Thermodynamic parameters of adsorption of adamantane and its derivatives on graphitized thermal carbon black

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The adsorption equilibrium constants for adamantane, 1-fluoro-, 1-chloro-, 1,3-difluoro-, 1,3-dichloro-, 1,3-dibromo-, and 1-hydroxyadamantane, and methyl 1-adamantyl ketone were determined by gas chromatography. The results were compared with molecular statistical calculations based on the known atomic-atomic potentials of the interaction of atoms of the sorbate molecule with the C atom of graphitized thermal carbon black (GTCB). The experimental adsorption heats exceed the calculated values by 3—10 kJ mol^{-1}. The reasons for this divergence are discussed. The changes in the adsorption entropy show that the molecules of the studied compounds form a layer of the ideal dimeric gas on the GTCB surface upon adsorption.

Key words: adamantane derivatives, adsorption, graphitized thermal carbon black, molecular statistical calculations.

The chromatographic behavior of adamantane derivatives was studied by gas-liquid chromatography in several works.[1—8] Data on adsorption of nonsubstituted adamantane and diadamantane from the gas phase on graphitized thermal carbon black (GTCB) are available in the literature.

The purpose of this work is to study the adsorption of some adamantane derivatives on GTCB and compare the experimental thermodynamic parameters of adsorption obtained by gas adsorption chromatography with the results of molecular statistical calculations.

Experimental

Gas chromatographic experiments were carried out on a Tsvet-100 chromatograph (flame-ionization detector, glass column 0.75 m × 1.5 mm, Sterling MT graphitized thermal carbon black with a weight of 0.815 g, grain diameter of 0.16—0.20 mm, and specific surface of 7.6 m^2 g^{-1}). Experimental Henry's constants ($K_{1,c}$) were calculated by the formula

$$K_{1,c} \equiv V_S{}^T = (t_R - t_M)\ F_{\bar{P},T_c}/W_S s, \qquad (1)$$

where $V_S{}^T$ (cm^3 m^{-2}) is the specific retention volume of the compound per GTCB surface unit, t_R is the retention time of the adsorbate, t_M is the retention time of the nonsorbed substance (methane), W_S is the weight of GTCB in the column, s (m^2 g^{-1}) is the specific surface of GTCB, and $F_{\bar{P},T_c}$ is the flow rate of the carrier gas (N$_2$) at the pressure $\bar{P}$ (average over the column length) and temperature of the column T_c.

Measurements were carried out at temperatures from 140 to 300 °C with an interval of ~10 °C (less volatile sorbates were chromatographed at higher temperatures). The temperature of the evaporator was 50 °C higher than that of the column. Small samples of solid powders were introduced directly into the chromatographic column using a special syringe (the weight of the introduced sample was at most 0.05 mg). This made it possible to obtain chromatograms with sufficiently symmetric peaks, whose retention times were independent of the amount of the substance in the sample.

It is difficult to measure the flow rate of the carrier gas at the outlet of the column when a glass column and a flame-ionization detector are used. Therefore, the flow rate was determined at the inlet of the column by a special flowmeter at room temperature directly during the chromatographic experiment. The flowmeter consists of two chambers with sensitive elements connected by a measuring loop (a steel pipe) with the known volume $V_{\rm mes}$. During analysis, H$_2$ was periodically fed into the carrier gas flow by a dosing valve, and its passage through the flowmeter was detected. The flow rate of the carrier gas in the column was calculated by the formula

$$F_{\bar{P},T_c} = F_{P_i,T_a}\, j\, \frac{P_i T_c}{P_a T_a} = \frac{V_{\rm mes}}{\Delta t}\, j\, \frac{P_i T_c}{P_a T_a}, \qquad (2)$$

where t is the distance (in time units) between maxima of the hydrogen peaks, $V_{\rm mes}$ is the volume of the measuring loop taking into account the volume of the chambers with the sensitive elements, T_a is room temperature, P_i is the carrier gas pressure at the inlet of the column, P_a is an atmospheric pressure, and $j = \dfrac{3(P_i/P_a)^2 - 1}{2(P_i/P_a)^3 - 1}$ is the correction factor to compressibility of the carrier gas.

The flow rate of the carrier gas in the column did not exceed 6.5 cm^3 min^{-1}, which corresponds to the pressure drop $\Delta P = P_i - P_a \approx 90$—120 kPa.

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The adsorption heats and Henry's constants were calculated by the semiempirical molecular statistical theory of adsorption.[9] The previously published values of atomic-atomic potential constants of the interaction of the A atom of the sorbate molecule with the carbon atom of GTCB $\varphi_{\mathrm{A...C(GTCB)}}$ in the form of Buckingham—Corner potentials[9—15] were used. The geometry of molecules was calculated by the semiempirical quantum-chemical PM3 method, which evolved the AM1 method.[16] The polarizabilities and dipole moments of the molecules under study were determined from the results of quantum-chemical calculations (Table 1).

Results and Discussion

Table 1 contains the experimental (at 503 K) and calculated adsorption equilibrium constants $K_{1,c} = \Gamma/c$, where Γ is the adsorption (μmol cm^{-2}), c is the sorbate concentration in the gas phase (μmol cm^{-3}), and index "1" indicates Henry's region.

At 503 K the adsorption on GTCB increases in the series adamantane > 1-fluoro- > 1-hydroxy- > 1,3-difluoro- > 1-chloro- > 1,3-dichloroadamantane > methyl 1-adamantyl ketone > 1,3-dibromoadamantane. This sequence is retained in a sufficiently broad temperature interval.

The replacement of the H atom in position 1 of the adamantyl framework by the F atom is accompanied by an insignificant decrease in the polarizability of the molecule and the appearance of a dipole moment. Correspondingly, both the dispersion and induction interactions contribute to the retention of 1-fluoroadamantane and, hence, it is retained more strongly than nonsubstituted adamantane. The 1-chloroadamantane molecules, which possess a close dipole moment, but a higher polarizability, are still more strongly retained on the GTCB surface. Dihalo-substituted adamantanes also exhibit an increase in retention on going from 1,3-difluoro- to 1,3-dichloro- and 1,3-dibromoadamantane, and 1,3-difluoroadamantane is eluted faster than 1-chloroadamantane. In the case of methyl 1-adamantyl ketone, the high Henry's constant is related, most likely, to the bulky substituent MeCO, which facilitates contact of the adsorbed molecule with the GTCB surface. The methyl 1-adamantyl ketone and 1,3-difluoroadamantane molecules are close in molecular weight and dipole moment, but substantially differ in polarizability and surface area of contact with GTCB. As a result, the retention strongly increases on going from 1,3-difluoroadamantane to methyl 1-adamantyl ketone.

Table 1. Parameters of adsorptives and Henry's constants for adsorption of adamantane derivatives on GTCB

Compound	M	α/Å^3	μ/D	$K_{1,c}$/cm^3 m^{-2} (503 K)	
				Experiment	Calculation
Adamantane	136	16.80	0	0.263	0.321
1-Fluoroadamantane	154	16.71	1.88	0.324	0.338
1-Chloroadamantane	170.5	18.73	1.81	0.958	0.824
1-Hydroxyadamantane	152	17.44	1.52	0.599	0.396
Methyl 1-adamantyl ketone	178	20.56	2.69	2.71	—
1,3-Difluoroadamantane	172	16.62	2.16	0.727	0.361
1,3-Dichloroadamantane	205	20.66	1.98	2.11	2.316
1,3-Dibromoadamantane	294	22.05	2.28	5.45	4.807

As a whole, however, the main contribution to the retention of the adamantane derivatives is made by the dispersion interaction of these molecules with the GTCB surface, which is confirmed by a correlation between the logarithms of Henry's constants and polarizability of the molecules (Fig. 1). Deviations from this correlation can be related to the differences between the contributions of the induction interactions or between the surface contact of the molecule with GTCB.

The temperature plots of Henry's constants are presented in Figs. 2—4. It is seen that for adamantane, methyl 1-adamantyl ketone, 1-fluoro-, 1,3-dichloro-, and 1,3-dibromoadamantane the plots are linear, and for 1-hydroxy-, 1-chloro-, and 1,3-difluoroadamantane they are described by curves that are convex downward to the abscissa. The maximum divergence of the experimental and calculated values is observed for 1-hydroxy- and 1,3-difluoroadamantane.

To process the linear plots of $\ln K_{1,c}$ *vs.* $1/T$, we used the approximate correlation[9,10,17]

$$\ln K_1 = \bar{q}_{\mathrm{dif},1}/(RT) + \mathrm{D}\bar{S}^{\mathrm{S}\circ}{}_{1,\mathrm{c}}/R + 1 = A + B/T, \qquad (3)$$

where $\bar{q}_{\mathrm{dif},1}$ is the differential molar adsorption heat; $\Delta\bar{S}^{\mathrm{S}\circ}_{1,c} = \bar{S}^{\mathrm{S}\circ}_{1,c} - \tilde{S}^{\circ}_{\mathrm{g},S}$ is the difference between the

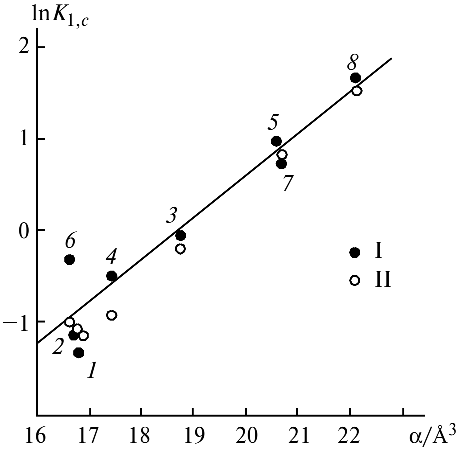

Fig. 1. Experimental (*I*) and calculated (*II*) plots of the logarithms of Henry's constants at 503 K *vs.* polarization of the adsorptives (the straight line was drawn through experimental points) for adamantane (*1*), 1-fluoro- (*2*), 1-chloro- (*3*), 1-hydroxyadamantane (*4*), methyl 1-adamantyl ketone (*5*), 1,3-difluoro- (*6*), 1,3-dichloro- (*7*), and 1,3-dibromoadamantane.

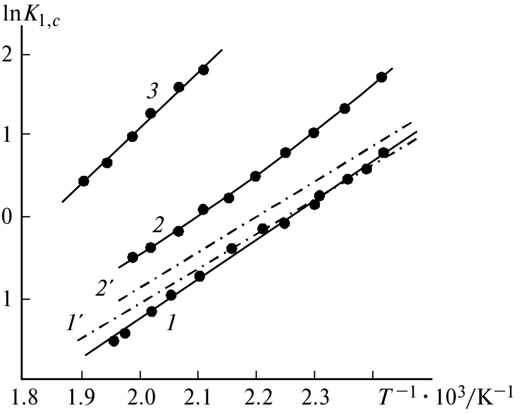

Fig. 2. Experimental (*1—3*) and calculated (*1′*, *2′*) Henry's constants at different temperatures for adamantane (*1*, *1′*), 1-hydroxyadamantane (*2*, *2′*), and methyl 1-adamantyl ketone (*3*).

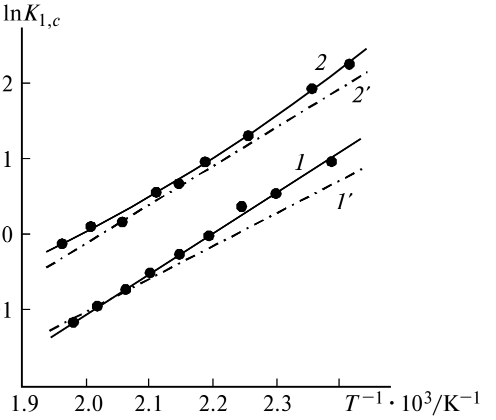

Fig. 3. Experimental (*1*, *2*) and calculated (*1′*, *2′*) Henry's constants at different temperatures for 1-fluoroadamantane (*1*, *1′*) and 1-chloroadamantane (*2*, *2′*).

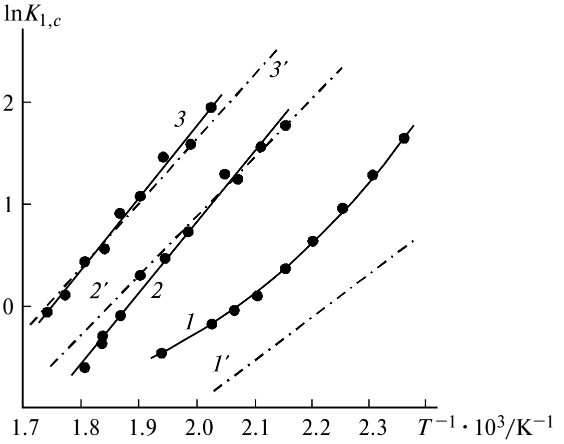

Fig. 4. Experimental (*1—3*) and calculated (*1′—3′*) Henry's constants at different temperatures for 1,3-difluoroadamantane (*1*, *1′*), 1,3-dichloroadamantane (*2*, *2′*), and 1,3-dibromoadamantane (*3*, *3′*).

standard differential entropy of an adsorbate (at the adsorption Γ = 1 μmol cm^{-2}) and the standard entropy of the adsorbate in the gas phase (at the concentration c = 1 μmol cm^{-3}).

A more complex correlation[17] was used for the nonlinear temperature plots $\ln K_{1,c}$—$1/T$

$$\begin{aligned}\ln K_1 = {} & (\bar{q}_{\mathrm{dif},1} + R\hat{T} + \Delta\bar{c}_{1,p}\hat{T})/(RT) + \\ & + [\Delta\bar{S}^{\mathrm{S}\circ}_{1,c} - \Delta\bar{c}_{1,p}(\ln\hat{T} + 1) - R\ln\hat{T}]/R + \\ & + (\Delta\bar{c}_{1,p}/R + 1)\ln T = A + B/T + C\ln T. \qquad (4)\end{aligned}$$

The coefficients of this equation are related to the thermodynamic parameters of adsorption, which are conventionally referred to the middle of the temperature interval; $\Delta\bar{c}_{1,p} = \bar{c}_{\mathrm{ads}} - \tilde{c}_{p,\mathrm{g}}$ is the difference of the differential molar thermal capacity of the adsorbate and molar thermal capacity of its vapor under a constant pressure.

The coefficients in Eq. (3) (or (4)) were found by the least-squares method from experimental Henry's constants and then used for calculation of the experimental values of the differential molar adsorption heat and change in entropy upon adsorption (Table 2).

The differential molar adsorption heat as a function of the polarizability of the adamantane derivatives is presented in Fig. 5. As a whole, an increase in the polarizability is accompanied by an increase in the differential molar adsorption heat. Thus, here we find the same tendency as that for Henry's constants. It is most likely that, as in the case of terpenes,[18,19] the retention and, correspondingly, the adsorption heats of the adamantane derivatives are determined, first, by the geometry and sizes of their molecules and to a lesser extent by the polarity of compounds. The obtained value of the differential molar adsorption heat for adamantane (40.6 kJ mol^{-1}) agrees with the published data (39.0 [8] and 41 kJ mol^{-1} [20]).

For all the compounds, we observed deviations of the calculated Henry's constants and adsorption heats from the experimental values by 3—10 kJ mol^{-1}, and $\bar{q}_{\mathrm{dif},1}$(exp.) > $\bar{q}_{\mathrm{dif},1}$(calc.). The divergence between the experimental and calculated Henry's constants is especially significant for 1-hydroxyadamantane and 1,3-difluoroadamantane.

This divergence is related, first, to the fact that we used in calculations the available constants of atomic-atomic potentials. Corrections[21] should likely be introduced into these values to take into account the nonequivalent character of the nodal and bridging C atoms of the adamantyl framework. For 1-hydroxyadamantane, one should introduce an additional correction into the atomic-atomic potential of the O atom because we used in calculations the potential of the O atom in ethers. In addition, a correction to the parameters of the atomic-atomic potentials $\varphi_{\mathrm{Hal...C(GTCB)}}$ is required because they were refined from the experimental data for halogen atoms conjugated with aromatic systems. For

Table 2. Thermodynamic parameters of adsorption of adamantane and its derivatives on GTCB

Compound	Parameters of temperature function of $\ln K_{1,c}$			ΔT	$\hat{T}$	$\bar{q}_{\mathrm{dif},1}$/kJ mol^{-1}		$-\Delta\bar{S}^{S^\circ}_{1,c}$/J mol^{-1} K^{-1}	
	$-A$	B	C	K		Experiment	Calculation[a]	Experiment	Calculation[b]
Adamantane	11.04	4884	—	414—511	463.0	40.6±1.8	35.3	100±4	111.2
1-Fluoroadamantane	11.86	5400	—	419—504	461.5	44.8±2.5	35.7	107±6	111.7
1-Chloroadamantane	227.40	19327	30.37	415—509	462.0	44.5±2.6	41.8	98±6	112.1
1-Hydroxyadamantane	163.46	14958	21.41	414—503	458.5	42.4±1.6	37.2	98±4	111.6
Methyl 1-adamantyl ketone	12.78	6931	—	474—525	499.5	57.6±5.6	—	115±11	112.6
1,3-Difluoroadamantane	396.18	30300	53.95	424—515	469.5	41.1±1.7	36.3	94±4	112.2
1,3-Dichloroadamantane	13.25	7042	—	465—554	509.5	58.6±3.4	48.7	119±7	113.3
1,3-Dibromoadamantane	12.59	7188	—	494—575	534.5	59.7±4.0	52.7	113±8	115.0

[a] Using the semiempirical molecular statistical theory of adsorption.

[b] Using formula (5) in the approximation of the ideal dimeric gas for the adsorbed substance.

1-fluoroadamantane we found satisfactory agreement between the experimental and calculated Henry's constants, whereas in the case of 1,3-difluoroadamantane, Henry's constants differ substantially, which can be related to the strong mutual influence of the F atoms.

The change in the differential molar entropy of the adsorbate on going from the gas phase to adsorbed state is an important thermodynamic parameter of sorption equilibrium. The difference between the entropies of the gaseous and adsorbed substance provides an insight into the state of the adsorbate molecules in the adsorption layer and their mobility on the adsorbent surface. Any entropy characteristics of the adsorption equilibrium reflect a change in the number and type of the degrees of freedom of molecules on going from the gas phase to the solid surface.[22] Let us restrict our consideration to the simplest molecular model in which the adsorbate—adsorbent interaction is mainly determined by van der Waals forces that act on the surface of nonspecific adsorbents at high temperature. In this case, the experimental values of a change in the differential molar entropy can be compared to those obtained by the molecular statistical theory under the assumption that the adsorbate is an ideal dimeric gas. The corresponding theoretical value was calculated by the equation, whose derivation assumed that the adsorbed molecules retained the rotational and vibrational degrees of freedom and lost one translational degree of freedom,[17,22]

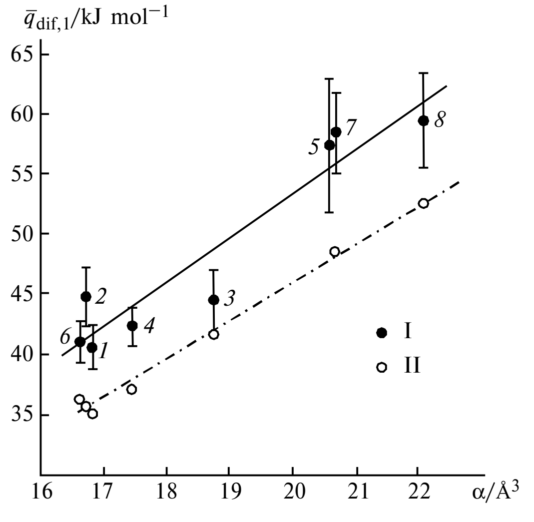

Fig. 5. Plots of the experimental (*I*) and calculated (*II*) differential molar heats of adsorption of the compounds under study *vs.* polarizability of their molecules: *1*, adamantane; *2*, 1-fluoroadamantane; *3*, 1-chloroadamantane; *4*, 1-hydroxyadamantane; *5*, methyl 1-adamantyl ketone; *6*, 1,3-difluoroadamantane; *7*, 1,3-dichloroadamantane; and *8*, 1,3-dibromoadamantane.

$$-\Delta\bar{S}^{S^\circ}_{1,c}(\text{theor.}) = R\hat{T}\ln(M\hat{T})^{1/2} + 56.95 + R, \qquad (5)$$

where *M* is the molecular weight of the adsorbent.

It can be seen from the data in Table 2 that, except for 1,3-dichloroadamantane and methyl 1-adamantyl ketone, the compounds under study obey the correlation

$$\left|-\Delta\bar{S}^{S^\circ}_{1,c}(\text{theor.})\right| \geq \left|-\Delta\bar{S}^{S^\circ}_{1,c}(\text{exp.})\right|, \qquad (6)$$

which is also observed for the majority of the described adsorbate—GTCB systems.[22—24]

Since the difference between the experimental and theoretical values of $-\Delta\bar{S}^{S^\circ}_{1,c}$ is low, the model of ideal dimeric gas gives a good approximation for the description of the behavior of the adamantane derivatives in Henry's region.

Thus, even when the semiempirical molecular statistical theory of adsorption uses unreliable structural parameters of molecules of adamantane derivatives and atomic-atomic potentials determined for non-framework compounds, it allows one to quantitatively estimate Henry′s constants and heats of adsorption. The change in entropy upon adsorption of the adamantane derivatives on GTCB can be estimated from the model of the ideal dimeric gas. The results obtained can serve as grounds for the development of procedures of the gas chromatographic separation of adamantane derivatives on GTCB and other carbon adsorbents.

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