The cell effect in adamantane adsorption on graphitized thermal carbon black

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Nonequivalence of the nodal and bridging carbon atoms of the adamantane molecule during adsorption on graphitized thermal carbon black was shown. The nonequivalence is related to a special type of intermolecular interaction, the cell effect. Based on the experimental data and the molecular statistical calculations of Henry's constants, the parameters of atom-atom potentials for the nodal carbon atoms in the adamantane molecule were found. This atom-atom potential differs from that known for the carbon atom in the sp^3-hybridization.

Key words: adamantane, adsorption, cell effect, graphitized thermal carbon black, molecular statistical calculation, atom-atom potential, Henry's constant.

Despite achievements in studying the physicochemical properties of adamantane and its derivatives, several questions concerning the specific features of the geometric and electronic structure of the adamantane framework remain unclear.[1,2] These features are distinctly manifested in the chromatographic properties of adamantane derivatives, in particular, a noticeable difference in retention of 1- and 2-substituted adamantanes. It has been assumed[3,4] that the so-called cell effect is a possible reason for the observed distinctions (Fig. 1). The essence of this intramolecular interaction, unusual for saturated cyclic systems, is overlapping of the rear sides of hybrid orbitals of tertiary carbon atoms in the framework, resulting in the direct contact of valence-unbound atoms and an increase in the electron density in the adamantyl cycle.[1] Either direct or indirect evidence for a possibility of a similar intramolecular electron interaction are available in the literature. Among them the following facts are most substantial: the higher stability of the tertiary carbocation and, as a consequence, the different chemical reactivities of the nodal and bridging carbon atoms of the framework[5]; the difference in charges on the tertiary (+0.18 C) and secondary (−0.09 C) carbon atoms in the adamantane molecule[6]; the slight deviation of bond angles in the adamantane framework from the ideal tetrahedral values[7]; the valence state of the nodal carbon atoms that differ from sp^3-hybridization[8]; the strong screening effect of the adamantane cycle on the α-substituents in the lateral chain that appears in the NMR spectra[9]; and unusually high dipole moments (especially for 1-derivatives) as compared to those of *tert*-butyl analogs, and others.[1,10]

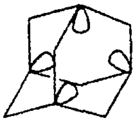

Fig. 1. Cell effect in the adamantane molecule.

Each property presented above is unusual for a saturated compound and is based on the unique geometric structure of the rigid adamantane framework and the character of electron density distribution in it. These peculiarities are as yet almost unstudied in detail.

It is known[11] that the thermodynamic characteristics of adsorption of organic molecules on the surface of a uniform, planar, and nonspecific adsorbent, graphitized thermal carbon black (GTCB), depend mainly on their geometric structure and polarizabilities of the molecular fragments. It was of interest to determine experimentally the thermodynamic parameters of adamantane adsorption on GTCB and estimate the influence of changing the geometric and electronic structure of this compound, which appears under the cell effect, on the adsorption by comparison of the experimental data with the results of semiempirical molecular statistical calculations. The calculation and experimental determination of Henry's constants are of special interest, because these values make it possible to monitor even insignificant changes in the geometric structure of adsorbent molecules and study the influence of the electronic structure on the character of intermolecular interactions during adsorption. Adamantane adsorption on GTCB has previously[12] been studied experimentally and by molecular statistics. A satisfactory agreement between the experiment and calculation was obtained only in the high-temperature region. Therefore, in this work, we

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determined once more the experimental values of Henry's constants in the low-temperature region where the probability of experimental errors increases and calculated the thermodynamic parameters of adsorption using the known and new (taking into account the cell effect) atom-atom potentials.

Experimental

Experiments on determination of Henry's constants (K_1) for adamantane were carried out on a Tsvet-100M gas chromatograph (flame-ionization detector, N_2 as the carrier gas, flow rate 24 cm^3 min^{-1}). A glass micropacked column 0.70 m × 1 mm packed with graphitized thermal black (trademark Sterling, specific surface 7.6 m^2 g^{-1}, weight 0.364 g) was used. A fraction of carbon black with a particle size of 0.20—0.25 mm was taken for packing the column. Experimental K_1 values were calculated by a known procedure.[11,12] The error in determination of Henry's constants was 1.5%.

Molecular statistical calculation of K_1 was performed by the algorithm described previously.[11] The obtained experimental and calculated K_1 values are presented in Tables 1—3. The geometric parameters of the molecule were either taken from the literature[7] or accepted to be equal to the ideal values of bond angles (109.5°) and bond lengths. To compare the experimental and calculated Henry's constants, correction factors obtained by different methods were introduced into the known atom-atom potentials (AAP).[11,14] Parameters of the dependences of the correction factor β on various molecular characteristics, which were plotted in the work, were determined by the least-squares method.

Results and Discussion

The adamantane molecule has a rigid geometric structure, free of conformational transformations, whose carbon atoms are nonequivalent due to the cell effect. Owing to this, it is an interesting object for calculations using the semiempirical molecular statistical theory of adsorption. According to this theory, the intermolecular interaction of the adsorbate with the adsorbent surface is described in the atom-atom approximation. The atoms that form the adsorbate molecule and adsorbent surface are considered as fixed force centers whose interaction is due to dispersion, induction, and electrostatic attraction forces and universal repulsion forces. The quantitative characteristics of interaction of the force centers in the adsorbate—adsorbent system is the AAP — the atom-atom potentials of intermolecular

Table 1. Comparison of Henry's constants and adsorption heats (coefficients in the equation $\ln K_1 = A + B/T$; $\ln K_1$, $-\Delta U$) of adamantane on graphitized thermal carbon black

Parameter	Published data[12]		Data of this work	
	experiment	calculation	experiment	calculation
$-A$	10.72	—	11.37	—
B	4707	—	4925	—
$\ln(K_1/\mathrm{cm^3\ m^{-2}})$*	2.43	2.28	2.42	2.28
$-\Delta U$/kJ mol^{-1}	39.1	38.8	41.0	40.6

* At 358 K.

Table 2. Experimental and calculated Henry's constants K_1 ($\ln K_1$) at different temperatures for adamantane adsorption on graphitized thermal carbon black obtained by different methods*

T/K	$\ln(K_1/\mathrm{cm^3\ m^{-2}})$			
	experiment		calculation	
	A	B	C	D
333	3.42	3.42	3.19	3.30
338	3.20	3.21	3.00	3.10
343	3.00	3.00	2.81	2.91
348	2.80	2.81	2.63	2.72
353	2.61	2.61	2.45	2.53
358	2.42	2.43	2.28	2.35
363	2.25	2.25	2.12	2.18
368	2.08	2.07	1.96	2.01
373	1.91	1.90	1.80	1.85
378	1.75	1.74	1.65	1.69
383	1.59	1.57	1.50	1.53
388	1.41	1.41	1.35	1.38
393	1.25	1.25	1.21	1.24
398	1.10	1.10	1.08	1.09
403	0.96	0.96	0.94	0.96
408	0.82	0.82	0.81	0.82
413	0.68	0.68	0.69	0.69
418	0.55	0.54	0.56	0.56
423	0.44	0.43	0.44	0.44

* *A* are the experimental values obtained in this work; *B* are the experimental data in Ref. 12; *C* are the values calculated under the assumption of ideal (tetrahedral) angles in the adamantane molecule (see Ref. 7); and *D* are the values calculated using the geometric parameters obtained by the electronographic method.[12]

Table 3. Henry's constants ($\ln K_1$) for adamantane adsorption calculated by the semiempirical molecular statistical method* using the geometric parameters obtained from the electronographic data[14]

T/K	$\ln(K_1/\mathrm{cm^3\ m^{-2}})$			
	A	B	C	D
333	3.37	3.31	3.34	3.37
353	2.59	2.54	2.56	2.59
373	1.90	1.85	1.87	1.90
393	1.29	1.24	1.26	1.29
413	0.74	0.69	0.71	0.74
423	0.48	0.44	0.46	0.48

* *A* is the correction coefficient β determined by matching of the experimental and calculated data[12] (method I); *B* is β = 1.002 (by the formula proposed in Ref. 15 (method II)); *C* is β = 1.01 (by Eq. (5)); and *D* is β = 1.019 (by Eq. (6), method III).

interaction (φ) depending on the valence state of the atom and its environment in the molecule.[11]

Published data on adsorption of adamantane and its derivatives are rather scarce. The K_1 constants for the adamantane molecules have been experimentally determined and theoretically calculated.[12] The calculation used the semiempirical Buckingham—Korner AAP for C and H atoms obtained previously[11] for adsorption of alkanes (alk) on graphite (gr):

$$\varphi_{\mathrm{H(alk)...C(gr)}} = -0.498 \cdot 10^{-3} \cdot r^{-6} - 0.950 \cdot 10^{-5} \cdot r^{-8} + 3.600 \cdot 10^{4} \cdot \exp(-35.7r), \quad (1)$$

$$\varphi_{\mathrm{C(alk)...C(gr)}} = -1.386 \cdot 10^{-3} \cdot r^{-6} - 2.148 \cdot 10^{-5} \cdot r^{-8} + 1.890 \cdot 10^{5} \cdot \exp(-35.7r), \quad (2)$$

where φ values are expressed in kJ mol^{-1}, and r is the distance from the adsorbent surface in nm. The C—C bonds in the adamantane molecules were assumed in the calculation to be 0.154 nm, and all angles were assumed to be 109.5° (an ideal molecular structure).

The authors of Ref. 12 achieved an agreement between the experimental and calculated K_1 values for the adamantane molecules only in the high-temperature region (from 388 to 430 K). In the 333—388 K temperature interval, the difference between the experimental and calculated values exceeds the experimental error. In this work, to verify the reliability of the experimental data,[12] we repeatedly determined the thermodynamic characteristics of adsorption in this temperature range. The obtained results in comparison with the published data[12] are presented in Table 1 along with the experimental and calculated Henry's constants K_1, adsorption heats, and coefficients of the equation (A and B) that approximate the experimental data. As follows from Table 1, the experimental K_1 values and adsorption heats determined in our work satisfactorily agree with the published data.[12]

The adsorption heats calculated[12] under the assumption of ideal tetrahedral angles are close to those determined in this work. The K_1 values calculated for the ideal adamantane structure (tetrahedral angles) by both us and the authors of the above mentioned work[12] are substantially (by 0.15 $\ln K_1$ units) lower than the experimental values (see Tables 1 and 2), and the divergence increases with the temperature decrease. The agreement between different experimental data suggests that the reason for the divergence between the experimental and calculated values is inaccuracy of either parameters of the geometric structure or AAP. Ignoring the approximate character of the additivity principle and the mathematical form of AAP in the mathematical statistical calculation of K_1, we have, most likely, two main sources of errors: the incorrectly specified AAP parameters or inaccurate parameters of the molecular structure (angles and bond lengths) of adamantane. It is known that the adamantane molecule has a slight internal strain (~25 kJ mol^{-1}), resulting in a deviation of the bond angles from tetrahedral and a slight change in the C—C and C—H bond lengths.[13] The geometric parameters of adamantane and other polyhedra have been determined by the electronographic method.[1] In all cases, the bond angles for the nodal C atoms differ somewhat from the ideal tetrahedral value (109.5°). We calculated Henry's constants for adamantane using the data obtained by the electronographic method[7] and that differed from the parameters of the "ideal" structure. The results are presented in Table 2. It is seen that the differences between the experimental Henry's constants and k_1 values calculated from the geometric parameters taken from the electronographic data decrease and amount, on the average, to 0.05 $\ln K_1$ units. Therefore, we may assume that the reason for the observed divergence between the calculated and experimental K_1 values is related to the incorrect application of the known AAP of carbon in the sp^3-hybridization state to the C atoms in the nodal sites of the adamantane molecules rather than to the error in determination of the experimental K_1 values.

To achieve a satisfactory coincidence of the data of the molecular statistical calculation with the experimental data, we introduced the corresponding correction factors related to the refinement of the AAP values for the nodal atoms of the adamantane molecule. The Henry's constants calculated taking into account each correction and their array are presented in Table 2.

Since in the adamantane molecule the nodal atoms are tetracoordinate and the bond angles at these atoms are close to tetrahedral, we used AAP for the sp^3-hybridized carbon atom (Eq. (2)) as the initial AAP.[11,14]

Presently, three types of AAP for the C atom are known: in the sp^3-, sp^2-, and sp-hybridization states in the corresponding compounds. The C atoms in the nodal sites of the adamantane molecules have been shown[8] to be intermediate between the sp^3- and sp^2-hybrid states, which is probably associated with the cell effect inside the adamantane framework (see Fig. 1).[1,5] The quantum-chemical calculation of the hybridization state (n) of the orbitals of the nodal C atoms participating in the formation of the cell effect gave n = 2.66.[8] The valence state of the bridging C and H atoms in adamantane was accepted to be the same as that in alkanes.

Taking into account the aforesaid, the expression for AAP of the nodal C atom in adamantane (AdH) can be written as follows:

$$\varphi_{\mathrm{C(AdH)...C(gr)}} = \beta\varphi_{\mathrm{C(alk)...C(gr)}}, \quad (3)$$

where β is the correction coefficient.

The simplest and most widely used method for the determination of the β coefficient is that which allows one to achieve an agreement between the experimental and calculated K_1 values by the arbitrary variation of the β values (the method of matching of experimental and calculated data[14] — method I). The δ coefficient for AAP of the nodal carbon atoms in adamantane found by us using a similar method is equal to 1.02. Thus, the expression for the refined AAP can be presented in the form

$$\varphi_{\mathrm{C(AdH)...C(gr)}} = -1.414 \cdot 10^{-3} \cdot r^{-6} - 2.191 \cdot 10^{-5} \cdot r^{-8} + 1.928 \cdot 10^{5} \cdot \exp(-35.7r). \qquad (4)$$

The K_1 values calculated using the introduced correction factors for the cell effect are presented in Table 3, from which it follows that the experimental and calculated K_1 values in the temperature interval under study almost coincide when the indicated correction factors are applied.

Although method I is simple and efficient, it possesses several disadvantages such as the absence of the physicochemical foundations due to which the introduction of the correction factor is reduced to sorting out various β values. At the same time, it is of interest to find the correction factor from independent experimental physicochemical characteristics of the molecules under study. Therefore, we used other methods to determine the β coefficient based on the study of the dependence of the β value on the valence state of atoms in the molecule under study and on the specific features of its geometric structure.

The dependence of β on the specific features of the geometric structure (internal strain in the molecules, deviation of the geometric parameters from ideal from the viewpoint of the concepts on hybridization, *etc.*) has been examined first for polycyclic strained hydrocarbons.[15] The ideal bond angles (cos α) and the corresponding AAP were used in Ref. 15 as the parameters determining the β value (method II). Using the dependence proposed,[15] we found the correction factor β equal to 1.002 and calculated Henry's constants (see Table 3). Comparison of the data in Tables 2 and 3 shows that this method achieves only an insignificant convergence of the experimental and calculated results.

Since method II is inefficient,[15] we examined the dependence of the β constant on the value of the bond angle (cos α) at the tertiary C atom in the adamantane molecule. The values of bond angles characteristic of the corresponding valence states of the carbon atom were used as reference points. The obtained dependence of the β value on the bond angle (Fig. 2, *a*) has the following form:

$$\beta = 1.267 + 0.329\lg(-\cos\alpha),\ s = 0.024, \qquad (5)$$

where s is the root-mean-square deviation of the experimental points from the plotted curve.

The correction coefficient found by Eq. (5) for the tertiary carbon atom of the framework is equal to 1.01. Examination of dependence (5) shows that the previously used procedure[15] (method II) does not allow the β value to be determined in the case of the adamantane molecule as well, which is indicated by the deviation of the β value calculated by Eq. (5) from that obtained by method I (1.02) using fitting of the experiment to the calculation.

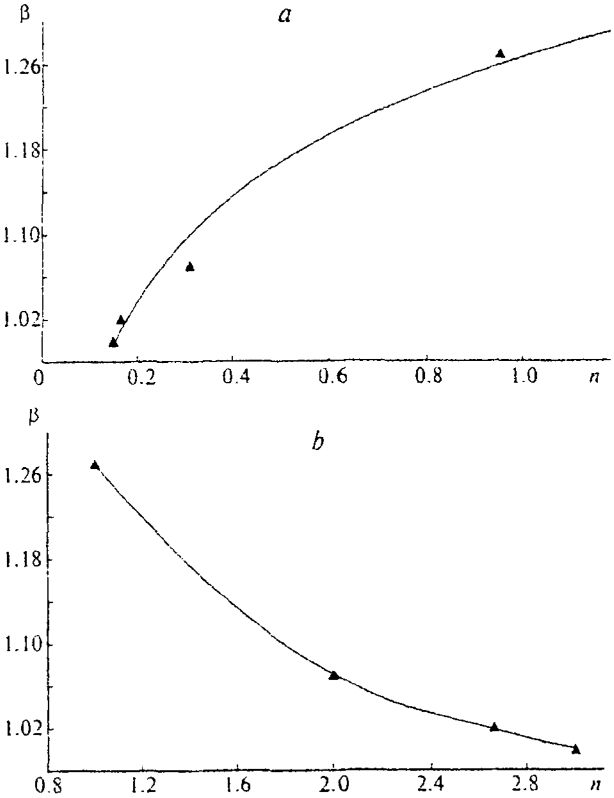

Fig. 2. Dependences of the correction coefficient (β) on the bond angle α (*a*) and hybridization *n* (*b*) in the adamantane molecule.

In addition to the geometric parameters, the valent state of the atom in the molecule is characterized, to a great extent, by the hybridization state (n) (see Fig. 2, *b*). The AAP value strongly depends on the n value, which is convincingly demonstrated by AAP for the C and H atoms.[16] Using the AAP value characteristic of each hybrid state of the atom, we found the following functional dependence of the β coefficient on the hybridization state of the carbon atom (method III) (see Fig. 2, *b*):

$$\beta = 1.263 - 0.575\log n,\ s = 0.017. \qquad (6)$$

The correction coefficient β for the C atom of the adamantane framework ($n = 2.66$) calculated by Eq. (6) is equal to 1.019. Similarity of the β values calculated by formula (6) and obtained by method I makes the dependence of β on n preferable to method II which takes into account the geometric parameters.

It is seen from the data in Tables 2 and 3 and Fig. 3 that the difference between the values calculated ignoring the β correction factors and experimental K_1 values decreases with the temperature increase. This fact can be attributed, in particular, to an increase in the inten-

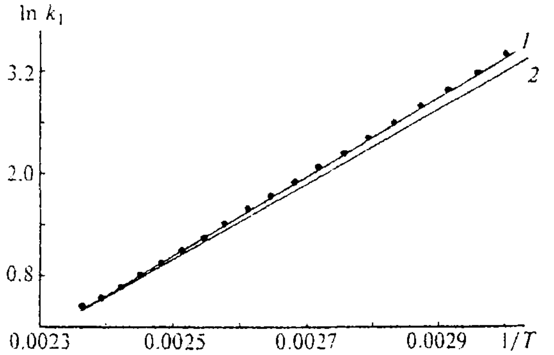

Fig. 3. Calculated (straight lines) and experimental (points) Henry's constants (K_1) for adamantane adsorption on GTCB: *1*, calculated using the correction factors for the special valence state of the nodal C atoms (cell effect); and *2*, without correction factors.

sity of libration vibrations in the adsorbate molecule with increase in temperature, which results in the deformation of the structure of the carbon framework in the adamantane molecule,[17] resulting in weakening of the intramolecular interaction (cell effect). The introduction of the correction factors is especially necessary in the low-temperature region ($\leq$388 K) in molecular statistical calculations of the adsorption parameters of the adamantane molecule and its derivatives.

The obtained results suggest that adamantane adsorption on GTCB manifests the cell effect-caused nonequivalence of the carbon atoms of the framework due to different intermolecular interactions of the nodal and bridging C atoms with the adsorbent surface. Therefore, the nodal and bridging C atoms differ in the AAP characteristics, and it is reasonable to introduce a β correction factor equal to 1.02 for the AAP parameters of the nodal carbon atoms in the molecular statistical calculation of the thermodynamic characteristics of adsorption of adamantane and its derivatives.

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