ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2016, Vol. 90, No. 10, pp. 2006–2010. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © V.Yu. Gus'kov, S.P. Ivanov, Yu.F. Shaikhitdinova, F.Kh. Kudasheva, 2016, published in Zhurnal Fizicheskoi Khimii, 2016, Vol. 90, No. 10, pp. 1517–1522.

PHYSICAL CHEMISTRY OF SURFACE PHENOMENA

Thermodynamics of the Adsorption of Organic Molecules on Graphitized Carbon Black Modified with a Monolayer of 5-Hydroxy-6-methyluracil

V. Yu. Gus'kov[a]*, S. P. Ivanov[b], Yu. F. Shaikhitdinova[a], and F. Kh. Kudasheva[a]
[a] *Bashkir State University, Ufa, 450076 Russia*
[b] *Ufa Institute of Chemistry, Russian Academy of Sciences, Ufa, 450054 Russia*
**e-mail: guscov@mail.ru*

Received September 16, 2015

Abstract—Thermodynamic characteristics of the adsorption of alkanes, alcohols, arenes, and esters on graphitized carbon black with a deposited monolayer (0.17%) of 5-hydroxy-6-methyluracil are studied by means of inverse gas chromatography at infinite dilution. It is established that size effects (violation of the additivity of molar changes in internal energy and the entropy of adsorption for pairs of molecules of one homologous series that differ by one methyl group) are observed when organic molecules are adsorbed on the surface of the resulting adsorbent. The size effects are similar to those observed when 1% 5-hydroxy-6-methyluracil is deposited on graphitized carbon black. It is concluded that the observed violation of additivity is associated with cavities in the supramolecular structure.

Keywords: specific retention volume of test sorbates of different natures, molar changes in internal energy and entropy of adsorption, inverse gas chromatography, 5-hydroxy-6-methyluracil, monolayers, graphitized carbon black

DOI: 10.1134/S0036024416100149

INTRODUCTION

Supramolecular chemistry is of interest to researchers due to the diversity of supramolecular structures, the ease with which they are obtained, and their widespread presence in nature [1]. One of the most interesting objects in supramolecular chemistry today is surfaces with two-dimensional ordered layers of supramolecular structures, due to their possible application in chemical sensors, nanoelectronics, and other areas where molecular recognition is necessary [2]. One effective way of studying these surfaces, inverse gas chromatography (IGC), allows us to obtain data on the constants of adsorption–desorption equilibrium, thermodynamic functions, and other important parameters of the adsorption of organic molecules of different types [3–5]. These data are of help in assessing the structure and properties of supramolecular structures.

Earlier, we studied sorbents based on supramolecular network uracil structures [6] and their derivatives [7–9] by means of IGC. The adsorption of organic molecules on them is accompanied by so-called size effects, at the heart of which lies violation of the additivity of molar changes in internal energy and the entropy of adsorption of pairs of molecules of one homologous series (alkanes, alcohols, arenes, and so on) that differ by one methyl group, one of which is smaller than the size of a cavity while the other is a bit larger [9]. The resulting effects correlate with the size of cavities in a supramolecular structure, determined by the independent means of scanning tunneling microscopy and X-ray analysis.

The most likely interpretation of the observed effects is the total or partial adsorption of organic molecules in the cavities of a supramolecular structure. In all similar investigations, however, the amount of deposited modifier ranged from 1 to 10%; i.e., it was deliberately higher than the amount necessary for layer formation. This results in the cavities of the first layer of a supramolecular structure not always coinciding with those of the second layer, and so on. This can change the actual size of the cavities in which molecules are adsorbed. We therefore cannot reliably confirm the relationship between the size of supramolecular network cavities and the observed size effects, based on the available data. To do so, we must study the size effects using a sample with a monolayer of supramolecular structure. The aim of this work was to study the thermodynamic characteristics of adsorption for a series of organic molecules on a sorbent with a monolayer of 5-hydroxy-6-methyluracil.

EXPERIMENTAL

5-Hydroxy-6-methyluracil (HMU) was chosen as the modifier because of the great volume of available data on the adsorption of organic molecules on surfaces of HMU-modified sorbents [6, 8]. The initial sorbent was a graphitized carbon black (GCB). This adsorbent was chosen because of its homogeneous plane surface, which allows us to calculate the amount of HMU necessary for monolayer formation. The specific surface of the initial adsorbent was determined via low-temperature nitrogen adsorption on a Monosorb instrument. Nitrogen adsorption on the surface was conducted in a continuous flow reactor at the nitrogen boiling point and atmospheric pressure. The quantity of adsorbed nitrogen was calculated from the change in the heat conductivity of a gaseous mixture of nitrogen in helium. The resulting specific surface area was 1 m^2/g.

Preliminary quantum-chemical calculations showed that one fragment of an HMU supramolecular structure consisting of 10 molecules has an area of ~408 $Å^2$. We therefore calculated that the amount of HMU needed to deposit a monolayer on its surface is 0.17% of the weight of initial sorbent. Deposition was performed in a diluted water–alcohol solution via solvent evaporation at room temperature. The weight of the initial adsorbent was 1.1342 g; that of the HMU, 19 mg.

Our study was conducted on a Chromos GC-1000 gas chromatograph (Khimanalitservis, Dzerzhinsk, Russia) equipped with a flame-ionization detector. A column 30 cm long with an internal diameter of 3 mm was used. The helium flow rate was 10 ± 0.1 mL/min. As adsorbates, we chose organic compounds of various natures that were capable of different kinds of intermolecular interactions: pentane, hexane, heptanes, octane, nonane, decane, undecane, dodecane, *iso*-octane, cyclohexane, benzene, toluene, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, *iso*-propanol, *iso*-butanol, *iso*-pentanol, *tert*-butanol, ethyl acetate, and butyl acetate. A diluted vapor–air mixture corresponding to the detector's limit of sensitivity (10 μL) was fed into the chromatograph's evaporator. The retention volumes ($V^0_{g(T)}$, mL/g) were measured in the temperature ranges of 55 to 80°C for hexanol, 60 to 95°C for heptanol, 70 to 95°C for octanol, 45 to 80°C for *tert*-butanol, and 40 to 70°C for the remaining compounds, at intervals of 5 K. The thermostat's accuracy of temperature control was 0.01 K. Each sample was preconditioned in a flow of mobile gas at 100°C for 10 h.

The desorption branches of peaks with different heights were superimposed on one another, and the values of the specific retention volumes were independent of the carrier gas flow rate. This allowed us to consider the experimental conditions as quasi-equilibrium and the Henry constants of adsorption–desorption equilibrium as proportional to the specific retention volumes at the column temperature [4, 10] (the standard states of a compound were an adsorbate concentration of 1 μmol/mL in the gaseous phase and an adsorbate concentration of 1 μmol/g in the adsorbed state).

Using dependence $\ln V^0_{g(T)}$ on $1/T$ according to the formula

$$\ln V^0_{g(T)} = \frac{\Delta S}{R} - \frac{\Delta U}{RT} + 1, \quad (1)$$

we calculated ΔS and ΔU, i.e., the molar changes in entropy and internal energy, J/(mol K) and kJ/mol, respectively. Our calculations were performed using the Advanced Grapher program.

Molar change in the adsorption free energy ΔF, kJ/mol, was calculated according to the formula

$$-\Delta F = RT\ln V^0_{g(T)} + RT. \quad (2)$$

The relative conditional surface polarity and contributions from different intermolecular interactions to ΔF were estimated via linear decomposition of the adsorption energy according to the procedure described in [8, 9, 11].

RESULTS AND DISCUSSION

Figure 1 presents the dependences of the logarithm of the specific retention volume on the inverse temperature for a graphitized carbon black modified with HMU monolayer. As can be seen from the diagram, all of the dependences are linear, allowing us to calculate reliably the values of the molar changes in internal energy and the entropy of adsorption. The resulting values of ΔU and ΔS are given in Table 1. The indicated measurement errors include the systematic errors of measuring the carrier gas flow rate and the temperature, the deviations from a linear dependence when plotting the diagrams for $\ln V^0_{g(T)}$ on $1/T$, along with random errors in measuring retention times. Our data show that for *n*-alkanes, we observe violation of the additivity of molar changes in internal energy and the entropy of adsorption due to the number of carbon atoms in a homologous series (Figs. 2 and 3).

For hexane–heptanes, the values of ΔU are thus virtually identical (the difference is a mere 0.1 kJ/mol), while those of ΔS differ within the limit of error. For the octane–nonane pair, the heat and entropy of adsorption coincide. The observed size effects are similar to those of 1% HMU-modified graphitized carbon black and inert supports [8]. We may therefore conclude that the size effects observed for sorbents containing uracil supramolecular structures and compounds of similar structure are most likely associated with the cavities of the supramolecular structure. Violations of additivity in the hexane–heptane and octane–nonane pairs correspond to cav-

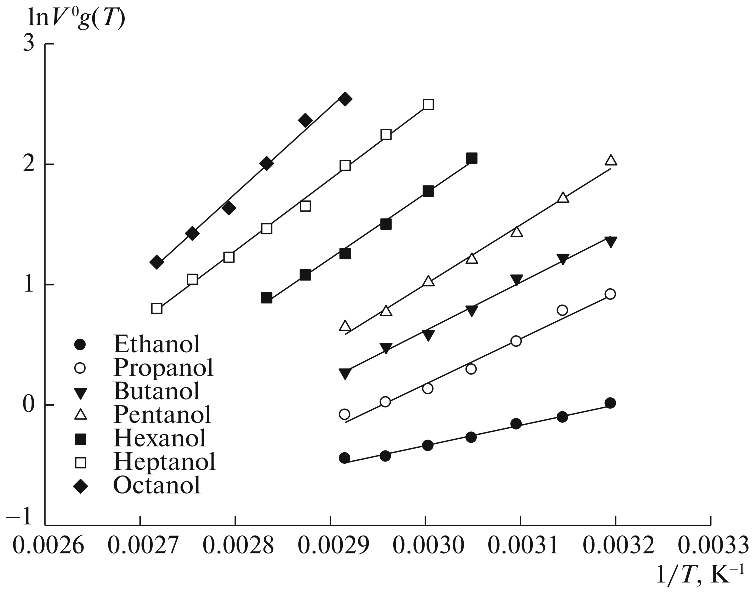

Fig. 1. Dependences of the logarithm of the specific retention volume on the inverse temperature for *n*-alcohols on GCB modified with a 5-hydroxy-6-methyluracil monolayer.

ities A and B, respectively (Fig. 4 [12]). A similar pattern is observed for the benzene–toluene pair (cavity A).

In homologous series of alcohols, such size effects as equalizing of the heats and entropies of adsorption are observed for C_3–C_4 and C_6–C_8 pairs of adsorption (Fig. 3), due likely to adsorption in cavities A and B, respectively. In analogy with alkanes, however, the sizes of the alcohol molecules were slightly smaller than needed. According to [9], the actual size of cavity B is thus 11 Å, while the maximum size of a molecule is ~9.3 Å for hexanol and 10.6 Å for heptanol. This can be explained by the ability of alcohols to form hydrogen bonds with HMU cavitites. A similar effect was observed earlier in a pyrimidinophane-based adsorbent [10].

The main difference between the size effects observed on an HMU monolayer and those on 1% HMU-containing GCB (~6 HMU layers) is that in the latter case, the thermodynamic characteristics of the adsorption of smaller molecules are notably higher than for bigger molecules. This is not true of a monolayer, since the heat and entropy of adsorption equalize. A comparison of the values of ΔU and ΔS for the deposition of a monolayer and the data on the thermodynamic functions of adsorption on 1% HMU-containing GCB [8] shows that the adsorption of organic

Table 1. Values of ΔU, kJ/mol, and ΔS, J/(mol K), of the adsorption of organic molecules on GCB modified with a monolayer of 5-hydroxy-6-methyluracil, along with coefficients r of linear correlation

Adsorbate	ΔU	ΔS	r	Adsorbate	ΔU	ΔS	r
Pentane	4.1 ± 0.4	25 ± 2	0.9801	Propanol	31 ± 3	101 ± 9	0.9915
Hexane	10.7 ± 0.8	44 ± 3	0.9920	*iso*-Propanol	27 ± 4	94 ± 13	0.9818
Heptane	13 ± 1	47 ± 4	0.9907	Butanol	33 ± 3	103 ± 9	0.9962
Octane	36 ± 4	117 ± 11	0.9963	*iso*-Butanol	30 ± 4	97 ± 11	0.9831
iso-Octane	14 ± 1	51 ± 4	0.9902	Pentanol	41 ± 4	122 ± 12	0.9981
Nonane	36 ± 5	111 ± 14	0.9892	*iso*-Pentanol	39 ± 2	118 ± 7	0.9966
Decane	48 ± 6	141 ± 16	0.9924	Hexanol	53 ± 5	152 ± 13	0.9995
Undecane	50 ± 9	140 ± 24	0.9962	Heptanol	50 ± 3	136 ± 8	0.9986
Cyclohexane	9 ± 1	38 ± 2	0.9946	Octanol	60 ± 6	161 ± 14	0.9950
Ethyl acetate	13 ± 2	48 ± 10	0.9635	*tert*-Butanol	17 ± 1	63 ± 4	0.9958
Butyl acetate	32 ± 7	92 ± 19	0.9828	Benzene	12 ± 2	48 ± 6	0.9763
Ethanol	14 ± 1	53 ± 5	0.9919	Toluene	13 ± 2	47 ± 6	0.9797

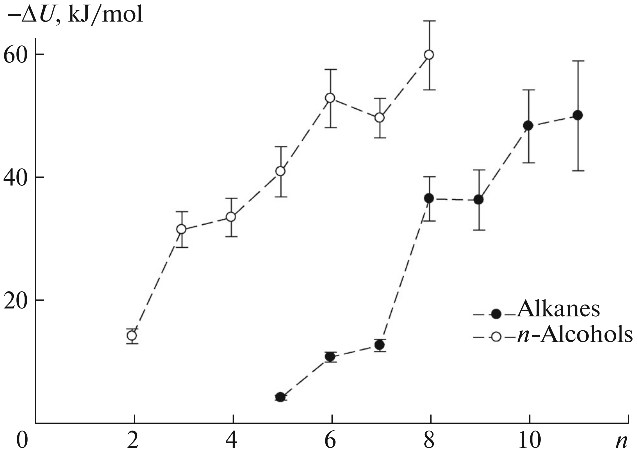

Fig. 2. Dependences of ΔU of adsorption for alkanes and alcohols on the number of carbon atoms on GCB modified with a 5-hydroxy-6-methyluracil monolayer.

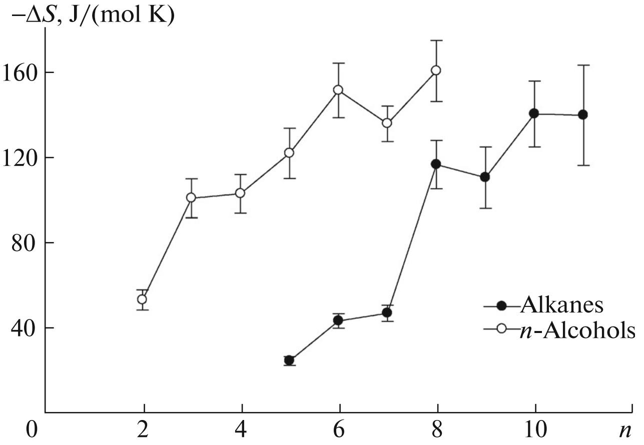

Fig. 3. Dependences of ΔS of adsorption for alkanes and alcohols on the number of carbon atoms on GCB modified with a 5-hydroxy-6-methyluracil monolayer.

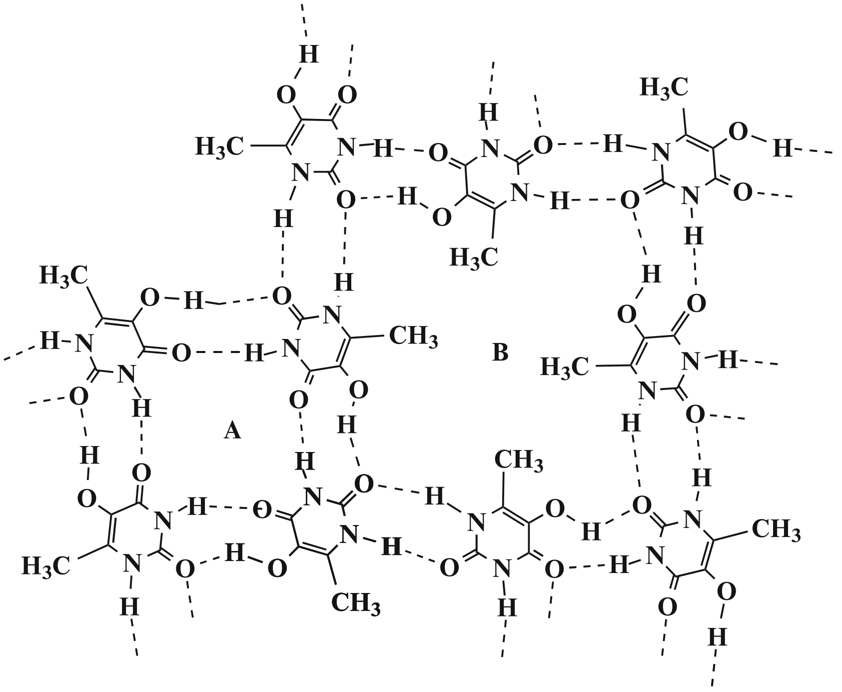

Fig. 4. Fragment of the supramolecular structure of 5-hydroxy-6-methyluracil.

compounds on the sample with 1% HMU is accompanied by a strong release of heat and a dramatic drop in entropy, compared to the HMU-monolayered adsorbent. Since the initial adsorbent was taken from the same lot, this difference can be explained only by the adsorption in the volume of HMU in the case of the sample with 1% modifier. This is possible only if the cavities of the overlaid HMU layers coincide at least partially with one another. The linear molecules of *n*-alkanes and *n*-alcohols can then permeate the HMU layers where micropore effects mainly occur: strong intermolecular interactions with micropore walls raise the energy of adsorption, while the spatial limits to adsorption help lower the entropy.

For nonlinear molecules, the molar changes in internal energy and the entropy of adsorption are lower in absolute value than for linear molecules. The values of ΔU and ΔS for *iso*-octane are thus equal to those for heptanes. *iso*-Octane therefore reacts with the sorbent's surface through seven carbon atoms only.

Table 2. Contributions (%) from different intermolecular interactions to the value of $-\Delta F$ for the adsorption of organic compounds on GCB modified with a layer of 5-hydroxy-6-methyluracil

Adsorbate	D	I + O	D/A	Adsorbate	D	I + O	D/A
Hexane	95	5	0	Propanol	58	11	31
Heptane	95	5	0	*iso*-Propanol	58	12	30
Octane	95	5	0	Butanol	60	11	29
Cyclohexane	95	5	0	*iso*-Butanol	60	11	29
Ethyl acetate	67	14	19	Benzene	89	4	7
Ethanol	54	12	34	Toluene	87	6	7

D, dispersive; I + O, inductive and orientational; D/A, donor–acceptor.

For *tert*-butanol, the thermodynamic characteristics of adsorption are remarkably lower than those for butanol and isobutanol.

The contributions from different intermolecular interactions to the Helmholtz adsorption energy are presented in Table 2. The relative conditional polarity of the surface, determined according to the procedures in [9–11], was 9.6; at the same time, it was equal to zero on the initial GCB. The deposition of the HMU layer onto the GCB thus raised the polarity of the studied adsorbent's surface. The main contribution to the increase in polarity came from the strong donor–acceptor interaction between alcohol molecules and the HMU monolayer.

CONCLUSIONS

Based on our data, it is sufficient to have one HMU layer on a GCB surface in order for the adsorption of organic molecules to be accompanied by size effects that are likely associated with the adsorption of organic molecules in the cavitites of the supramolecular structure. According to A.V. Kiselev's classification, the investigated samples could be categorized as low-polarity adsorbents of a mixed type (I + II).

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 14-03-31025 mol_a; by the RF Ministry of Education and Science as part of a Basic State Task, project no. 2522; and by a grant from the Republic of Bashkortostan for young scientists and scientific teams of 2015.

REFERENCES

1. J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives* (VCH, Weinheim, 1995).
2. H.-M. Zhang, X.-X. Zhao, L.-S. Long, et al., J. Phys. Chem. C **112**, 4209 (2008).
3. A. V. Kiselev, *Intermolecular Interactions in Adsorption and Chromatography* (Vysshaya Shkola, Moscow, 1986) [in Russian].
4. L. D. Belyakova, A. K. Buryak, and O. G. Larionov, Prot. Met. Phys. Chem. Surf. **49**, 605 (2013).
5. K. A. Kopytin, S. Yu. Kudryashov, and L. A. Onuchak, Russ. J. Phys. Chem. A **86**, 147 (2012).
6. V. Yu. Gus'kov, Yu. Yu. Gainullina, S. P. Ivanov, and F. Kh. Kudasheva, Prot. Met. Phys. Chem. Surf. **50**, 55 (2014).
7. V. Yu. Gus'kov, S. P. Ivanov, R. A. Khabibullina, R. R. Garafutdinov, and F. Kh. Kudasheva, Russ. J. Phys. Chem. A **86**, 475 (2012).
8. V. Yu. Gus'kov, Yu. Yu. Gainullina, S. P. Ivanov, and F. Kh. Kudasheva, Russ. J. Phys. Chem. A **88**, 1042 (2014).
9. V. Yu. Gus'kov, Yu. Yu. Gainullina, S. P. Ivanov, and F. Kh. Kudasheva, J. Chromatogr., A **1356**, 230 (2014).
10. F. Kh. Kudasheva, V. Yu. Gus'kov, and E. R. Valinurova, *Adsorption. Theory and Practice* (Bashkir. Gos. Univ., Ufa, 2014) [in Russian].
11. V. Yu. Gus'kov, V. E. Semenov, Yu. Yu. Gainullina, A. S. Mikhailov, and F. Kh. Kudasheva, Russ. Chem. Bull. **64**, 800 (2015).
12. S. P. Ivanov, K. A. Lysenko, O. A. Kolyadina, Z. A. Starikova, and Yu. I. Murinov, Russ. J. Phys. Chem. A **79**, 215 (2005).

Translated by L. Rocha