Modelling and parameter estimation of diethyl phthalate partitioning behaviour on glass and aluminum surfaces

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Abstract: The knowledge of the partitioning behaviour of semi-volatile organic compounds (SVOCs), such as phthalates, between different materials and their surrounding air is of extreme importance for quantifying levels of human exposure to these compounds, which have been associated with adverse health effects. Phthalates’ partitioning behaviour also represents a key property for modelling and assessing polymer degradation mechanisms associated with plasticiser loss. However, the characterisation of phthalates partitioning behaviour has been reported only for a limited number of compounds, mainly involving di-2-ethylhexyl phthalate (DEHP), di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP), while the characterisation of diethyl phthalate (DEP) partitioning has been overlooked. As one of the first plasticisers employed in the production of semi-synthetic plastics produced industrially in the late 19th and early 20th century, DEP plays an important role for understanding stability issues associated with historically significant artefacts in museum collections and archives. Here we show that the partitioning behaviour of DEP between borosilicate glass and aluminum surfaces and their surrounding air can be described by an exponential function of temperature, presenting a model to describe this relationship for the first time. Model parameters are
estimated using nonlinear regression from experimental measurements acquired using 109 samples which have been equilibrated at different temperatures between 20 and 80 °C in sealed environments. Measured partition coefficients have been predicted accurately by our proposed model. The knowledge of DEP equilibrium distribution between adsorptive surfaces and neighbouring environments will be relevant for developing improved mathematical descriptions of degradation mechanisms related to plasticiser loss.

*Keywords:* diethyl phthalate, partition coefficient, phthalates adsorption, building materials, parameter estimation.
1. Introduction

Semi-volatile organic compounds (SVOCs), such as phthalates, can partition between different materials and their surrounding air in indoor environments, affecting levels of human exposure to these compounds, which have been associated with adverse health effects, including endocrine disruption, cancer, birth defects and alteration of insulin signalling molecules which could trigger type 2 diabetes (Miles-Richardson, 2017; Mondal and Mukherjee, 2020). Thus, understanding the distribution of these compounds is fundamental for properly assessing and quantifying levels of human exposure (Cao et al., 2016; Eichler et al., 2018; Xu and Little, 2006). Characterising the partitioning behaviour of phthalates is also of extreme importance to allow for the mathematical description of material degradation processes, including, for instance, degradation mechanisms in plastic objects which can be initiated or promoted by the loss of phthalates plasticisers (King et al., 2020).

Diethyl phthalate (DEP) represents one of the first plasticisers employed industrially in the production of semi-synthetic plastics in the late 19th and early 20th century (Macht and Fletcher, 1938; Mossman, 1997; Walsh et al., 1933; Zimmerli, 1932). Therefore, understanding diethyl phthalate loss is important for addressing stability issues associated with historically significant artefacts in museum collections and archives. For instance, the loss of plasticisers such as DEP from cellulose acetate-based artefacts is known to initiate or promote physical changes, such as warping, crazing, cracking and brittleness, which could ultimately reduce the value of these art objects (Da Ros et al., 2021; Richardson et al., 2014; Shashoua, 2008; Strlič et al., 2013). Furthermore, although the partial substitution of DEP by less volatile phthalates has led to a reduction of its worldwide consumption (IHS Markit, 2018), DEP still finds application in a wide range of consumer products, including orthodontic adhesives and dentures, cosmetic formulations (such as bath oils, tablets and salts; eye shadow, perfumes, hair sprays, nail polish and enamel removers, nail extenders, detergents, aftershave lotions and
skin care products), and pharmaceutical products (such as in coatings for drug controlled release) (Mondal and Mukherjee, 2020; Sekizawa et al., 2003; Wypych, 2017). Thus, it is not surprising that DEP is still found as an important constituent of pollutants in indoor (Fromme et al., 2004; Yang et al., 2020) and outdoor (Vasiljevic et al., 2021) environments. However, while research has advanced on understanding the partition behaviour of phthalates such as di-2-ethylhexyl phthalate (DEHP), benzyl butyl phthalate (BBP), di-n-butyl phthalate (DnBP) and di-isobutyl phthalate (DiBP) on a wide range of materials (Wei et al., 2018), our knowledge on the partition behaviour of DEP remains limited to a few systems, Table 1. For instance, the partition coefficient of DEP between cotton fabric and air, $K_{\text{cotton-air}}$, has been reported as equal to $2.6 \cdot 10^5$ (unitless) at 25 °C by a study which highlighted the risks of non-dietary phthalate ingestion by toddlers mouthing cotton and dermal uptake (Morrison et al., 2015a). In another study, the relationship between temperature and $K_{\text{cotton-air}}$ values for DEP between 20 and 40 °C was reported, where an approximately exponential reduction in $K_{\text{cotton-air}}$ with the increase of temperature was demonstrated (Eftekhari and Morrison, 2018), corroborating similar observations reported for additional phthalates between vinyl flooring and air (Bi et al., 2015).

**Table 1** - Partition coefficients calculated or experimentally measured for diethyl phthalate for different systems.

<table>
<thead>
<tr>
<th>Based on the ratio between</th>
<th>$K$ (unitless)</th>
<th>T (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indoor airborne particles/air</td>
<td>$1.8 \cdot 10^{-4}$</td>
<td>25</td>
<td>(Weschler et al., 2008)</td>
</tr>
<tr>
<td></td>
<td>$0.67 \cdot 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Octanol/air</td>
<td>$3.5481 \cdot 10^7$</td>
<td>25</td>
<td>(Cousins and Mackay, 2000)</td>
</tr>
<tr>
<td>Air/water</td>
<td>$9.7724 \cdot 10^{-6}$</td>
<td>25</td>
<td>(Cousins and Mackay, 2000)</td>
</tr>
<tr>
<td>Octanol/water</td>
<td>346.7</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Octanol/water</td>
<td>263.03</td>
<td>25</td>
<td>(Ellington and Floyd, 1996)</td>
</tr>
<tr>
<td>Material</td>
<td>K (m²/s) ± Error</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>------------------</td>
<td>----------------------------</td>
<td></td>
</tr>
<tr>
<td>Polydimethylsiloxane/water</td>
<td>59 ± 14</td>
<td>(Kotowska et al., 2006)</td>
<td></td>
</tr>
<tr>
<td>Polyacrylate/water</td>
<td>53.70</td>
<td></td>
<td></td>
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<tr>
<td>Hexane/acetonitrile</td>
<td>218 ± 10</td>
<td></td>
<td></td>
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<tr>
<td>Hexane/nitromethane</td>
<td>0.09 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outershirt cotton fabric/air</td>
<td>2.6⋅10³</td>
<td>(Morrison et al., 2015a)</td>
<td></td>
</tr>
<tr>
<td>Undershirt cotton fabric/air</td>
<td>2.5⋅10³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jeans cotton fabric/air</td>
<td>(5.6 ± 0.2)⋅10⁵</td>
<td>(Eftekhari and Morrison, 2018)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1.5 ± 0.01)⋅10⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1.1 ± 0.1)⋅10⁴</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>(0.75 ± 0.01)⋅10⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cotton fabric/air</td>
<td>630957</td>
<td>(Saini et al., 2017)</td>
<td></td>
</tr>
<tr>
<td>Rayon fabric/air</td>
<td>1584893</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Latex wall paint/air</td>
<td>1.6596⋅10⁷</td>
<td>(Schripp et al., 2014)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0417⋅10⁷</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.5481⋅10⁷</td>
<td></td>
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<tr>
<td></td>
<td>2.7542⋅10⁷</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>2.3442⋅10⁷</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC film (5 wt%)/n-hexane</td>
<td>521.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC film (5 wt%)/isoctane</td>
<td>5233.33</td>
<td>(Yuan et al., 2019)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>513.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC film (5 wt%)/ethanol</td>
<td>1057.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>131.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.77</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Calculated using correlation developed by (Naumova et al., 2003) for polycyclic aromatic hydrocarbons;

bCalculated using correlation developed by (Finizio et al., 1997) using octanol/air partition coefficients for Air.
polycyclic aromatic hydrocarbons; ‘Calculated using correlations developed using water and air solubility and octanol/water partition coefficients for phthalate esters.

As it can be seen from Table 1, there are many indoor built materials for which the partition behaviour of DEP is unknown, including impervious surfaces such as glass and aluminum. However, due to their presence in a variety of domestic interior surfaces, in addition to many scientific laboratory tools and instruments, characterising the partitioning of DEP on these surfaces is essential for understanding how DEP is transported and distributed through environments. For instance, environmental chambers used in emission studies are usually made of glass and/or aluminum elements (Afshari et al., 2003; Clausen et al., 2004; Even et al., 2020; Xu and Little, 2006), and glass and/or aluminum are also often involved in experimental methods concerning measurements of phthalates concentrations (Clausen et al., 2016; Eftekhari and Morrison, 2018; Vasiljevic et al., 2021).

In this context, the partitioning of DEHP on aluminum, steel, glass and acrylic surfaces has been characterised at 25 °C (Wu et al., 2017), suggesting that $K_{i-air}$ values for DEHP could depend not only on the nature of the adsorptive surface, but also on its roughness, defined as the ratio between the true surface area and the geometric area of the material. In another study, the characterisation of the partitioning of triethyl phosphate (TEP), tributyl phosphate (TBP) and tris-(chloropropyl)-phosphate (TCP) on borosilicate glass has also indicated the likely existence of a relationship between these compounds’ volatility and their partition coefficients at 23 °C (Ghislain et al., 2017), a finding also observed for the partitioning behaviour of DINP, DEHP, BBP and DnBP over stainless steel at 25 °C (Liang and Xu, 2014a).

However, even for the most widely researched SVOCs, significantly different partition coefficients have been reported at similar temperatures, stressing the urgent need for further research in this field, as also pointed out by (Wei et al., 2019). For instance, values for the
partition coefficient of DEHP on glass surfaces have been reported as equal to 3800 m at 22 °C (Xu and Little, 2006), 600 m at 25 °C (Wu et al., 2017) and 0.26 m at 23 °C (Ghislain et al., 2017).

Thus, this work has characterised the partitioning behaviour of DEP on glass and aluminum surfaces for the first time in a wide range of temperatures ranging between 20 and 80 °C. Additionally, we quantified the effect of temperature on the partitioning behaviour of DEP between these surfaces and their surrounding air, presenting a model to describe this relationship. Model parameters are estimated using nonlinear regression from experimental measurements acquired using 109 samples which have been equilibrated between 20 and 80 °C in sealed environments. The knowledge of DEP equilibrium distribution between adsorptive surfaces and neighbouring environments will be relevant for developing improved mathematical descriptions of degradation mechanisms related to plasticiser loss. Furthermore, we anticipate our model to be a starting point for understanding and quantifying the partition behaviour of DEP in additional systems.

2. Materials and Methods

2.1 Determination of DEP partitioning between enclosure surfaces and air

Sample enclosures used in this work consisted of 20 mL borosilicate glass vials (referred to here as “enclosure vials”) equipped with a polypropylene lid presenting a pulp-backed aluminum foil liner inner surface, which were acquired from Fisher Scientific (London, catalogue number 12383317). Vials were dried at 150 °C (glass) and 90 °C (lid) for 12 h prior to experiments to minimise contamination. In order to measure the equilibrium concentration ratio of DEP between the inner surfaces of the enclosure vial and the gas-phase within, a smaller, open 2 mL glass vial, filled with 1 mL of pure DEP (99.5 %, purchased from Sigma Aldrich, London, used as received), was placed at the centre of the enclosure vial, as illustrated
in Fig. S1. After the enclosure vial was sealed, the system was then equilibrated at different
temperatures (20, 30, 40, 50, 60, 70, 80 and 90 °C) by keeping the vials in environments with
temperature control. The actual temperature and relative humidity (RH) during the
experimental period were recorded using TinyTag dataloggers. Several replicated experiments
at each temperature were performed to guarantee reproducibility and assess equilibration,
totalling 109 individual measurements.

At the end of the experiment, enclosure vials were removed from ovens and allowed to
stabilise at room temperature while still sealed for approximately 1 h to minimise fluctuations
that would otherwise be present were vials analysed while still hot. DEP-containing vials were
then removed using tweezers and the aluminum and glass vial inner surfaces were immediately
and individually washed with 4 mL of solvent each. Finally, washing solutions were analysed
by UV-Vis spectroscopy, as detailed in the next section.

2.2 Quantification of DEP adsorbed on enclosure surfaces

The UV-Vis spectroscopic method used to quantify the amount of DEP adsorbed on
the sample enclosure surface was based on the absorbance intensity of DEP at 226 nm
(Monakhova et al., 2011). Calibration solutions were prepared by diluting a stock solution of
DEP, prepared at the concentration of 15 mg·mL$^{-1}$, using an aqueous ethanolic solution (60/40
%vol. ethanol/distilled water) as solvent. Ethanol (96 %vol.) was purchased from Fisher
Scientific (London, UK) and used without further purification. Measurements were performed
in a double-beam Shimadzu spectrophotometer 2700 using quartz cuvettes of 1 cm pathlength.
After each analysis, the quartz cuvette was washed and the solvent analysed for phthalate
contamination. This procedure was performed also to ensure that the quartz cuvette was free
from contamination from the preceding analysis. Spectra were recorded between 200 and 350
nm with a spectral resolution of 1 nm, as illustrated in the Fig. S2 of the Supplementary
Information (SI). A seven-point calibration curve ranging between 0.47 and 18.75 μg·mL$^{-1}$
DEP was always built at the beginning of the analysis day, as illustrated in Fig. S3 of the SI. Limits of quantification (LOQ) ranged between 22.6 and 58.6 ng among calibrations and were well below quantified ranges among experiments.

The efficiency of the washing procedure applied for transferring the DEP from the sample enclosure surface to the solvent solution prior to UV-Vis spectroscopic measurements was evaluated by four replicated experiments in which an accurate amount of DEP (5.60, 0.86, 0.79 and 0.76 mg) was added within a sample enclosure vial that was then sealed and allowed to stabilise at 60 °C for 13 h. Washing solutions were diluted accordingly to result in absorbances within the linear range of the calibration curve. From these, an average recovery efficiency of 105.95 ± 7.01 % was recorded, as further illustrated in Table S1 of the SI, which was considered excellent (Cao et al., 2016; Ghislain et al., 2017; Wu et al., 2017).

2.3 Modelling the effect of temperature on DEP partitioning between enclosure surfaces and air

The partition coefficient of DEP, $K_{i-air}$, between the sample enclosure surface $i$ (where $i$ represents either the glass or aluminum vial inner surface) and the DEP gas-phase concentration, $C_{g,DEP}$, was calculated using Eq. (1), in which $C_{s,i}$ represents the quantified amount of DEP adsorbed on the surface $i$, in mg·m$^{-2}$.

$$K_{i-air} = \frac{C_{s,i}}{C_{g,DEP}} \quad (1)$$

Values of $C_{g,DEP}$, in mg·m$^{-3}$, at each experimental temperature, $T$ (in Kelvin), were calculated using Eq. (2), in which the DEP saturation vapour pressure, $p^*$, was calculated using the three-parameter form of the Cox equation, Eq. (3) (Roháč et al., 2004). In Eq. (2), $M_{DEP}$ is the molecular mass of DEP and $R$ is the ideal gas constant. In Eq. (3), $p_0$ and $T_0$ represent the pressure and temperature at the triple-point, equal to 0.0029 Pa and 269.922 K, respectively,
and $A_0$, $A_1$ and $A_2$ denote the coefficients estimated by (Roháč et al., 2004), equal to $3.844479$, $-9.201487 \cdot 10^{-4}$ and $-5.406641 \cdot 10^{-7}$, respectively.

$$C_{g, \text{DEP}} = \left( \frac{P^*}{RT} \cdot M_{\text{DEP}} \right) \times 1000 \quad (2)$$

$$\ln \left( \frac{P^*}{P_0} \right) = \left( 1 - \frac{T_0}{T} \right) \exp (A_0 + A_1 \cdot T + A_2 \cdot T^2) \quad (3)$$

In order to calculate $C_{s,i}$ in mg·m$^{-2}$, the quantified amount of DEP adsorbed on the sample enclosure surface, in mg, was divided by the geometric exposed area, $A$, which was calculated as equal to 43.99 and 2.01 cm$^2$ for the glass and aluminum surfaces, respectively, from the vial dimensions, Fig. S1.

Finally, the dependence of obtained $K_{i-\text{air}}$ values towards temperature was quantified using a reparameterised form of the van’t Hoff equation, Eq. (4), to minimise the correlation of estimated coefficients (Koretsky, 2013; Schwaab and Pinto, 2007a). In Eq. (4), $T$ is the measured temperature, in K, and $T_{\text{ref}}$ was defined as equal to 322 K for both the glass and aluminum surfaces. Usually, $T_{\text{ref}}$ is defined as the average temperature of the analysed experimental range, even though the choice criterion for $T_{\text{ref}}$ should be based on its capacity to reduce or minimise the correlation between parameters estimates (Schwaab and Pinto, 2007a). Thus, we performed several parameter estimation procedures using different $T_{\text{ref}}$ values within the experimental range to assess its impact on resultant estimated coefficients correlation, resulting in the selection of 322 K as $T_{\text{ref}}$.

$$K_{i-\text{air}} = \exp \left( A_i + B_i \left( \frac{T - T_{\text{ref}}}{T} \right) \right) \quad (4)$$
In Eq. (4), the $A_i$ constant is related to the pre-exponential factor of the integrated form of the van’t Hoff equation, $K_{i\text{-air,ref}}$, according to Eq. (5) and $B_i$ relates to the DEP adsorption/desorption enthalpy, $\Delta H^\circ$, according to Eq. (6).

$$A_i = \ln(K_{i\text{-air,ref}})$$

$$B_i = \frac{\Delta H^\circ}{R \cdot T_{\text{ref}}}$$

Thus, a constant enthalpy for the DEP adsorption/desorption was assumed, which was considered a reasonable hypothesis given that all experiments were performed at atmospheric pressure and low temperatures.

**2.4 Parameter estimation and statistical evaluation of results**

The estimation of the $A_i$ and $B_i$ parameters from Eq. (4) was performed through the minimisation of the weighed-least-squares objective function (Da Ros et al., 2017b; Schwaab and Pinto, 2007b), $F_{\text{obj}}(\theta)$, Eq. (7), in which $NE$ is the number of experimental data points, $K_{i\text{-air,j}}^{exp}$ denotes the experimental value at the experimental conditions $j$ as calculated from UV-Vis spectroscopic measurements, $K_{i\text{-air,j}}^{mod}$ is the value predicted using Eq. (4), $x_j^{exp}$ represents the experimental condition of temperature, $\theta$ represents a vector with the best set of parameter estimates for $A_i$ and $B_i$, and $\sigma_j^2$ denotes the variance associated with the measurement fluctuations of $K_{i\text{-air,j}}^{exp}$ at the experiment condition $j$.

$$F_{\text{obj}}(\theta) = \sum_{j=1}^{NE} \left( \frac{K_{i\text{-air,j}}^{exp} - K_{i\text{-air,j}}^{mod}(x_j^{exp}, \theta)}{\sigma_j^2} \right)^2$$

The minimisation of Eq. (7) was performed using a hybrid optimisation method implemented in Fortran 90, in which the Particle Swarm Optimization (PSO) algorithm (Kennedy, J., Eberhart, 1995) is used in the initial phase of minimisation (Noronha et al., 1993;
The best estimate of the point of the minimum is used as an initial guess for a second estimation round, using the Gauss-Newton method (Da Ros et al., 2017b; Schwaab and Pinto, 2007b). The initial phase of minimisation using the PSO algorithm was performed using 30 particles and 50000 iterations, resulting in 1500000 evaluations of the objective function. Convergence was achieved when the relative modification of the objective function was smaller than $1.0 \times 10^{-6}$. Statistical significance of parameters estimates was assessed with the standard t-test (Box, G.P., Hunter, J.S., Hunter, 2005), with 95% confidence level. The quality of the $A_i$ and $B_i$ parameter estimates was further assessed by evaluating the parameters correlation according to Eq. (8), in which $\rho_{ij}$ represents the element $ij$ of the covariance matrix of parameter estimates, $V_\theta$, defined by Eq. (9), where $B$ is the sensitivity matrix that contains the first derivatives of the model responses in respect to the model parameters and $V_y$ denotes the covariance matrix of experimental fluctuations (Schwaab et al., 2008).

$$\rho_{ij} = \frac{V_{ij}}{\sqrt{V_{ii}V_{jj}}}$$ (8)

$$V_\theta = \left[ B^T V_y B \right]^{-1}$$ (9)

Additionally, the likelihood confidence region of $A_i$ and $B_i$ parameter estimates was characterised by Eq. (10) (Beale, 1960; Schwaab et al., 2008), where $F_{obj}(\hat{\Theta})$ represents the objective function at the point of minimum, $NP$ is the number of parameters, and $F_{NP,NE-NP}^\alpha$ is the F probability distribution value for $NP$ and $NE-NP$ degrees of freedom and 95% confidence level, which is equal to 6.94 in this work.

$$F_{obj}(\Theta) \leq F_{obj}(\hat{\Theta}) \left(1 + \frac{NP}{NE-NP} F_{NP,NE-NP}^\alpha\right)$$ (10)

Finally, the evaluation of the model adequacy was performed by comparing the final value of the objective function ($Final \ SSE$) with the limits of the Chi-square distribution with $NE-2$
degrees of freedom and 95 % confidence level (Schwaab and Pinto, 2007b). In addition, model predictions were compared with experimental measurements, in which prediction errors were calculated by Eq. (11).

\[ \hat{V}_y = B V_a B^T \]  

(11)

3. Results and Discussion

3.1 Assessment of equilibrium

To verify that equilibration had occurred in each investigated condition, a period of at least 4-52 days was selected for our experiments. Fig. 1 illustrates the quantified amounts of DEP adsorbed on the inner glass surface of the enclosure vials, \( m_{\text{glass}} \), as a function of time. As it can be seen, measurements supported the hypothesis that equilibration times were long enough to allow the system to equilibrate at each temperature. A similar conclusion could be inferred from measurements on the aluminum surface of the enclosure vials, Fig. S4.

It is important to note that observed equilibration times are in agreement with previous findings. For instance, the adsorption of DEHP, emitted from a PVC flooring containing 23 ± 3 wt % of DEHP, on aluminum, polished glass and acrylic surfaces was estimated to equilibrate after 13 h at 25 °C in an approximately 0.45 cm³ sealed chamber presenting an emitting source and adsorptive surface area of 3.2 cm² (Wu et al., 2017). In
Fig. 1 - Quantified DEP on the vial inner glass surface (in µg), $m_{\text{glass}}$, as a function of equilibration time at 20, 30, 40, 50, 70 and 80 °C. Equilibration data at 60 °C is presented as Fig. S5. Error bars represent absolute standard deviations ($\sigma$). The confidence interval (--) was built assuming averages ($\bar{u}$, —) follow the $t$-Student distribution of probabilities with $NE-1$.
degrees of freedom and 95% confidence level, where NE denotes the total number of measurements ($\bullet$) at each temperature, as $\bar{u} \pm \sigma \times t$-Student.

Another example, the adsorption TEP, TBP and TCPP emitted from a polyurethane foam containing between 5 and 7.6 wt% of the above compounds, on borosilicate glass was observed to equilibrate after between 2 to 5 h at 23 °C in a 60 cm$^3$ sealed chamber presenting an emitting source of 17 cm$^2$ and an adsorptive surface of approximately 50 cm$^2$ (Ghislain et al., 2017).

Therefore, it follows that the adsorption equilibration time of diethyl phthalate, a more volatile compound when compared to DEHP, TBP and TCPP, involving its diffusion from the layer just above its pure liquid state to the surrounding air and adsorptive surfaces within the sealed sample enclosures used in this work, was expected to be shorter than the above-mentioned examples, further supporting our conclusion that acquired measurements had achieved equilibration.

3.2 Modelling the effect of temperature on the DEP partitioning between enclosure surfaces and air

Fig. 2 illustrates the relationship between adsorbed quantities and temperature for the glass and aluminum surfaces. This figure presents the global averages of adsorbed DEP, as illustrated in Fig. 1 and S4 ($\bar{u}$, ---), divided by the respective geometrical area of the exposed surface, resulting in global averages of DEP concentrations on the glass, $C_{s,\text{glass}}$, and aluminum, $C_{s,\text{Al}}$, surfaces, in mg·m$^{-2}$.

As it can be seen from Fig. 2, while an exponential increase in $C_{s,\text{glass}}$ was observed as the equilibration temperature was raised, the same tendency was not verified for $C_{s,\text{Al}}$. This could indicate that experimental fluctuations associated with measurements on the aluminum surface were too large to allow for the observation of the temperature effect. Indeed, while
adsorbed DEP quantities ranged between approximately 9.4 and 38.7 μg for the glass surface among investigated temperatures, this amount for the aluminum surface was significantly smaller, ranging between 1.5 and 3 μg (but still well above LOQ). In general, this resulted in more precise measurements associated with the glass surface, which presented global relative standard deviations (RSDs) ranging from 15.9 to 39.6 %, being smaller than 24 % for 5 of the 7 experimental conditions investigated. For the aluminum surface, RSDs values varied between 20 and 48 %, being smaller than 28 % for 5 of the 7 experimental conditions.

Regardless of the distinct variabilities among experimental conditions, indicating, as expected, that the precision of measurements could depend on the range of concentrations analysed (Da Ros et al., 2017a), one must note that several replicates have been performed to ensure the reproducibility of experimental measurements, as already illustrated in Fig. 1 and S4. Thus, global averages obtained for $C_{s,\text{glass}}$ and $C_{s,\text{Al}}$ were considered suitable for calculating DEP partition coefficients between the adsorptive surfaces and the surrounding gas-phase,

![Diagram showing quantified DEP concentration averages for glass and aluminum surfaces.](image-url)
$K_{\text{glass-air}}$ and $K_{\text{Al-air}}$, calculated using Eqs. (1-3), and resultant values are summarised in Table 2, along with average temperatures, relative humidities (RH) and DEP surface concentrations quantified at each equilibration condition.

Table 2 – Average temperature, relative humidity (RH), DEP surface concentrations and partition coefficients quantified at each equilibration condition along with respective absolute standard deviations.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>RH (%)</th>
<th>$C_{s,\text{glass}}$ (mg·m⁻²)</th>
<th>$C_{s,\text{Al}}$ (mg·m⁻²)</th>
<th>$K_{\text{glass-air}}$ (m)</th>
<th>$K_{\text{Al-air}}$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.1 ± 0.18</td>
<td>51 ± 6.4</td>
<td>2.13 ± 0.36</td>
<td>7.60 ± 2.3</td>
<td>4.11·10⁻¹ ± 6.97·10⁻²</td>
<td>1.47 ± 4.43·10⁻¹</td>
</tr>
<tr>
<td>32.2 ± 0.56</td>
<td>17 ± 2.1</td>
<td>2.49 ± 0.61</td>
<td>7.41 ± 1.5</td>
<td>1.41·10⁻¹ ± 3.43·10⁻²</td>
<td>4.18·10⁻¹ ± 8.46·10⁻²</td>
</tr>
<tr>
<td>39.1 ± 0.12</td>
<td>16.4 ± 2.4</td>
<td>3.61 ± 0.57</td>
<td>8.7 ± 2.31</td>
<td>9.72·10⁻² ± 1.54·10⁻²</td>
<td>2.34·10⁻¹ ± 6.23·10⁻²</td>
</tr>
<tr>
<td>50.0 ± 0.03</td>
<td>8.6 ± 1.7</td>
<td>4.75 ± 0.99</td>
<td>10 ± 2.86</td>
<td>4.73·10⁻² ± 9.81·10⁻³</td>
<td>9.96·10⁻² ± 2.85·10⁻²</td>
</tr>
<tr>
<td>59.9 ± 0.03</td>
<td>6.1 ± 0.7</td>
<td>5.48 ± 1.91</td>
<td>8.82 ± 2.04</td>
<td>2.45·10⁻² ± 8.54·10⁻³</td>
<td>3.95·10⁻² ± 9.11·10⁻³</td>
</tr>
<tr>
<td>70.1 ± 0.05</td>
<td>5.9 ± 0.5</td>
<td>6.97 ± 2.76</td>
<td>15.13 ± 7.27</td>
<td>1.32·10⁻² ± 5.24·10⁻³</td>
<td>2.87·10⁻² ± 1.38·10⁻²</td>
</tr>
<tr>
<td>79.3 ± 0.04</td>
<td>4.9 ± 0.3</td>
<td>8.79 ± 2.07</td>
<td>7.33 ± 1.52</td>
<td>8.48·10⁻³ ± 2.0·10⁻³</td>
<td>7.07·10⁻³ ± 1.46·10⁻³</td>
</tr>
</tbody>
</table>

Furthermore, one should also note that as values of DEP partial pressure rise with temperature, increasing the DEP gas-phase concentration, $C_{g,\text{DEP}}$, Eqs. (2-3), the observed reduction in $K_{\text{glass-air}}$ and $K_{\text{Al-air}}$ values with temperature could be expected. However, as calculated $K_{\text{glass-air}}$ and $K_{\text{Al-air}}$ values represent independent measurements at each temperature which also take into account the adsorptive properties of the investigated surfaces (Eq. (1)), quantified values of $K_{\text{glass-air}}$ and $K_{\text{Al-air}}$ can be used to assess the relationship between these partition coefficients and temperature, through Eqs. (4-6).

In order to model the effect of temperature, values of temperature (in Kelvin) and $K_{i-air}$ as presented in Table 1 were used to adjust Eq. (4), as described in Sections 2.3 and 2.4.
However, measurements obtained at 40 °C were not included in the parameter estimation, to allow them to be used as an independent validation set. Fig. 3 illustrates the $K_{i\text{-air}}$ predicted and experimental values for the borosilicate glass (a) and aluminum (b) surfaces; estimated parameters of Eq. (4) are summarised in Table 3.

![Fig. 3](image)

**Fig. 3** – Experimental (●, ⭐) and predicted (—) values for $K_{\text{glass-air}}$ (a) and $K_{\text{Al-air}}$ (b) as a function of equilibration temperature. The symbol (●) denotes data sets used in the parameter estimation and (⭐) indicates the measurements used as independent validation set.

**Table 3** – Parameter estimates and their associated standard deviations obtained from the fitting of Eq. (4) to the experimental values of $K_{i\text{-air}}$. Correlation of parameter estimates, Eq. (8), Final SEE and $Chi^2$ limits for model adequacy are also summarised.

<table>
<thead>
<tr>
<th>Estimates</th>
<th>Glass</th>
<th>Aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$ (m)</td>
<td>-3.008 ± 0.101</td>
<td>-2.413 ± 0.104</td>
</tr>
<tr>
<td>$B_i$ (unitless)</td>
<td>-20.95 ± 1.443</td>
<td>-28.424 ± 1.547</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Statistical analysis of estimated parameters and model adequacy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{AB}$*</td>
</tr>
<tr>
<td>0.27</td>
</tr>
</tbody>
</table>
As it can be seen from Fig. 3, predicted values for $K_{\text{glass-air}}$ and $K_{\text{Al-air}}$ presented excellent agreement with experimental observations, with linear correlation coefficients being equal to 0.99. In addition, Fig. 3 also presents quantified averages for $K_{\text{glass-air}}$ and $K_{\text{Al-air}}$ at 40 °C (represented as ‘★’) which have not been used in the parameter estimation. As it can be also seen, these measurements support the validity of the developed relationships for predicting $K_{\text{glass-air}}$ and $K_{\text{Al-air}}$ within the range of investigated temperatures. In addition, it is also important to note that although the role of RH may be important for the partition behaviour of some compounds depending on the surface sink material (Mader and Pankow, 2000; Morrison et al., 2015b; Storey et al., 1995), our results suggest that effects from the competitive adsorption between water and DEP molecules on the investigated adsorptive surfaces could be neglected within evaluated experimental ranges, as developed relationships were able to accurately predict experimental observations despite different RH conditions (Table 2).

Table 3 also presents the correlation of parameter estimates, as calculated using Eq. (8), demonstrating how the reparameterisation of the integrated form of the van’t Hoff equation with the selected reference temperature was efficient in reducing the characteristic high correlation observed for parameter estimates from Arrhenius-like functions, thus improving the quality of the parameter estimation procedure (Schwaab and Pinto, 2007a). Fig. S6 illustrates the confidence region of parameter estimates as calculated using Eq. (10), where the broad shape of the regions further illustrates the low correlation between the $A_i$ and $B_i$ estimated coefficients. Finally, model adequacy was also confirmed by the comparison of the objective

<table>
<thead>
<tr>
<th>$Final SSE$</th>
<th>0.58</th>
<th>1.69</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Chi^2$ limits for adequacy $^b$</td>
<td>$0.48 &lt; Final SSE &lt; 11.14$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Calculated using Eq. (8). $^b$ $Chi^2$ limits are for 4 degrees of freedom and 95% confidence level.
function at the point of minimum (Final SSE) with the limits of the \( \text{Chi}^2 \) distribution with 4 degrees of freedom and a 95% confidence level, as illustrated in Table 3.

Table 4 summarises the calculated values for the pre-exponential factors of the integrated form of the van’t Hoff equation (\( K_{\text{glass-air,} \text{ref}} \) and \( K_{\text{Al-air,} \text{ref}} \)), which represents the value of \( K_{\text{glass-air}} \) and \( K_{\text{Al-air}} \) at the reference temperature, and the values obtained for the DEP adsorption/desorption enthalpy, \( \Delta H^\gamma \). For \( K_{i-\text{air,} \text{ref}} \), similar values to the experimentally observed ones have been verified (see Table 2 and 3), as expected. In turn, calculated enthalpies, equal to \(-56.1 \pm 3.86 \) and \(-76.1 \pm 4.14 \) kJ\( \cdot \)mol\(^{-1} \) for the glass and aluminum surfaces, respectively, are slightly smaller (in absolute terms) than reported values for the condensation enthalpy of DEP at 298 K, equal to \(-82.1 \pm 1.6 \) kJ\( \cdot \)mol\(^{-1} \) (Gobble et al., 2014; Roháč et al., 2004). This is in contrast to previous findings, in which researchers found higher enthalpies for evaporation of phthalates (DEHP, DINP and DnBP) from vinyl flooring than from the pure compound (Liang and Xu, 2014b). Liang and Xu concluded that there were stronger interactions between the studied phthalates and vinyl flooring than within the pure phthalates. Our results suggest that the opposite is true for glass and aluminium.

Table 4 – Resultant constants calculated using Eq. (5-6) with the estimated parameters (\( A_i \) and \( B_i \)) as presented in Table 3.

<table>
<thead>
<tr>
<th>Calculated constants</th>
<th>Glass</th>
<th>Aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{i-\text{air,} \text{ref}} ) (m) (^a)</td>
<td>4.94 ( \cdot ) 10(^{-2} ) ± 5.22 ( \cdot ) 10(^{-3} )</td>
<td>8.96 ( \cdot ) 10(^{-2} ) ± 9.85 ( \cdot ) 10(^{-3} )</td>
</tr>
<tr>
<td>( \Delta H^\gamma ) (kJ ( \cdot ) mol(^{-1} )) (^b)</td>
<td>-56.09 ± 3.864</td>
<td>-76.09 ± 4.142</td>
</tr>
</tbody>
</table>

\(^a\) \( K_{i-\text{air,} \text{ref}} \) was calculated using Eq. (5) with the estimated value of \( A_i \) (Table 3). \(^b\) \( \Delta H^\gamma \) was calculated using Eq. (6) with the estimated value of \( B_i \) (Table 3) and \( T_{\text{ref}} \) defined as equal to 322 K for both the glass and aluminum surfaces.
To the best of our knowledge, this is the first work reporting the partitioning behaviour of DEP on glass and aluminum surfaces. In spite of that, some interesting comparisons can be made with previous reports. For instance, (Ghislain et al., 2017) proposed that the partition coefficient of DEHP on borosilicate glass at 23 °C could be predicted by Eq. (12).

\[
\log(K_{glass}) = -0.51 \cdot \log(p^*) - 2.88
\]  

Although the characterisation of prediction errors was not reported, one could calculate the partition coefficient of DEHP on glass as equal to 0.33 m by using the above relationship, assuming DEHP partial pressure as equal to 2.039 \cdot 10^{-5} Pa (Gobble et al., 2014). In another study, the partition coefficient of DEHP on polished glass at 25 °C was reported as equal to 600 m. At 23 °C, our proposed model predicts the partition coefficient of DEP between glass and air as equal to 0.31 ± 0.06 m, being therefore likely smaller than predicted values for DEHP, as would be expected given the higher volatility of DEP. Furthermore, (Liang and Xu, 2014a) have investigated the partition behaviour of several phthalates, including DINP, DEHP, BBP and DnBP, between stainless steel and air at 25 °C, proposing that their partition coefficient, \( K_s \), could be related to these compounds’ vapour pressures through Eq. (13).

\[
\log(K_s) = -0.53 \cdot \log(p^*) + 0.63
\]  

Using this proposed relationship, one could calculate \( K_s \) as equal to 1113.5 m for DEHP, a value very similar to ones reported by (Wu et al., 2017) for this same phthalate and adsorptive surface. However, for an aluminum surface, the DEHP partition coefficient has been reported to be nearly reduced by half when compared to stainless steel (Wu et al., 2017). While it is unclear if Eq. (13) could be valid for DEP, one could calculate its \( K_s \) as equal to 14.55 m at 25 °C, which, if reduced by half to account for an aluminum surface, would not be so far from values estimated in our study, which ranged from approximately 1 to 2 m at 20 °C. Therefore,
while comparisons may be difficult, our values are in reasonable agreement with previous reports.

Further studies are required to assess the impact of additional environmental conditions on the diethyl phthalate partitioning behaviour, for instance, including ventilated (and unsealed) scenarios. However, we note that sealed environments are commonly used as a method of storage in museums collections and archives, where minimising the extent to which an artefact perceive external fluctuations in temperature and relative humidity is a common aim.

4. Conclusions

This work has investigated the partitioning behaviour of diethyl phthalate on borosilicate glass and aluminum surfaces in a wide range of temperatures between 20 and 80 °C for the first time. Measured partition coefficients for the glass and aluminum surfaces ranged between $0.41 \pm 6.9 \cdot 10^{-3}$ and $8.48 \cdot 10^{-3} \pm 2 \cdot 10^{-3}$ m and between $1.47 \pm 0.44$ and $7.1 \cdot 10^{-3} \pm 1.4 \cdot 10^{-3}$ m, respectively, within the investigated temperature range.

In addition, it was demonstrated that the relationship between DEP partition coefficients, $K_{\text{glass-air}}$, and temperature can be accurately predicted by a reparameterised form of the van’t Hoff equation, in which $K_{\text{glass-air}}$ values are exponentially reduced with temperature, supporting the assumption that DEP adsorption enthalpy can be considered constant for the investigated systems.

We anticipate that the developed models can prove useful for the mathematical description of degradation phenomena involving plasticiser loss in modern and contemporary artefacts, and also be a starting point for characterising the partitioning behaviour of this historically significant phthalate on different storage materials used in museum collections and archives. In addition, we hope this work will further contribute to ongoing efforts dedicated to determine levels of human exposure to this and additional phthalates.
5. Acknowledgments

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6. References


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