -3.22R_2 + 1.28\alpha^H_2 + 2.73\beta^H_2 + 2.05\log L^{16} - 1.65 \\
R &= 0.949 \text{ S.D.} = 0.332 \text{ N} = 20 \\
\log K_p &= -3.37R_2 + 1.65\alpha^H_2 + 2.02\beta^H_2 + 2.23\log L^{16} - 1.36 \\
R &= 0.954 \text{ S.D.} = 0.343 \text{ N} = 20
\end{align*}

At 80% humidity it can readily be seen that the term $b\beta^H_2$ has now become significant with $b$ constants of 2.73 and 2.02 for log $K_e$ and log $K_p$ respectively. This shows a strong increase in hydrogen bond acidity towards hydrogen bond base adsorbates. On the other hand the $a$ constant, reflecting hydrogen bond basicity towards hydrogen bond acid adsorbates has decreased for both log $K_e$ and log $K_p$. The effect is much the same as that observed with 207A, discussed previously, and is probably due to water on the adsorbent surface increasing the acidity of the adsorbent but blocking of the basic oxygen sites to effectively lower the basicity. The terms in $R_2$ and in $\log L^{16}$ do not change in the same manner as 207A at 80% humidity. The equation for log $K_p$ shows only a slight increase in the $R_2$ constant ($r = -3.69$ to $r = -3.37$) and the $\log L^{16}$ constant actually increases its value ($l = 1.92$ to $l = 2.23$). The effects are more marked for the log $K_e$ equations with the $R_2$ constant decreasing ($r = -2.08$ to $r = -3.22$), and the $\log L^{16}$ constant increasing markedly ($l = 1.36$ to $l = 2.05$).

It is difficult to explain these effects mechanistically, water on the surface should not increase the dispersion potential of the surface above that of carbon. Neither should the
presence of water reduce the polarisability of the surface, water being more polarisable than carbon. A possible explanation may be found in the choice of adsorbates for the two respective studies. The mean of all the log$L^1$ parameters at 0% humidity was 0.96, whereas at 80% humidity it was 1.52. This was because it was possible to inject larger molecules under the humid conditions which would not have eluted for some considerable time on the dry column. The heterogenous nature of these adsorbents is well known and it may be that the proportion of active sites available to a molecule increases with its molecular size. The reason for this is found in the TVFM theory for micropores, [15,16]. According to the TVFM theory molecules are adsorbed by interacting with the electronic force fields of opposing micropore walls, it may be that for small molecules these pore walls are too far apart for the molecule to interact with the opposing force fields and become nested between them. Such molecules would be poorly adsorbed, indeed for such molecules a micropore would be no different in its adsorbing potential than a mesopore, the micropore merely providing a surface for adsorption but no enhanced adsorption, from the opposing pore wall, characteristic of micropores. As the molecular size increases the molecules are able to find an increasing number of these 'nesting' sites, where they are able to interact with opposing pore walls. Once interaction has taken place, then the micropore filling process can begin to take place and TVFM would hold true.

It may be that the smaller average size of molecules for the 0% study resulted in a lower value for the adsorbent’s $I$ constant than might have been found if larger molecules had been studied. Indeed if methane is dropped from the regression at 0% humidity the overall $I$ constant does increase by about 0.4 log units implying that methane is adsorbing by a different mechanism than larger molecules. However, the increase does not account fully for the increase in $I$ on moving from a 0% to an 80% humidity carrier gas.

An alternative explanation is that the adsorbent contains highly non–polar areas which repel water but which are highly active towards non–polar adsorbates. These highly active
sites would not be covered by water and there strong interaction potential increases the average strength of the dispersion potential compared with the average of the sites available at 0% humidity. This increase in the average dispersion potential of sites at 80% humidity would be reflected in an increased I value at this humidity. In such circumstances the constant term in the regression equation would be expected to decrease in size, reflecting a reduction in the number of sites available for adsorption. This is indeed the case with reductions of 2.58 and 2.29 log units for the log $K_e$ and log $K_p$ constants respectively.
AMBERSORB CARBONACEOUS ADSORBENTS

INTRODUCTION

Ambersorb 572 is the first of three synthetic carbonaceous adsorbents studied. The synthetic adsorbents are derived from highly sulphonated styrene/divinylbenzene copolymers. The copolymers are macroreticular (highly macroporous) ion exchange resins with moderate surface area. The resins are pyrolysed in a patented process. During pyrolysis the macroreticular structure remains intact while there is a large increase in microporosity and a slight increase in mesoporosity. Applications of the Ambersorb adsorbents include; groundwater remediation, spillage clean up, waste water treatment, vapour phase treatment of toxic air emissions, odour control and protective clothing.

It will be interesting to compare the synthetic adsorbents with those derived from natural sources. The Ambersorb adsorbents are also claimed to be more hydrophobic and consequently more reliable under wet conditions. It will be interesting to test this by comparing adsorption characteristics under humid conditions with the non synthetic adsorbents 207A and ASC Whetlerite.
The parameters, $R_j$, $\pi H_2$, $\alpha H_2$, $\beta H_2$ and $\log L^{16}$ for each adsorbate studied are shown in table 7.11 for the adsorbates studied at 0% and table 7.12 for the adsorbates studied at 80% humidity.

### TABLE 7.11

Parameters for the Adsorbates Studied at 0% Humidity on Ambersorb 572 at 298.15K

<table>
<thead>
<tr>
<th>Set</th>
<th>C.N. Adsorbate Name</th>
<th>$R_j$</th>
<th>$\pi H_2$</th>
<th>$\alpha H_2$</th>
<th>$\beta H_2$</th>
<th>$\log L^{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>101 Methane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.323</td>
</tr>
<tr>
<td>2</td>
<td>102 Ethane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.492</td>
</tr>
<tr>
<td>3</td>
<td>103 Propane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>4</td>
<td>1001 Ethene</td>
<td>0.107</td>
<td>0.100</td>
<td>0.000</td>
<td>0.070</td>
<td>0.289</td>
</tr>
<tr>
<td>5</td>
<td>1002 Propene</td>
<td>0.103</td>
<td>0.080</td>
<td>0.000</td>
<td>0.070</td>
<td>0.946</td>
</tr>
<tr>
<td>6</td>
<td>2501 Chloromethane</td>
<td>0.249</td>
<td>0.430</td>
<td>0.000</td>
<td>0.080</td>
<td>1.163</td>
</tr>
<tr>
<td>7</td>
<td>2502 Dichloromethane</td>
<td>0.387</td>
<td>0.570</td>
<td>0.100</td>
<td>0.050</td>
<td>2.019</td>
</tr>
<tr>
<td>8</td>
<td>2504 Tetrachloromethane</td>
<td>0.458</td>
<td>0.380</td>
<td>0.000</td>
<td>0.000</td>
<td>2.823</td>
</tr>
<tr>
<td>9</td>
<td>4025 Fluorodichloromethane</td>
<td>0.206</td>
<td>0.400</td>
<td>0.200</td>
<td>0.000</td>
<td>1.614</td>
</tr>
<tr>
<td>10</td>
<td>4026 Difluorochloromethane</td>
<td>0.000</td>
<td>0.250</td>
<td>0.200</td>
<td>0.000</td>
<td>0.690</td>
</tr>
<tr>
<td>11</td>
<td>4051 Difluorodichloromethane</td>
<td>0.001</td>
<td>0.140</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
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</table>
### TABLE 7.12
Parameters for the Adsorbates Studied at 80% Humidity on Ambersorb 572 at 298.15K

<table>
<thead>
<tr>
<th>Set</th>
<th>C.N. Adsorbate Name</th>
<th>$R_2$</th>
<th>$\pi^H_2$</th>
<th>$\alpha^H_2$</th>
<th>$\beta^H_2$</th>
<th>$\log L^{16}$</th>
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</thead>
<tbody>
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<td>1</td>
<td>103 Propane</td>
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<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>2</td>
<td>104 n-Butane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.615</td>
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<tr>
<td>3</td>
<td>106 n-Pentane</td>
<td>0.000</td>
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<td>0.000</td>
<td>0.000</td>
<td>2.162</td>
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<tr>
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<td>109 n-Hexane</td>
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<td>2.668</td>
</tr>
<tr>
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<td>1002 Propene</td>
<td>0.103</td>
<td>0.080</td>
<td>0.000</td>
<td>0.070</td>
<td>0.946</td>
</tr>
<tr>
<td>6</td>
<td>2154 1,1,2,2-Tetrafluoroethane</td>
<td>-0.280</td>
<td>-0.300</td>
<td>0.300</td>
<td>0.000</td>
<td>0.289</td>
</tr>
<tr>
<td>7</td>
<td>2502 Dichloromethane</td>
<td>0.387</td>
<td>0.570</td>
<td>0.100</td>
<td>0.050</td>
<td>2.019</td>
</tr>
<tr>
<td>8</td>
<td>2503 Trichloromethane</td>
<td>0.425</td>
<td>0.490</td>
<td>0.150</td>
<td>0.020</td>
<td>2.480</td>
</tr>
<tr>
<td>9</td>
<td>2504 Tetrachloromethane</td>
<td>0.458</td>
<td>0.380</td>
<td>0.000</td>
<td>0.000</td>
<td>2.823</td>
</tr>
<tr>
<td>10</td>
<td>4025 Fluorodichloromethane</td>
<td>0.206</td>
<td>0.400</td>
<td>0.200</td>
<td>0.000</td>
<td>1.614</td>
</tr>
<tr>
<td>11</td>
<td>4026 Difluorochloromethane</td>
<td>0.000</td>
<td>0.250</td>
<td>0.200</td>
<td>0.000</td>
<td>0.690</td>
</tr>
<tr>
<td>12</td>
<td>4051 Difluorodichloromethane</td>
<td>0.001</td>
<td>0.140</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>13</td>
<td>4154 1-fluoro-1,1-dichloroethane</td>
<td>0.160</td>
<td>0.400</td>
<td>0.000</td>
<td>0.000</td>
<td>1.932</td>
</tr>
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<td>14</td>
<td>4206 1,1,1-Trifluoro-2-chloroethane</td>
<td>0.010</td>
<td>0.400</td>
<td>0.150</td>
<td>0.000</td>
<td>1.168</td>
</tr>
<tr>
<td>15</td>
<td>5302 Acetaldehyde</td>
<td>0.208</td>
<td>0.670</td>
<td>0.000</td>
<td>0.450</td>
<td>1.230</td>
</tr>
<tr>
<td>16</td>
<td>5501 Propanone</td>
<td>0.179</td>
<td>0.700</td>
<td>0.040</td>
<td>0.510</td>
<td>1.696</td>
</tr>
<tr>
<td>17</td>
<td>6001 Methyl formate</td>
<td>0.192</td>
<td>0.680</td>
<td>0.000</td>
<td>0.380</td>
<td>1.285</td>
</tr>
<tr>
<td>18</td>
<td>6601 Acetonitrile</td>
<td>0.237</td>
<td>0.900</td>
<td>0.090</td>
<td>0.300</td>
<td>1.739</td>
</tr>
<tr>
<td>19</td>
<td>8001 Methanol</td>
<td>0.278</td>
<td>0.440</td>
<td>0.430</td>
<td>0.470</td>
<td>0.970</td>
</tr>
<tr>
<td>20</td>
<td>8002 Ethanol</td>
<td>0.246</td>
<td>0.420</td>
<td>0.370</td>
<td>0.480</td>
<td>1.485</td>
</tr>
<tr>
<td>21</td>
<td>8303 2,2,2-Trifluoroethanol</td>
<td>0.015</td>
<td>0.600</td>
<td>0.570</td>
<td>0.150</td>
<td>1.224</td>
</tr>
</tbody>
</table>

The regression equations for log $K_e$ and log $K_p$ values at 0% humidity are shown below.

$$\log K_e = 1.09 \log L^{16} + 1.15$$
$$R = 0.9213 \text{ S.D.} = 0.414 \text{ N} = 11 \quad (7.9)$$

$$\log K_p = 1.38 \log L^{16} + 1.19$$
$$R = 0.9179 \text{ S.D.} = 0.540 \text{ N} = 11 \quad (7.10)$$

The two equations both show a simple relationship between partition constant and $1, \log L^{16}$. Other parameter constants were found to be insignificant at 0% humidity. The $I$ values are both lower than those found for 207A and for ASC Whetlerite but the constant terms are higher. The implication is that Ambersorb 572 has a greater number of adsorption sites but that they are weaker than those found on the natural carbons.

There is however, an interesting aspect to these results if one considers heterogeneity. The regression changes quite markedly if one drops the smaller molecules methane,
ethane, ethene and chloromethane from the regression. The regression equations in this instance are shown below.

\[
\begin{align*}
\log K_\varepsilon &= 0.74 \log L^16 + 1.85 \\
R &= 0.9726 \text{ S.D.} = 0.146 \text{ N} = 7 \\
\log K_\varepsilon &= 0.91 \log L^16 + 2.14 \\
R &= 0.9395 \text{ S.D.} = 0.272 \text{ N} = 7
\end{align*}
\]

The constant terms have now increased markedly implying that the larger molecules have a much greater adsorption surface available to them. In addition the dispersive strength of these sites has now decreased, reflected in lower \( I \) values.

The effect can be more clearly seen in figure 7.1. There are at least two different series in figure 7.1 as illustrated. However, it is probable that there is an intermediate series which is constituted of the small cluster of compounds between \( \log L^16 \) of 0.60 and 1.20. It is likely that the adsorbates on either side of this cluster are adsorbed by entirely different mechanisms. While adsorbates in the cluster are probably being adsorbed by a combined mechanism.

The reason for this is presumably connected with the range of widths in the micropores. There could be a relatively small number of narrow and highly active sites which are able to adsorb small molecules such as methane. However, the main bulk of the micropores are wider and unable to adsorb such small molecules. The wider parts of the micropore are used in adsorbing larger molecules but they are not adsorbed as strongly as the small molecules in the narrower areas of the microporous surface. The availability of sites for adsorption of larger molecules far outweighs the stronger but less numerous sites for adsorption of small molecules in influencing adsorption. This conclusion is gleaned from the difference in the constant terms of the equation of the full data set and the equation of the limited data set of larger molecules only. The limited data set gives a constant term for \( \log K_p \) of 2.14 compared with 1.19 for the full data set. This implies an almost tenfold increase in the average number of adsorption sites available. The corresponding
reduction in the dispersive strength of these sites 1.38 to 0.91 is about a threefold decrease. Thus despite the small molecules being adsorbed more strongly on individual sites, the lack of availability of such sites results in them having a low partition constant.

FIGURE 7.1

The regression equations for log $K_e$ and log $K_p$ at 80% humidity are shown below.

$$\log K_e = -2.76R_e + 2.76H_2 + 2.07\log L_{16} - 0.90$$ (7.13)

R = 0.9750, S.D. = 0.264, N = 21

$$\log K_p = -3.14R_e + 2.30H_2 + 2.33\log L_{16} - 0.65$$ (7.14)

R = 0.9554, S.D. = 0.369, N = 21

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The changes in I and in the constant values follow the same pattern as in ASC Whetlerite. There is presumably a decrease in available surface area as the water occupies the micropores, causing a reduction in the constant term in both equations at this humidity. Similarly, the rise in I values implies that either the sites unoccupied by water are highly active dispersion sites or that the higher average \( \log L^{16} \) value in the humid study allows occupation of highly dispersive sites (p.180–182).

The \( b \) value is now significant, indicating an increase in hydrogen bond acidity. The \( a \) constant is however not significant. The inherent acidity of water, \( (\alpha^H_2 = 0.85, \alpha_1 = 1.17, [109]) \), which is greater than its basicity, \( (\beta^H_2 = 0.35, \beta_1 = 0.18, [109]) \), is likely to cause the \( b \) constant to be greater than the \( a \) constant in the final regression equation. But, nevertheless, the complete absence of a significant \( a \) constant warrants some explanation. The absence of any significance to the \( a \) term may be due to the orientation of adsorption of water. The water may be attaching to the carbon surface by the oxygen centre only, leaving the acidic hydrogen exposed in the micropore, giving the microporous surface an acidic but no basic character. Indeed, the absence of any acidic or basic sites on the dry carbon, which could act as nuclei for water adsorption, would indicate that water could only be adsorbed by dispersive forces, which rest more heavily on the oxygen portion of the molecule causing oriented adsorption at the oxygen only. If this were the case the wet carbon would then be expected to have a significant \( b \) but no significant \( a \) constant.
AMBERSORB 563

Ambersorb 563 is the second in the series of Ambersorb adsorbents and is used as a hydrophobic adsorbent due to its low water uptake.

The parameters, $R_2$, $\pi^H_2$, $\alpha^H_2$, $\beta^H_2$ and $\log L^{16}$ for each adsorbate studied are shown in table 7.13 for the adsorbates studied at 0% and table 7.14 for the adsorbates studied at 80% humidity.

TABLE 7.13

Parameters for the Adsorbates Studied at 0% Humidity on Ambersorb 563 at 298.15K

<table>
<thead>
<tr>
<th>Set</th>
<th>C.N. Adsorbate Name</th>
<th>$R_2$</th>
<th>$\pi^H_2$</th>
<th>$\alpha^H_2$</th>
<th>$\beta^H_2$</th>
<th>$\log L^{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>101 Methane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.323</td>
</tr>
<tr>
<td>2</td>
<td>102 Ethane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.492</td>
</tr>
<tr>
<td>3</td>
<td>103 Propane</td>
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<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>4</td>
<td>1001 Ethene</td>
<td>0.107</td>
<td>0.100</td>
<td>0.000</td>
<td>0.070</td>
<td>0.289</td>
</tr>
<tr>
<td>5</td>
<td>1002 Propene</td>
<td>0.103</td>
<td>0.080</td>
<td>0.000</td>
<td>0.070</td>
<td>0.946</td>
</tr>
<tr>
<td>6</td>
<td>2153 1,1,1,2-Tetrafluoroethane</td>
<td>-0.280</td>
<td>-0.300</td>
<td>0.200</td>
<td>0.000</td>
<td>0.226</td>
</tr>
<tr>
<td>7</td>
<td>2154 1,1,2,2-Tetrafluoroethane</td>
<td>-0.280</td>
<td>-0.300</td>
<td>0.300</td>
<td>0.000</td>
<td>0.289</td>
</tr>
<tr>
<td>8</td>
<td>2502 Dichloromethane</td>
<td>0.387</td>
<td>0.570</td>
<td>0.100</td>
<td>0.050</td>
<td>2.019</td>
</tr>
<tr>
<td>9</td>
<td>4025 Fluorodichloromethane</td>
<td>0.206</td>
<td>0.400</td>
<td>0.200</td>
<td>0.000</td>
<td>1.614</td>
</tr>
<tr>
<td>10</td>
<td>4026 Difluorochloromethane</td>
<td>0.000</td>
<td>0.250</td>
<td>0.200</td>
<td>0.000</td>
<td>0.690</td>
</tr>
<tr>
<td>11</td>
<td>4051 Difluorodichloromethane</td>
<td>0.001</td>
<td>0.140</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>12</td>
<td>5302 Acetaldehyde</td>
<td>0.208</td>
<td>0.670</td>
<td>0.000</td>
<td>0.450</td>
<td>1.230</td>
</tr>
<tr>
<td>13</td>
<td>8001 Methanol</td>
<td>0.278</td>
<td>0.440</td>
<td>0.430</td>
<td>0.470</td>
<td>0.970</td>
</tr>
<tr>
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<td>α&lt;sup&gt;H&lt;sub&gt;2&lt;/sub&gt;&lt;/sup&gt;</td>
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<td>0.000</td>
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<td>0.492</td>
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<td>Propane</td>
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<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
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<tr>
<td>3</td>
<td>Ethene</td>
<td>0.107</td>
<td>0.100</td>
<td>0.000</td>
<td>0.070</td>
<td>0.289</td>
</tr>
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<td>Propene</td>
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<td>0.080</td>
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<td>0.946</td>
</tr>
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<td>1,1,1,2-Tetrafluoroethane</td>
<td>−0.280</td>
<td>−0.300</td>
<td>0.200</td>
<td>0.000</td>
<td>0.226</td>
</tr>
<tr>
<td>6</td>
<td>1,1,2,2-Tetrafluoroethane</td>
<td>−0.280</td>
<td>−0.300</td>
<td>0.300</td>
<td>0.000</td>
<td>0.289</td>
</tr>
<tr>
<td>7</td>
<td>Dichloromethane</td>
<td>0.387</td>
<td>0.570</td>
<td>0.100</td>
<td>0.050</td>
<td>2.019</td>
</tr>
<tr>
<td>8</td>
<td>Tetrachloromethane</td>
<td>0.458</td>
<td>0.380</td>
<td>0.000</td>
<td>0.000</td>
<td>2.823</td>
</tr>
<tr>
<td>9</td>
<td>Fluorodichloromethane</td>
<td>0.206</td>
<td>0.400</td>
<td>0.200</td>
<td>0.000</td>
<td>1.614</td>
</tr>
<tr>
<td>10</td>
<td>Difluorochloromethane</td>
<td>0.000</td>
<td>0.250</td>
<td>0.200</td>
<td>0.000</td>
<td>0.690</td>
</tr>
<tr>
<td>11</td>
<td>Difluorodichloromethane</td>
<td>0.001</td>
<td>0.140</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>12</td>
<td>1,1,1-Trifluoro-2-chloroethane</td>
<td>0.010</td>
<td>0.400</td>
<td>0.150</td>
<td>0.000</td>
<td>1.168</td>
</tr>
<tr>
<td>13</td>
<td>Acetaldehyde</td>
<td>0.208</td>
<td>0.670</td>
<td>0.000</td>
<td>0.450</td>
<td>1.230</td>
</tr>
<tr>
<td>14</td>
<td>Methyl formate</td>
<td>0.192</td>
<td>0.680</td>
<td>0.000</td>
<td>0.380</td>
<td>1.285</td>
</tr>
<tr>
<td>15</td>
<td>Methylamine</td>
<td>0.250</td>
<td>0.350</td>
<td>0.100</td>
<td>0.640</td>
<td>1.300</td>
</tr>
<tr>
<td>16</td>
<td>Methanol</td>
<td>0.278</td>
<td>0.440</td>
<td>0.430</td>
<td>0.470</td>
<td>0.970</td>
</tr>
<tr>
<td>17</td>
<td>Ethanol</td>
<td>0.246</td>
<td>0.420</td>
<td>0.370</td>
<td>0.480</td>
<td>1.485</td>
</tr>
<tr>
<td>18</td>
<td>2,2,2-Trifluoroethanol</td>
<td>0.015</td>
<td>0.600</td>
<td>0.570</td>
<td>0.150</td>
<td>1.224</td>
</tr>
</tbody>
</table>

The regression equations for log K<sub>e</sub> and log K<sub>p</sub> values at 0% humidity are shown below.

\[
\log K_e = -3.36R_2 + 2.30\log L^{16} + 0.52 \\
R = 0.9558 \text{ S.D. } = 0.366 \text{ N } = 13
\]  
(7.15)

\[
\log K_p = -4.93R_2 + 2.84\log L^{16} + 0.51 \\
R = 0.9574 \text{ S.D. } = 0.428 \text{ N } = 13
\]  
(7.16)

The equations show the highest \( I \) values so far, indicative of strong dispersive adsorption. The \( R_2 \) value is significant and is comparable to the values for 207A indicating a low polarisability. The constant term is less than that for Ambersorb 572 and is probably a reflection of the lower surface area of Ambersorb 563.
The regression equations for Ambersorb 563 at 80% humidity are shown below.

\[
\log K_e = -3.56R_3 + 1.91pH + 2.03\log L_{16} + 0.15 \\
R = 0.9316, \quad \text{S.D.} = 0.375, \quad N = 18
\]

\[
\log K_p = -4.99R_3 + 1.66pH + 2.53\log L_{16} + 0.19 \\
R = 0.9242, \quad \text{S.D.} = 0.450, \quad N = 18
\]

The equations when compared with those at 0% humidity show only a small change in \( I \) values with a drop of around 0.3 log units in both cases. The constant term shows a small drop of around 0.3 log units also. The \( r \) values have changed little within experimental error and the only significant change is the appearance of a significant \( b \) value. The \( b \) value is indicative of the appearance of acidic water sites on the adsorbent as discussed previously.

The hydrophobicity of Ambersorb 563 has presumably led to a low adsorbance of water and thus the surface has been least affected in its adsorbance characteristics compared with Ambersorb 572 or the non-synthetic carbons.
AMBERSORB 564

Ambersorb 564 is the third adsorbent in the Ambersorb series to be studied. It has a similar surface area to Ambersorb 563 but is known to be less hydrophobic.

The parameters, $R_2$, $\pi^H_2$, $\alpha^H_2$, $\beta^H_2$ and $\log L^{16}$ for each adsorbate studied are shown in table 7.15 for the adsorbates studied at 0% and table 7.16 for the adsorbates studied at 80% humidity.

TABLE 7.15
Parameters for the Adsorbates Studied at 0% Humidity on Ambersorb 564 at 298.15K

<table>
<thead>
<tr>
<th>Set</th>
<th>C.N.</th>
<th>Adsorbate Name</th>
<th>$R_2$</th>
<th>$\pi^H_2$</th>
<th>$\alpha^H_2$</th>
<th>$\beta^H_2$</th>
<th>$\log L^{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>101</td>
<td>Methane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.323</td>
</tr>
<tr>
<td>2</td>
<td>102</td>
<td>Ethane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.492</td>
</tr>
<tr>
<td>3</td>
<td>2502</td>
<td>Dichloromethane</td>
<td>0.387</td>
<td>0.570</td>
<td>0.100</td>
<td>0.050</td>
<td>2.019</td>
</tr>
<tr>
<td>4</td>
<td>4025</td>
<td>Fluorodichloromethane</td>
<td>0.206</td>
<td>0.400</td>
<td>0.200</td>
<td>0.000</td>
<td>1.614</td>
</tr>
<tr>
<td>5</td>
<td>4051</td>
<td>Difluorodichloromethane</td>
<td>0.001</td>
<td>0.140</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>6</td>
<td>8001</td>
<td>Methanol</td>
<td>0.278</td>
<td>0.440</td>
<td>0.430</td>
<td>0.470</td>
<td>0.970</td>
</tr>
</tbody>
</table>

The regression equations for log $K_e$ and log $K_p$ values at 0% humidity are shown below.

$$
\text{Log } K_e = 1.09 \log L^{16} + 1.41
$$

$$
R = 0.9676 \text{ S.D.} = 0.263 \text{ N} = 6
$$

$$
\text{Log } K_p = 1.45 \log L^{16} + 1.37
$$

$$
R = 0.9744 \text{ S.D.} = 0.309 \text{ N} = 6
$$

The equations show $I$ values very similar to those obtained for Ambersorb 572 but the constant term is a little higher in both cases for Ambersorb 564. Indeed, the constants are the highest obtained on any of the five adsorbents and are indicative of strong adsorption even for an adsorbate with a rather small $\log L^{16}$ value, e.g. 0. Such a compound would be between methane and ethane in its $\log L^{16}$ value. The 564 adsorbent
would be ideally suited to adsorption of small molecules but would be superseded by the carbon with its high \( I \) value when adsorption of larger molecules is necessary.

### TABLE 7.16

Parameters for the Adsorbates Studied at 80% Humidity on Ambersorb 564 at 298.15K

<table>
<thead>
<tr>
<th>Set</th>
<th>C.N. Adsorbate Name</th>
<th>( R_1 )</th>
<th>( \pi^H_2 )</th>
<th>( \alpha^H_2 )</th>
<th>( \beta^H_2 )</th>
<th>( \log L^{16} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>102 Ethane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.492</td>
</tr>
<tr>
<td>2</td>
<td>103 Propane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>3</td>
<td>104 n-Butane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.615</td>
</tr>
<tr>
<td>4</td>
<td>1001 Ethene</td>
<td>0.107</td>
<td>0.100</td>
<td>0.000</td>
<td>0.070</td>
<td>0.289</td>
</tr>
<tr>
<td>5</td>
<td>1002 Propene</td>
<td>0.103</td>
<td>0.080</td>
<td>0.000</td>
<td>0.070</td>
<td>0.946</td>
</tr>
<tr>
<td>6</td>
<td>2153 1,1,1,2-Tetrafluoroethane</td>
<td>-0.280</td>
<td>-0.300</td>
<td>0.200</td>
<td>0.000</td>
<td>0.226</td>
</tr>
<tr>
<td>7</td>
<td>2154 1,1,2,2-Tetrafluoroethane</td>
<td>-0.280</td>
<td>-0.300</td>
<td>0.300</td>
<td>0.000</td>
<td>0.289</td>
</tr>
<tr>
<td>8</td>
<td>2501 Chloromethane</td>
<td>0.249</td>
<td>0.430</td>
<td>0.000</td>
<td>0.080</td>
<td>1.163</td>
</tr>
<tr>
<td>9</td>
<td>2502 Dichloromethane</td>
<td>0.387</td>
<td>0.570</td>
<td>0.100</td>
<td>0.050</td>
<td>2.019</td>
</tr>
<tr>
<td>10</td>
<td>2504 Tetrachloromethane</td>
<td>0.458</td>
<td>0.380</td>
<td>0.000</td>
<td>0.000</td>
<td>2.823</td>
</tr>
<tr>
<td>11</td>
<td>4025 Fluorodichloromethane</td>
<td>0.206</td>
<td>0.400</td>
<td>0.200</td>
<td>0.000</td>
<td>1.614</td>
</tr>
<tr>
<td>12</td>
<td>4026 Difluorochloromethane</td>
<td>0.000</td>
<td>0.250</td>
<td>0.200</td>
<td>0.000</td>
<td>0.690</td>
</tr>
<tr>
<td>13</td>
<td>4051 Difluorodichloromethane</td>
<td>0.001</td>
<td>0.140</td>
<td>0.000</td>
<td>0.000</td>
<td>1.050</td>
</tr>
<tr>
<td>14</td>
<td>4206 1,1,1-Trifluor-2-chloroethane</td>
<td>0.010</td>
<td>0.400</td>
<td>0.150</td>
<td>0.000</td>
<td>1.168</td>
</tr>
<tr>
<td>15</td>
<td>5302 Acetaldehyde</td>
<td>0.208</td>
<td>0.670</td>
<td>0.000</td>
<td>0.450</td>
<td>1.230</td>
</tr>
<tr>
<td>16</td>
<td>6001 Methyl formate</td>
<td>0.192</td>
<td>0.680</td>
<td>0.000</td>
<td>0.380</td>
<td>1.285</td>
</tr>
<tr>
<td>17</td>
<td>6801 Methylamine</td>
<td>0.250</td>
<td>0.350</td>
<td>0.100</td>
<td>0.640</td>
<td>1.300</td>
</tr>
<tr>
<td>18</td>
<td>8001 Methanol</td>
<td>0.278</td>
<td>0.440</td>
<td>0.430</td>
<td>0.470</td>
<td>0.970</td>
</tr>
<tr>
<td>19</td>
<td>8002 Ethanol</td>
<td>0.246</td>
<td>0.420</td>
<td>0.370</td>
<td>0.480</td>
<td>1.485</td>
</tr>
<tr>
<td>20</td>
<td>8303 2,2,2-Trifluoroethanol</td>
<td>0.015</td>
<td>0.600</td>
<td>0.570</td>
<td>0.150</td>
<td>1.224</td>
</tr>
</tbody>
</table>

The regression equations for \( \log K_e \) and \( \log K_p \) values at 80% humidity are shown below.

\[
\log K_e = -2.48 R_2 + (0.83)\pi^H_2 + 2.25 \beta^H_2 + 1.57 \log L^{16} - (0.18) \\
R = 0.9578 \text{ S.D.} = 0.313 \text{ N} = 20
\]

\[
\log K_p = -3.75 R_2 + 1.20 \pi^H_2 + 1.80 \beta^H_2 + 1.91 \log L^{16} - (0.06) \\
R = 0.9697 \text{ S.D.} = 0.279 \text{ N} = 20
\]

The results at 80% humidity show drops in the constant terms of 1.59 and 1.43 for \( \log K_e \) and \( \log K_p \) respectively. The constants are statistically insignificant simply because the coefficients are closer to zero than their own standard deviation and in this case statistical
insignificance should not be taken to mean that the values are unreliable.

The increase in the \( I \) values of 0.48 and 0.46 for \( \log K_e \) and \( \log K_p \) respectively indicates that greater distinction is made between compounds with differing \( \log L^{16} \) values than was made at 0% humidity. The phenomenon is a parallel one to that observed on both ASC Whetlerite and Ambersorb 572 and has been explained previously (p.180–182). The significance of \( b \) and \( r \) is also analogous to the previous carbons studied and is of the usual order of magnitude.

The significance of \( s \) for \( \log K_p \) values is interesting. In actual fact the \( s \) coefficient for \( \log K_e \) has a 94% confidence level. It may be then that dipolarity is playing a small part in the adsorption process at 80% humidity. However, it may be simply an artifact of the regression. Indeed, \( R_3 \) and \( \pi_{H_2} \) are highly correlated with a coefficient of 0.755 and it may be the cross correlation which is causing the significance of \( s \pi_{H_2} \) rather than any physicochemical phenomena on the carbon surface.
CONCLUSIONS

The adsorption mechanism for water onto activated carbon depends on the initial surface characteristics of the dry carbon.

With Sutcliffe Speakman 207A, which has both hydrogen bond base and hydrogen bond acid capabilities when dry, and ASC Whetlerite, which is hydrogen bond basic when dry, the adsorption of water probably takes place on the basic and to some extent on the acidic sites. The evidence for this is gleaned from the changes in the $a$ and $b$ constants for the regression equations at 80% humidity. The $a$ constant falls in the presence of water, which is indicative of covering of basic sites by water.

The adsorption of water on all carbons results in an increase in $b$, the hydrogen bond acid constant except in the case of 207A. There is an absence of acidic or basic sites to act as nuclei for water adsorption in the dry Ambersorb adsorbents and this implies that the mode of adsorption of water is by dispersion. From the accompanying rise in $b$, which is indicative of acidity, one can infer that adsorption takes place at the oxygen portion of the molecule, leaving the hydrogen portion to impart the acidity to the carbon surface.

In the case of 207A the appearance of these acidic sites on the carbon surface through dispersive adsorption is outweighed by the disappearance of the acidic sites already present on the dry surface, which presumably act as nuclei for water adsorption. The result is a slight fall in hydrogen bond acidity.
TABLE 7.17

Summary of Regression Equations for Log $K_p$ at 0% Humidity

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$R_2$</th>
<th>$\alpha^H_2$</th>
<th>$\log L^{16}$</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sutcliffe Speakman</td>
<td>-4.29</td>
<td>1.85</td>
<td>2.18</td>
<td>0.25</td>
</tr>
<tr>
<td>207A</td>
<td>-3.69</td>
<td>2.23</td>
<td>1.92</td>
<td>0.93</td>
</tr>
<tr>
<td>ASC Whetlerite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambersorb 572</td>
<td></td>
<td></td>
<td>1.38</td>
<td>1.19</td>
</tr>
<tr>
<td>Ambersorb 563</td>
<td>-4.93</td>
<td>-</td>
<td>2.84</td>
<td>0.51</td>
</tr>
<tr>
<td>Ambersorb 564</td>
<td></td>
<td></td>
<td>1.45</td>
<td>1.37</td>
</tr>
</tbody>
</table>

From table 7.17 it can be seen that the strongest adsorbent by dispersion is Ambersorb 563. The adsorbents can be grouped in order of decreasing dispersion strength, where; 563 > 207A > ASC_W > 564 > 572. Alternatively, if the constant term is taken into account which is important for adsorbates with small $\log L^{16}$ values, the series, 564 > 572 > ASC_W > 563 > 207A, emerges.

If the dipolarity term $R_2$ and the hydrogen bond acidity term $\alpha^H_2$ which have less of an influence on adsorption than $\log L^{16}$ are ignored, a plot of log $K_p$ against $\log L^{16}$ can be obtained. The plot shows the effect of dispersion forces only on adsorption at 0% humidity.

The plots of log $K_p$ values against $\log L^{16}$ are shown in fig 7.2 for each adsorbent.
At low log$L_{16}$ values the log $K_p$ values cover a range of about 1.5 log units with 564 and 572 being stronger, ASC_W medium, and 563 and 207A weaker adsorbents. As log$L_{16}$ increases there are several changes. 563 becomes increasingly stronger and at a log$L_{16}$ value of approximately 0.75 becomes the strongest adsorbent and remains so as log$L_{16}$ increases. ASC_W and 207A also become increasingly stronger and for higher log$L_{16}$ values are the medium strength adsorbents. 564 and 572 become increasingly weak compared with the other adsorbents and for higher log$L_{16}$ values are the weaker adsorbents.

The plot of log$L_{16}$ against log $K_p$ at 80% humidity is shown in figure 7.3. It must be stressed, however, that the contribution of $\beta H_2$ and $R_2$ are not included in the figure and these are considerable although not as great as log$L_{16}$.
FIGURE 7.3 The Plot of $\log L^{16}$ against $\log K_p$ at 80% Humidity

The figure shows that the contribution of dispersion to adsorbance is strongest for 563 at both high and low $\log L^{16}$ values. At low values of $\log L^{16}$ the difference between $\log K_p$ values is about 1.5 log units. ASC_W is the weakest adsorbent, 572 is of medium strength and the others are more or less equally the strongest. As $\log L^{16}$ increases 563, 572 and ASC_W remain more or less parallel with a slight divergence so that the difference at high $\log L^{16}$ values is approximately 2.5 log units. 207A and 564 change in their relative adsorbing strength as $\log L^{16}$ increases, becoming less adsorbent compared with the other three. 564 crosses 572 at about 1.25 $\log L^{16}$. This means that for compounds with $\log L^{16}$ values below 1.25, 564 has a stronger dispersive power but for compounds with $\log L^{16}$ above 1.25, 572 has the stronger dispersive power. Similar crossovers occur for 207A. This type of prediction could be very useful where the size of the adsorbates varied for different applications.
To summarise 572 and particularly 563 hold their dispersion strength at high levels of humidity. ASC_W decreases in strength but still retains a reasonably strong increase in adsorbance as \( \log L^16 \) increases. 564 and particularly 207A are more affected by humidity and only have a relatively weak increase in adsorbance with \( \log L^16 \).

### TABLE 7.18
Summary of Regression Equations for Log \( K_p \) at 80% Humidity

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( R_2 )</th>
<th>( \pi_H )</th>
<th>( \alpha_H )</th>
<th>( \beta_H )</th>
<th>( \log L^{16} )</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sutcliffe Speakman</td>
<td>-1.25</td>
<td>-</td>
<td>1.68</td>
<td>0.93</td>
<td>1.43</td>
<td>-0.39</td>
</tr>
<tr>
<td>207A</td>
<td>-3.37</td>
<td>-</td>
<td>1.65</td>
<td>2.02</td>
<td>2.23</td>
<td>-1.36</td>
</tr>
<tr>
<td>ASC Whetlerite</td>
<td>-3.14</td>
<td>-</td>
<td>-</td>
<td>2.30</td>
<td>2.33</td>
<td>-0.65</td>
</tr>
<tr>
<td>Ambersorb 572</td>
<td>-4.99</td>
<td>-</td>
<td>-</td>
<td>1.66</td>
<td>2.53</td>
<td>0.19</td>
</tr>
<tr>
<td>Ambersorb 563</td>
<td>-3.75</td>
<td>1.20</td>
<td>-</td>
<td>1.80</td>
<td>1.91</td>
<td>-0.06</td>
</tr>
<tr>
<td>Ambersorb 564</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From table 7.18 it can be seen that the effect of humidity has altered the adsorption series for the adsorbents. In terms of \( \log L^{16} \) the series is now; 563 > 572 > ASC_W > 564 > 207A. While in terms of the constant the series is now; 563 > 564 > 207A > 572 > ASC_W. It is clear from this that the 563 adsorbent is least affected by humidity as is expected by its hydrophobic nature. This hydrophobicity obviously confers a great advantage on its ability to adsorb under humid conditions.

There are also two other series obtainable under humid conditions. In terms of the hydrogen bond acidity of the adsorbent; 572 > ASC_W > 564 > 563 > 207A. Also in terms of polarisability the series is; 207A > 572 > ASC_W > 564 > 563. Due to the presence of basic sites on dry 207A and ASC Whetlerite, adsorption of water molecules would probably take place there. Such adsorption would be at the hydrogen portion of the water molecule leaving the oxygen portion free in the micropore. This adsorption
mechanism is the opposite of what would take place in the synthetic resins where dispersive attraction of the oxygen portion of the water molecule for the carbon surface leaves the hydrogen portion free in the micropore. However, this latter mechanism is probably taking place in the natural adsorbents aswell, at dispersive sites. This explains why the synthetic adsorbents only show significant hydrogen bond acidity when wet but the natural adsorbents show both significant hydrogen bond acidity and basicity.

A study of the effect of pore size distribution on adsorbance at 80% humidity can be carried out using the same compounds as at 0% humidity. The increasing strength of 572 as \( \log L_{16} \) increases is the opposite of what took place at 0% humidity and may be a result of the mesopores providing intermediate surfaces for adsorption of larger molecules.

All three of the synthetic Ambersorb adsorbents out perform the coal based carbons at higher levels of \( \log L_{16} \) at 80% humidity and a possible explanation is the presence of mesopores and macropores on the synthetic carbons. Indeed, the higher proportion of these larger pores on Ambersorb 563 (table 7.1), may account for its strength at higher levels of humidity and could be the cause of its apparent hydrophobicity. A possible explanation could be that water adsorption takes place in the micropores, reducing the availability of such sites for adsorption but the presence of mesopores on the carbon surface provides alternative adsorption sites less affected by the wet conditions. The higher proportion of mesopores on the Ambersorb adsorbents may explain their resilience under wet conditions, especially in the case of 563 which has the greatest proportion of mesopores.

Another cause for the greater effectiveness of the synthetic resins when exposed to humid gas streams could be a lower water uptake. As has already been discussed the coal based carbons contain significant hydrogen bond basicity and acidity and these may not only provide strong water adsorption sites but may result in greater water uptake. The absence of such sites on the synthetic surface probably lowers water uptake, resulting in a greater facility for adsorption when wet. Confirmation is found in the adsorption
isotherms of the synthetic carbons (figure 5.7), which display their lower water uptake compared with BPL carbon which is the precursor of ASC Whetlerite.

The lower affinity of the synthetic carbons for adsorbates with smaller \( \log L^{16} \) values may also explain its low affinity for water (\( \log L^{16} = 0.26 \)). This low affinity is not so easily seen in the best fit plots of figure 7.2 and 7.3 but is better seen in the ‘split’ plot of figure 7.1.

It is clear that in order to understand the effect of humidity, pore structures as well as the chemical nature of the carbon surface ought to be taken into account. However, it should be pointed out that carbons with similar pore structures can have very different properties. This is apparent when one considers the relative adsorption of 207A and ASC_W at 80% humidity. The two adsorbents have a very similar pore size distribution and surface area, 207A having a slightly larger surface area. The crossover that takes place as \( \log L^{16} \) is increased can only be accounted for by differences in the chemical nature of the adsorbents not by differences in the pore size distribution. The chemical nature of these two adsorbents is revealed quantitatively by the LSER equations shown earlier. A study of these equations reveals far more about the factors governing adsorption for these carbons than attempts to explain it in terms of pore size distributions, which do not take the nature of the particular carbon surface into account. Nevertheless, the only explanation for the apparent hydrophobicity of Ambersorb 563 is obtained from consideration of the pore structure. Thus, in characterisation of active carbon it is found that the pore structure and the chemical nature of the surface are both important in understanding the adsorption processes.
COMPARITIVE STUDY OF CHEMICAL AGENT MODELS ON ADSORBENTS

One of the main aims of this work has been to compare the adsorbance of models for chemical agents. The models are halogenated compounds covering a range of boiling points. In this work four models were studied on seven adsorbents. The sources of the first five of the adsorbents have been described previously in chapter vii, the remaining two, SCII and SAR-O are both commercial microporous carbons. The partition constants on the adsorbents of the challenge vapours; tetrachloromethane, dichloromethane, fluorodichloromethane (Arcton 21) and difluorodichloromethane (Arcton 12) are shown below in table 7.19.

TABLE 7.19 Log K_e values for Some Model Compounds on Several Adsorbents at 0% Humidity

<table>
<thead>
<tr>
<th>ADSORBENT</th>
<th>A-564</th>
<th>A-572</th>
<th>A-563</th>
<th>S-207A</th>
<th>ASC_W</th>
<th>SCII</th>
<th>SAR-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Log K_e</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>3.87</td>
<td>3.33</td>
<td>3.59</td>
<td>3.20</td>
<td>3.60</td>
<td>3.59</td>
<td>3.60</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>3.71</td>
<td>3.17</td>
<td>2.82</td>
<td>3.39</td>
<td>3.84</td>
<td>3.22</td>
<td>3.96</td>
</tr>
<tr>
<td>Fluorodichloromethane</td>
<td>2.40</td>
<td>2.82</td>
<td>2.80</td>
<td>2.33</td>
<td>2.41</td>
<td>2.28</td>
<td>2.28</td>
</tr>
<tr>
<td>Difluorodichloromethane</td>
<td>4.67</td>
<td>4.18</td>
<td>4.13</td>
<td>3.70</td>
<td>4.01</td>
<td>3.45</td>
<td>3.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.35</td>
<td>4.38</td>
<td>4.39</td>
<td>4.40</td>
<td>3.71</td>
<td>3.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.25</td>
<td>3.50</td>
<td>3.50</td>
<td>3.50</td>
<td>3.50</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.02</td>
<td>3.22</td>
<td>3.10</td>
<td>2.97</td>
<td>3.02</td>
<td>2.97</td>
</tr>
</tbody>
</table>

TABLE 7.20 Log K_p values for Some Model Compounds on Several Adsorbents at 0% Humidity

<table>
<thead>
<tr>
<th>ADSORBENT</th>
<th>A-564</th>
<th>A-572</th>
<th>A-563</th>
<th>S-207A</th>
<th>ASC_W</th>
<th>SCII</th>
<th>SAR-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Log K_p</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>4.67</td>
<td>4.35</td>
<td>4.38</td>
<td>4.39</td>
<td>4.40</td>
<td>3.71</td>
<td>3.10</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>4.25</td>
<td>3.70</td>
<td>3.77</td>
<td>3.63</td>
<td>3.55</td>
<td>3.02</td>
<td>2.97</td>
</tr>
<tr>
<td>Fluorodichloromethane</td>
<td>3.94</td>
<td>3.50</td>
<td>3.50</td>
<td>3.50</td>
<td>3.50</td>
<td>3.50</td>
<td>3.50</td>
</tr>
<tr>
<td>Difluorodichloromethane</td>
<td>3.10</td>
<td>3.52</td>
<td>3.50</td>
<td>3.02</td>
<td>3.22</td>
<td>3.10</td>
<td>2.97</td>
</tr>
</tbody>
</table>
### TABLE 7.21

Log $K_p$ values for Some Model Compounds on Several Adsorbents at 80% Humidity

<table>
<thead>
<tr>
<th>ADSORBENT</th>
<th>A-564</th>
<th>A-572</th>
<th>A-563</th>
<th>S-207A</th>
<th>ASC_W</th>
<th>SCII</th>
<th>SAR-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Log $K_e$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>2.90</td>
<td>3.65</td>
<td>3.58</td>
<td>2.40</td>
<td>2.55</td>
<td>3.05</td>
<td>3.17</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>2.68</td>
<td>2.74</td>
<td>3.14</td>
<td>1.49</td>
<td>1.75</td>
<td>2.50</td>
<td>2.40</td>
</tr>
<tr>
<td>Fluorodichloromethane</td>
<td>2.69</td>
<td>1.85</td>
<td>3.11</td>
<td>1.18</td>
<td>1.38</td>
<td>2.23</td>
<td>2.44</td>
</tr>
<tr>
<td>Difluorodichloromethane</td>
<td>1.50</td>
<td>1.47</td>
<td>2.67</td>
<td>0.50</td>
<td>0.32</td>
<td>1.41</td>
<td>1.44</td>
</tr>
</tbody>
</table>

### TABLE 7.22

Log $K_p$ values for Some Model Compounds on Several Adsorbents at 80% Humidity.

<table>
<thead>
<tr>
<th>ADSORBENT</th>
<th>A-564</th>
<th>A-572</th>
<th>A-563</th>
<th>S-207A</th>
<th>ASC_W</th>
<th>SCII</th>
<th>SAR-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Log $K_e$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>3.70</td>
<td>4.45</td>
<td>4.38</td>
<td>3.20</td>
<td>3.34</td>
<td>3.85</td>
<td>3.97</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>3.22</td>
<td>3.28</td>
<td>3.68</td>
<td>2.03</td>
<td>2.29</td>
<td>3.04</td>
<td>2.93</td>
</tr>
<tr>
<td>Fluorodichloromethane</td>
<td>3.32</td>
<td>2.48</td>
<td>3.74</td>
<td>1.80</td>
<td>2.01</td>
<td>2.85</td>
<td>3.06</td>
</tr>
<tr>
<td>Difluorodichloromethane</td>
<td>2.20</td>
<td>2.16</td>
<td>3.36</td>
<td>1.19</td>
<td>1.01</td>
<td>2.10</td>
<td>2.13</td>
</tr>
</tbody>
</table>

The adsorbent log $K_p$ values are compared in fig 7.4 and fig 7.5 at both 0% and 80% humidity. From the figures one can observe the trends in log $K_p$ as adsorbate log$L^{16}$ increases for each adsorbent. The use of log$L^{16}$ as an adsorbate parameter is somewhat limited as it has already been shown that other types of intermolecular forces influence adsorption such as acidity, basicity and polarity. However, dispersion forces, represented by log$L^{16}$, have by far the most influence on adsorption. The purpose of using log$L^{16}$ is
to show the changes that can occur in adsorption with variations in the size of adsorbate.

The trends are not linear and vary with each adsorbent. An interesting observation is that
the strongest adsorbent for difluorodichloromethane, which is the weakest adsorbate, is
not necessarily the strongest adsorbent for tetrachloromethane, which is the strongest
adsorbate. This "cross-over" effect is present at both levels of humidity and shows quite
clearly the need to experiment with a range of challenge vapours in order to more fully
understand the relative adsorbing ability of different adsorbents. The adsorption plots
completely change as the humidity is increased from 0% to 80% and this underlines the
need to consider the importance of humidity when identifying adsorbents for particular
applications.

The variation in adsorbance at 0% humidity, as represented by log $K_p$ values, does not
exceed one log unit for any of the model vapours. There are several "crossovers" in
figure 7.4 which make it difficult to derive general trends. However, a general
classification with 207A as the weakest adsorbent, with ASC_W, SCII and SAR-O as
medium strength adsorbents and the Ambersorb carbons as strong adsorbents is not too
unreasonable. There are a few exceptions to this classification, notably 564 shows only
medium strength when adsorbing weaker adsorbates, and ASC_W shows adsorption
behaviour of a strong adsorbent when adsorbing the medium strength adsorbates.

The variation in adsorbance for the challenge vapours usually covers over two log units.
A very general classification from figure 7.5 would place ASC_W and 207A as weak
adsorbents, 564, SCII and SAR-O as medium adsorbents, 563 as a strong adsorbent and
572 as a "crossover" from medium to strong as log$L^{16}$ increases.
CONCLUSIONS

A few broad conclusions can be drawn from the behaviour of the model vapours on the adsorbents studied. The hydrophobic adsorbent 563 is hardly affected by the change in humidity and remains a strong adsorbent. All the other adsorbents were affected by the high level of humidity. SCII, SAR-O, 564 and 572 were all weaker adsorbents at 80% humidity, although 572 showed a considerable improvement at higher log$L^16$ values. The two adsorbents ASC_W and 207A were weakened considerably by the humidity.

The possible use of 563 in humid applications would certainly warrant some attention, judging by its behaviour in this study. On the other hand there is a considerable question mark over the use of ASC_W where high levels of humidity are present. The Ambersorb carbons obtained by pyrolysis of copolymers have performed consistently better than the coal and coconut based carbons in this study and the inclusion of them in air and water purification applications would seem worthy of examination.
Figure 7.4 A Plot of Log $K_p$ values versus Log $L^16$ for Four Model Vapours at 0% Humidity and 298.15K
Figure 7.5 A Plot of $\log K_p$ values versus $\log L^*_1$ for Four Model Vapours at 80% Humidity and 298.15K
Figure 7.6 A 3-D BAR GRAPH OF LOG $K_p$ VALUES FOR FOUR MODEL COMPOUNDS ON SEVEN ADSORBENTS AT 298.15K AND 0% HUMIDITY
Figure 7.7 A 3-D bar graph of log $K_p$ values for four model compounds on seven adsorbents at 298.15 K and 80% humidity.
FUTURE WORK

A microtechnique has been developed which provides a convenient way of obtaining adsorbent partition data for a whole range of adsorbates. The application of multiple linear regression, (MLR), and known adsorbate parameters to the data provides a characteristic equation for the adsorbent studied. Adsorbents can be compared either directly using the partition data or more quantitatively by using the characteristic equations. The microtechnique can be used at varying levels of humidity thus allowing the important influence of water on adsorption to be ascertained.

Work to compare the results from the microtechnique with those of a parallel study using the more tedious breakthrough methods in fixed beds is already underway. If the results obtained using the two techniques are comparable then the way is clear to replace the classical technique with the more convenient gas chromatographic procedure. Although breakthrough times have not been studied in this work due to their dependence on concentration, a standard technique of determining breakthrough times by GC should be developed. This would be possible if a fixed molar amount of adsorbate was injected in each case, allowing comparisons of breakthrough times to be meaningful.

The effect of humidity on adsorption has been shown to be far too important to be ignored any longer. A large number of applications of activated carbon involve exposure of the carbon to water, or water vapour in the air, and the effect of water on adsorbance ought to be taken into account in any future testing procedures developed. Indeed, the failure to take into account the effect of water when testing adsorbents may cause the most appropriate adsorbent to be ignored while a less appropriate one is chosen for the particular application. This was found to be the case with ASC_Whetlerite, which promised to be quite a good adsorbent when tested dry but proved to be one of the weakest adsorbents when wet.

The variation in adsorbance when dry covered only one log unit for the adsorbents studied and it could be argued that this difference was not large enough to warrant a
classification of adsorbents. However, the work at 80% humidity showed a variation of over two log units in partition constants. The large difference found in the presence of water implies that an adsorbent scale may be called for, especially for adsorbance under humid conditions. An adsorbent scale should provide adsorbent users with a very useful indication of a particular adsorbents properties and relative adsorbing strength compared with 'competitive' adsorbents.

The adsorption of water vapour by carbon has been shown to be affected by the presence of polar sites on the adsobent surface. It is likely that the non-synthetic carbons which have polar sites on the surface would perform better under wet conditions if these sites could be removed. It would be of benefit to ascertain the effect of removing these sites, if a technique can be found, on adsorption.

The variation with adsorbents made in different batches by the manufacturer has not been studied in any detail. It is likely that there will be some variation in adsorption properties from batch to batch and the amount of variation will depend on the particular manufacturing process. In order for a scale of carbon adsorbents to be developed batch variation should be taken into account. In this manner a more reliable averaged value for an adsorbent would be available.

The use of the adsorbent characteristic constants are recommended for the future classification of adsorbents. The constants provide an useful means of placing adsorbents in a scale and take into account not only dispersion forces but more specific forces such as hydrogen bond acidity, hydrogen bond basicity, and polarisability, all of which have proved important in the characterisation of the adsorbents studied here.

Finally, the effect of mesopores on adsorption, particularly under wet conditions, has been shown to be of interest. A more rigorous study of the effect of mesopores on water adsorption and possible hydrophobicity of resins is now called for so that a greater understanding of the adsorption process is gained and so that adsorbent manufacturers can move closer to producing adsorbents that remain effective under wet conditions.
CHAPTER VIII
THE ADSORPTION OF CHLOROFLUOROCARBONS

INTRODUCTION

In the coming years, when it will be necessary to remove the banned chlorofluorocarbon (CFC) compounds from air streams or to simply trap the gases prior to analysis of environmental samples, information regarding the relative adsorption of CFC compounds on various adsorbents under both dry and wet conditions will be very useful.

DETERMINATION OF CFC PARAMETERS AND PARTITION DATA

The log L^16 values for a variety of CFC's have been determined by experiments on hexadecane at 298.15K. The πH, αH, βH, and R values have been determined by back calculation from available retention data and these are in table 8.1.

Table 8.1
Experimental and Back Calculated CFC Parameters

<table>
<thead>
<tr>
<th>COMPOUND NAME</th>
<th>Arcton #</th>
<th>log L^16</th>
<th>R</th>
<th>πH</th>
<th>αH</th>
<th>βH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichlorofluoromethane</td>
<td>Arcton 21</td>
<td>1.614</td>
<td>0.210</td>
<td>0.40</td>
<td>0.20</td>
<td>0.00</td>
</tr>
<tr>
<td>1,1-Dichloro-1-fluoroethane</td>
<td>Arcton 141b</td>
<td>1.932</td>
<td>0.160</td>
<td>0.40</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>1,1-Dichloro-2,2,2-trifluoroethane</td>
<td>Arcton 123</td>
<td>1.746</td>
<td>-0.160</td>
<td>0.40</td>
<td>0.22</td>
<td>0.00</td>
</tr>
<tr>
<td>Dichlorodifluoromethane</td>
<td>Arcton 12</td>
<td>1.050</td>
<td>0.001</td>
<td>0.14</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Chlorodifluoromethane</td>
<td>Arcton 22</td>
<td>0.690</td>
<td>0.000</td>
<td>0.25</td>
<td>0.20</td>
<td>0.00</td>
</tr>
<tr>
<td>1,1,1,2-tetrafluoroethane</td>
<td>Arcton 134a</td>
<td>0.226</td>
<td>-0.280</td>
<td>-0.30</td>
<td>0.20</td>
<td>0.00</td>
</tr>
<tr>
<td>1,1,2,2-tetrafluoroethane</td>
<td>Arcton 134</td>
<td>0.289</td>
<td>-0.280</td>
<td>-0.30</td>
<td>0.30</td>
<td>0.00</td>
</tr>
<tr>
<td>1-Chloro-2,2,2-trifluoroethane</td>
<td>Arcton 133a</td>
<td>1.168</td>
<td>0.010</td>
<td>0.40</td>
<td>0.15</td>
<td>0.00</td>
</tr>
<tr>
<td>Bromochlorodifluoromethane</td>
<td>Arcton 12B1</td>
<td>1.489</td>
<td>0.220</td>
<td>0.40</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The solute parameters were determined by experiment or back calculation. The parameters that are now available allow the adsorption behaviour of this important class of compounds to be calculated on any adsorbent for which a characteristic equation is
The partition constants for several of these compounds have been determined on several adsorbents and these together with those calculated, by substitution into the equations given in chapter vii, are given in tables 8.2 and 8.3. A list of the adsorbents and their properties are given in table 8.4 for convenience and the characteristic constants of the equations used for calculation of some of the parameters are summarised in table 8.5 and table 8.6.

### TABLE 8.2 Arcton Log K<sub>p</sub> Values at 0% Humidity on Various Adsorbents

<table>
<thead>
<tr>
<th>ADSORBENT</th>
<th>A-564</th>
<th>A-572</th>
<th>A-563</th>
<th>S-207A</th>
<th>ASC_W</th>
<th>SCII</th>
<th>SAR-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arcton #</td>
<td>Log K&lt;sub&gt;p&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcton 134a</td>
<td>1.70+</td>
<td>2.34+</td>
<td>2.91</td>
<td>2.58</td>
<td>2.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcton 134</td>
<td>1.79+</td>
<td>2.40+</td>
<td>2.80</td>
<td>2.94</td>
<td>2.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcton 22</td>
<td>2.37+</td>
<td>2.76</td>
<td>2.85</td>
<td>2.39</td>
<td>2.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcton 133a</td>
<td>3.06+</td>
<td>3.20+</td>
<td>3.00</td>
<td>3.03+</td>
<td>3.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcton 12</td>
<td>3.10</td>
<td>3.52</td>
<td>3.50</td>
<td>3.02</td>
<td>3.22</td>
<td>3.10</td>
<td>2.97</td>
</tr>
<tr>
<td>Arcton 21</td>
<td>3.94</td>
<td>3.79</td>
<td>4.01</td>
<td>3.45</td>
<td>3.84</td>
<td>3.60</td>
<td>3.55</td>
</tr>
<tr>
<td>Arcton 141b</td>
<td>4.17+</td>
<td>3.90+</td>
<td>4.18+</td>
<td>3.83</td>
<td>4.04+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcton 123</td>
<td>3.90+</td>
<td>3.72+</td>
<td>5.23+</td>
<td>5.14+</td>
<td>5.36+</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

+ Calculated from the characteristic equation of the adsorbent

### TABLE 8.3 Arcton Log K<sub>p</sub> Values at 80% Humidity on Various Adsorbents

<table>
<thead>
<tr>
<th>ADSORBENT</th>
<th>A-564</th>
<th>A-572</th>
<th>A-563</th>
<th>S-207A</th>
<th>ASC_W</th>
<th>SCII</th>
<th>SAR-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arcton #</td>
<td>Log K&lt;sub&gt;p&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcton 134a</td>
<td>0.80</td>
<td>1.17</td>
<td>1.95</td>
<td>0.62+</td>
<td>0.42+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcton 134</td>
<td>1.29</td>
<td>1.35</td>
<td>2.04</td>
<td>0.82</td>
<td>0.72+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcton 22</td>
<td>1.64</td>
<td>1.16</td>
<td>2.26</td>
<td>0.75</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcton 133a</td>
<td>2.48</td>
<td>2.21</td>
<td>2.71+</td>
<td>1.44</td>
<td>1.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcton 12</td>
<td>2.20</td>
<td>2.16</td>
<td>3.36</td>
<td>1.19</td>
<td>1.01</td>
<td>2.10</td>
<td>2.13</td>
</tr>
<tr>
<td>Arcton 21</td>
<td>3.32</td>
<td>2.48</td>
<td>3.74</td>
<td>1.80</td>
<td>2.01</td>
<td>2.85</td>
<td>3.06</td>
</tr>
<tr>
<td>Arcton 141b</td>
<td>3.51+</td>
<td>3.46</td>
<td>3.90+</td>
<td>2.65</td>
<td>2.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcton 123</td>
<td>4.35+</td>
<td>3.65</td>
<td>5.02+</td>
<td>2.68+</td>
<td>3.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

+ Calculated from the characteristic equation of the adsorbent

213
The partition constants given in table 8.2 and 8.3 are also shown in figures 8.1 and 8.2. From the figures it can readily be seen that there are significant differences in the relative performances of the adsorbents at different levels of humidity. At 0% humidity the strongest adsorbents are difficult to discern, and to some extent relative adsorption appears to vary with different arcton compounds. At 80% humidity the situation has changed and clear differences now exist between the general adsorption properties of each adsorbent. Ambersorb 563 has now emerged as the strongest adsorbent at 80% humidity, while Ambersorb 564 and Ambersorb 572 also appear to have held up rather well to the wet conditions. ASC Whetlerite and to a lesser extent Sutcliffe Speakman 207A are the most severely affected by the humidity and can no longer compete with the Ambersorb series of adsorbents. Although only a small number of results were available the adsorbents Chem Viron SCII and SAR-O SGM performed reasonably well at 80% humidity, their adsorption properties being comparable to Ambersorb 564 or 572 but less than Ambersorb 563.

It appears that the hydrophobic adsorbent Ambersorb 563 may be well suited to humid applications and could be a possible replacement for ASC-Whetlerite in applications where water vapour may significantly reduce the effectiveness of the latter to CFC samples.
<table>
<thead>
<tr>
<th>Adsorbent(^1)</th>
<th>Lot No.</th>
<th>BET Surface Area ((m^2 g^{-1}))</th>
<th>Micropore Volume ((cm^3 g^{-1}))</th>
<th>Mesopore Volume ((cm^3 g^{-1}))</th>
<th>Macropore Volume ((cm^3 g^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambersorb 564</td>
<td>88/007</td>
<td>486(606)</td>
<td>0.25</td>
<td>0.16</td>
<td>0.13</td>
</tr>
<tr>
<td>Ambersorb 572</td>
<td>89/2147</td>
<td>738(917)</td>
<td>0.38</td>
<td>0.21</td>
<td>0.19</td>
</tr>
<tr>
<td>ASC Whetlerite</td>
<td></td>
<td>708(856)</td>
<td>0.36</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Sutcliffe–Speakman 207A</td>
<td></td>
<td>796(923)</td>
<td>0.40</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>SAR–O SGM1701–1</td>
<td>SGM1701–1</td>
<td>914(1131)</td>
<td>0.46</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Ambersorb* 563</td>
<td>550</td>
<td>0.24</td>
<td>0.24</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Chem–Viron SCII</td>
<td>TE10102A</td>
<td>1253</td>
<td>0.51</td>
<td>0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

\(^1\) All adsorbents are 20/30 mesh. \(^2\) Manufacturers Estimate Only. Data obtained from Rohm and Haas Ltd, USA. Figures in parenthesis are BET multipoint values.
Figure 8.1

ADSORPTION PARTITION LEVELS OF ARCTON COMPOUNDS ON VARIOUS ADSORBENTS AT 0% HUMIDITY AND 298.15K.
Figure 8.2

Adsorption Partition Levels of Arcton Compounds on Various Adsorbents at 80% Humidity and 298.15K.
### TABLE 8.5+

Summary of Characteristic Equations for Log $K_p$ at 0% Humidity

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$R_2$</th>
<th>$\alpha^H_2$</th>
<th>$\logL^{16}$</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sutcliffe Speakman</td>
<td>-4.29</td>
<td>1.85</td>
<td>2.18</td>
<td>0.25</td>
</tr>
<tr>
<td>207A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASC Whetlerite</td>
<td>-3.69</td>
<td>2.23</td>
<td>1.92</td>
<td>0.93</td>
</tr>
<tr>
<td>Ambersorb 572</td>
<td>-</td>
<td>-</td>
<td>1.38</td>
<td>1.19</td>
</tr>
<tr>
<td>Ambersorb 563</td>
<td>-4.93</td>
<td>-</td>
<td>2.84</td>
<td>0.51</td>
</tr>
<tr>
<td>Ambersorb 564</td>
<td>-</td>
<td>-</td>
<td>1.45</td>
<td>1.37</td>
</tr>
</tbody>
</table>

* Derived from results in Chapter VII

### TABLE 8.6+

Summary of Characteristic Equations for Log $K_p$ at 80% Humidity

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$R_2$</th>
<th>$\pi^H_2$</th>
<th>$\alpha^H_2$</th>
<th>$\beta^H_2$</th>
<th>$\logL^{16}$</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sutcliffe Speakman</td>
<td>-1.25</td>
<td>-</td>
<td>1.68</td>
<td>0.93</td>
<td>1.43</td>
<td>-0.39</td>
</tr>
<tr>
<td>207A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASC Whetlerite</td>
<td>-3.37</td>
<td>-</td>
<td>1.65</td>
<td>2.02</td>
<td>2.23</td>
<td>-1.36</td>
</tr>
<tr>
<td>Ambersorb 572</td>
<td>-3.14</td>
<td>-</td>
<td>-</td>
<td>2.30</td>
<td>2.33</td>
<td>-0.65</td>
</tr>
<tr>
<td>Ambersorb 563</td>
<td>-4.99</td>
<td>-</td>
<td>-</td>
<td>1.66</td>
<td>2.53</td>
<td>0.19</td>
</tr>
<tr>
<td>Ambersorb 564</td>
<td>-3.75</td>
<td>1.20</td>
<td>-</td>
<td>1.80</td>
<td>1.91</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

* Derived from results in Chapter VII
CHAPTER IX
EXPERIMENTAL

INTRODUCTION
Due to the fact that much of the experimental methodology has been developed during the course of this work, much of the information which would normally be contained in this chapter has already been presented in chapter v. Information contained in chapter v is not repeated here and a full experimental account can best be gleaned by considering chapters v and ix together.

THE MEASUREMENT OF FLAME IONISATION DETECTOR PARTITION COEFFICIENTS
Partition coefficients were measured on several specially adapted Perkin-Elmer F11 and F33 flame ionisation detector (FID) gas chromatographs, the flow controllers supplied with the machines having been replaced by high precision Negretti and Zambra M2545 units, to guarantee readily reproducible and stable gas flow rates of around 60ml/minute. As most work was carried out at 298.15K it was preferable to use a water bath thermo-stat. The head of the gas chromatograph was simply placed over a thermo-stat water bath such as a Grant SE-50, and the columns completely immersed in water. Accurate temperature regulation to within +/- 0.05K is possible using this method. There is a distinct advantage to using older equipment such as the Perkin-Elmer F11 and F33, as opposed to modern gas chromatographs, in that they can be easily modified, taken apart, and used in this way. If room temperature rose to, or exceeded 298.15K, cooling units such as the Townson & Mercer Laboratory Refrigeration Unit, along with the water bath heater could also be used to ensure isothermal conditions and minimize effects due to laboratory temperature variations. A special customised water bath, with simultaneous heating and cooling facilities was also available for this purpose.
Flame ionisation detector systems were used exclusively with moisture free helium as carrier gas (dried by passing the source gas for the chromatograph through a silica gel/molecular sieve absorbent column obtained from Phase Sep Ltd.). Gas flow rates were typically 60ml/minute. But for some of the more retentive adsorbates a flow rate of 120ml/minute was used.

The flame gases were air and hydrogen. In this work the flame is set at maximum sensitivity which allows detection of eluting adsorbates at concentrations as low as 0.001 μg. This compares with the lowest TCD concentration of 0.5 μg dm⁻³. The columns used are 0.3 and 0.18 mm i.d., 0.6mm o.d. and are obtained from Analytical Columns Ltd.

Column temperatures were measured using mercury thermometers (+/-0.05K) calibrated against thermometers from the National Physical Laboratory, Teddington.

THERMAL CONDUCTIVITY (TCD) MEASUREMENTS OF PARTITION COEFFICIENTS

TCD partition coefficients were measured using a specially adapted Pye-Unicam 104 system, with a replacement amplifier and detector by AMS Ltd. Flow controllers were again Negretti and Zambra M2545 units, and column temperatures were thermostatted and measured exactly as that described for FID measurements. Thermal conductivity detector or katharometer systems were used with helium as carrier gas, dried in the same manner as the FID method detailed above.

At the end of the column is the detector, which detects changes in the current being passed across a Wheatstone bridge due to changes in the thermal conductivity of the eluting carrier gas. The titanium filaments in the Wheatstone bridge are very sensitive and care must be taken to keep them in an inert environment, exposure to oxygen will cause them to burn out. In order to protect the filaments from an inadvertent introduction of oxygen; most commonly taking place when the helium supply is turned off allowing oxygen to diffuse into the detector, an emergency pressure sensing switch is placed in the
carrier gas supply line, this will shut down the bridge current to the detector if the helium supply falls below a critical pressure.

The experimental set up for both FID and TCD systems is shown diagrammatically in fig 9.1.

HUMIDITY EXPERIMENTAL

Dreschel bottles containing salt solution had specially widened internal inlet tubes of 1cm to avoid blocking due to salt deposition. Indeed, the first Dreschel bottle contained a solution that was not quite saturated in order to increase the lifetime of the system and minimise the salt deposition in the 2nd bottle.

Humidity levels were measured gravimetrically using a 1:1 CaCl₂/molecular sieve mixture in a series of three separately weighed U-tubes. The wet helium stream was collected for between 5 and 24 hrs and then the U-tubes were reweighed.

All other experimental details for the humidity control can be found in chapter v.

MEASUREMENT OF LOG L₁⁶ VALUES

The measurements are carried out by gas liquid chromatography, GLC, on hexadecane columns.

GLC Packing and Column Preparation

The hexadecane stationary phase is simply coated onto the chromosorb support by rotary evaporation of a solution/slurry of stationary phase and support respectively, in a suitable volatile solvent. The stationary phase is accurately weighed out into a round-bottomed flask, along with the chosen 'inert' support. Sufficient suitable solvent is then added to completely dissolve the stationary phase, and produce a slurry of support. The same flask is used throughout the coating procedure, to avoid any errors in phase/support/solvent transfer.
The mixture is slowly agitated by turning with vacuum off on a rotary evaporator for about an hour. Care is taken here to joint all glass joints with PTFE tape, to avoid vacuum grease contamination of the mixture, and weighing errors. The solvent is then slowly extracted using vacuum over the course of the next hour. Depending on solvent volatility, heat can also applied to the bottom of the flask from a heated water bath. When all solvent has been removed, as checked by repeated weighings, the coated support is sieved to ensure a uniform mesh range, typically mesh 40/60. Care with the support is necessary throughout the whole coating procedure to ensure the particle size is not significantly decreased through attrition. The resulting coated support can now be used to pack a column. The support used was Chromosorb G with loadings of around 10%, which is quite high, specifically to try to minimize adsorption effects.

The FID system was used to obtain \( \log L_1^\ast \) values relative to the alkane standards on hexadecane, thereby indirectly obtaining absolute values for the unknown. For \( n\text{-hexadecane} \) many absolute values have already been determined. So to get an absolute \( L_1^\ast \) value for an unknown solute, it need only be chromatogrammed on \( n\text{-hexadecane} \) at 298.15K with a solute for which \( L_1^\ast \) is already known, such as octane, and from the following relationship \( L_1^\ast \) can be easily calculated.

\[
\frac{L^\ast \text{(UNKNOWN)}}{L^\ast \text{(STANDARD)}} = \frac{T^\prime \text{(UNKNOWN)}}{T^\prime \text{(STANDARD)}} \quad \text{(9.1)}
\]
FIGURE 9.1 SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS

Key: FC Flow Controller
I Injection Port
M Manometer
AC Adsorbent Column
FID Flame Ionisation Detector
A Amplifier
CR Chart Recorder
A/D Analog Digital Converter
C Computer
GC Gas Cylinders and Pressure Regulators
DC Drying Column
PR Pressure Regulator

He O2 H2 GC

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ADSORBENT COLUMN PACKING AND CONDITIONING

The adsorbent material is first sieved to obtain 20–30 mesh size and then a portion of this is added to a preweighed glass column containing an inert teflon stopper to hold the adsorbent in place, the weight of added adsorbent is obtained and another teflon stopper is used to fully enclose the column. The column is then tapped lightly for a few minutes to make sure it is packed down and the final weight of the preconditioned column is obtained. The column is then conditioned at 110°C, using helium, for 24 hours, it is then reweighed. The process is repeated until there is no change in column weight at which time the column is ready for use.

Typically Ambersorb 572 and 564 lose 1–3% of their weight in the first 24 hour period and no more after that.

LABORATORY TEMPERATURE CONTROL

The laboratory temperature was kept between 21°C and 23°C during humidity measurements. This was found necessary to avoid condensation in the humidity lines at the lower temperature and loss of 25°C thermo-stat control at the higher temperature. The increased air temperature in the laboratory was effected using a 3000W oil heater obtained from Delonghi Ltd. If air temperatures became excessive, experimental work was continued by incorporating cooling units to maintain low bath temperatures.

FLOW MEASUREMENTS

Flow measurements were made using a soap bubble meter. After equilibration, it was found that a minimum of five bubbles were necessary to give a reproducible value for flow that did not vary with an increasing number of bubbles. Below this number the error was of the order of a 1–2% decrease in flow, this was probably due to a lack of equilibrium with the walls of the bubble meter and thus the water vapour saturation pressure above the surface of the bubble was not attained. The presence of water vapour
in the meter has an additive effect on pressure of column eluent and this increases the observed flow rate, correction for this increase, which is detailed in chapter v (equation 5.36), assumes 100% water vapour pressure in the meter and thus if 100% is not attained the correction will over compensate and give an artificially retarded flow. Thus, as the flow correction in this work assumes water vapour saturation above the bubble it is important that equilibration has taken place in the flow meter. And it has been found that once equilibration has been reached around five bubbles are needed to maintain a repeatable measurement.

A digital hand held thermometer (+/-0.1K, type Tempcon TC1100) was used to measure the temperature of the soap solution and carrier gas in the flow meter for two reasons. Water saturated carrier gas will condense on a mercury bulb thermometer, (the resultant latent heat effect giving very slight inaccuracies) and simply because it was easier to introduce a thermocouple into the narrow flow meter than a thermometer. The thermocouple was previously calibrated at the experimental temperature using the accurate mercury thermometers. The inlet and outlet gas pressures were measured using manometers filled with mercury, and a correction for the pressure drop across the column also applied.

SAMPLE SIZES

Generally, sample sizes injected varied between 0.01–1000μl for a gas and 0.01–20μl for a liquid. Samples were injected using Hamilton 7000 series syringes, into a column injection heater at a temperature sufficiently high to volatilize the solute, ensuring that the solute interacts with the column head as a vapour.

DATA RECORDING

Chromatograms were displayed on a number of chart recorders, eg. Goerz Electronic RE 511, Perkin Elmer model 1002 and Philips PM 8251. Retention measurements were made
either directly from the chart paper (especially where elution times were very large), or by
using a personal computer. The personal computer was either an Amstrad 2286 IBM
compatible with maths coprocessor or an Elonex 386B, in both cases Unkelscope Level II
data acquisition software with a Metrabyte DAS-8 PGA analogue/digital conversion
board was used.

CALCULATION OF PARTITION COEFFICIENTS USING UNKELSCOPE LEVEL II
SOFTWARE AND IN-HOUSE SOFTWARE.
The analog signal from the detector amplifier is passed to the computer interface,
converted to a digital signal and stored in data file for processing at a later date.
To effect this Unkelscope level II data acquisition software and a DAS 8-PGA analog
digital converter were used. Peaks were smoothed using a Fourier transform smoothing
function and read directly into the adsorption program Inputest.Bas for baseline,
diffusion and flow rate corrections. The output of Inputest.Bas was read into the 'C'
program GFAD.C for calculation of partition coefficients as detailed in chapter v. All the
program outputs can be stored and used in plots, as evidenced throughout this thesis.
The programs are shown in Appendix 1 & 2.
APPENDIX 1
DECLARE SUB bcorr (i%, sum!, ave!, conc!, xtime!, peakend%, x%, tang!, numb%, cmass#, sens#, ubfile$)
REM This program corrects for diffusion and other experimental parameters
REM but differs from input2.bas by not correcting for baseline drift.
DECLARE SUB mass (mass1#)
DECLARE SUB findretvol (P%, LVG, xtime!())
DECLARE SUB bcorr (i%, sum!, ave!, conc!, xtime!, peakend%, x%, tang!, numb%, cmass#, sens#, ubfile$)
DECLARE SUB corrdiff (P%, pleft%, pright%, pcorr%, ldata!, i%, maxlen%, conc!, xtime!, corrt!, pcorr!, ubfile$)
DO
CONST maxlen = 8200
CLS
100 REM This subroutine should set the dimensions of the file depending on
REM number of analog signals. Maximum number of signals four.
REM make the array parameters variable
REM Warning 1st letter of array variable must not coincide with any other variable
REM $DYNAMIC
COLOR 0, 14: CLS
DEFINT T
BEEP
REM 110 INPUT "How many traces in the file (1,2)"; T
REM T = 1
REM IF T = 1 THEN
REM proceed time with x as T is a separate variable
REDIM conc(maxlen), horz(1), xtime(maxlen), pcorr(maxlen), corrt(maxlen)
REM ELSEIF T = 2 THEN
REM 130 REDIM conc(maxlen), horz(1), xtime(maxlen), pcorr(maxlen), corrt(maxlen)
REM 135 REDIM conc2(maxlen), horz2(1), xtime2(maxlen), pcorr2(maxlen), corrt2(maxlen)
REM IF T = 4 THEN
REM REDIM conc(1024), horz(1024), xtime(1024)
REM REDIM conc2(1024), horz2(1024), xtime2(1024)
REM
REM BEEP
REM PRINT "1,2 or 4 NOT entered"
REM GOTO 110
REM END IF
DEFINT I-N, Q
DEFSNG A, C-H, O-P, R-Z
DEFSTR U
CLS
REM Now ask for and read the input file
BEEP
DIM SHARED file.asc$
INPUT "INPUT FILE "; file.asc$
PRINT
OPEN file.asc$ FOR INPUT AS #1
REM read titles
bhead1$ = INPUT$(40, #1)
bhead2$ = INPUT$(40, #1)
REM PRINT "THE PRIMARY TITLE IS ", bhead1$
REM PRINT
REM PRINT "THE SECONDARY TITLE IS ", bhead2$
REM PRINT
REM read # of channels & number of data points
INPUT #1, space, chan, MAXLENG%
PRINT "THE NO. OF TRACES IS ", chan
PRINT
PRINT "THE NUMBER OF POINTS IN PEAK TRACE IS ", MAXLENG%
REM read in data points
IF (chan < 1) THEN GOTO 9000
INPUT #1, npt1
REM PRINT npt1; "(# OF DATA POINTS)"
BEEP
PRINT
PRINT "READING DATA TRACE 
FOR i = 1 TO MAXLENG%
INPUT #1, conc(i)
NEXT
REM PRINT "conc(MAXLEN) is"; conc(maxlen);
PRINT
PRINT "DATA TRACE READ 
BEEP
INPUT #1, space
PRINT
PRINT "READING TIME TRACE 
FOR i = 1 TO MAXLENG%
INPUT #1, xtime(i + n)
NEXT
PRINT
PRINT "TIME TRACE READ"
PRINT
INPUT #1, m
REM split the label
INPUT #1, ulong$
uc1$ = MID$(ulong$, 1, 20)
uh1$ = MID$(ulong$, 21, 20)
ut1$ = MID$(ulong$, 41, 20)
REM PRINT
REM PRINT bhead1$
REM PRINT
REM PRINT bhead2$
REM PRINT uc1$
REM PRINT uh1$
REM PRINT ut1$
BEEP
IF T = 2 THEN
   PRINT "Press any key to read second trace"
WHILE INKEY$ = ""
   WEND
CLS
INPUT #1, npt1
PRINT npt1, "(# of data points)"
PRINT "Reading data into array"
FOR i = 1 TO MAXLENG%
   REM INPUT #1, conc2(i + n)
NEXT
PRINT "Vertical trace read"

BEEP
INPUT "Is there a set of horizontal data values y/n"; hashor$
REM Read in the space between voltage values and time values
REM Read in horizontal axis
INPUT #1, m
IF LCASE$(hashor$) = "n" THEN
   GOTO 148
END IF
PRINT "Reading horizontal trace"
FOR i = 1 TO MAXLENG%
   REM INPUT #1, horz2(i)
NEXT
REM Read in space between horz. values & time values
REM Read in the data points for time
INPUT #1, m
148 PRINT "Reading time trace"
FOR i = 1 TO MAXLENG%
   REM INPUT #1, xtime2(i + n)
NEXT
PRINT "ok?"
230
REM To find the end of the peak in conc() array ie cursor point
REM QB fills remainder of array with 0's if not enough points from Unkel.asc
PRINT "FINDING END OF TRACE. WAIT!"
FOR z% = 1 TO maxlen
    IF conc(z%) <> 0! THEN
        peakend% = z%
    ELSEIF conc(z% - 1) <> 0! THEN
        peakend% = z% - 1
    END IF
NEXT
PRINT
PRINT "PEAKEND IS GIVEN THE VALUE OF POINT"; peakend%
PRINT
IF peakend% = 0 THEN
    PRINT
    PRINT "Correction to peakend"
    peakend% = MAXLENG%
    PRINT "CORRECTED PEAKEND TO "; peakend%
END IF
CALL mass(massg#)
PRINT
PRINT "CORRECTING FOR BASELINE DRIFT "
CALL bcorr(im%, sum!, ave!, conc(), xtime(), peakend%, x%, tang!, numb%, massg#, csens#, ubfile$)
LET P% = 0
FOR i = 1 TO peakend%
    IF conc(P%) < conc(i + 1) THEN
        P% = i + 1
    END IF
NEXT
PRINT "Peak at"; P%; "D.P.'s"
CALL corrdiff(P%, pleft%, pright%, pcorr%, ldata!, q, npt1%, conc(), xtime(), corrt(), pcorr(), ubfile$)
PRINT "New peak at"; P%; "D.P.'s"
CALL findretvol(P%, vg, xtime())
REM INPUT "What is the LogVg compound file", vgfile$
REM OPEN vgfile$ FOR APPEND AS #1
REM INPUT "What is the name of the adsorbate for LogVg storage", comp$
PRINT
PRINT "LOG Vg IS"; vg
PRINT
REM WRITE #1, vg, comp$
REM CLOSE #1
INPUT "ANOTHER FILE? (Y/N)", AN$
LOOP UNTIL UCASE$(AN$) = "N"
9000 END
REM/*******************************************************************************/
REM/*******************************************************************************/
REM/----------- BASELINE CORRECTION FUNCTION -----------
REM/*******************************************************************************/
REM/*******************************************************************************/

DEFINT I-N, Q
DEFSTR U
SUB bcorr (i, sum!, ave!, conc(), xtime(), peakend%, x%, tang!, numb%, cmass#, sens#, ubfile$)

REM Calculate number of points for initial baseline calcn. based on number
REM of points in subsequent peak.
IF peakend% > 1000 THEN
    numb% = INT(peakend% / 500)
ELSEIF peakend% <= 1000 THEN
    numb% = 5
ELSEIF peakend% <= 100 THEN
    numb% = 3
END IF

REM Mean value of initial baseline
sum! = 0
REM Baseline beginning
FOR i = 1 TO numb%
    sum! = sum! + conc(i)
NEXT
ave! = sum! / numb%

REM tangent of drift calculation using opposite/adjacent
tang! = (conc(peakend%) - ave!) / xtime(peakend% - numb%)
REM recalculate conc(I) values with corrected baseline
x% = 0
FOR x% = 0 TO numb%
    conc(x%) = 0
NEXT
FOR x% = numb% + 1 TO peakend%
    conc(x%) = conc(x%) - (xtime(x% - numb%) * tang!) - ave!
NEXT
PRINT
PRINT "CORRECTED"; x% - numb%; "VALUES NEGLECTING BASELINE DRIFT."
PRINT
PRINT "CALCULATING SENSITIVITY WAIT!"
INTSUM# = 0
x% = 1
WHILE x% <= peakend%
    INTSUM# = INTSUM# + conc(x%)
    x% = x% + 1
WEND
INTSUM# = INTSUM# * (xtime(2) - xtime(1))
PRINT
PRINT USING "THE AREA UNDER THE PEAK IS #######.# VOLTS.SECS"; INTSUM#
BEEP
REM PRINT "Check 1: The value of insum is"; insum#; "volts.secs"

232
REM PRINT "Check 2: The value of cmass is"; cmass#; "grams"
sens# = INTSUM# / cmass#
REM Determine length of Mother file
leng% = LEN(file.asc$)
pos2% = 1
REM Loop to find final occurrence if any of AS
DO
pos1% = INSTR(pos2%, UCASE$(file.asc$), "AS")
pos2% = INSTR((pos1% + 1), UCASE$(file.asc$), "AS")
BEEP
LOOP UNTIL pos2% = 0 OR pos1% = 0
REM Test for existence of AS and that AS are the final letters of the
IF pos1% > 0 AND pos1% + 1 = leng% THEN
BEEP
REM PRINT pos1%
REM Add one to string length to replace AS file with longer COR file
ubfile$ = STRING$(leng% + 1, 42)
REM Modify corfile with original ascii file
MID$(ubfile$, 1) = UCASE$(file.asc$)
REM Modify name end
MID$(ubfile$, pos1%) = "COR"
PRINT
PRINT "INPUT FILE IS ", UCASE$(file.asc$)
PRINT
PRINT "OUTPUT FILE IS ", ubfile$
PRINT
BEEP
ELSE
PRINT "WHAT IS THE NAME OF THE DIFFUSION CORRECTED WRITE FILE? 
INPUT "Use ______COR type filename", ubfile$
END IF
OPEN ubfile$ FOR OUTPUT AS #2
WRITE #2, sens#
BEEP
REM PRINT "sensitivity factor is"; sens#; "volts.secs/gram solute"
END SUB
REM END IF
REM<*---------------------------------------------------------------*/
REM<*---------------------------------------------------------------*/
REM<********************* DIFFUSION CORRECTION FUNCTION *************/
REM<*---------------------------------------------------------------*/
REM<*---------------------------------------------------------------*/
REM IDENTIFY ARRAY POSITION OF PEAK
REM WRITE THE CORRECTED PEAK TIME
REM Optional correction for diffusion.
REM Error check P% incorrectly assigned.
REM Step down left (diffusion only) side
REM Use midpoint of two points as cutoff for greater accuracy
REM Check the points on the right (adsorption and diffusion) side
REM for cast out criteria
REM Start diffusion correction loop.
REM Increment loop start so that cast out point is lost from array
REM Cast out criteria (COC); IF THIS IS TRUE ARRAY VALUE IS THROWN OUT.
REM NEXT VALUE TO PASS COC IS PLACED IN NEXT ARRAY POSITION.
REM THEREFORE # POINTS CAST OUT = # POINTS FRONT BOUNDARY
REM Warning drifting points may cause loop exit BY PASSING COC
REM Improve cast out criteria at later date
REM If exit loop criteria satisfied point not saved
REM Default diffusion corrected pcorr!() array to 0
REM n = n + 1
REM LET pcorr!(n) = conc(pright%)
REM PRINT
970 PRINT "EXITED LOOP BY ELUTION BOUNDARY"
PRINT
PRINT n; " POINTS IN DIFFUSION CORRECTED PEAK"
990 DO WHILE pright% < maxlen%
   n = n + 1
   pright% = pright% + 1
   pcorr!(n) = conc(pright%)
LOOP
   REM PRINT pright%; "is it"
   REM PRINT "writing"; xtime(i); ";"; pcorr!(i);
ELSEIF UCASE$(DC$) = "N" THEN
   PRINT "NOT CORRECTING FOR DIFFUSION"
   LET n = 0
   FOR pright% = pcorr% TO maxlen%
      n = n + 1
      pcorr!(n) = conc(pright%)
   NEXT pright%
ELSE
   PRINT "Y OR N NOT GIVEN - TRY AGAIN!"
GOTO 948
END IF
LET diff! = xtime(2) - xtime(1)
PRINT
PRINT "TIME BETWEEN DATA POINTS IS ", diff!; "SECS"
REM CORRECT FOR NEW MAXLEN%
   b& = diff! * maxlen%
REM WHILE INKEYS = ""
REM WEND
PRINT
PRINT "POINTS IN PEAK BEFORE DIFFUSION CORRECTION"; maxlen%
   LET maxlen% = n
   b& = diff! * maxlen%
REM WHILE INKEYS = ""
REM WEND
REM PRINT "1"
REM PRINT "POINTS IN PEAK AFTER DIFFUSION CORRECTION"; maxlen%
PRINT
REM Optional correction for mid-run injections
   P1% = 0
   DP% = 0
REM CONVERSION TO ABSOLUTE DATA POINT
REM WHILE INKEYS = ""
REM WEND
REM PRINT "2"
   P1% = (xtime(1) / diff!) + P%
REM WHILE INKEYS = ""
REM WEND
REM PRINT "3"
REM PRINT b&; diff!; xtime(1)
REM WHILE INKEYS = ""
REM WEND
C& = xtime(1)
REM WHILE INKEY$ = ""
REM WEND
REM PRINT "4"
PRINT "ELUTION STARTS AT "; C&; " SECONDS."
C& = diff! * P%
PRINT
PRINT "RELATIVE PEAK MAXIMA AT "; C&; " SECONDS ("; P%; ")."
C& = diff! * P1%
PRINT
PRINT "ABSOLUTE PEAK MAXIMA AT "; C&; " SECONDS ("; P1%; ")."
PRINT
INPUT "WAS THE INJECTION TIME AT 0 SECONDS (Y/N)", ITS
IF UCASES(ITS) = "N" THEN
PRINT
INPUT "WHAT WAS THE INJECTION DATA POINT STORAGE NUMBER", DP%
P1% = P1% - DP%
PRINT "NEW ABSOLUTE PEAK MAXIMA AT ", P1%; "DATA POINTS"
END IF
WRITE #2, P1%
WRITE #2, diff!
BEEP
1012 FOR i = 1 TO maxlen% - 1
1013 WRITE #2, pcorr!(i), i
1014 NEXT i
PRINT "WRITING"; i - 1; "POINTS TO DISK FILE"
PRINT
P% = P1%
1015 CLOSE #1, #2
1050 END SUB
REM/*******************************************************************************
REM/*******************************************************************************
REM/******************** RETENTION VOLUME FUNCTION ***************/
REM/*******************************************************************************
REM/*******************************************************************************
REM/*******************************************************************************

SUB findretvol (P%, vg, xtime())
b$ = "N"
DO WHILE UCASE$(b$) = "N"
1500 INPUT "FLOW RATE (sec/10cm3)? ", f!
f! = 1 / ((f! / 10) / 60)
PRINT
PRINT "FLOW IS "; f!; "CM3/MIN"
PRINT
REM CALCULATE RETENTION VOLUME
VR! = f! * (xtime(P%) / 60)
INPUT "GAS HOLDUP TIME (MINS)? "; th!
PRINT
REM CALCULATE HOLDUP VOLUME
VH! = f! * th!
INPUT "ATMOSPHERIC PRESS. (MM/Hg) "; po!
PRINT
INPUT "INPUT GAS LINE MANOMETER READING (MM/Hg) I.E. PRESSURE DROP "; pi!
PRINT
1560 REM CALCULATE ACTUAL INPUT PRESSURE
CPI! = po! + pi!
INPUT "TEMPERATURE OF THE COLUMN (°C) "; tcc!
tc! = tcc! + 273.2
PRINT
INPUT "TEMPERATURE OF THE FLOW METER(°C) "; tfc!
tf! = tfc! + 273.2
PRINT
INPUT "WATER VAPOUR PRESSURE AT TEMP OF FLOW METER(MM/Hg) "; pw!
PRINT
INPUT "ACTIVE WEIGHT OF ADSORBENT(G) = "; w!
PRINT
1586 svr! = VR! - VH!
REM CORRECT SVR FOR PRESSURE DROP ACCROSS THE COLUMN
REM (1) PRESSURE DROP CORRECTION FACTOR
PDCF! = 3 / 2 * (((CPI! / po!) ^ 2) - 1) / (((CPI! / po!) ^ 3) - 1))
REM (2) FLOW RATE PRESSURE CORRECTION
FRPC! = (po! - pw!) / po!
REM (3) FLOW RATE TEMPERATURE CORRECTION
FRTC! = tc! / tf!
VC! = PDCF! * svr! * FRPC! * FRTC!
REM INPUT "DO YOU WANT TO CORRECT FOR HUMIDITY(Y/N) "; A$
REM PRINT
REM IF UCASE$(A$) = "Y" THEN
REM INPUT "WHAT IS PRESSURE OF WATER VAPOUR IN THE COLUMN (MM/Hg) = "
; PWC!
REM PRINT
REM VC! = VC! * (pi! / (pi! - PWC!))
REM ELSEIF UCASE$(A$) = "N" THEN

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REM END IF
REM CALCULATE SPECIFIC RETENTION VOLUME
vg! = VC! / w1!
vg! = (LOG(vg!)) / (LOG(IO))
PRINT
PRINT "THE VALUE OF LOG10Vg IS "; vg!
PRINT
INPUT "CONTINUE PRESS Y TO ALTER EXPERIMENTAL DATA PRESS N"; b$
LOOP
REM Determine length of Mother file
leng% - LEN(file.asc$)
pos2% = 1
REM Loop to find final occurrence if any of AS
DO
pos1% = INSTR(pos2%, UCASE$(file.asc$), "AS")
pos2% = INSTR((pos1% + 1), UCASE$(file.asc$), "AS")
BEEP
LOOP UNTIL pos2% = 0 OR pos1% = 0
REM Test for existence of AS and that AS are the final letters of the filename
IF pos1% > 0 AND pos1% + 1 = leng% THEN
BEEP
REM Add one to string length to replace AS file with longer DAT file
filedat$ = STRING$(leng% + 1, 42)
REM Modify corfile with original ascii file
MID$(filedat$, 1) = UCASE$(file.asc$)
REM Modify name end
MID$(filedat$, pos1%) = "DAT"
PRINT
PRINT "DATA FILE IS NAMED ", filedat$
BEEP
ELSE
1645 INPUT "Give filename to store this data in ", filedat$
END IF
OPEN filedat$ FOR OUTPUT AS #3
WRITE #3, w1!
WRITE #3, tcc!
WRITE #3, fl!
WRITE #3, po!
WRITE #3, pi!
WRITE #3, tfc!
WRITE #3, pw!
CLOSE #3
1646 END SUB
REM/******************************************************************************
REM******************************************************************************
REM/**************************** MASS DETERMINATION FUNCTION ********************/
REM******************************************************************************
REM******************************************************************************

SUB mass (mass1#)
  INPUT "WHAT WAS THE AMOUNT OF ADSORBATE INJECTED UL ", volmic#
  PRINT
  volmil# = volmic# / 1000
  INPUT "WHAT WAS THE DENSITY OF THE ADSORBATE (G/CM3) ", dens#
  mass1# = volmil# * dens#
  PRINT
END SUB
APPENDIX 2
# include <stdio.h>
# include <stdlib.h>
# include "head.h"
# include "gfa.c"

main()
{
  int dummy3;
  char ubfile[40];
  char rpt[1];
  char dummy[1];
  char dummy2[1];
  float sens, point, time, *pcorr, *cmem;

  FILE *pointer, *fopen();

  Initialize();
  MainTitle(header, header1, header2, header3, header4);
  MainWindow();
  Pause();
  Closegraf();
  do
  {
    printf("What is the compound file ");
    scanf("%s", ubfile);
    cmem = (float *)calloc(MAXLEN, sizeof(float));
    if (!cmem) {
      printf("calloc failure for pcorr exiting");
      exit(1);
    }
    pcorr = cmem;
    if ((pointer = fopen(ubfile, "r")) != NULL) {
      fscanf(pointer, "%f%c", &sens, dummy);
      fscanf(pointer, "%f%c", &point, dummy);
      fscanf(pointer, "%f%c", &time, dummy);
      printf("time %f", time);
      while (!feof(pointer))
      {
        fscanf(pointer, "%f%c", pcorr++, dummy2, &dummy3);
      }
      *(pcorr - 1) = NULL; /*Marks end of array*/
    }
    else
    {
  
  }
}

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{ 
    printf("\nFile %s does not exist",ubfile);
    exit(0);
}

printf("\nFile loaded into C array");
printf("Passing %s%10.2f%5.0f%15.8f%5.0f\n",ubfile,sens,time,*cmem,point);
areas(ubfile,sens,time,cmem,point);
free(cmem);
printf("\n\n\nReturned to function main successfully\n\n\n");
fclose(pointer);
printf("\n\n\nClosed %s successfully\n\n\n",ubfile);
printf("\nDo you want to process another file? (Y/N)\n");
scanf("%s",rpt);
}
while (!strcmp(strupr(rpt),"Y"));

/**************************** END GFADS.C *****************************/
/***************************** INCLUDE FILES *****************************
#include<stdio.h>
#include<alloc.h>
#include<math.h>
#include<string.h>

#define START 0
#define FINISH 90
#define MAXLEN 8192
#define MAXOUT 16384

/************************** FUNCTION PROTOTYPES **************************/
void areas(char ahinp[20],float s_l,float time,float *adsorb,float peak_point);  
float fr_conv(FILE *fp_data,float f_m,float t_cc);
float corr_h();
float p_area();
float vol_g();
float process(float time dl, float *volts_al, float mass_l);
void adsplot(float far *Y,float far *X,int end);  
float leastsqr(float far *Kc,float far *Cg,int N);

/**************************** END PROTOTYPES *****************************/
/************************* FUNCTION AREAS *************************/

void areas(char ahinp[20],float s_l,float time,float *adsoib,float point)
{

char areasfil[20];
char datafil[20];
static char sout[5]={"out"};
static char sdat[5]={'rdatrr};
static char sinp[5]={"cor"};
char ♦endchk;
char rchk[l];
int len,flen;
int ah=0,n;
float dtimec=time;
float peak_area=0, srec, big recjso a re aj 0,f l,w l,t c,t k,m 2,ght;
float r_c=0.082056;/*Units of (dnT3.atm)/(moLdeg)*/
float far *Kc;
float far *Cg;
float far *Cs;
float far *P2;
float far *K_c;
float far *C g;
float far *C_s;
float far *P_2;
float far *Kcr,
float far *Cgr,
double Kp,kc,fl_l,p_c;
/♦Read File Name & Data file Open both Files with Error Trap.*/
FILE *ah_input, *fopen();
FILE *fp_data, *fopen();
printf( "\nFunction receives
%s%82Zf%5.0fy©15.8f%5.0f\n'f,strupr(ahmp),s_l,time,*adsorb,point);
endchk=strrchr(stiiwr(ahinp)/c');
if(!stmcmp(endchk,sinp, 10))
{

flen=strlen(ahinp);
printf("\nString length is %d",flen);
len=flen-3;
printf("\nProcessing yos'Xstrupi^ahinp));
stmcpy(areasfil,ahinp,len);
stmcpy(datafil,ahinp,len);
areasfil[len]=NULL;
datafil[len]=NULL;
stmcat(areasfil,sout,3);
stmcat(datafil,sdat,3);
printf("\nThe output file is %s\n",strupr(areasfil));
printf^XnThe datafile is assumed to be %s\n',,strupr(datafil));
)

else
1

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What is the adsorbate areas output file? 

scanf("%s",areasfil);

What is the data file? 

scanf("%s",datafil);

if((ah_input=fopen(areasfil,"w"))==NULL) {
puts("Cannot open the file");
exit(1);
}

if((fp_data=fopen(datafil,"r"))==NULL) {
puts("Cannot open the data file");
exit(1);
}

/* Allocate memory for arrays*/
K_c = farcalloc(MAXLEN,sizeof(float));
if(!K_c){
    printf("NULL pointer for buffer from calloc_2 exiting");
    exit(1);
}

C_g = farcalloc(MAXLEN,sizeof(float));
if(!C_g){
    printf("NULL pointer for buffer from calloc_3 exiting");
    exit(1);
}

C_s = farcalloc(MAXLEN,sizeof(float));
if(!C_s){
    printf("NULL pointer for buffer from calloc_4 exiting");
    exit(1);
}

P_2 = farcalloc(MAXLEN,sizeof(float));
if(!P_2){
    printf("NULL pointer for buffer from calloc_5 exiting");
    exit(1);
}

/* Move pointers to end of arrays*/
Kc = K_c + ((MAXLEN-1) * sizeof(float));
C_g = C_g + ((MAXLEN-1) * sizeof(float));
C_s = C_s + ((MAXLEN-1) * sizeof(float));
P_2 = P_2 + ((MAXLEN-1) * sizeof(float));
printf("Pointers OK");
/* Read in values from data file*/
 fscanf(fp_data,"%f",&w_l);
 printf("Pointers OK w_l");
 fscanf(fp_data,"%f",&t_c);
 printf("Pointers OK tc");
 fscanf(fp_data,"%f",&f_0);
 printf("Pointers OK f0");
t_k=t_c + 273.2;

/*Convert flow rate to cm^3/sec*/
f_1=(f_0/10));

/*Correct flow rate to actual flow rate in the column*/
 printf("\nCorrecting flow %f & temp °C %f",f_1,t_c);
f_1 = fr_conv(fp_data,f_1,t_c);

/*Convert flow rate to dm^3/secs*/
 f_1 = f_1/1000;

/*Read in molecular weight of adsorbate*/
 printf("\nWhat is the molecular weight of the adsorbate in grams per mole:\n");
 scanf("%f",&m_2);

/* Calculate constant p_c(R.K/Mr) for conversion of Kc to Kp */
p_c = (r_c * t_k) / m_2;

/*Get peak area from srec function.*/
peak_area = p_area(adsorb);

/*Initialise ah to position of first data point i.e.peakmax point*/
ah = point;

fprintf(ah_input," P2 Cs Cg Kc \n");
/* Calculate Kc & Cg values*/
 while(*adsorb != NULL)
 {
  /*Calculate area of rectangle preceeding characteristic point.*/
  big_rec = *adsorb * ah;
  /*Calculate total area before and after characteristic point.*/
  iso_area = peak_area + big_rec;
  /*Convert *iso_area from volts to volt.secs.*/
  iso_area *= dtimec;
}
/*Calculate Henry's constants and Cg and output to a file*/

*Kc=(*adsorb * w_1)/(iso_area * fl_1);
*Cg=(*adsorb)/ (fl_1 * s_l);
*Cs=iso_area/(s_l*w_1);
*P2=*Cg * p_c;

fprintf(ah_input,"%18.6e%11.6f%18.6e%11.6f\n",*P2,—,*Cs,—,*Cg,—,*Kc—);

/*Calculate the area of the current first height/time segment and subtract*/
/*from the current area. Increment adsorb and ah.

srec = *adsorb++;  
peak_area -= srec;  
ah++;  
*/

/*Print to screen some confirmatory remarks & close up any files still open.*/
puts("\nCleared loop ok\n");

fclose(ah_input);

printf("\nClosed %s successfully\n",areasfil);

/* Move pointers to first data values*/
Kc++;  
Cg++;  

/*Calculate Henry's constants of final value in array as good approximation.*/
Kp=*Kc * p_c;

kc=-log10(*Kc);  
Kp=-log10(Kp);
printf("\nThe approximate Henry's constants are as follows;\n");
printf("\n -logKc = %3.2f -logKp = %3.2f",kc,Kp);

/*Set maximum number of points for least squares regression*/
ah = ah - point;
do{
  Kcr=Kc;  
  Cgr=Cg;
/*Input # points for least squares regression*/
printf("\nHow many points for least squares regression out of %d? ",ah);  
scanf("%d",&n);
/*adsplot(Kcr,Cgr,ah);*/
*K_c = leastsqr(Kcr,Cgr,n);
printf("\nLeast squares function returns %f",*K_c);
Kp = *K_c * p_c;
Kp = -log10(Kp);
*K_c = -log10(*K_c);
printf("\nLog10 of least squares function is %f",*K_c);
printf("\nLog10 of least squares function is %f",Kp);
printf("\nDo you want to repeat least squares regression with new number? (Y/N)\n");
scanf("%s",rchk);
}
while (!strcmp(strupr(rchk),("Y")));

farfree(K_c);
farfree(C_g);

/**************************** FUNCTION END ****************************/
float p_area(voltage)
float *voltage;
{
float intsum=0;
while(*voltage!=NULL)/*End of loop criteria depends on user*/
{
intsum= intsum + *voltage++;
}
return (intsum);
}
*************** FUNCTION FR_CONV ******************

FUNCTION FR_CONV

CORRECTION OF FLOW RATE

The measured flow rate needs to be corrected to the actual flow rate in the column. Due to gas compressibility, differences in temperature of column(Tc) and flowmeter(Tf), water vapour pressure(Pwf) contributing to gas stream pressure against atmospheric pressure (Po) in flow meter, water vapour pressure in column itself when taking humidity measurements and also pressure drop(P.D.) across the column. The measured flow rate is not the same as the actual flow rate across the column. The correcting eqn, is:

F_a = F_m * J_23 * ((P_o - Pwf) / P_o) * (T_c / T_f) * (P_i / (P_i - P_wc))

where:
- F_a - Actual flow rate
- F_m - Measured flow rate
- J_23 - Pressure correction factor
- P_i - Inlet pressure
- P_o - Outlet pressure
- T_c - Column temperature
- T_f - Flowmeter temperature
- P_wf - Water vapour pressure
- P_wc - Water vapour pressure in column
- P_d - Pressure drop

float fr_conv(FILE *fp_data, float f_m, float t_cc)
{
    float p_o = 0, p_i = 0, p_d = 0, j_23 = 0, t_fk = 0, t_ck = 0, p_wc = 0, p_wf = 0, p_f = 0, p_f2 = 0, p_f3 = 0, f_a = 0;
    char ans;

    /* Correct column temp. */
    t_ck = t_cc + 273.2;

    /* Calculation of J_23 */
    /* J_23 = 3/2[(P_i/P_o)^2 - 1]/[(P_i/P_o)^3 - 1] */

    /* Read data */
    fscanf(fp_data, "%f", &p_o);
    fscanf(fp_data, "%f", &p_d);

    /* Calculation */
    p_f = p_i / p_o;
    p_f2 = p_f * p_f;
    p_f3 = p_f2 * p_f;
    j_23 = 1.5 * ((p_f2 - 1) / (p_f3 - 1));

    /* Correct flow meter temp. */
    fscanf(fp_data, "%f", &t_fc);
    t_fk = t_fc + 273.2;

    /* Humidity correction option */
    /* printf("\nCorrection for humidity(y/n): "); */
    /* ans = getche(); */
    /* if (ans == 'y') */
    /* */

    /* Correction for flow rate */
    f_a = f_m * j_23 * ((p_o - p_wf) / p_o) * (t_ck / t_fk) * (p_i / (p_i - p_wc));
}
/*         */
/* printf("Correcting for humidity: "); */
/* p_wc=corr_h(); */
/*         */

/* Read water vapour pressure and correct flow */
 fscanf(fp_data, "%f", &p_wf);

    f_a=f_m*j_23*(t_ck/t_fk)*((p_o-p_wf)/p_o)*(p_i/(p_i-p_wc));
    printf("The value of corrected flow is %f", f_a);

/* Close data file */
fclose(fp_data);

return(f_a);
}

/****************** FUNCTION END **********************/
float corr_h()
{
    /*Humidity correction*/
    float per_h=0, wvcf=0, p_wc=0; /*Percentage humidity, water vapour correction /
    /*factor, pressure of water in the column (mm/Hg)*/

    printf("What is the percentage humidity? ");
    scanf("%f", &per_h);

    printf("What is the water vapour correction factor? ");
    scanf("%f", &wvcf);

    p_wc = wvcf * (per_h / 100);

    return(p_wc);
}

float vol_g()
{
    float size_mic = 0, dens = 0, size_mil = 0, mass_g = 0;

    /*Take ul input and get cm3*/
    printf("What was the sample size in µl:");
    scanf("%f", &size_mic);
    size_mil = size_mic / 1000;

    /*convert cm3 to grams*/
    printf("What is the density in g/cm3:");
    scanf("%f", &dens);

    mass_g = size_mil * dens;

    return(mass_g);
}

}
float process(float time_d1, float *volts_a1, float mass_l)
{
    float intsum_1=0;
    int count=START;
    float sens_1;

    while (count<=FINISH)
    {
        intsum_1=intsum_1 + *volts_a1++;
        count++;
    }

    intsum_1=intsum_1*time_d1;
    sens_1=intsum_1 / mass_l;

    return(sens_1);
}
/************************* FUNCTION END ******************************/
```c
void adsplot(float *Y, float *X, int end)
{
    int i;

    Initialize();

    for(int i=0; i<=end; i++)
    {
        putpixel(int(*X)*1000000, (400-((int)((*Y)-5000)/100)), 1);
    }
}

float leastsqr(float *Y, float *X, int N)
{
    float sum_x=0, sum_y=0, sum_x2=0, sum_y2=0, sum_xy=0, s_xx, s_yy, s_xy, M, C;
    int i;

    for (i=1; i<=N; i++)
    {
        sum_x += *X;
        sum_y += *Y;
        sum_xy += (*X) * (*Y);
        sum_x2 += (*X) * (*X);
        sum_y2 += (*Y) * (*Y);
    }

    s_xx = sum_x2 - (sum_x * sum_x) / N;
    s_yy = sum_y2 - (sum_y * sum_y) / N;
    s_yy = sum_y2 - (sum_y * sum_y) / N;
    s_xy = sum_xy - (sum_x * sum_y) / N;
    M = s_xy / s_xx;
    C = (((sum_x2 * sum_y) - (sum_x * sum_xy)) / N) / s_xx;

    printf("The value of the intercept is %f\n", C);
    return(C);
}
```
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