Adsorption of adamantanol isomers on graphitized thermal carbon black

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The thermodynamic characteristics of adsorption of some adamantanol isomers on graphitized thermal carbon black were calculated and determined experimentally. The parameters of the potential function for the intermolecular interaction between hydroxyl oxygen and carbon of the graphite basis plane were determined for the first time. The adsorption properties of adamantanols are largely determined by electron density distribution in the adamantane cage, which are related to the "cage" effect.

Key words: adamantanol isomers, adsorption, thermodynamic characteristics of adsorption, molecular statistic theory of adsorption, hydroxyl hydrogen atom, "cage" effect.

An interesting aspect in the chemistry of carbocyclic compounds is the difference in the biological activity and physicochemical and chromatographic properties of 1- and 2-substituted adamantanes.[1,2]

A ^{13}C NMR-spectroscopic study of the influence of the β- and γ-effects of substituents in hydroxy-substituted adamantanes showed that the changes in the chemical shifts of the bridging and bridgehead carbon atoms depend on the energy of intramolecular nonvalence interactions within the adamantane cage.[3] It is known that adamantan-1- and -2-ols differ markedly in physicochemical properties,[4,5] reactivity,[1,6—8] and chromatographic retention on stationary phases of various polarities.[9,10] The spectral characteristics, the reactivity, and the physicochemical properties of adamantan-1-ols are related to the existence of the so-called "cage" effect, *i.e.*, the overlap of the back ends of the hybrid orbitals of the tertiary carbon atoms in the cage. This brings atoms not linked by valence bonds in contact and increases the electron density in the adamantyl unit (Fig. 1).

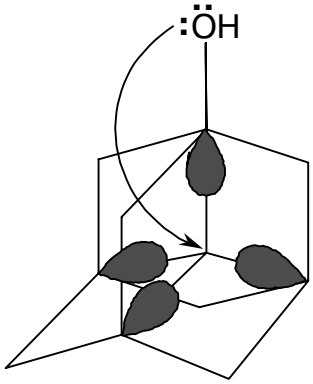

Fig. 1. Cage effect in adamantan-1-ol molecule.

The best agreement between experimental and calculated thermodynamic characteristics of adsorption (TCA) of the adamantane molecule on graphitized thermal carbon black (GTCB) is achieved by introducing a correction allowing for the cage effect in the parameters of the potential function describing intermolecular interactions of the tertiary carbon atom in the adamantane cage.[11] In this connection, it is of interest to study the chromatographic behavior of adamantan-1- and -2-ols on GTCB using the semiempirical molecular-statistic theory of adsorption, which provides a quantitative estimate of the effects of various intermolecular interactions on the TCA values. Unfortunately, no data on the parameters of atom—atom potential functions (AAP) for intermolecular interactions between hydroxyl oxygen and carbon atoms on the GTCB surface can be found in the literature. However, AAP parameters for the oxygen atoms in ether and carbonyl groups[12] and in five- and six-membered heterocyclic systems[13] have been determined; the AAP of the OH group has been proposed for the description of the chromatographic properties of some aliphatic and aromatic alcohols.[14]

The purpose of this study is to examine the influence of the cage effect on the adsorption behavior of adamantan-1- and 2-ols on GTCB and to determine the AAP parameters for the alcohol oxygen atom with a quasi-rigid structure. In addition, it is of interest to compare the AAP parameters for the oxygen atoms contained in various functional groups and to determine the influence of differences in the AAP on adsorption.

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Table 1. Experimental (I) and calculated (II) thermodynamic characteristics of adsorption of some alcohols and hydrocarbons on GTCB

Compound	ΔT/K	Constant of the equation[a]		$-\Delta\bar{U}_1$/kJ mol^{-1}			K_1 (423 K)/cm^3 m^{-2}		
		$-A$ (I)	B (I)	I		II	I		II
Propan-2-ol	313—383	10.49	3251.83	27.0[b]	28.0[c]	27.1	0.17[b]	0.16[c]	0.17
2-Methylpropane	296—326	10.45	3173.53	26.4[b]	26.4[c]	—	0.14[b]	0.14[c]	—
2-Methylpropan-2-ol	328—403	10.49	3450.42	28.7[b]	30.2[c]	27.6	0.29[b]	0.29[c]	0.29
2,2-Dimethylpropane	295—364	9.65	3118.03	26.0[b]	26.0[c]	—	0.28[b]	0.28[c]	—
2-Methylbutan-2-ol	343—423	10.53	3939.14	32.8[b]	32.7[c]	33.5	1.03[b]	1.07[c]	1.11
2,2-Dimethylbutane	323—383	9.85	3621.32	—	—	29.3	—	—	0.87

[a] The constants of the equation $\ln K_1 = A + B/T$.
[b] This work.
[c] The data were taken from the literature.[15,20,21]

Experimental

The compounds studied in this work were synthesized at the Chair of Organic Chemistry of the Samara State Technical University. The purity of compounds was checked by GC/MS.

The experimental determination of the Henry constants (K_1) for propan-2-ol, 2-methylpropan-2-ol, 2-methylbutan-2-ol, phenol (chemically pure grade), adamantan-1-ol, and adamantan-2-ol was carried out using a Tsvet-100M gas chromatograph with a flame ionization detector (N_2 as the carrier gas, flow rate 20 cm^3 min^{-1}, a 0.7 m × 1.5 mm glass micropacked column). The Sterling-MT graphitized thermal carbon black (GTCB) (specific surface area 7.6 m^2 g^{-1}, granule size 0.18—0.25 mm, weight portion of the adsorbent 0.86 g) served as the adsorbent. The substances to be analyzed were introduced from the gas phase. The experimental K_1 values and the values of differential adsorption heats ($\Delta\bar{U}_1$) were calculated using the known procedure[15] (error of the experiment ≤5%). The differential heats of adsorption ($\Delta\bar{U}_1$) were calculated from the equation

$$\Delta\bar{U}_1 = -RB. \qquad (1)$$

Table 2. Experimental (I) and calculated (II) thermodynamic characteristics of adsorption of adamantanol isomers on GTCB in the 393—473 K temperature range

TCA	Adamantan-1-ol	Adamantan-2-ol
Constant of the equation		
$-A$ (I)	11.24	11.02
B (I)	5147.94	5111.86
$-\Delta\bar{U}_1$/kJ mol^{-1}	42.8 (I)	42.5 (I)
	43.1 (II)[a]	42.2 (II)[a]
	43.5 (II)[b]	42.4 (II)[b]
	42.6 (II)[c]	—
K_1 (423 K)/cm^3 m^{-2}	2.53 (I)	2.91 (I)
	2.56 (II)[a]	2.74 (II)[a]
	2.72 (II)[b]	2.89 (II)[b]
	2.53 (II)[c]	—

[a] Without correction applied.
[b] A correction for the adsorption nonequivalence of the carbon atoms in the adamantane cage was applied.
[c] A correction for the nonequivalence of the oxygen and carbon atoms in the adamantane cage was applied.

The B parameter was found by the least-squares method from the temperature dependence of $\ln K_1$

$$\ln K_1 = A + B/T. \qquad (2)$$

Comparison of the thermodynamic characteristics of adsorption found experimentally and calculated theoretically is presented in Tables 1 and 2.

The polarizability[16] (α/Å^3) was determined using the values of molecular refraction (MR) found from the experimental refraction indices (n_D) and densities (d). The results of calculations are listed in Table 3. The atomic polarizability of the hydroxyl oxygen atom (α_O) was calculated in terms of an additive scheme in which the polarizabilities of carbon and hydrogen atoms were taken to be 0.96 and 0.43 Å^3, respectively. It can be seen from the presented data that the α_O values for three alcohols are somewhat different; therefore, the average value $\bar{\alpha}_O = 0.6580$ Å^3 found from the α_O values for propan-2-ol, 2-methylpropan-2-ol, and 2-methylbutan-2-ol was used in the molecular-statistic calculations. The geometric parameters of the compounds involved in the molecular-statistic calculation were determined by gas electron diffraction and microwave spectroscopy.[17—19]

The thermodynamic characteristics of adsorption of hydrocarbons and alcohols were taken from Ref. 15.

Results and Discussion

Data on the chromatographic properties of hydroxyl-containing compounds on GTCB have been reported in the literature.[14,20,21] An attempt at predicting the TCA

Table 3. Molecular refraction (MR), refraction index (n_D), density (d), polarizability of molecules (α_M) and oxygen (α_O) in some alcohols at ~20 °C

Compound	MR	n_D	d /g cm^{-3}	α_M	α_O
				Å^3	
Propan-2-ol	60.09	1.3771	0.7858	6.9812	0.6612
2-Methyl-propan-2-ol	74.12	1.3878	0.7887	8.7959	0.6559
2-Methyl-butan-2-ol	88.15	1.4052	0.8079	10.6168	0.6568

of some alcohols in terms of the atom—atom approximation of the molecular-statistic theory of adsorption is documented.[14] Although some authors[14] believe that alcohols are adsorbed on GTCB more weakly than the corresponding hydrocarbons, other researchers[15,20,21] insist that alcohols are adsorbed on GTCB more strongly than the related hydrocarbons. It can be seen from comparison of the experimental TCA determined in this work with the published data for the compounds under study[15,20,21] (see Tables 1, 2) that the differences between the values lie within the experimental error. However, since the TCA for alcohols are still greater than the corresponding values for hydrocarbons, it can be concluded that the OH group makes a greater energetic contribution to the total energy of adsorption of the sorbate molecule than the Me group.

The most significant contribution to the adsorption on GTCB is known to be made by dispersion forces. The energy of dispersion interaction is largely dictated by the size and polarizability of the molecules being adsorbed. In this study, the TCA were calculated using a semiempirical AAP parameter in the form of the Backinham—Corner potential:

$$\varphi = -C_1 r^{-6} - C_2 r^{-8} + B\exp(-qr) = \\ = -C_1 r^{-6}[1 + C_2/(C_1 r^2)] + B\exp(-qr), \qquad (3)$$

where C_1 and C_2 are attraction constants; B and q are the repulsion constants. The constants were calculated from the Kirkwood—Müller formulas:

$$C_1 = -6m_e c^2 \frac{\alpha_a \alpha_b}{(\alpha_a/\chi_a) + (\alpha_b/\chi_b)}, \qquad (4)$$

$$C_2 = \frac{45h^2}{32\pi^2 m_e}\alpha_a\alpha_b\left[1\Big/2\left(\frac{\alpha_b/\chi_b}{\alpha_a/\chi_a}+1\right) + 1\Big/2\left(\frac{\alpha_a/\chi_a}{\alpha_b/\chi_b}+1\right)\right], \qquad (5)$$

$$B = \frac{6C_1\exp(qr_0)}{qr_0^7}\left(1 + \frac{4C_2}{3C_1 r_0^2}\right), \qquad (6)$$

where h is the Planck constant; m_e is the mass of an electron; c is the light velocity; α is the atomic polarizability; χ is the atomic diamagnetic susceptibility; and r_0 is the equilibrium distance between the GTCB carbon atom and the corresponding atom of the adsorbate molecule.

The AAP parameters of the oxygen atom in the hydroxyl group were determined using propan-2-ol, 2-methylpropan-2-ol, and 2-methylbutan-2-ol as reference molecules. The molecules of these alcohols form no rotational isomers upon internal rotation, and the potential barrier to the internal rotation is markedly greater than the change in the potential energy of the interaction with the adsorbate surface caused by this rotation. Thus, in the calculations of the TCA on the graphite basis face, these molecules can be regarded as being quasi-rigid. The geometric parameters needed for the calculation were taken from gas electron diffraction and microwave spectroscopy data.[17,18]

Apart from the atomic polarizability α, relations (4)—(6) contain the diamagnetic susceptibility χ and the equilibrium distance r_0. The diamagnetic susceptibility for an oxygen atom incorporated in a hydroxyl group was taken from the literature[22] ($\chi_O = -7.66 \cdot 10^{-6}$ Å^3). Since no r_O values for the $O_{(OH)}...C_{GTCB}$ interaction of atoms are available, in calculation of the parameters of Eq. (3), the r_O value was varied until a satisfactory agreement between experimental and calculated TCA values was attained (Table 4). The equilibrium $O_{ketone}...C_{GTCB}$ (0.290 nm)[12] and $O_{furan}...C_{GTCB}$ (0.350 nm) distances were taken as the boundary values in the variation of r_O.[13] The best results were obtained with r_O equal to 0.316 nm. The $O_{(OH)}...C_{GTCB}$ equilibrium distance accepted in this work is approximately equal to the sum of the van der Waals radii of the oxygen (0.129 nm) and carbon (0.191 nm) atoms, which were taken from Ref. 17; this makes 0.320 nm. The potential parameters appearing in Eq. (3), which were calculated in this study using relations (4)—(6) for the oxygen atom of hydroxyl, together with the data obtained previously[12,13] for ether, carbonyl and heterocyclic oxygen atoms are listed in Table 5. The variation of the AAP describing the pair intermolecular interactions between oxygen atoms in different valence states and the graphite carbon atom is shown in Fig. 2. It can be seen that the deepest energy minimum (−0.653 kJ mol^{-1}) is observed for ketone oxygen, while the smallest (in magnitude) potential function was found for the oxygen atom in furan (−0.355 kJ mol^{-1}). The interaction of the alcohol oxygen atom with GTCB is characterized by a medium-depth energy minimum (−0.539 kJ mol^{-1}). Thus, in terms of the energy of interaction with GTCB, oxygen atoms can be arranged in the sequence $O_{ketone} > O_{alcohol} > O_{ether}$.

The reliability of the resulting AAP parameters for a hydroxyl oxygen atom could be confirmed by the possi-

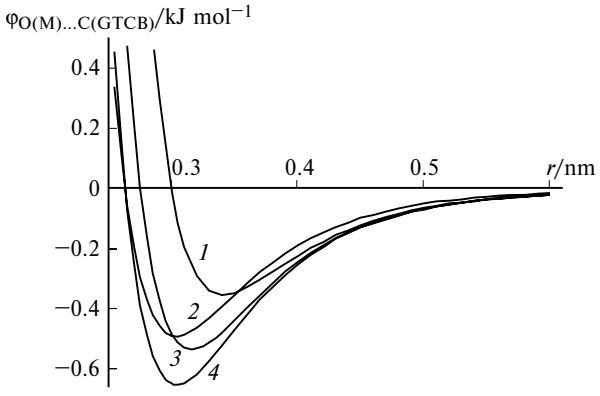

Fig. 2. Atom—atom potentials of the intermolecular interaction between the oxygen atom and the GTCB carbon atom ($\varphi_{O(M)...C(GTCB)}$) in various compounds: (*1*) furan;[12] (*2*) ethers;[11] (*3*) alcohols; (*4*) ketones.[11]

Table 4. Henry constants ($\ln K_1$) at various r_0 values for the OH...C_{GTCB} pair interactions of alcohols

r_O/ nm	2-Methyl-propan-2-ol (373 K)	2-Methyl-butan-2-ol[a] (373 K)	Adamantan-1-ol (423 K)			Adamantan-2-ol (423 K)	
			1[b]	2[c]	3[d]	1[b]	2[c]
0.290	−0.87	0.42	1.07	1.12	1.05	1.24	1.29
0.300	−1.03	0.30	1.02	1.06	1.00	1.14	1.19
0.310	−1.18	0.18	0.97	1.01	0.96	1.06	1.10
0.316	**−1.26**	**0.11**	**0.94**	**0.98**	**0.93**	**1.01**	**1.06**
0.320	−1.32	0.06	0.92	0.97	0.92	0.98	1.03
0.330	−1.45	−0.05	0.87	0.92	0.88	0.92	0.96
0.340	−1.56	−0.16	0.83	0.88	0.84	0.86	0.91
0.350	−1.67	−0.26	0.79	0.84	0.80	0.81	0.85
Experiment	**−1.26**	**0.07**		**0.93**		**1.06**	

[a] The calculation was performed for one of the possible rotation isomers of 2-methylbutan-2-ol.
[b] Without corrections applied.
[c] A correction for the adsorption nonequivalence of the carbon atoms in the adamantane cage was applied.
[d] A correction for the nonequivalence of the oxygen and carbon atoms in the adamantane cage was applied.

Table 5. Comparison of the parameters of the Backingham—Corner potential for the O(M)...C_{GTCB} pair interaction of alcohols and related compounds

O (molecule)	$C_1 \cdot 10^3$ /kJ nm^6 mol^{-1}	$C_2 \cdot 10^5$ /kJ nm^8 mol^{-1}	$B \cdot 10^{-4}$ /kJ mol^{-1}	r_O /nm
O (alcohol; adamantan-2-ol)	1.042	1.693	5.373	0.316
O (adamantan-1-ol)	0.983	1.597	5.069	0.316
O (ketone)[12]	1.066	1.464	4.630	0.297
O (ether)[12]	0.801	1.098	3.473	0.297
O (furan)[13]	1.005	1.628	7.230	0.341

bility of using them in the calculations of TCA for other adsorbates. The applicability of the AAP was verified by calculating the TCA for adamantanol isomers and comparing the results with the corresponding experimental values (see Table 2). This was done using the method of isostructural fragments, which allows simulating the structure of a molecule based on geometric data for compounds with related structures. Unsubstituted adamantane was taken as the isostructural molecule. The use of AAP of the oxygen atom in the calculations does not provide a satisfactory agreement between the calculated and experimental values for the adamantan-2-ol molecule. In the molecular-statistic calculation, the known AAP values for an sp^3-hybridized carbon atom were used for the carbon atoms of the adamantane cage.[12] Previously,[11] the non-equivalent properties of carbon atoms in the adamantane fragment was established and a correction for the AAP of the bridgehead carbon atoms was calculated. After introduction of this adjustment, an agreement between the calculated and experimental data is attained for adamantan-2-ol; however, in the case of adamantan-1-ol, the calculated TCA values are still markedly greater than the experimental ones. In the adamantan-1-ol molecule, unlike adamantan-2-ol, the electron density of the OH group is delocalized over the C—C bonds of the adamantane unit.[1,3,4,7] Therefore, in the former case, apart from the corrections for the nonequivalence of the bridgehead and bridging carbon atoms, a correction for delocalization of the electron density of the OH group is required.

The experimental and theoretical values for the thermodynamic characteristics of adsorption coincide if the correction β[15] equal to 0.943 is applied to the AAP parameters of a hydroxyl oxygen atom found for the reference molecules and applicable to adamantan-2-ol. The φ_O^* potential for the interaction of oxygen in adamantan-1-ol with the GTCB carbon atom that ensures an agreement between the calculated and experimental TAA parameters to within the experimental error (see Table 3) has the following form:

$$\varphi_O^* = -0.983 \cdot 10^{-3} \cdot r^{-6} - 1.597 \cdot 10^{-5} \cdot r^{-8} + \\ + 5.069 \cdot 10^4 \exp(-35.7 \cdot r). \quad (7)$$

Thus, the oxygen atoms in the molecules of adamantanol isomers, similarly to the carbon atoms in the adamantane cage, possess different parameters of the potential function describing the intermolecular in-

teraction with the carbon atoms of graphitized thermal carbon black. The nonadditive behavior of the atom—atom potential parameters might be due to the cage effect of the adamantane framework, resulting in an additional interaction of the OH group at the α-position with the adamantane unit.

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