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## Gas Chromatographic Study of a Composite Sorbent Based on Metal-Organic Framework MIL-53(Al)

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**Abstract**—The retention regularities and the thermodynamic characteristics of the sorption of volatile organic compounds from the gas phase were studied for the chromatography columns packed with composite sorbents based on the MIL-53(Al) metal-organic framework and polydiphenyldimethylsiloxane (PPMS). It was shown that with an increase in the content of MIL-53(Al) in the binary sorbent to 73 wt %, retention is predominantly associated with adsorption in the microporous structure of MIL-53(Al) rather than dissolution in the PFMS film. It has been shown that the adsorbate–adsorbent interaction in the orthorhombic channels of MIL-53(Al) depends to a greater extent on the dispersion attractive forces than the dipole–dipole and specific interactions.

**Keywords:** metal-organic framework polymers, MIL-53(Al), composite sorbent, gas chromatography, retention mechanism

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### INTRODUCTION

Metal organic frameworks (MOFs) or metal-organic coordination polymers (MOCPs) are a class of micro- and mesoporous materials obtained through the self-assembly of various metal-containing structural groups and organic linkers. A wide variety of building blocks of MOCPs provides the possibility of a wide variation of their porous structure, and the relatively high thermal stability and stability in various liquid media makes MOCPs promising materials for gas storage technology [1], extraction [2, 3], catalysis [4, 5], and chromatography [6–10]. The use of both packed and capillary columns filled with different MOCPs for the separation of light gases, alkanes, arenes, and polar compounds in gas chromatography have been described [11]. It should be noted that the use of MOCPs as sorbents for gas chromatography (GC) is associated with some difficulties, such as the inhomogeneity of the particle sizes of the synthesized crystals and their low mechanical strength, which makes it difficult to obtain highly efficient columns with good operational properties. Therefore, the production of composite sorbents of various types is a more promising direction in the field of practical application of MOCPs in GC. Thus, copper-based MOCP (Cu-BTC) was supported [12] on a wide-pore silica carrier Chromosorb W, the surface of which was deactivated with 3% polymethylsiloxane phase SE-30. In [13], directed synthesis (crystallization) of MOF-5 was carried out on microspheres of polydimethylsilox-

ane, providing particles with the morphology “polymer core–MOCP shell.” The possibility of producing a composite sorbent based on carbon material (graphene) and MOCP ZIF-8 is demonstrated in work [14]. It should, however, be noted that most of these works are devoted to the study of the separation properties of columns with sorbents based on MOCPs. There are no works in which the effect of the polymer phase and the degree of availability of the internal pores of the MOCP in the composite on its sorption properties are analyzed. In this regard, the aim of this work is to study the sorption of organic compounds from the gas phase by a composite sorbent based on MIL-53(Al) metal-organic framework and polydiphenyldimethylsiloxane at various ratios of MOCP and polymer to establish the contribution of adsorption in the porous structure of MOCPs to gas chromatographic retention and thermodynamics of sorption redistribution.

### EXPERIMENTAL

The original MIL-53(Al) (Sigma-Aldrich) was dispersed using ultrasound in acetone to obtain a fraction with a particle size of  $\leq 1 \mu\text{m}$ . The composite sorbent was obtained by depositing MIL-53(Al) microparticles on wide-pore silica support Chromaton N AW ( $s_{\text{sp}} = 1 \text{ m}^2/\text{g}$ ), preliminarily modified with 5.5% polydiphenyldimethylsiloxane phase SP-2250 (50% phenyl groups). Two packed columns with different con-

tents of MIL-53(Al) in a binary sorbent “MOCP–polymer” were made. In column no. 1 (1.2 m × 2.5 mm), the composite sorbent contained 6.7% MIL-53(Al) and 5.5 wt % polydiphenyldimethylsiloxane (PPMS) relative to the mass of Chromaton N AW, and in column no. 2 (0.9 m × 2 mm), 15% and 5.5 wt %, respectively. The columns were conditioned in a stream of nitrogen at a temperature of 280°C for 10 h.

The experiment was carried out on a Kristall-5000.2 gas chromatograph equipped with a flame ionization detector. The excess pressure  $\Delta P$  at the column inlet was varied in the range 80–120 kPa, which corresponded to the gas flow rate (nitrogen) at the column outlet  $F_{p_a, T_c} = 20\text{--}30$  mL/min.

The retention factor  $k$  was calculated using the formula:

$$k = \frac{t_R - t_M}{t_M},$$

where  $t_R$ ,  $t_M$  is the retention time of the sorbate and the nonsorbing substance (methane), respectively. The specific retention volume of sorbates  $V_g^T$  was determined per unit mass of the binary sorbent according to the equation:

$$V_g^T = \frac{(t_R - t_M)F_{p_a, T_c}j_3^2}{W_S} = \frac{(t_R - t_M)F_{\bar{p}, T_c}}{W_S},$$

where  $W_S$  is the mass of the stationary phase ( $W_S = W_{\text{MIL-53}} + W_{\text{SP-2250}}$ ),  $F_{p_a, T_c}$  is the space velocity of the carrier gas at the outlet of the column at the column temperature  $T_c$  and atmospheric pressure  $P_a$ ,  $j_3^2$  is James and Martin coefficient, and  $F_{\bar{p}, T_c}$  is the volumetric velocity reduced to the column temperature  $T_c$  and the pressure  $\bar{P}_x$  averaged over the column length.

To calculate  $F_{\bar{p}, T_c}$  we used a traditional method of using a soap-film flowmeter, and the method of cold column calibration proposed in [15]. Both methods showed close values of volumetric gas flow rate inside the column  $F_{\bar{p}, T_c}$ . Due to simplicity, especially when working in a wide temperature range, the method of cold calibration of the column was mainly used. The error in determining  $V_g^T$  did not exceed 5% on average, and the retention factor  $k$ , 8%.

Sorption characteristics (specific retention volume  $V_g^T$ , retention factor  $k$ ) were determined for each of the studied compounds in the range of gas flow rates in which they remain practically constant for small samples of sorbates.

The change in the internal energy  $\Delta\bar{U}$  (heat) of sorption and the value proportional to the standard change in entropy  $\Delta S^*$  were determined from experimental data on the temperature dependences of the

specific retention volumes of sorbates according to the equation:

$$\ln V_g^T = -\frac{\Delta\bar{U}}{RT} + \frac{\Delta S^*}{R}.$$

A general array of experimental data on the retention of 21 studied compounds was obtained in the temperature range from 110 to 230°C. However, for each substance, the  $\ln V_g^T - 1/T$  dependences were determined in a narrower  $\Delta T$  range, in which the chromatographic peaks were not too blurred and had a symmetric shape.

The studied sorbates were *n*-alkanes ( $C_5\text{--}C_7$ ), octane isomers, arenes (benzene, *o*- and *m*-xylenes), cyclohexane, alkanols and isoalkanols ( $C_3\text{--}C_5$ ), chloromethanes, and nitromethane. Using the Spartan software package, some molecular parameters were calculated for them—length  $l$ , volume  $V_m$ , polarizability  $\alpha$ , and dipole moment of the molecule  $\mu$ .

## RESULTS AND DISCUSSION

The metal-organic framework polymer MIL-53(Al) (Al–OH–benzene-1,4-dicarboxylate) has a rhombic channel system. After synthesis, a framework with a channel cross section of  $7.3 \times 7.7$  Å is obtained, which contains the linker residues (terephthalic acid molecules). Thermal activation leads to the release of channels and an increase in their cross-sectional dimensions to  $8.5 \times 8.5$  Å [16] (Fig. 1).

For the tasks of practical GC, it is necessary to obtain such an MOCP-based sorbent that provides a fast mass exchange between the gas phase and its microporous structure, and also has good operational properties (mechanical strength, thermal stability). The use of a wide-pore (pore diameter  $\sim 10$  μm) silica support, as well as layer-by-layer application of a thin film (0.055 μm) of a medium-polarity polymer PPMS and a layer of aggregated microcrystallites MIL-53(Al) contributes not only to facilitating the transfer of the substance to the pores, but also to better adhesion and fixation of particles on the deactivated surface of the support.

Thus, both adsorption in pores and dissolution in polymer film (adsorption–absorption version of GC) occur simultaneously on the studied sorbents [17]. In the process of conditioning the column at a sufficiently high temperature (280°C), part of the polymer phase from the polymer layer can penetrate into the space between the microcrystallines and thereby shield their surface. This effect should be reduced by increasing the amount of MOCP in the sorbent and leads to a significant increase in retention. The  $\ln V_g^T - 1/T$  dependences presented in Fig. 2, obtained on columns with different amounts of MOCPs in the composite sorbent, confirm the above assumption.

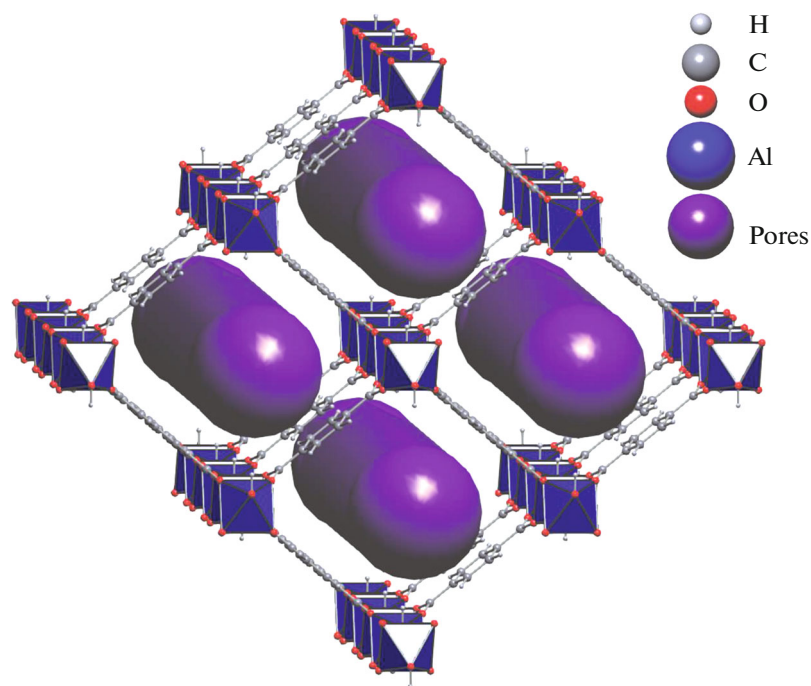


Fig. 1. Canal structure of MIL-53(Al) metal-organic framework polymer.

From Fig. 2 it follows that an increase in the mass fraction of MOCP in the composite sorbent from 0.55 (column no. 1) to 0.73 (column no. 2) leads to an increase in the retention of xylenes by about 6–7 times. Such a multiple increase in the specific retention volume  $V_g^T$  is observed for other studied hydrocarbons, and this increase is usually accompanied by an increase in the heat of sorption  $|\Delta\bar{U}|$  by 3–10 kJ/mol. For polar compounds (alcohols, dichloromethane), the increase in retention is much less, and the value  $|\Delta\bar{U}|$  for them, either changes little or even decreases (propanol-1, butanol-1).

The regularities found indicate the prevailing contribution of adsorption to retention on column no. 2 with a composite sorbent containing 73% MIL-53(Al) and 27% PPMS, and also that the surface of the pore walls of this MOCP has a greater tendency to nonspecific interactions with adsorbates, than to specific ones, which was found in works [18, 19]. That is why the retention of *o*-xylene is less than that of *m*-xylene, since the molecular length of the latter (6.5 Å) is longer than that of *o*-xylene (5.9 Å), which leads to an increase in the dispersion forces of attraction of *m*-xylene by hydrophobic pore walls MIL-53(Al).

An increase in the amount of MOCP in the sorbent affects the sequence of elution from the column of chlorine derivatives of methane. On a sorbent with a lower content of MIL-53(Al) (column no. 1), retention increases with an increase in the dipole moment  $\mu$  of molecules in the series carbon tetrachloride (0 D) →

trichloromethane (1.02 D) → dichloromethane (1.36 D). This retention sequence is obvious, associated with influence PFMS. On column no. 2, the retention of these compounds increases with the volume of  $V_m$  and the polarizability of  $\alpha$  molecules in the dichloromethane → trichloromethane → carbon tetrachloride series (Table 1).

Thus, the effect of the polymer layer on sorption in column no. 2 is very small, and the retention charac-

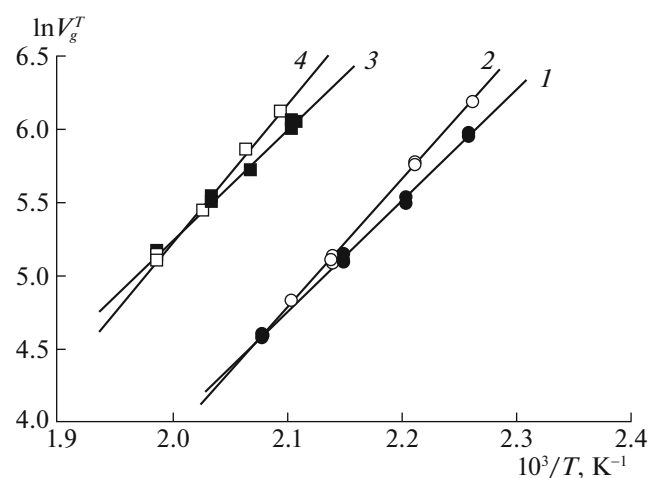


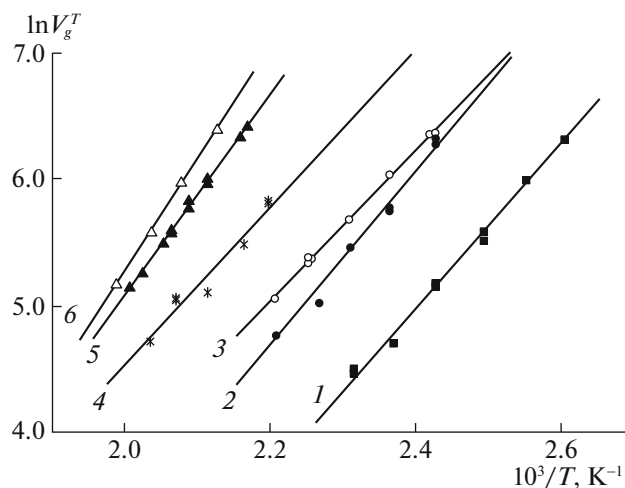
Fig. 2. Dependences  $\ln V_g^T - 1/T$  of xylene isomers obtained on columns with a composite sorbent “MIL-53(Al)–PPMS”: 1, 2—column no. 1 (55% MIL-53(Al)); 3, 4—column no. 2 (73% MIL-53(Al)); 1, 3—*o*-xylene; 2, 4—*m*-xylene.

**Table 1.** Molecular parameters and thermodynamic sorption characteristics of the studied compounds

No.	Sorbates	$V_m, \text{\AA}^3$	$\alpha, \text{\AA}^3$	$\mu, \text{D}$	$V_g^T, 170^\circ\text{C}, \text{cm}^3/\text{g}$	$k, 170^\circ\text{C}$	$-\Delta\bar{U}, \text{kJ/mol}$	$-\Delta S^*, \text{J}/(\text{mol K})$
1	Pentane	106.5	9.95	0	57.5	2.1	54.1	88.3
2	Hexane	124.8	11.78	0	160.5	6.1	57.6	87.7
3	Heptane	143.1	13.62	0	1254.9	37.5	66.2	90.0
4	2,2-Dimethylhexane	160.7	15.45	0	2063.1	71.7	73.4	102.3
5	2,3-Dimethylhexane	160.8	15.45	0	1796.2	61.7	67.3	89.5
6	2,3,4-Trimethylpentane	160.6	15.45	0	2284.9	60.3	72.7	99.8
7	2,2,4-Trimethylpentane	160.3	15.45	0	1897.9	60.9	73.2	102.3
8	Cyclohexane	111.5	11.01	0	215.3	8.1	49.7	67.5
9	Benzene	99.2	10.43	0	463.2	13.2	52.1	66.5
10	<i>o</i> -Xylene	135.3	14.10	0.46	1283.2	41.3	62.5	81.5
11	<i>m</i> -Xylene	135.6	14.10	0.27	2052.2	60.9	78.4	113.6
12	Propanol-1	77.4	6.92	1.68	267.4	7.7	37.3	37.8
13	Propanol-2	77.4	6.92	1.63	56.2	1.3	49.6	78.3
14	Butanol-1	95.7	8.75	1.68	660.1	25.9	41.8	40.3
15	2-Methylpropanol-1	93.7	8.75	1.62	239.9	6.0	61.7	93.6
16	2-Methylpropanol-2	93.6	8.75	1.63	69.4	2.0	53.4	85.3
17	3-Methylbutanol-1	113.8	10.59	1.51	810.0	22.5	64.0	88.7
18	Dichloromethane	60.9	6.47	1.36	80.2	2.5	44.6	64.1
19	Trichloromethane	74.9	8.39	1.02	82.5	2.7	53.2	83.8
20	Tetrachloromethane	89.1	10.32	0	255.0	9.4	57.0	82.8
21	Nitromethane	55.4	4.45	3.98	84.7	2.6	42.2	58.3

teristics of the studied compounds on this column are mainly due to adsorption in the porous structure of MIL-53(Al); therefore, detailed studies of the ther-

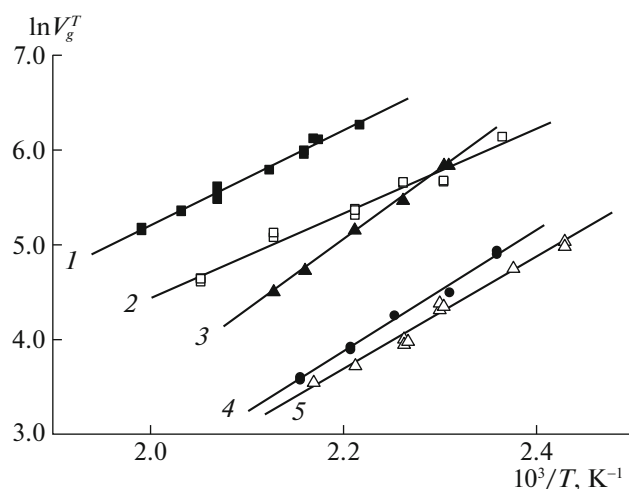
modynamics of sorption were carried out using this column.



**Fig. 3.** Dependences  $\ln V_g^T - 1/T$  of hydrocarbons on a column with a composite sorbent "MIL-53(Al)-PPMS" (73% MIL-53(Al)): 1—*n*-pentane, 2—*n*-hexane, 3—cyclohexane, 4—benzene, 5—*n*-heptane, 6—2,2,3-trimethylpentane.

Figure 3 shows the dependences  $\ln V_g^T - 1/T$  obtained on column no. 2 for *n*-alkanes  $C_5$ – $C_7$ , 2,2,3-trimethylpentane, cyclohexane, and benzene. It can be seen from the presented figure that the elution temperature range significantly depends on the volume of the molecule  $V_m$ . As  $V_m$  increases, this range shifts to higher temperatures.

Adsorption on MIL-53(Al) is sensitive to the structure of the carbon skeleton of the molecule. Thus, in the case of compounds with six carbon atoms in their structure, the retention increases in the series *n*-hexane → cyclohexane → benzene. At the same time, based on a comparison of the heats of adsorption  $|\Delta\bar{U}|$  (Table 1), it can be argued that linear *n*-hexane molecules interact more strongly with the pore walls of the framework than cyclic molecules of cyclohexane and benzene. Consequently, the greater retention of cyclic hydrocarbons in comparison with *n*-hexane is associated with a smaller drop in entropy during the transition of their rigid (benzene) and semi-rigid (cyclohexane) molecules from the gas phase to the porous structure of the framework. *n*-Octane eluted from the column only at  $t > 250^\circ\text{C}$ , forming strongly blurred



**Fig. 4.** Dependences  $\ln V_g^T - 1/T$  alcohols on a column with a composite sorbent “MIL-53(Al)–PPMS” (73% MIL-53(Al)): 1—*n*-butanol-1, 2—*n*-propanol-1, 3—2-methylpropanol-1, 4—2-methylpropanol-2, 5—*n*-propanol-2.

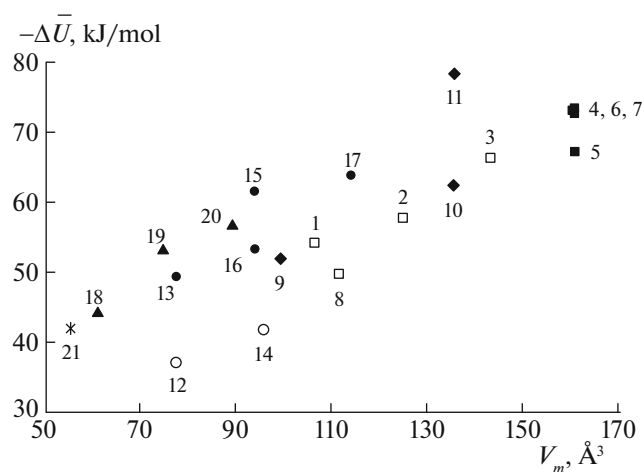
and asymmetric peaks, which made it difficult to determine the retention characteristics. The linear sizes of isomeric octanes ( $t = 6.8\text{--}8.1 \text{ \AA}$ ) better correspond to the sizes of MIL-53(Al) orthorhombic channels, and they eluted from the column in the temperature range 200–230°C.

The branching of the alcohol molecule leads to an increase in dispersion interactions with the walls of the MIL-53(Al) channel, and, as a consequence, to an increase in the heat of adsorption  $|\Delta\bar{U}|$  for isoalkanols compared to their linear counterparts. This leads to a strong increase in the slope of the  $\ln V_g^T - 1/T$  dependence for isoalkanols compared with the corresponding *n*-alkanols (Fig. 4).

However, despite the higher values of  $|\Delta\bar{U}|$  for isoalkanols, their retention is significantly lower. From a comparison of the values of the entropy drop during adsorption (Table 1), it can be concluded that the lower retention of isomeric alcohols is due to the lower mobility of their molecules in the porous structure of the framework as compared to the behavior of linear alcohols.

We have analyzed the influence of the dipole moment  $\mu$ , linear size  $l$ , and volume  $V_m$  of molecules of the studied sorbates on the heat of adsorption  $|\Delta\bar{U}|$ . Thus, the smallest values  $|\Delta\bar{U}|$  found for nitromethane ( $\mu = 3.98 \text{ D}$ ), propanol-1, and butanol-1 ( $\mu = 1.68 \text{ D}$ ), the polar molecules of which have a linear structure. The maximum values  $|\Delta\bar{U}|$  were obtained for *m*-xylene and octane isomers ( $\sim 70\text{--}78 \text{ kJ/mol}$ ).

For the investigated set of compounds, the linear dimensions of which vary from  $l = 2.84 \text{ \AA}$  (dichloro-



**Fig. 5.** Change in internal energy during sorption by the composite sorbent “MIL-53(Al)–PPMS” (73% MIL-53(Al)), presented in the coordinates  $|\Delta\bar{U}|$ –the volume of the molecule  $V_m$  (the numbering of the points corresponds to Table 1).

methane) to  $l = 9.33 \text{ \AA}$  (*n*-heptane), no correlation was found between  $l$  and  $|\Delta\bar{U}|$ . Thus, for chlorine derivatives of methane ( $l \approx 2.85 \text{ \AA}$ ), the value  $|\Delta\bar{U}|$  increases in the order dichloromethane  $\rightarrow$  trichloromethane  $\rightarrow$  tetrachloromethane. At close values of  $l$  for *n*-butanol and 3-methylbutanol-1 ( $l = 6.55 \text{ \AA}$ ), the heats of adsorption are 41.8 and 64.0 kJ/mol, respectively. The growth trend is more pronounced  $|\Delta\bar{U}|$  with increasing  $V_m$  (Fig. 5) and polarizability of molecules.

It should be noted that the values obtained for the compounds under study on column no. 2 are higher (by 10–20 kJ/mol) than during adsorption on a flat surface of graphitized soot [20] and sorption on PPMS. Thus, for *n*-hexane and *n*-heptane, the values  $|\Delta\bar{U}|$  on “pure” PPMS, they were 24.6 and 38.2 kJ/mol, respectively; for aromatic compounds, they vary from 25.5 (benzene) to 42.8 (*o*-xylene). This confirms the assumption that retention on column no. 2 is mainly associated with adsorption in the microporous structure of MIL-53(Al) rather than dissolution in the PPMS film.

Thus, upon adsorption in orthorhombic channels of MIL-53(Al), the manifestation of dipole–dipole interactions,  $\pi$ – $\pi$ -stacking, and specific interactions (hydrogen bond, donor–acceptor interactions) is hindered. The adsorbate–adsorbent interaction, characterized by the value  $|\Delta\bar{U}|$ , depends to a greater extent on nonspecific dispersion attractive forces, the contribution of which, upon adsorption in narrow cavities of the MOCP, increases with an increase in the volume of the molecule, branching of the hydrocarbon chain, and with an increase in the degree of sphericity of the shape of molecules (for example, in a series of

dichloromethane—trichloromethane—tetrachloromethane).

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