Experimental and molecular-statistical investigation of adsorption of aminoadamantanes on graphitized thermal carbon black

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Thermodynamic characteristics of adsorption of some isomeric aminoadamantanes on graphitized thermal carbon black were determined by molecular-statistic calculations and gas-chromatographic measurements. The parameters of the potential function for the pairwise intermolecular interactions between nitrogen in saturated amines and carbon in graphite were calculated. The best agreement between the experimental and calculated Henry constants for 1-aminoadamantane is attained by introducting a correction taking into account the influence of the "cage" effect on α-substituents in the adamantane unit in the parameters of the $\varphi_{N...C(GTCB)}$ atom-atom potential.

Key words: aminoadamantane isomers, adsorption, gas solid chromatography, graphitized thermal carbon black, Henry constant, heat of adsorption, nitrogen atom in the amino group, atom-atom potentials, "cage" effect.

Among adamantane derivatives, aminoadamantanes possessing a broad spectrum of biological activities are encountered most frequently and have found the widest practical use.[1—10] The advances in the synthetic chemistry of adamantane derivatives have resulted in the development of a number of adamantane-containing analogs of natural alkaloids.[10] When comparing the biological activities of 1- and 2-substituted adamantanes, including amino derivatives, it can be found that 1-derivatives exhibit higher biological activities.[11] Apparently, this is related to the features of geometric and electronic structures of the adamantyl group and to different effects of the adamantane unit on bridging and bridgehead substituents.[12,13] The permeability and adsorption of adamantane derivatives on cell membranes dictate the direction and the efficiency of biological action;[2,5,11,12] therefore, it is of interest to study the influence of the position of the amino group, which is the pharmacophore used most frequently in medicinal adamantane derivatives, on the adsorption properties of the compounds. In addition, the increasing interest in the chemistry of aminoadamantanes requires that reliable methods for their identifications in mixtures of various origins be developed. Currently, gas chromatography on various stationary phases holds the key position in the analysis of adamantane and its derivatives.[13—16]

The 1- and 2-aminoadamantane isomers are model adsorbates for investigation of the influence of the geometric and electronic structures of amino-substituted hydrocarbons with framework structures on their adsorption behavior on the surface of graphitized thermal carbon black (GTCB).

Thermodynamic characteristics of adsorption (TCA) on the GTCB surface are largely determined by the geometric structure and polarizability of the adsorbate molecules. Due to the high sensitivity of TCA to the positions of functional groups in the corresponding structural isomers, high selectivity of the chromatographic separation of isomers on columns with GTCB can be attained. In addition, owing to the high sensitivity of TCA to the valence state of atoms in a molecule adsorbed on a GTCB surface, this adsorbent can be used to separate representatives of various classes of organic compounds.

This work deals with a gas-chromatographic study of the influence of electronic and geometric structures of mono- and diaminoadamantane isomers on their adsorption on the GTCB surface. In addition, the parameters of the atom—atom potential functions (AAP) for the pairwise intermolecular interactions (IMI) in the adsorbate—adsorbent system for the N atoms in saturated amines were determined and molecular-statistic calculations of the thermodynamic characteristics of aminoadamantane adsorption on GTCB were performed.

Experimental

Gas chromatography was carried out on a Tsvet-100M gas chromatograph with a flame ionization detector; nitrogen was

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used as the carrier gas; flow rate 20 cm^3 min^{-1}. The separation was carried out on a glass micropacked column, 0.7 m × 1.5 mm. The Sterling-MT graphitized thermal black (GTCB) (0.86 g) with a specific surface area of 7.6 m^2 g^{-1} and a pellet size of 0.18—0.25 mm was used as the adsorbent. Aminoadamantanes were introduced into the chromatograph as solutions in hexane, which was used as the extractant to isolate pure amines from alkaline aqueous solutions (3 *M*) of their hydrochlorides. The reference adsorbate, 2-methyl-2-propylamine (b.p. 46.4 °C), used to determine the AAP of the N atom in the amino group, was introduced from the gas phase. The experimental values of Henry constants (K_1) were determined by a known procedure,[17] and the molar differential heats of adsorption ($\Delta\bar{U}_1$) were found using the relation[17]

$$\ln K_{1,C} = A + B/T = (\Delta\bar{S}_1 + R)/R - \Delta\bar{U}_1/(RT), \qquad (1)$$

where *A*, *B* are the coefficients that account for the change in the entropy (ΔS) and in the internal energy (ΔU) upon adsorption.

The error of the gas-chromatographic experiment did not exceed 3.5%.

The semiempirical molecular-statistic calculations of TCA for the 2-methyl-2-propylamine, 1- and 2-aminoadamantane, and 1,2-, 1,3-, *cis*-1,4-, and *trans*-1,4-diaminoadamantane molecules were done using the adamantanol isomers as examples.[18] The AAP IMI parameters of the C, H, and N atoms in the adsorbate with the C atoms of the graphite basal face, needed to calculate the TCA, were chosen in the Backingam—Corner potential form[17]

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

where C_1 and C_2/kJ nm mol^{-1} are parameters of the attraction forces; and B/kJ mol^{-1} and q/nm are parameters of the repulsion forces.

The atomic polarizability of nitrogen in the amino group (α_N/m^{-30}) was calculated on the basis of experimental data on the molecular refraction (MR) of the reference 2-methyl-2-propylamine molecule.[19] The diamagnetic susceptibility of nitrogen (χ_N/m^{-36}) was taken from a handbook.[20] The geometric parameters of molecules of compounds under study were obtained by gas electron diffraction analysis[21,22] or determined using isostructural fragments.[23] The data used in the calculations of the AAP parameters for the N atoms in saturated amines are presented below

Atom	$\alpha \cdot 10^{-30}$	$\chi \cdot 10^{-36}$	$r_{N...C(ГТС)}$/nm	
	m^3		I	II
N (amine)	1.576	−9.25	0.360	0.415
C (graphite)*	0.937	−10.54		

Note. I — present work. II — see Ref. 25 * See Ref. 17

The GC/MS experiment was carried out on a JMS-D300 instrument with an HP-5980 chromatograph. The mass chromatogram was obtained from chromatograms recorded for the total current using a standard procedure.

Results and Discussion

Table 1 lists the experimental TCA values for the 1- and 2-aminoadamantane isomers determined on a column with GTCB. The plot of the logarithm of the Henry constant *vs.* reciprocal temperature for 1- and 2-aminoadamantanes constructed on the basis of ten points was approximated by a linear dependence.[17] The close values of the entropy terms *A* in Eq. (1) indicate that on passing from the gas phase to the adsorbed state, the adsorbate molecules lose the same number of degrees of freedom. However, since the molar heats and entropies of adsorption for 1- and 2-derivatives of adamantane are somewhat different, the $K_{1,C}$ values are sensitive to the position of functional groups in the adamantane cage. The lower $K_{1,C}$ value found for the 1-aminoadamantane molecule compared to $K_{1,C}$ for 2-aminoadamantane implies that the 1-isomer should be eluted first from a chromatographic column with GTCB; this is actually observed in experiments on chromatography of a mixture of these isomers. Figure 1 shows the chromatogram for the separation of a mixture of 1- and 2-aminoadamantane isomers on a micropacked column with GTCB. Thus, on the basis of experimental data, it can be concluded that adsorption of aminoadamantane isomers on GTCB is largely dependent on the position of the amino group in the adsorbate mol-

Table 1. Calculated (I—III) and experimental TCA values of some aminoadamantanes on GTCB (373—493 K)

Compound	$\ln K_{1,C} = A + B/T$		$-\Delta\bar{U}_1$/kJ mol^{-1}				$\ln K_{1,C}$ (423 K)/cm^3 m^{-2}			
	$-A$*	B*	Experiment	I	II	III	Experiment	I	II	III
1-Aminoadamantane	11.24	5256	43.7	43.8	44.0	43.6	1.19	1.24	1.29	1.19
2-Aminoadamantane	11.32	5401	44.9	44.6	44.7	—	1.45	1.41	1.46	—
1,2-Diaminoadamantane	—	—	—	45.7	45.8	45.5	—	2.31	2.35	2.29
1,3-Diaminoadamantane	—	—	—	47.2	47.4	46.7	—	2.44	2.48	2.34
cis-1,4-Diaminoadamantane	—	—	—	45.7	45.9	45.5	—	2.39	2.44	2.38
trans-1,4-Diaminoadamantane	—	—	—	49.2	49.4	49.0	—	2.69	2.74	2.68

Note. Calculations: I, without corrections; II, with a correction for the adsorption nonequivalence of the C atoms in the cage; III, with a correction for the nonequivalence of N atoms as well as the C atoms in the cage.
* Experiment.

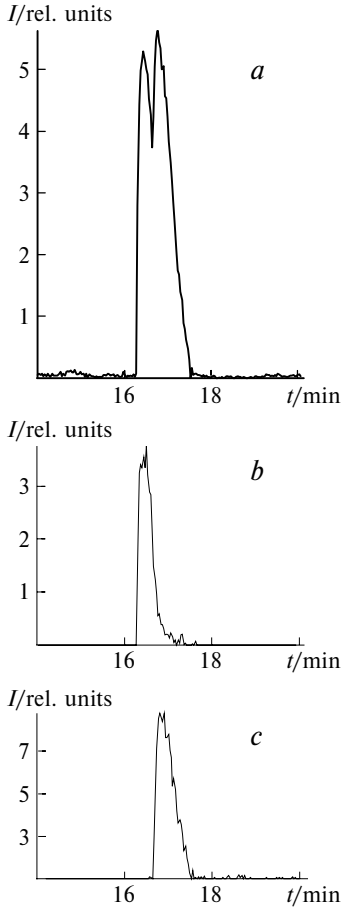

Fig. 1. Chromatogram of separation of a mixture of 1- and 2-aminoadamantanes on a micropacked column with GTCB (*a*) based on total ion current and characteristic ions (*b*) of 1-aminoadamantane (95) and 2-aminoadamantane (150).

ecule and that GTCB is suitable for satisfactory separation of these compounds under conditions of gas chromatography (see Fig. 1).

The correctness of the TCA values found for aminoadamantanes could be verified reliably by semiempirical molecular-statistic calculations. These calculations would allow one to determine the TCA for aminoadamantane molecules that are difficult to prepare or have not been synthesized yet. However, it is difficult to carry out these calculations for the amines of the adamantane series because no AAP values for the intermolecular interaction of the nitrogen atom in the amino group with the carbon atom of the graphite basal face can be found in the literature.

Data on the adsorption behavior of saturated[24] and aromatic[24,25] amines in gas chromatography on GTCB have been reported. The AAP parameters for the N(arom. amine)...C(GTCB) pairs of the interacting atoms were determined[25] and employed in the molecular-statistic calculations of TCA for aniline, 1- and 2-naphthylamines, and phenylenediamine isomers. However, this AAP parameter is inapplicable for the calculation of TCA of the *o*-phenylenediamine molecule because the calculated and experimental values of the Henry constants are found to deviate markedly from each other (*ortho*-effect).[23] It can be assumed that the differences between the chemical and physicochemical properties of saturated and aromatic amines caused by the nearest environment and the valence state of the N atom in the amino group would substantially influence the AAP parameters for the N atoms in the molecules of the corresponding amines. The assumption concerning the considerable differences between the AAP parameters of the N atoms in saturated and aromatic amines is consistent with the previously obtained data on the dependence of the AAP for the C and O atoms on their electronic configurations.[13,17,18]

The quasi-rigid 2-methyl-2-propylamine (*tert*-butylamine) molecule was chosen as the reference molecule for determination of the AAP parameters. The TCA values for *tert*-butylamine found experimentally in this work are presented below.

Parameter	Experiment	I	II	III
$-\Delta\bar{U}_1$/kJ mol^{-1}	29.0	28.0	25.4	29.1
$\ln K_{1,C}$ (373 K)/cm^3 m^{-2}	−1.00	−0.76	−1.52	−1.00

Note. I is calculation with the AAP;[25] II is the calculation with the AAP found in this work for $r_{N...C(GTCB)}$ = 0.415 nm; III is the calculation with the AAP found in this work for $r_{N...C(GTCB)}$ = 0.360 nm. The *A* and *B* parameters in Eq. (1) are −10.25 and 3488, respectively.

The resulting TCA values are in good agreement with the data obtained previously.[24] When the nitrogen AAP proposed for aromatic amines (Table 2, I) is used in the molecular-statistic calculations of TCA of *tert*-butylamine, the resulting molar differential heats of adsorption are comparable with the experimental results. However, the calculated and experimental Henry constants are markedly dissimilar; this precludes the use of the AAP of nitrogen proposed for aromatic amines for the description of the adsorption properties of *tert*-butylamine on GTCB.

Using known Kirkwood—Müller quantum-chemical formulas[17] and the electron diffraction data on the

Table 2. AAP parameters for q = 35.7 nm^{-1} for the N atom in amines determined in Ref. 25 (I) and calculated in this work for various r (I, II)

Calculation	$C_1 \cdot 10^3$ /kJ nm^6 mol^{-1}	$C_2 \cdot 10^5$ /kJ nm^8 mol^{-1}	$B \cdot 10^{-5}$ /kJ mol^{-1}
I	3.190	4.850	7.680
II	1.684	4.055	4.304
III	1.684	4.055	1.719
IV	1.583	3.812	1.616

Note. II, $r_{N...C(GTCB)}$ = 0.415 nm; III, $r_{N...C(GTCB)}$ = 0.360 nm; IV, the correction β = 0.94 for the cage effect in 1-aminoadamantane was applied.

geometry of the reference molecules in the gas phase,[21] in this work, we calculated the AAP parameters of the N atom in the 2-methyl-2-propylamine molecule. The equilibrium distance r_0 for the N(NH_2—)...C(GTCB) pair of interacting atoms needed for the calculations was taken from a study published previously.[25] The resulting (II) AAP parameters are listed in Table 2. The use of the determined AAP for the calculation of TCA of 2-methyl-2-propylamine did not provide a satisfactory agreement between the experimental and calculated $K_{1,C}$ values either (see above). Apparently, the observed discrepancy is due to the fact that the r_0 value (0.415 nm) used in the calculation of AAP parameters is somewhat overestimated because it poorly agrees with the sum of the van der Waals radii (r_v) of the nitrogen (0.150 nm)[26] and GTCB carbon (0.191 nm)[17] atoms, which is equal to 0.341 nm. The overestimated r_0 value results in an overestimated value for the parameter B of the universal repulsive forces in the expression (2) for the Backingam—Corner potential. Thus, the TCA values obtained for *tert*-butylamine should be lower than those determined experimentally, and that is actually observed when comparing the calculated and experimental results (see above).

Let us attempt to determine the r_0 value by comparing the experimental $K_{1,C}$ values with those calculated theoretically for various equilibrium distances r_0 and various parameters C_1 and C_2 for the attractive forces in the Backingam—Corner potential (2). It can be seen from Table 3 that the best agreement between the experimental and theoretical $K_{1,C}$ values is attained for r_0 = 0.360 nm, which is in good agreement with the data obtained by summing the r_v values for the N and C atoms. Thus, the semiempirical molecular-statistic theory of adsorption allows one to calculate the AAP parameters of the N atoms in saturated amines that provide a satisfactory description of the adsorption properties of the reference molecule, 2-methyl-2-propylamine, on the GTCB surface (see Table 3, III). The AAP values found for the N atom in *tert*-butylamine differ from those determined previously for nitrogen in aromatic amines; this is yet another piece of evidence supporting the assumption that the AAP parameters of nitrogen depend on its electronic configuration.

Table 3. Values $\ln K_{1,C}$ ($cm^3\ m^{-2}$) calculated (I—III) at different $r_{N...C(GTCB)}$

r_0 /nm	2-Methyl-2-propylamine (373 K)	1-Aminoadamantane (423 K)			2-Aminoadamantane (423 K)	
		I	II	III	I	II
0.341	−0.73	1.35	1.39	1.27	1.52	1.54
0.345	−0.79	1.33	1.38	1.26	1.49	1.52
0.350	−0.87	1.31	1.36	1.24	1.47	1.50
0.355	−0.94	1.30	1.34	1.23	1.45	1.47
0.360	**−1.00**	**1.28**	**1.32**	**1.21**	**1.42**	**1.45**
0.365	−1.07	1.26	1.31	1.20	1.40	1.43
0.370	−1.13	1.24	1.29	1.18	1.37	1.41
0.375	−1.18	1.22	1.27	1.17	1.34	1.38
0.380	−1.23	1.21	1.25	1.16	1.31	1.36
0.415	−1.52	1.07	1.12	1.05	1.19	1.24
Exp.	**−1.00**		**1.20**		**1.45**	

Note. I, without corrections; II, with a correction for the adsorption nonequivalence of the C atoms in the cage; III, with a correction for the nonequivalence of N atoms as well as the C atoms in the cage.

The data presented in Table 1 indicate that the AAP parameters determined for the N atom in *tert*-butylamine are applicable only to the description of adsorption of 2-aminoadamantane. In this case, only one adjustment to the AAP parameters of the C atoms of the adamantane unit is needed to take into account the nonequivalence of the bridgehead and bridging C atoms,[13,18] related to the existence of the cage effect[12,13,18,27] (Fig. 2). However, the introduction of this correction does not provide a satisfactory agreement between the theoretical and experimental TCA for 1-aminoadamantane. The role of the cage effect in the physicochemical behavior of aminoadamantane isomers has been described in detail in the literature.[13,27—30] It is known that, due to the direct influence of the adamantyl group on the amino group in position 1 of the adamantane cage, the electron density on the N atom is markedly decreased and, hence, the 1-aminoadamantane molecule is less polarizable than the 2-aminoadamantane molecule.[13,27—30] Apparently, the lower polarizability of the 1-isomer accounts for the observed order of elution of aminoadamantane isomers from the column with GTCB. Using the algorithm for introducing an adjustment in the AAP parameters of the O atom in the α-position of the adamantane cage proposed previously,[18] we can determine more precisely the corresponding AAP values for the N atom in 1-aminoadamantane. The correction factor β for the parameters of the reference AAP of the N atom in 1-aminoadamantane is 0.94. The AAP corrected in this way provides a satisfactory agreement between the calculated and experimental TCA values for 1-aminoadamantane (see Table 1). Table 3 contains (IV) the

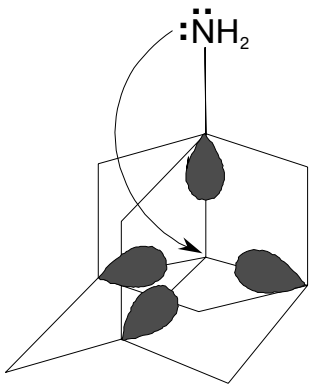

Fig. 2. Cage effect in 1-aminoadamantane molecule.

AAP parameters for the N atoms in the 1-aminoadamantane molecule. Note that the $K_{1,C}$ values for different r_0, calculated with the adjustments introduced to take into account the specific features of the electronic structure of the adamantane cage are also equal to the experimental values at the equilibrium distance, equal to 0.360 nm (see Table 3). This, apparently, can also serve as a criterion for the reliability of the AAP parameters found for the N atom in saturated amines. Thus, in the adsorption of aminoadamantane isomers on the GTCB surface, both the cage C atoms and the N atoms in different positions of the molecule are nonequivalent.

Table 1 gives the TCA for the following diamines of the adamantane series: 1,2-, 1,3-, *cis*-1,4-, and *trans*-1,4-diaminoadamantanes. The molecular-statistic calculations were performed with introduction of various adjustments to the AAP parameters for the C and N atoms. The calculation gives different TCA values for the molecules of diaminoadamantane isomers; this may indicate the possibility of separating them by gas chromatography on a column with GTCB. In some cases, the order of elution of isomers from the chromatographic column can change depending on the type of correction introduced to the AAP parameters. Indeed, if the molecular-statistic calculation of TCA is carried out without corrections for the nonequivalence of the C and N atoms, the following order of elution of the isomers is expected: 1,2-, *cis*-1,4-, 1,3- and *trans*-1,4-isomers. More accurate determination of the AAP parameters of the bridgehead C atoms in the adamantane cage does not change the order of elution. However, when the correction for the adsorption nonequivalence of the C and N atoms in the 1- and 2-amino groups of the adamantane cage is applied, the order of elution of diaminoadamantanes becomes as follows: 1,2-, 1,3-, *cis*-1,4-, and *trans*-1,4-isomers. In view of the additive character of TCA on the GTCB surface, the calculated TCA values of diaminoadamantanes can be considered to be reliable because all the main features of the molecular structure have been taken into account.

However, the use of additive schemes for the calculation of TCA of cage adamantane derivatives is complicated by the fact that, depending on the position of the substituent in the adamantane cage, identical molecular fragments can make different contributions to one or another thermodynamic parameter because the crucial role in adsorption is played by the arrangement of the bulky adamantyl group on the planar GTCB surface.

The increments of the heats of adsorption ($\Delta(-\Delta\bar{U}_1)$/kJ mol^{-1}) introduced by amino groups in different positions of the adamantane cage are listed in Table 4. The $\Delta(-\Delta\bar{U}_1)$ values were calculated using the experimental heats of adsorption for 1- and 2-aminoadamantanes and for the nonsubstituted adamantane (40 kJ mol^{-1}).[13] For molecules that are adsorbed with the amino group located most closely to the GTCB surface, the increments of the corresponding heats of adsorption coincide to within the error of gas-chromatographic experiment. For example, in 1-amino-, 1,3-, and *trans*-1,4-diaminoadamantane molecules, the contribution made by the NH_2 group in position 1 is, on average, 3.6±0.6 kJ mol^{-1}, while in 2-amino- and *trans*-1,4-diaminoadamantane molecules, the increment of the NH_2 group in position 2 is 5.0±0.3 kJ mol^{-1}. In 1,2- and *cis*-1,4-diaminoadamantane molecules, the increments of the NH_2 groups are much lower, 0.6 and 1.8 kJ mol^{-1} for positions 1 and 2, respectively. These low $\Delta(-\Delta\bar{U}_1)$ values are explained, apparently, by a specific arrangement of these molecules on the GTCB surface. The $\Delta(-\Delta\bar{U}_1)$ values of the NH_2 groups in position 1 are lower than the corresponding values for the NH_2 groups in position 2 of the adamantane cage. This might be due to the nonequivalence of N atoms in positions 1 and 2 of the adamantyl group caused by

Table 4. Comparison of the increments of amino groups to the heat of adsorption of aminoadamantane isomers on GTCB found from experimental and theoretically calculated (I—III) data

Compound	$\Delta(-\Delta\bar{U}_1)$/kJ mol^{-1}							
	Experiment		I		II		III	
	1-NH_2[a]	2-NH_2[b]	1-NH_2	2-NH_2	1-NH_2	2-NH_2	1-NH_2	2-NH_2
1-Aminoadamantane	3.7	—	3.8	—	4.0	—	3.6	—
2-Aminoadamantane	—	4.9	—	4.6	—	4.7	—	4.7
1,2-Diaminoadamantane	—	—	0.8	2.0	0.9	2.1	0.6	1.8
1,3-Diaminoadamantane	—	—	3.5	—	3.7	—	3.0	—
cis-1,4-Diaminoadamantane	—	—	0.8	2.0	1.0	2.2	0.6	1.8
trans-1,4-Diaminoadamantane	—	—	4.3	5.5	4.5	5.7	4.1	5.3

Note. Calculations: I, without corrections; II, with a correction for the adsorption nonequivalence of the C atoms in the cage; III, with a correction for the nonequivalence of N atoms as well as the C atoms in the cage.

[a] The contribution made by the NH_2 group in position 1 of the cage.

[b] The contribution made by the NH_2 group in position 2 of the cage.

different influences of the cage effect on substituents in the bridgehead and bridging positions.

Thus, the TCA values for aminoadamantane isomers found in this study lead to the conclusion that nonporous carbon adsorbents like GTCB can be used to analyze these compounds by gas chromatography. The AAP parameters of the N atoms in saturated amines can be used to perform molecular-statistic calculation of TCA on the graphite surface, which provide data comparable with experimental results. The cage effect in adamantane accounts for the adsorption nonequivalence of the N atoms in aminoadamantane isomers; it should be taken into account in molecular-statistic calculations.

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