Adsorptivity of Copper Nanoparticles to Some Organic Compounds

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Abstract—Adsorptivity of some organic compounds to the copper nanoparticles prepared by levitation-jet generator was characterized by inverse gas chromatography. The measured values of specific volume of retained sorbate were used to calculate adsorption heats and entropy factors of the process.

Keywords: levitation-jet generator, inverse gas chromatography, copper nanoparticles, gas adsorption on nanoparticles

INTRODUCTION

Information on the absorptivity of compounds and materials is important for numerous applications such as drug delivery [1], effective/selective catalysis, [2, 3], gas sensors [4], and environment safety [5]. To date, a number of publications have been devoted to the absorptivity of commonly used organic compounds to such adsorbents as zeolites [6], polymers [7], and carbon materials [8].

As for Cu nanoparticles, their unique adsorption behavior has been reported by Soldatenko et al. [9, 10]. The catalytic activity of Co nanoparticles deposited onto shungite was studied by Yartsev et al. [11].

In this work, we explored the adsorptivity of some hydrocarbons and alcohols to copper nanoparticles produced at ISMAN by levitation-jet generator [12]. High catalytic activity of Cu nanoparticles loaded onto polycarbonate in hydrogenation of benzene was reported in [13].

EXPERIMENTAL

In experiments, we used the Cu nanoparticles home-made at ISMAN by using the levitation-jet generator [12]. The experimental setup and procedure for inverse gas chromatography were described in detail elsewhere [14]. A 97-cm column (3 mm in inner diameter) was stuffed with Inerton sorbent loaded with Cu nanoparticles. Chromatographic experiments were conducted within the temperature range 343–383 K.

Specific volume of retained gaseous sorbate V_{g}^{T} (mL/g) was calculated using formula (1):

$$V_{\mathrm{g}}^{T} = \frac{(t_{\mathrm{R}} - t_{\mathrm{M}})F_{PT}}{W_{\mathrm{ad}}} \qquad (1)$$

where t_{R}, t_{M} stand for the retention time of sorbate and non-adsorbing compound, respectively; W_{ad} is the weight of adsorbent in a column, and F_{PT} the averaged volumetric velocity of gas-carrier.

Thermodynamic parameters A and B were derived from linear plots (2) of $\ln V_{\mathrm{g}}^{T}$ $(1/T)$ functions:

$$\ln V_{\mathrm{g}}^{T} = A + \frac{B}{T} \qquad (2)$$

where A is the entropy component of sorption and $B = \bar{Q}_1/R$ relates to molar change in internal energy U; in our case, $\bar{Q}_1 = -\Delta U$, R is absolute gas constant.

RESULTS AND DISCUSSION

Figure 1 presents the SEM image of Cu nanoparticles prepared by levitation-jet method. It follows that the size of Cu nanoparticles is within the range 70–100 nm.

The values of V_{g}^{T} (mL/g) as derived from the linear plots in Figs. 2–4 are collected in Table 1 while the values of $\bar{Q}_1$ and $-A$, in Table 2.

In the homological series of *n*-alkanes, the values of $\bar{Q}_1$ and $-A$ are seen (Table 2) to gradually grow with an increase in molecular weight. Similar trend is observed [15] for higher *n*-alcohols: the larger molecular weight, the lower absorptivity.

In the row hexene-1–hexine-1–benzene (Table 2), adsorption heat $\bar{Q}_1$ increases, thus indicating the presence of specific interactions with the adsorbent. Their contributions can be estimated by analyzing the magnitude of $\Delta\bar{Q}_1$ (formula 3).

$$\Delta\bar{Q}_1 = \bar{Q}_1 - \bar{Q}_{1\mathrm{h}} \tag{3}$$

Here $\bar{Q}_1$ is the adsorption heat of sorbate and $\bar{Q}_{1\mathrm{h}}$ is that of a hypothetic alkane with the same polarizability. The results are presented in Table 3.

As follows from Table 3, an increase in $\bar{Q}_1$ is accompanied by a sharp increase of contributions from specific interactions ($\Delta\bar{Q}_1 / \bar{Q}_1$), whose magnitude can attain a value of 83% in case of benzene (third column in Table 3).

Figure 5 shows the entropy factor (–*A*) plotted versus differential molar adsorption heat $\bar{Q}_1$. This plot, also known as thermodynamic compensation, allows us to conclude that, in case of *n*-alkanes, unsaturated hydrocarbons, and aromatics, the mechanisms of sorption are similar, in contrast to those in case of alcohols.

CONCLUSIONS

For the organic compounds tested, their adsorption heat to Cu nanoparticles was found to grow in the order: unsaturated hydrocarbons → *n*-alkanes → benzene → *n*-alcohols.

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Table 1. The values of V_{g}^{T} (mL/g) as measured at T = 356 K

n-Heptane	0.22
n-Octane	0.46
n-Nonane	1.17
Methanol	0.20
Ethanol	0.17
Benzene	0.38
Hexine-1	0.15
Hexene-1	0.11

Table 2. The values of $\bar{Q}_1$ (kJ/mol) and –*A* as derived from linear plots in Figs. 2–4

	$\bar{Q}_1$, kJ/mol	–*A*
n-Heptane	13.2	5.9
n-Octane	18.8	7.1
n-Nonane	25.2	8.5
Methanol	20.9	8.7
Ethanol	18.4	8.1
Benzene	18.6	7.4
Hexine-1	11.4	5.8
Hexene-1	7.9	4.8

Table 3. The magnitudes of $\bar{Q}_1$, $\Delta\bar{Q}_1$, and extent of adsorption $\Delta\bar{Q}_1/\bar{Q}_1$

	$\bar{Q}_1$, kJ/mol	$\Delta\bar{Q}_1$, kJ/mol	$\Delta\bar{Q}_1/\bar{Q}_1$, %
Hexene-1	7.9	1.4	18
Hexine-1	11.4	8.0	70
Benzene	18.6	15.5	83

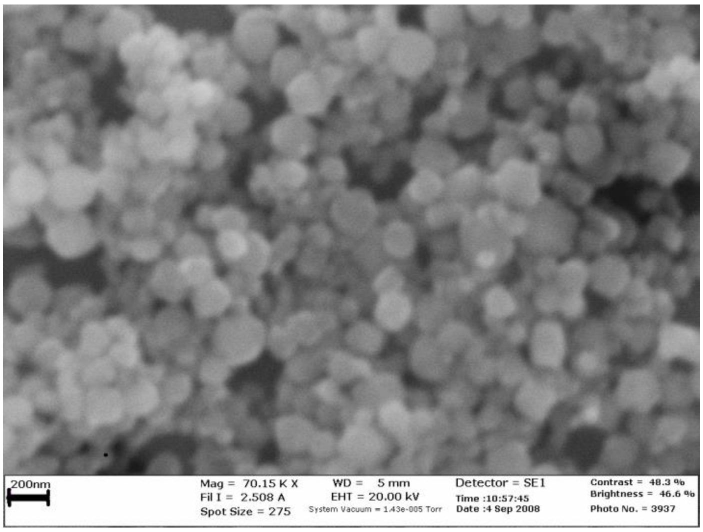
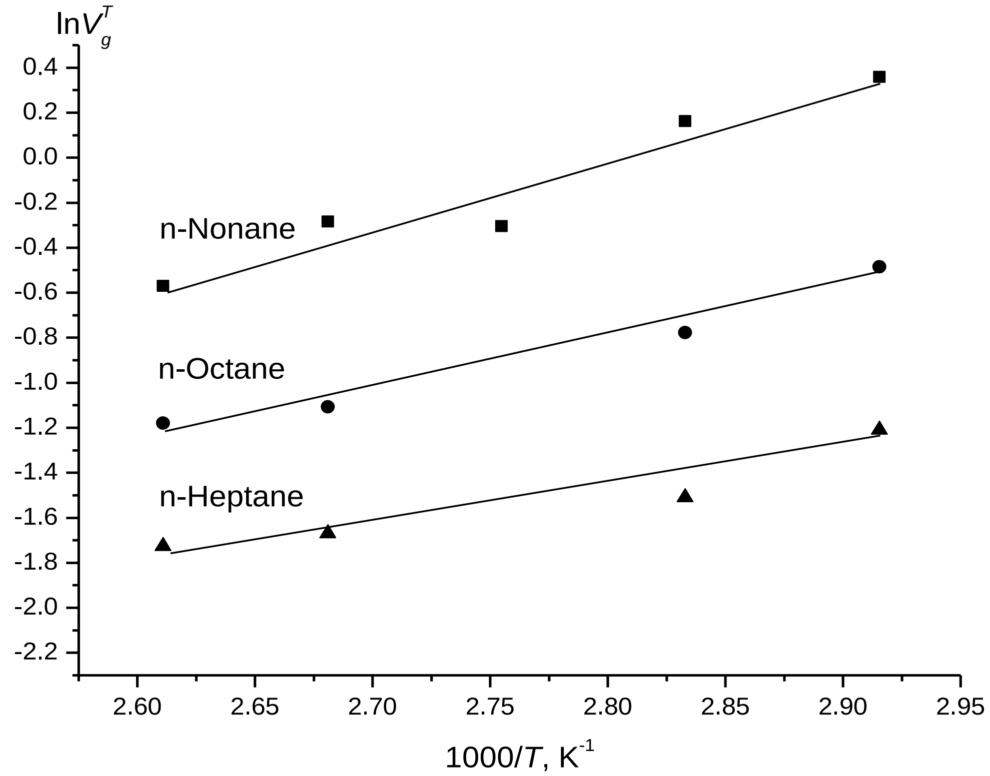
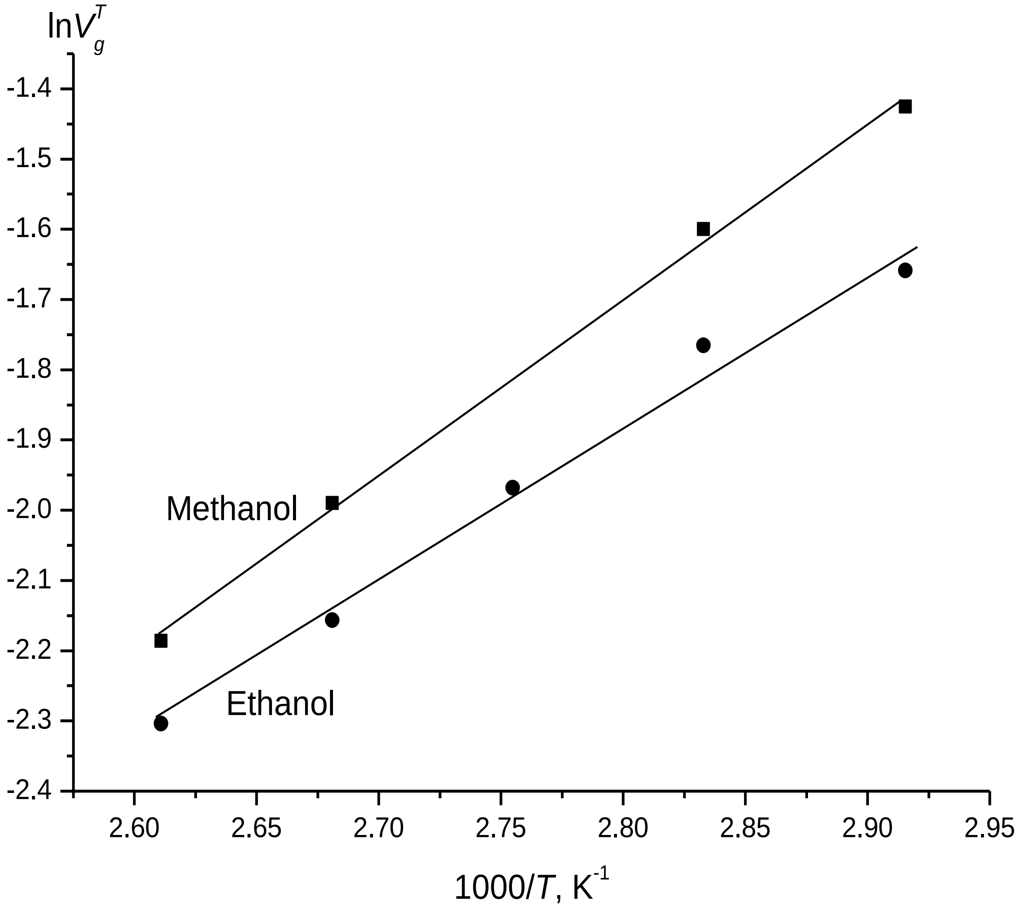


Fig. 1. SEM image of Cu nanoparticles prepared by using a levitation-jet generator.



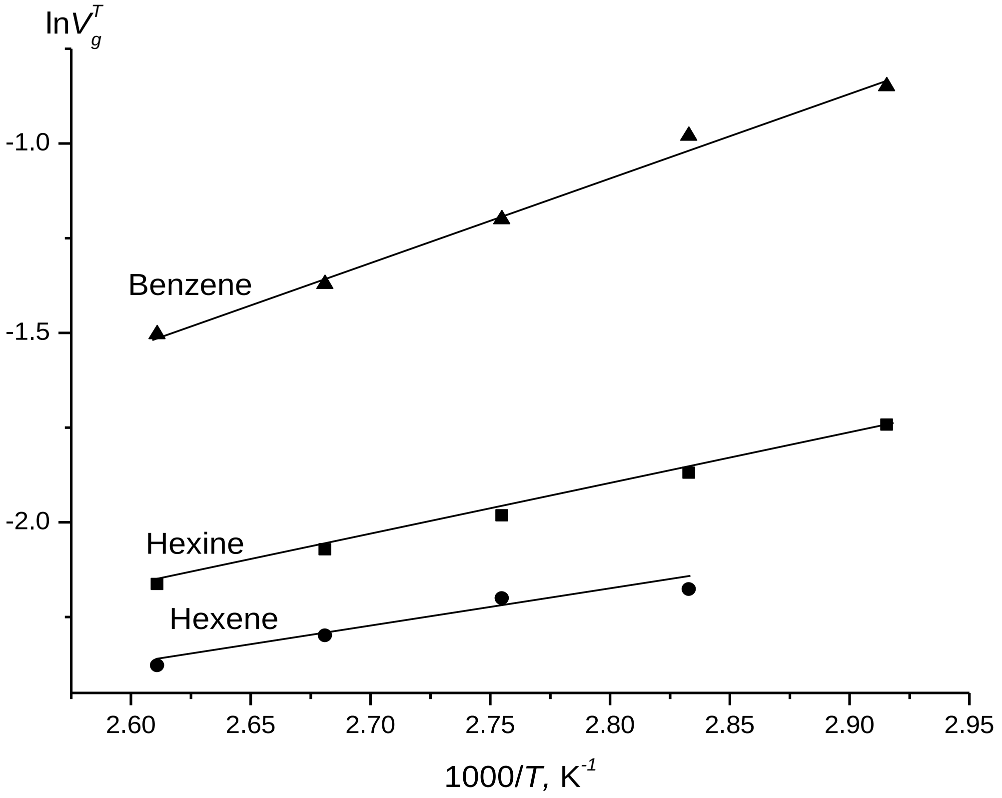
Key: $\ln V_g^T$ 1000/*T*, K^{-1}

Fig. 2. Linear $\ln V_g^T$ (1/*T*) plots according Eq. (2) for *n*-alkanes.



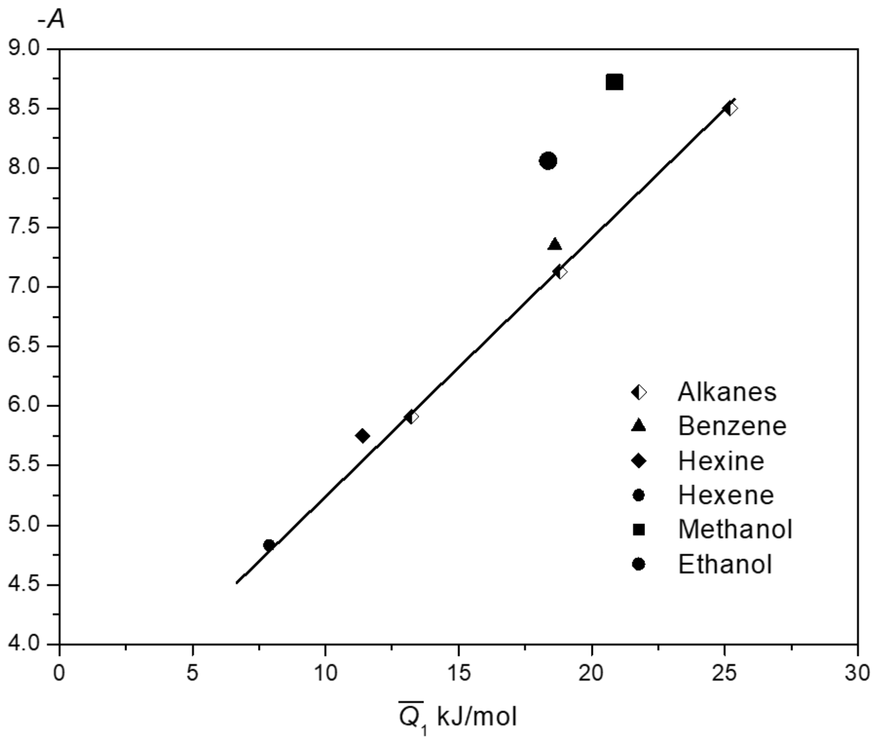
Key: $\ln V_g^T$ 1000/T, K^{-1}

Fig. 3. Linear $\ln V_g^T$ (1/T) plots according to Eq. (2) for methanol and ethanol.



Key: $\ln V_{\mathrm{g}}^{T}$ 1000/T, K^{-1}

Fig. 4. Linear $\ln V_{\mathrm{g}}^{T}$ (1/T) plots according to Eq. (2) for unsaturated hydrocarbons and benzene.



Key: –*A* $\overline{Q}_1$, kJ/mol

Fig. 5. Entropy component (–*A*) plotted versus differential molar adsorption heat $\overline{Q}_1$.