# Molecular statistical calculation of thermodynamic characteristics of adsorption of O-, S-, and Se-containing heteroadamantanes on graphitized thermal carbon black

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The thermodynamic characteristics of adsorption (TCA) on the basal face of graphite have been calculated in terms of the semiempirical molecular statistical theory of adsorption for molecules of O-, S-, and Se-containing heteroadamantanes of different structure and isostructural cyclohexane derivatives. The influence of the nature, number, and position of heteroatoms in the adamantane framework on the TCA values was studied in detail, which made it possible to predict the retention of the compounds considered on the surface of graphitized thermal carbon black under the conditions of equilibrium gas adsorption chromatography. The introduction of each subsequent heteroatom into a polyheteroadamantane molecule makes a non-additive contribution to the TCA values. The contributions of various fragments to the total adsorption energy were calculated by the TCA of isostructural heterocyclohexane molecules, and the most preferential orientations of the framework molecules of the adsorbates relative to the planar graphite surface were determined.

**Key words:** oxaadamantanes, thiaadamantanes, selenaadamantanes, graphitized thermal carbon black, molecular statistical calculations, Henry constant, heat of adsorption, entropy of adsorption, atom-atomic potentials, model of two-dimensional ideal gas, sorption—structure correlations, retention indices.

Heteroadamantanes are saturated polycyclic compounds in which one or several carbon atoms are substituted for heteroatoms. They form a large group of organic compounds and, due to the unusual molecular structure, occupy a special position in chemistry of polyhedral structures. The most studied representatives of these compounds are nitrogen-, sulfur-, and boron-containing heteroadamantanes.[1—6] Heteroadamantanes can also include other elements, predominantly from the IV, V, and VI Groups of the Periodical system; however, the properties of these compounds still remain poorly studied.[7—9] Heteroadamantane structures are convenient model systems for theoretical investigation of mechanisms of transfer of various intramolecular effects in framework molecules, which extends the known concepts on the nature of chemical bonds and electronic structure of carbo- and heterocyclic compounds of complicated structure.[1,10,11]

The majority of known heteroadamantanes is represented by synthetic products. At the same time, some substances with the heteroadamantane structure are met in nature, particularly, thiaadamantanes of diverse structure, whose content in some oils is rather high.[12] The sulfur-containing polyadamantane structures have recently been found in petroleum,[13] and synthetic chemistry of these compound started to develop vigorously at the stage of obtaining various precursors for the development of nanoobjects.[14] Heteroadamantane moieties were also found in the composition of some molecules of alkaloids[15] and other natural compounds.[16] Accordingly, there is a need for the development of modern methods for separating and concentrating adamantane compounds, which include a sound choice of the sorbent and separation conditions combined with versatility and relatively simple procedure of the method.

Graphitized thermal carbon black (GTC) is highly selective in the gas chromatographic separation of adamantane[17] and its functional derivatives.[18—20] Under the HPLC conditions, analogous results for these compounds were obtained[21] when the graphite-like adsorbent Hypercarb was used as a stationary phase. The molecular statistical calculations of the thermodynamic characteristics of adsorption of the adamantane derivatives on the surface of the basal graphite face showed their good agreement with the experimental gas chromatographic data determined on the GTC.[18—23] This served as a reliable basis for

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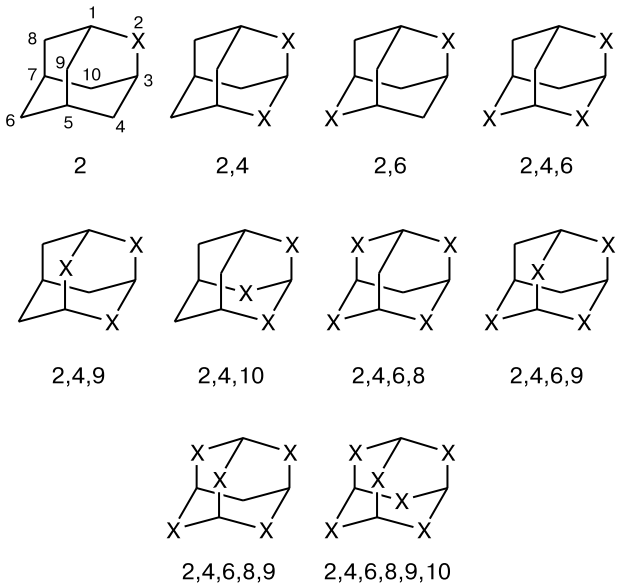
the prediction of thermodynamic retention conditions on the GTC of many adamantane derivatives, a considerable part of which represented stereoisomers similar in properties.[20] The accumulated vast experimental material on the retention values on the GTC in combination with molecular statistical calculations was successfully used for the identification of particular isomers in complicated synthetic[24] and natural[25] mixtures.

The purpose of this work is the molecular statistical study of the thermodynamics of adsorption of molecules of various oxygen-, sulfur-, and selenium-containing hetroadamantanes and isostructural cyclohexane derivatives. The study includes the calculation of the main thermodynamic characteristics of adsorption of these compounds on the surface of the basal graphite base such as adsorption equilibrium constants, molar differential heats of adsorption, and others. The calculations were supplemented by evaluation of the influence of the nature, number, and position of heteroatoms in the framework on the energy of the adsorbate—adsorbent intermolecular interaction. It was of interest to estimate the selectivity and possibility of separation of the heteroadamantanes considered on columns packed with the GTC under the conditions of equilibrium gas adsorption chromatography (GAC).

## Calculation Procedures

Structural formulas of the heteroadamantanes under study are given below (figures designate the position of the heteroatom X = O, S, or Se in the adamantane framework).




Molecular statistical calculations of the adsorption equilibrium constants (Henry constants $K_{1,C}$) were performed in terms of the semiempirical molecular statistical theory of adsorption (SMSTA)[26] based on the atom-atomic approximation for the potential function ($\Phi$) of pair intermolecular interactions of adsorbate molecules with the surface of the basal graphite face

$$\Phi = \sum_{A(M)} \sum_{C(gr)} \varphi_{A...C(gr)}, \qquad (1)$$

where $\varphi_{A...C(gr)}$ is the atom-atomic potential (AAP) function of interaction of each atom of the adsorbate molecule (A) with each carbon atom of the basal graphite face (kJ mol$^{-1}$).

The type of the AAP was chosen in the form of the Buckingham—Corner potential[27]:

$$\varphi_{A...C(gr)} = -C_1 r^{-6} - C_2 r^{-8} + B\exp(-qr), \qquad (2)$$

where $C_1$ and $C_2$ are the parameters of dipole—dipole and dipole—quadrupole dispersion attraction forces, $B$ and $q$ are the parameters of universal repulsion forces, and $r$ is the interatomic distance. Among the forms of intermolecular interaction potentials frequently used in the theory of adsorption (Lennard-Jones, Buckingham, *etc.*), the Buckingham—Corner potential is the most theoretically substantiated and full, because it contains the exponential expression for repulsion forces, while the first two terms of the multipole decomposition of the energy of this interaction are taken into account.[26] In addition, a considerable amount of data on the values of the Buckingham—Corner potential was accumulated for many atom-organogens in various valence states, which allows one to perform molecular statistical calculations comparable with experiment for equilibrium adsorption parameters of organic compounds on the graphite surface.[25] The used values of the parameters $C_1$, $C_2$, $B$, and $q$ for various atoms were taken from the literature data[26,28] and are listed in Table 1.

The $K_{1,C}$ values were calculated assuming the free motion of quasi-rigid adsorbate molecules along the mathematically

**Table 1.** Parameters of Eq. (2) used for the calculation of the TCA of the studied heterocyclic adamantane and cyclohexane derivatives

| Atom | $C_1 \cdot 10^3$/kJ nm$^6$ mol$^{-1}$ | $C_2 \cdot 10^5$/kJ nm$^8$ mol$^{-1}$ | $B \cdot 10^{-5}$/kJ mol$^{-1}$ | $q$/nm$^{-1}$ | $r_0$ | $r_{eff}$ |
|---|---|---|---|---|---|---|
| | | | | | nm | |
| C(sp$^3$) | 1.386 | 2.148 | 1.890 | 35.7 | 0.382 | 0.170 |
| CH$_2$(sp$^3$) | 2.860 | 4.970 | 6.870 | 35.7 | 0.403 | 0.190 |
| O | 1.005 | 1.628 | 0.723 | 35.7 | 0.341 | 0.129 |
| S | 3.472 | 6.667 | 5.953 | 35.7 | 0.393 | 0.181 |
| Se | 4.962 | 7.260 | 10.670 | 35.7 | 0.409 | 0.195 |
| H | 0.489 | 0.950 | 0.360 | 35.7 | 0.341 | 0.128 |

uniform graphite surface and the harmonic oscillation perpendicularly to the surface[26]:

$$K_{1,C} = \frac{1}{4\pi}\int\int\left(\frac{2\pi kT}{\Phi_z''}\right)^{1/2}\exp\left(-\frac{\Phi_0}{kT}\right)\sin\theta d\theta d\Psi, \qquad (3)$$

where $\Phi_0$ and $\Phi_z''$ are the values of the potential function $\Phi$ in the potential minimum and its second derivative with respect to the distance $z$ from the center of gravity of the molecule to the adsorbent surface; $\theta$ and $\Psi$ are the Euler angles determining the orientation of the molecule relative to the adsorbent surface.

The geometric parameters of the adsorbate molecules in the gas phase necessary for molecular statistical calculations were taken from the literature.[29,30] Quantum chemical calculations using the Gamess v.6.0 program package in terms of the *ab initio* RHF/6-31G** method were performed to establish the geometric structures of heteryladamantane molecules.

Based on the $K_{1,C}$ values determined by the above described procedure, we calculated the molar differential heats $\bar{q}_{dif,1}$ (kJ mol$^{-1}$) and changes in entropies $\Delta(\bar{S}_{1,C}^{\circ})^s$ (J mol$^{-1}$ K$^{-1}$) of adsorption. For this purpose, the equation $\ln K_{1,C} = f(T)$ taking into account the temperature dependences of $\bar{q}_{dif,1}$ and $\Delta(\bar{S}_{1,C}^{\circ})^s$ was used

$$\ln K_{1,C} = \frac{\Delta(\bar{S}_{1,C}^{\circ})^s - \Delta\bar{C}_{1,p}^s(\ln T_{av}+1) - R\ln T_{av}}{R} + \frac{\bar{q}_{dif,1} + T_{av}(\Delta\bar{C}_{1,p}^s + R)}{RT} + \left[\frac{\Delta\bar{C}_{1,p}^s + R}{R}\right]\ln T = A + \frac{B}{T} + C\ln T, \qquad (4)$$

where $\Delta\bar{C}_{1,p}^s = \Delta\bar{C}_{ads,p}^{\circ} - \bar{C}_{gas,p}$ is the difference between the difference between the molar differential heat capacity of the substance in the adsorbed state ($\Delta\bar{C}_{ads,p}^{\circ}$, J mol$^{-1}$ K$^{-1}$) and the molar heat capacity of the substance in the equilibrium gas phase at $p$ = const ($\bar{C}_{gas,p}^{\circ}$, J mol$^{-1}$ K$^{-1}$); $T_{av}$ is the middle of the temperature range studied (K); $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$). The calculated values of $K_{1,C}$, $\bar{q}_{dif,1}$, and $\Delta(\bar{S}_{1,C}^{\circ})^s$ are given in Table 2. The number of significant digits in the values presented corresponds to the accuracy of their experimental determination achieved under the conditions of standard gas chromatographic measurements on columns with the GTC for analogous sorbates and external conditions.[20]

Accepting that the state of the adsorbate molecules on the GTC surface is close to that of a two-dimensional ideal gas, which at non-specific adsorption is characterized by the loss of

**Table 2.** Thermodynamic characteristics of adsorption (TCA) calculated by the molecular statistical method and formula (5) for molecules of the O-, S-, and Se-containing heteroadamantanes on the basal face of graphite in the temperature range from 333.15 to 473.15 K

| Adsorbate | $\ln K_{1,C}$ | | | $\bar{q}_{dif,1}$[a] | $-\Delta(\bar{S}_{1,C}^{\circ})^s$[b] | | $\Delta\bar{C}_{1,p}^s$[b] |
|---|---|---|---|---|---|---|---|
| | 333.15 K | 403.15 K | 473.15 K | | I[c] | II[d] | |
| | | | | Adamantane derivatives | | | |
| Adamantane | 3.46 | 1.17 | −0.43 | 36.5 | 89.8 | 110.6 | 1.0 |
| 2-Oxa- (**1**) | 3.46 | 1.04 | −0.61 | 37.9 | 93.7 | 110.7 | 11.4 |
| 2,4-Dioxa- (**2**) | 3.18 | 0.80 | −0.82 | 37.2 | 94.0 | 110.8 | 9.5 |
| 2,6-Dioxa- (**3**) | 3.50 | 1.02 | −0.67 | 38.9 | 96.3 | 110.8 | 12.3 |
| 2,4,6-Trioxa- (**4**) | 2.97 | 0.61 | −0.99 | 36.9 | 94.9 | 110.8 | 8.9 |
| 2,4,9-Trioxa- (**5**) | 3.20 | 0.75 | −0.90 | 38.2 | 96.9 | 110.8 | 15.3 |
| 2,4,10-Trioxa- (**6**) | 2.79 | 0.49 | −1.08 | 36.0 | 93.6 | 110.8 | 7.1 |
| 2,4,6,8-Tetraoxa- (**7**) | 2.55 | 0.28 | −1.27 | 35.6 | 94.2 | 110.9 | 6.2 |
| 2,4,6,9-Tetraoxa- (**8**) | 2.83 | 0.46 | −1.15 | 37.1 | 96.5 | 110.9 | 12.8 |
| 2,4,6,8,9-Pentaoxa- (**9**) | 2.66 | 0.30 | −1.30 | 36.9 | 97.4 | 110.9 | 13.1 |
| 2,4,6,8,9,10-Hexaoxa- (**10**) | 2.59 | 0.22 | −1.38 | 37.0 | 98.2 | 111.0 | 11.5 |
| 2-Thia- (**11**) | 3.74 | 1.36 | −0.28 | 37.5 | 90.0 | 111.1 | 0.8 |
| 2,4-Dithia- (**12**) | 4.24 | 1.73 | 0.01 | 39.5 | 91.9 | 111.6 | 5.3 |
| 2,6-Dithia- (**13**) | 4.11 | 1.65 | −0.05 | 38.8 | 90.9 | 111.6 | 2.1 |
| 2,4,6-Trithia- (**14**) | 4.69 | 2.07 | 0.28 | 41.1 | 93.1 | 112.0 | 6.9 |
| 2,4,9-Trithia- (**15**) | 4.74 | 2.09 | 0.28 | 41.5 | 94.0 | 112.0 | 10.5 |
| 2,4,10-Trithia- (**16**) | 4.69 | 2.07 | 0.27 | 41.2 | 93.4 | 112.0 | 7.6 |
| 2,4,6,8-Tetrathia- (**17**) | 5.09 | 2.39 | 0.53 | 42.6 | 94.1 | 112.4 | 7.6 |
| 2,4,6,9-Tetrathia- (**18**) | 5.16 | 2.41 | 0.54 | 43.0 | 94.9 | 112.4 | 10.3 |
| 2,4,6,8,9-Pentathia- (**19**) | 5.67 | 2.79 | 0.83 | 45.1 | 96.9 | 112.7 | 13.1 |
| 2,4,6,8,9,10-Hexathia- (**20**) | 6.11 | 3.13 | 1.09 | 46.7 | 98.3 | 113.1 | 13.4 |
| 2-Selena- (**21**) | 4.28 | 1.80 | 0.08 | 39.2 | 90.7 | 112.3 | 1.8 |
| 2,4-Diselena- (**22**) | 5.21 | 2.51 | 0.66 | 42.4 | 92.7 | 113.4 | 5.5 |
| 2,6-Diselena- (**23**) | 5.16 | 2.51 | 0.67 | 41.9 | 91.6 | 113.4 | 1.8 |
| 2,4,6-Triselena- (**24**) | 6.11 | 3.23 | 1.24 | 45.4 | 94.1 | 114.3 | 6.7 |
| 2,4,9-Triselena- (**25**) | 6.11 | 3.19 | 1.20 | 44.9 | 95.3 | 114.3 | 12.7 |
| 2,4,10-Triselena- (**26**) | 6.05 | 3.17 | 1.19 | 45.3 | 94.4 | 114.3 | 7.5 |

(*to be continued*)

**Table 2** (*continued*)

| Adsorbate | $\ln K_{1,C}$ | | | $\bar{q}_{dif,1}$[a] | $-\Delta(\bar{S}_{1,C}^{\circ})^{s}$[b] | | $\Delta\bar{C}_{1,p}^{s}$[b] |
|---|---|---|---|---|---|---|---|
| | 333.15 K | 403.15 K | 473.15 K | | I[c] | II[d] | |
| | | | | Adamantane derivatives | | | |
| 2,4,6,8-Tetraselena- (**27**) | 6.83 | 3.81 | 1.72 | 47.6 | 94.7 | 115.1 | 6.1 |
| 2,4,6,9-Tetraselena- (**28**) | 6.85 | 3.80 | 1.70 | 47.9 | 95.7 | 115.1 | 10.1 |
| 2,4,6,8,9-Pentaselena- (**29**) | 7.66 | 4.43 | 2.21 | 50.8 | 97.7 | 115.7 | 12.5 |
| 2,4,6,8,9,10-Hexaselena- (**30**) | 8.36 | 5.00 | 2.63 | 53.3 | 99.5 | 116.2 | 13.6 |
| | | | | Cyclohexane derivatives | | | |
| Cyclohexane | 1.01 | -0.93 | −2.25 | 30.4 | 94.4 | 108.6 | 5.0 |
| Oxa- (**31**) | 0.78 | -1.19 | −2.51 | 30.5 | 93.9 | 108.7 | 13.2 |
| 1,3-Dioxa- (**32**) | 0.31 | -1.57 | −2.83 | 29.2 | 93.8 | 108.8 | 11.7 |
| 1,4-Dioxa- (**33**) | 0.48 | -1.46 | −2.75 | 30.1 | 95.0 | 108.8 | 13.4 |
| 1,3,5-Trioxa- (**34**) | 0.35 | -1.66 | −2.97 | 30.7 | 98.4 | 108.9 | 23.5 |
| Thia- (**35**) | 1.64 | -0.45 | −1.88 | 32.7 | 93.3 | 109.4 | 8.3 |
| 1,3-Dithia- (**36**) | 2.32 | 0.05 | −1.48 | 35.4 | 95.8 | 110.1 | 12.9 |
| 1,4-Dithia- (**37**) | 2.20 | -0.02 | −1.53 | 34.7 | 94.7 | 110.1 | 9.6 |
| 1,3,5-Trithia- (**38**) | 3.04 | 0.57 | −1.09 | 38.4 | 98.8 | 110.7 | 18.5 |
| Selena- (**39**) | 2.33 | 0.09 | −1.43 | 35.0 | 94.5 | 111.0 | 9.6 |
| 1,3-Diselena- (**40**) | 3.64 | 1.09 | −0.64 | 39.8 | 98.0 | 112.5 | 14.1 |
| 1,4-Diselena- (**41**) | 3.60 | 1.08 | −0.64 | 39.5 | 97.4 | 112.5 | 12.3 |
| 1,3,5-Triselena- (**42**) | 4.89 | 2.05 | 0.13 | 44.4 | 101.4 | 113.6 | 18.5 |

[a] In kJ mol$^{-1}$.
[b] In J mol$^{-1}$ K$^{-1}$.
[c] Calculation by formula (4).
[d] Calculation by formula (5) at $T_{av}$ = 403.15 K.

**Table 3.** Calculated values of logarithmic retention indices ($I_i$) of molecules of O-, S-, and Se-containing heteroadamantanes and heterocyclohexanes on GTC in the temperature range from 333.15 to 473.15 K

| Adsorbate | $I_i$ | | | Adsorbate | $I_i$ | | |
|---|---|---|---|---|---|---|---|
| | 333.15 K | 403.15 K | 473.15 K | | 333.15 K | 403.15 K | 473.15 K |
| | Adamantane derivatives | | | | Adamantane derivatives | | |
| Adamantane | 644.0 | 665.6 | 691.2 | **23** | 751.7 | 774.0 | 802.2 |
| **1** | 644.0 | 655.0 | 673.3 | **24** | 812.1 | 832.0 | 865.5 |
| **2** | 626.4 | 636.1 | 652.4 | **25** | 812.3 | 831.0 | 860.7 |
| **3** | 646.5 | 653.1 | 666.9 | **26** | 808.6 | 829.6 | 860.3 |
| **4** | 613.0 | 620.5 | 634.4 | **27** | 858.1 | 883.2 | 915.9 |
| **5** | 627.7 | 631.7 | 643.4 | **28** | 859.4 | 882.3 | 913.9 |
| **6** | 601.5 | 610.9 | 626.2 | **29** | 911.8 | 933.3 | 961.6 |
| **7** | 586.7 | 594.2 | 606.8 | **30** | 956.4 | 975.5 | 1001.9 |
| **8** | 604.2 | 607.9 | 618.6 | | | | |
| **9** | 593.9 | 595.5 | 603.5 | | Cyclohexane derivatives | | |
| **10** | 589.3 | 589.9 | 596.0 | Cyclohexane | 493.1 | 503.5 | 517.8 |
| **11** | 661.3 | 681.2 | 706.3 | **31** | 478.6 | 482.6 | 494.1 |
| **12** | 693.2 | 711.0 | 735.2 | **32** | 449.3 | 451.5 | 460.5 |
| **13** | 685.0 | 704.5 | 729.7 | **33** | 460.1 | 460.8 | 468.5 |
| **14** | 721.5 | 738.6 | 762.4 | **34** | 441.9 | 444.5 | 446.1 |
| **15** | 724.8 | 740.1 | 763.1 | **35** | 531.6 | 539.1 | 551.5 |
| **16** | 721.7 | 738.4 | 761.9 | **36** | 573.2 | 576.9 | 586.7 |
| **17** | 747.4 | 764.2 | 787.9 | **37** | 566.0 | 571.8 | 582.8 |
| **18** | 751.4 | 766.6 | 789.4 | **38** | 615.6 | 617.3 | 625.2 |
| **19** | 784.3 | 797.5 | 820.6 | **39** | 573.4 | 579.7 | 591.1 |
| **20** | 812.1 | 825.5 | 849.1 | **40** | 655.0 | 659.0 | 670.4 |
| **21** | 695.7 | 716.3 | 742.4 | **41** | 652.9 | 658.0 | 670.1 |
| **22** | 754.7 | 774.6 | 801.3 | **42** | 734.7 | 736.7 | 747.3 |

one translational degree of freedom, we calculated the $\Delta(\bar{S}_{1,C}^{\circ})^{s}_{calc}$ values using the known expression[31]

$$\Delta(\bar{S}_{1,C}^{\circ})^{s}_{calc} = R\ln(MT_{av})^{0.5} + 56.95 + R, \quad (5)$$

where $M$ is the molecular weight of the adsorbate.

The logarithmic retention indices ($I_i$) were calculated by the standard procedure[32] using the experimental $K_{1,C}$ values preliminarily obtained for *n*-alkanes on the columns with the GTC in a wide temperature range

$$I_i = 100\frac{\log K_{1,C(i)} - \log K_{1,C(z)}}{\log K_{1,C(z+1)} - \log K_{1,C(z)}} + 100z, \quad (6)$$

where $z$ is the number of carbon atoms in the *n*-alkane molecule eluted before the analyzed substance ($i$); $z + 1$ is the number of carbon atoms in the *n*-alkane molecules eluted after the analyzed substance ($i$). For the chromatographic determination of the $K_{1,C}$ values of *n*-alkanes, we used a glass column 1.00 m×1.5 mm in size packed with the hydrogen-treated GTC (Carbopack C HT) with a diameter of carbon black particles of 60—80 mesh, a weight of 2.203 g, and a specific surface of 10 $m^2 g^{-1}$ (Supelco, USA). The properties of the adsorbent used and the procedure of determination of the $K_{1,C}$ values on the basis of gas chromatographic data have earlier been described in detail.[18—20] Thus determined $I_i$ values are listed in Table 3.

## Results and Discussion

Literature data describe the use of the results of molecular statistical calculations for the prediction of retention in the GTC of various saturated heterocycles containing oxygen and sulfur atoms.[25] For example, the conformational composition, separation on the GTC, and identification by chromatography coupled with mass spectrometry of stereoisomeric perhydrothioxanthenes, perhydroxanthenes, and perhydro-4-thia-*s*-indacenes have been studied earlier.[24,33—35] Good agreement between the experimental and theoretically calculated TCA values (in particular, $K_{1,C}$ and $\bar{q}_{dif,1}$) for diverse stereoisomers was established[24,33—35] when the earlier[27,28] determined AAP parameters were used in the form of Eq. (2). In addition, the molecular statistical calculations were performed for the conformers presented by hypothetical structures, which made it possible to theoretically estimate the energy of their interaction with the graphite surface and to predict the order of elution on columns with the GTC under the conditions of equilibrium GAC.

On the basis of the electronic configurations of oxygen, sulfur, and selenium atoms on can expect that the corresponding heteroadamantanes contain the indicated heteroatoms only in the bridging positions of the framework and the maximum number of heteroatoms in these compounds cannot exceed six. Therefore, the structures of oxa-, thia-, and selenaadamantanes can include both substituted and unsubstituted cyclohexane moieties, whose ratio is determined by the number and position of heteroatoms in the molecule. Since in perhydroxanthenes and perhydro-4-thia-*s*-indacenes the oxygen and sulfur atoms also substitute the $CH_2$ groups in the saturated cyclohexane ring, our molecular statistical calculations of the TCA of heteroadamantanes are based on the AAP parameters known from the literature[34,35] (see Table 1). In addition, we used the AAP parameters for the selenium atoms calculated earlier[36] and approved by us for molecules of tetrahydroselenophene, selenophene, and benzoselenophene.

A comparison of the parameters of Eq. (2) listed in Table 1 and the values of the $\varphi_{A...C(gr)}$ function in the potential minimum ($r = r_0$) makes it possible to arrange the atoms forming the framework of heteroadamantanes in the order of decreasing adsorption potential on the graphite surface: Se > S > $CH_2(sp^3)$ > $C(sp^3)$ > O. The consideration of the adsorption potential of the $CH_2(sp^3)$ group in this sequence is not occasional, because only the bridging $CH_2(sp^3)$ group can be substituted upon the introduction of the O, S, and Se atoms in the adamantane framework. The $K_{1,C}$ and $\bar{q}_{dif,1}$ values in the series of monoheteroadamantanes and adamantane decrease in the same order (see Table 2). However, for the 2-oxaadamantane molecule the $K_{1,C}$ values almost coincide with the corresponding values for adamantane, whereas the $\bar{q}_{dif,1}$ value for 2-oxaadamantane is even by 0.4 kJ $mol^{-1}$ higher than the analogous value for 2-thiaadamantane. A possible reason for the enhanced adsorption potential of 2-oxaadamantane is a strong distortion of the highly symmetric bulky adamantane framework upon the introduction of the oxygen atom, due to which a tighter contact of the adsorbate molecule with the planar adsorbent surface can be anticipated. The example considered demonstrates clearly that the TCA of heteroadamantanes depend on the values of the AAP parameters of the heteroatom in the framework and also on specific features of the geometry of bulky molecule caused by the appearance of the heteroatom in its structure.

The TCA values change non-monotonically with an increase in the number of oxygen atoms in the molecules of oxaadamantanes studied. For instance, on going from 2-oxaadamantane to 2,4-dioxaadamantane the $K_{1,C}$ and $\bar{q}_{dif,1}$ values decrease noticeably, whereas on going to 2,6-dioxaadamantane they remain almost unchanged. The lower $K_{1,C}$ values for the 2,4-isomer suggest that this isomer is more weakly retained on columns with the GTC compared to the 2,6-isomer, and the difference observed in the $K_{1,C}$ values indicates that the degree of separation of these isomers can be rather high ($K_{1,C}(2,4)/K_{1,C}(2,6) = 0.83$ ($T = 423$ K)). The latter conclusion is confirmed by the high degree of separation of *cis*/*trans*-1,4-dimethyladamantanes ($K_{1,C}(cis)/K_{1,C}(trans) = 0.59$ ($T = 423$ K)) achieved under the conditions of experiments on GAC using the column packed with the GTC.[20] Among the trioxaadamantanes considered, the molecule of the

2,4,10-isomer is characterized by the lowest $K_{1,C}$ and $\bar{q}_{dif,1}$ values, while the highest values belong to the molecule of the 2,4,9-isomer. The $K_{1,C}$ values for all possible trioxaadamantanes are much lower than those of the 2-oxaadamantane molecule. This suggests that they are more weakly retained on the GTC-packed columns under the GAC conditions. In addition, the difference in the $K_{1,C}$ values of the isomers also indicates that they can be separated completely. At the same time, the $\bar{q}_{dif,1}$ value for 2,4,9-trioxaadamantane substantially exceeds the corresponding values for other isomers and 2-oxaadamantane. For two isomeric tetraoxaadamantanes, the 2,4,6,9-isomer is characterized by high $K_{1,C}$ and $\bar{q}_{dif,1}$ values; however, the both isomers has lower TCA values compared to those of the 2-oxaadamantane molecule. A similar pattern is observed for penta- and hexaoxaadamantanes. A comparative analysis of the $K_{1,C}$ values for all considered oxaadamantanes makes it possible to arrange them in the order of decreasing the $K_{1,C}$ values: **1** ≈ **5** > **4** > **6** ≈ **8** > **9** ≈ **7** ≈ **10** (sign ≈ separates the compounds with the close $K_{1,C}$ values, the difference between which is observed only with the temperature change (see Table 2)). The dependence presented shows that an increase in the number of oxygen atoms in the adamantane framework decreases, as a whole, the values of the free energy of adsorption $\Delta(\bar{F}_{1,C}^{\circ})^{s}$, which is proportional to the $K_{1,C}$ value. The dependence of the $\bar{q}_{dif,1}$ value in the oxaadamantane series on the number of oxygen atoms in the molecule is complicated and cannot be presented as a simple analytical expression (Fig. 1).

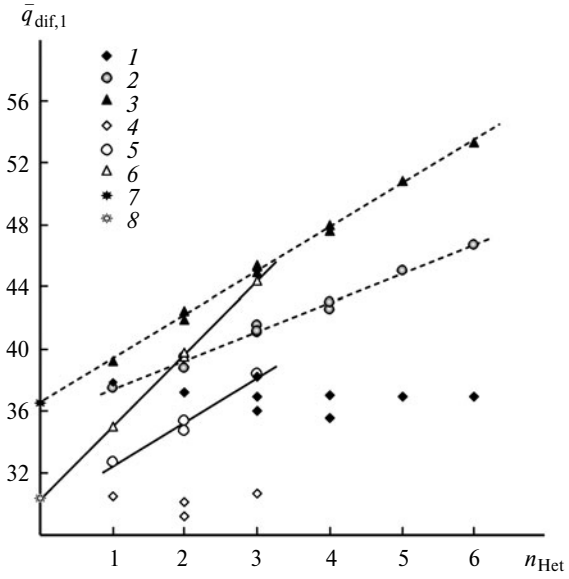



**Fig. 1.** Plots of the $\bar{q}_{dif,1}$ values for oxa- (*1*), thia- (*2*), and selenaadamantanes (*3*) and the corresponding oxa- (*4*), thia- (*5*), and selenium-containing (*6*) heterocyclic derivatives of cyclohexane and unsubstituted adamantane (*7*) and cyclohexane (*8*) *vs* number of heteroatoms in the molecule ($n_{Het}$).

Let us consider the change in heat capacity $\Delta\bar{C}_{1,p}^{s}$, whose values suggest that the real state of the adsorbed molecules is close to that of the ideal two-dimensional gas, because adsorption localization on the surface always results in an increase in the $\Delta\bar{C}_{1,p}^{s}$ values.[37] In addition, it is seen for isomeric alkyladamantanes[20] as an example that the adsorbate molecules having one, energetically most favorable equilibrium orientation relative to the planar graphite surface are characterized by the increased $\Delta\bar{C}_{1,p}^{s}$ values compared to other compounds similar in structure. The data in Table 2 show that the $\Delta\bar{C}_{1,p}^{s}$ values for a 2-oxaadamantane molecule is 10.4 J mol$^{-1}$ K$^{-1}$ higher than the $\Delta\bar{C}_{1,p}^{s}$ value for an adamantane molecule, indicating the existence of one, energetically most favorable orientation of the 2-oxaadamantane molecule relative to the planar graphite surface. Only dispersion intermolecular adsorbate—graphite interactions are taken into account in the molecular statistical calculations performed and, hence, the numerical TCA values *a priori* contain no contributions of any specific interactions, whose occurrence would also increase the TCA. Therefore, the observed increase in the $K_{1,C}$, $\bar{q}_{dif,1}$, and $\Delta\bar{C}_{1,p}^{s}$ values for 2-oxaadamantane relative to unsubstituted adamantane and 2-thiadamantane is due only to specific features of the geometric structure of their molecules and van der Waals sizes of the heteroatoms. This increase is not associated with the additional specific interactions on the easily polarizable graphite surface, which are characteristic of the strongly electronegative oxygen atom, and this is especially important for an analysis of the experimental TCA values of the oxygen-containing compounds on the GTC.

Other regularities in the TCA, as a function of the number of heteroatoms, are observed in the case of the thiaadamantane molecules considered. The close $\Delta\bar{C}_{1,p}^{s}$ values for adamantane and 2-thiaadamantane (see Table 2) indicate similarity of the adsorbed states of molecules of these compounds, which is related, first of all, to the absence of one predominant orientation of the molecule relative to the planar graphite surface. It is most likely that all cyclohexane fragments of 2-thiaadamantane, including the cyclohexane ring with the sulfur atom, behave in the same manner during adsorption. The relatively close mobilities of the adamantane and 2-thiaadamantane molecules on the graphite surface are also indicated by the almost equal $\Delta(\bar{S}_{1,C}^{\circ})^{s}$, whose numerical values depend directly on the number of the degrees of freedom lost by these molecules on going from the equilibrium gas phase to the adsorbed state. The most probable reason for the small differences in mobilities of adamantane and 2-thiaadamantane is that the values of the equilibrium state ($r_0$) and effect radius ($r_{eff}$), as well as the AAP parameters for the $CH_2$ group and the sulfur atom, are close (see Table 1). At the same time, for 2-thiaadamantane the $\bar{q}_{dif,1}$ and $K_{1,C}$ values are a little higher than the corresponding values for adamantane, which is due to the easier polarizability of

the sulfur atom compared to that of the $CH_2$ group (3.000 and 1.835 Å$^3$).[38]

Unlike isomeric dioxaadamantanes, 2,4-dithiaadamantane is characterized by the higher TCA values than those of 2,6-dithiaadamantane, and the both isomers interact more strongly with the graphite surface than 2-thiaadamantane does. Interestingly, the $\Delta\bar{C}_{1,p}{}^{s}$ values for 2,4-dithiaadamantane containing the both heteroatoms in one cyclohexane fragment are 2.5 times those for 2,6-dithiaadamantane containing the heteroatoms in different cyclohexane fragments. Probably, the introduction of each consecutive sulfur atom into the composition of thiaadamantanes exerts a stronger effect on the arrangement of their framework molecules relative to the planar surface. As a result, the isomer containing the maximum number of heteroatoms is the fragment that is in the closest vicinity of the surface. The $\Delta(\bar{S}_{1,C}{}^{\circ})^{s}$ values change similarly and for the 2,4-isomer they exceed the $\Delta(\bar{S}_{1,C}{}^{\circ})^{s}$ values for the 2,6-isomer. The relative difference in the $K_{1,C}$ values for isomeric dithiaadamantanes is lower than that for dioxaadamantane molecules, suggesting a lower degree of separation of dithiaadamantanes on the GTC-packed columns compared to the oxygen-containing structural analogs.

The character of changing the TCA values in the series of isomeric tri- and tetrathiaadamantanes is completely analogous to that described for dithiaadamantanes: the isomer containing the maximum number of sulfur atoms in the same cyclohexane fragment has the highest TCA values, and the difference in the Henry constants for the isomers is substantially lower compared to the corresponding isomeric tri- and tetraoxaadamantanes. The relative difference in the $\bar{q}_{dif,1}$ and $\Delta(\bar{S}_{1,C}{}^{\circ})^{s}$ values for isomeric thiaadamantanes with the equal numbers of sulfur atoms is also low. At the same time, the $\delta(\bar{q}_{dif,1})$ values corresponding to the contribution of the sulfur atom to the heat of adsorption upon the substitution of the $CH_2$ group differs for different isomers. For the isomer containing the sulfur atoms in one cyclohexane fragment, the $\delta(\bar{q}_{dif,1})$ value is ~2 kJ mol$^{-1}$, whereas for that with the sulfur atoms in different cyclohexane fragments it is ~1.5 kJ mol$^{-1}$. The dependences of $\bar{q}_{dif,1}$ on the number of heteroatoms in heteroadamantane molecules are presented in Fig. 2. It is seen that, unlike oxaadamantanes, the corresponding dependences for thiaadamantanes and selenaadamantanes are described by the linear plots ($\bar{q}_{dif,1} = 1.87n_S + 35.54$, $r^2 = 0.99$; $\bar{q}_{dif,1} = 2.82n_{Se} + 36.58$, $r^2 = 0.99$).

On going from 2,4,6,8,9-penta- (**19**) to 2,4,6,8,9,10-hexathiaadamantanes (**20**), the TCA increase monotonically, which agrees well with the above obtained results for other thiaadamantanes. However, the $\Delta\bar{C}_{1,p}{}^{s}$ values calculated for the 2,4,6,8,9,10-hexathiaadamantane molecule (**20**) turned out to be the highest among the thiaadamantane molecules considered. Evidently, for

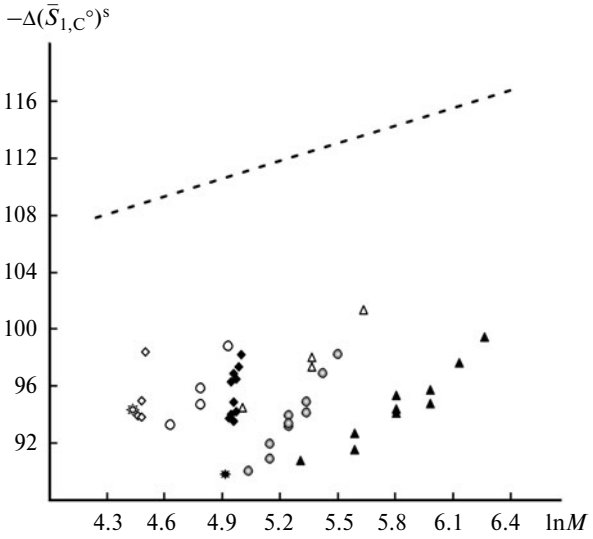



**Fig. 2.** Plots of the $\Delta(\bar{S}_{1,C}{}^{\circ})^{s}$ values *vs* molecular weight of the studied heterocyclic adamantane and cyclohexane derivatives: the dashed line corresponds to the $\Delta(\bar{S}_{1,C}{}^{\circ})^{s}$ values calculated by formula (5), and the signs (for designation of points, see Fig. 2) correspond to the $\Delta(\bar{S}_{1,C}{}^{\circ})^{s}$ values calculated by the molecular statistical method.

highly symmetric molecule **20**, as in the case of a molecule of unsubstituted adamantane, four energetically equivalent orientations relative to the planar graphite surface are possible. In terms of the discussed model of adsorption, this should result in a substantial decrease in the $\Delta\bar{C}_{1,p}{}^{s}$ value. It is most likely that in the case of compound **20**, as well as other isostructural compounds (**10** and **30**), additional factors will predominantly affect the numerical values of $\Delta\bar{C}_{1,p}{}^{s}$.

In spite of small differences in the TCA values in groups of isomeric thiaadamantanes, an increase in the number of sulfur atoms in the molecule results, in a whole, in a noticeable increase in the TCA values. An opposite tendency is observed for oxaadamantanes. For instance, $\ln K_{1,C}$ at $T = 333.15$ K for 2,4,6,8,9,10-hexathiaadamantane (**20**) is 1.6-fold higher than the corresponding value for 2-thiaadamantane, whereas for oxaheteroadamantanes analogous in structure this parameter is 0.75. These differences will be especially pronounced in the values of retention indices.

The influence of specific features of the molecular structure of selenaadamantanes on the character of changing the TCA is entirely analogous to the regularities established for thiaadamantanes. The only difference is that the contribution of selenium atoms to the $K_{1,C}$ and $\bar{q}_{dif,1}$ values is much higher compared to that from the oxygen and sulfur atoms in the isostructural compounds. This is well consistent with the AAP parameters presented in Table 1. In the series of isomeric selenaadamantanes, the difference in the $K_{1,C}$ values is insignificant, whereas the introduction of each new selenium atom should be

accompanied by a more considerable increase in the TCA values compared to the thiaadamantanes considered above.

The results of calculation of the $\Delta(\bar{S}_{1,C}^{\circ})^s$ values by formula (5) are listed in Table 2. Formula (5) is based on the assumption that adsorbate—adsorbent interaction involved in physical adsorption on non-specific adsorbents is predominantly determined by the van der Waals forces and the temperatures are rather high. In this case, adsorption is accompanied by the loss of only one translational degree of freedom. The adsorbed substance is conventionally named the two-dimensional ideal gas. The data in Table 2 show that for all heteroadamantanes studied the $\Delta(\bar{S}_{1,C}^{\circ})^s$ values calculated by formula (5) is by 15—20 entropy units higher than the corresponding $\Delta(\bar{S}_{1,C}^{\circ})^s$ values calculated by the molecular statistical method.

An analogous situation is observed for the heterocyclic cyclohexane derivatives. The $\Delta(\bar{S}_{1,C}^{\circ})^s$ values calculated by different methods are compared in Fig. 2. The reason for such a deviation is related to the nonplanar structure of the compounds studied, due to which not all fragments in the adsorbate molecules are in a direct contact with the adsorbent surface. As a consequence, the low-frequency vibrations are retained in the adsorbed molecule. They are directed perpendicular to the surface and impart the adsorbate molecule additional degrees of freedom that decrease the numerical $\Delta(\bar{S}_{1,C}^{\circ})^s$ values. The data in Fig. 2 shows that the difference in the $\Delta(\bar{S}_{1,C}^{\circ})^s$ values decreases with an increase in the molecular weight of the adsorbate, and this tendency is pronounced to a greater extent for the oxygen-containing compounds. An interesting regularity of the $\Delta(\bar{S}_{1,C}^{\circ})^s$ values as a function of the arrangement of heteroatoms in the framework is observed in the series of the corresponding isomers: the isomers containing the maximum number of heteroatoms in the same cyclohexane fragment are characterized by the highest $\Delta(\bar{S}_{1,C}^{\circ})^s$ values relative to other isomers (the only exception is the pair of isomers of 2,4- and 2,6-dioxaadamantanes). The most probable reason for the enhanced $\Delta(\bar{S}_{1,C}^{\circ})^s$ values of these compounds can be the real shift of the center of gravity in these molecules toward the most substituted cyclohexane ring, which is in a direct contact with the adsorbent surface. The "shift" is schematically shown in Fig. 3 for isomeric trithiaadamantanes as an example. As a result, it seems that the framework molecule becomes more planar, which is not related, of course, to the distortion of the true geometry of the adamantane fragment. The latter cannot change under the effect of the field from forces arising from adsorption on graphite and only corresponds to the shift of the center of gravity of the molecule to the adsorbent surface. Thus, during adsorption of framework conformationally rigid heteroadamantanes, the low-frequency vibration of the center of gravity of the molecule directed perpendicularly from the adsorbent surface is retained and decreases the numerical value of $\Delta(\bar{S}_{1,C}^{\circ})^s$. In the case of molecules **5**, **8**, **12**, **15, 18**, **22**, **25**, and **28**, this should be less pronounced compared to the corresponding isomeric molecules in which the center of gravity is considerably displaced to the adsorbent. As follows from the data of the present work, the model of "two-dimensional" ideal gas is inappropriate for the *a priori* calculation of the $\Delta(\bar{S}_{1,C}^{\circ})^s$ values in the series of the compounds studied and should include corrections to the bulky structure of the adsorbate molecules. This assumption agrees well with the earlier obtained experimental data for the adamantane derivatives with the nodal substituents in the framework[20] and the theoretical concepts presented[39] in detail.

The above considered "shift" of the center of gravity in the framework molecule related to an increase in the number of heteroatoms in the same cyclohexane fragment affects other TCA as well, in particular, $K_{1,C}$ and $\bar{q}_{dif,1}$. The results of calculation of the contributions from the $CH(CH_2)_3$ fragment (superstructure) in the adamantane and heteroadamantane fragment to the TCA

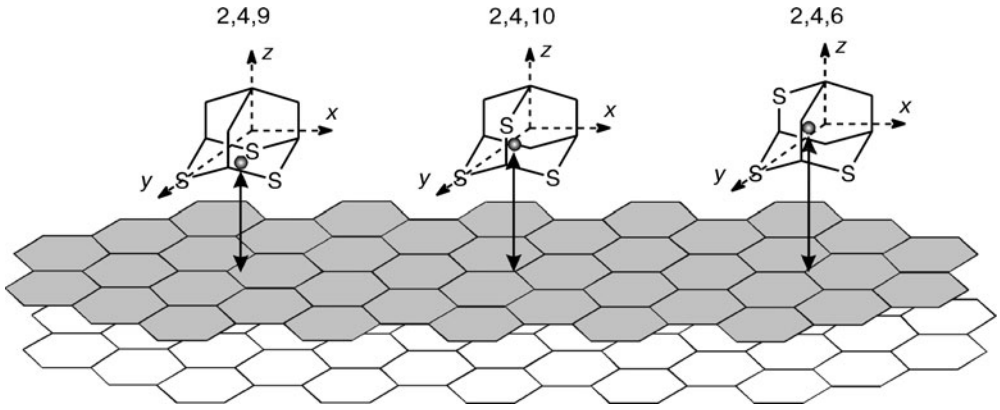



**Fig. 3.** Scheme illustrating the "shift" of the center of gravity in isomeric trithiaadamantane molecules relative to the graphite surface caused by a change in the position of the heteroatom in the framework.

**Table 4.** Contributions of the $CH(CH_2)_3$ moiety in the adamantane and heteroadamantane framework to the TCA values for various pairs of structural analogs

| Pair of analogs | $\delta(\ln K_{1,C})$ ($T = 333.15$ K) | $\delta(\bar{q}_{dif,1})$ | $\delta(\Delta(\bar{S}_{1,C}^{\circ})^s)$ | $-\delta(\Delta\bar{C}_{1,p}^s)$ |
|---|---|---|---|---|
| Adamantane—cyclohexane | 2.45 | 6.1 | 4.6 | 4.0 |
| **1—31** | 2.68 | 7.4 | 0.2 | 1.8 |
| **2—32** | 2.87 | 8.0 | −0.2 | 2.2 |
| **5—34** | 2.85 | 7.5 | 1.5 | 8.2 |
| **11—35** | 2.10 | 4.8 | 3.3 | 7.5 |
| **12—36** | 1.92 | 4.1 | 3.9 | 7.6 |
| **15—38** | 1.70 | 3.1 | 4.8 | 8.0 |
| **21—39** | 1.95 | 4.2 | 3.8 | 7.8 |
| **22—40** | 1.57 | 2.6 | 5.3 | 8.6 |
| **25—41** | 1.22 | 0.5 | 6.1 | 5.8 |

values for different pairs of structural analogs containing the same cyclohexane fragment are given in Table 4. The data presented show that for the pairs of the oxygen-containing compounds an increase in the number of oxygen atoms exerts almost no effect on the $\delta(\ln K_{1,C})$ and $\delta(\bar{q}_{dif,1})$ parameters, whose numerical mean values are 2.80 and 7.6 kJ mol$^{-1}$, respectively. The values obtained are close to those for the adamantane—cyclohexane pair. However, in the series of thia- and selenaadamantanes, the $\delta(\ln K_{1,C})$ and $\delta(\bar{q}_{dif,1})$ values decrease monotonically with an increase in the number of heteroatoms. The latter indicates that for thia- and selenaadamantanes the main contribution to the TCA values will be made by the most substituted cyclohexane fragment, and the contribution from the $CH(CH_2)_3$ fragment can be neglected in several cases. For example, for the 2,4,9-triselenaadamantane molecule, the contribution to the $\bar{q}_{dif,1}$ value from the $CH(CH_2)_3$ fragment is only 0.5 kJ mol$^{-1}$, which is comparable with the experimental inaccuracy of determination of the $\bar{q}_{dif,1}$ value under the conditions of the gas chromatographic experiment. An opposite trend is observed for the $\delta(\Delta(\bar{S}_{1,C}^{\circ})^s)$ values in the series of the pairs of structural analogs considered.

Let us try to compare the influence of the enthalpy ($\bar{q}_{dif,1}/(RT)$) and entropy ($[\Delta(\bar{S}_{1,C}^{\circ})^s + R]/R$) contributions to the total energy of intermolecular interaction using the plot in the corresponding coordinates (Fig. 4). It is seen from the data in Fig. 4 that for adsorption on graphite of all heteroadamantanes studied ($T_{av} = 403.15$ K) the enthalpy factor predominates, and its role increases with an increase in the heteroatom size. The points belonging only to cyclohexane, oxacyclohexane, and thia- and 1,4-dithiacyclohexanes lie below the line of enthalpy—entropy compensation. Under these conditions, the main contribution to the $K_{1,C}$ value of the unsubstituted adamantane molecule is made by the enthalpy factor.

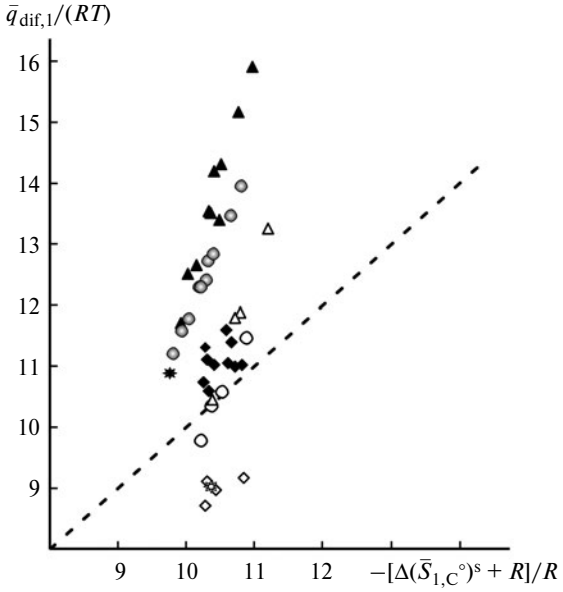



**Fig. 4.** Ratio between the enthalpy ($\bar{q}_{dif,1}/(RT)$) and entropy ($[\Delta(\bar{S}_{1,C}^{\circ})^s + R]/R$) contributions to the adsorption equilibrium constant on graphite at $T = 403.15$ K in the series of the studied heterocyclic adamantane and cyclohexane derivatives (for designations of points, see Fig. 2; the dashed line corresponds to the equality of the enthalpy and entropy contributions to the $K_{1,C}$ value).

According to the classification accepted in chromatography, the above considered $K_{1,C}$ values are classified as the so-called absolute retention values, which are rather rarely used in the practice of gas chromatographic analysis because of labor-consuming experimental determination, the absence in databases, and other reasons.[40] The relative retention characteristics found wide use in gas chromatography, and the leading position among them belongs to the Kovács retention indices ($I_i$).[41] The values of the Kovács retention indices of heteroadamantanes at different temperatures calculated from the $K_{1,C}$ values calculated in the present work are given in Table 3. The way in which molecular structure affects $I_i$ values is entirely analogous to the above obtained regularities for the $K_{1,C}$ values. At the same time, the numerical $I_i$ values of various heteroadamantanes can serve as a reliable basis for their identification in complex synthetic mixtures.

It is seen from the data in Table 3 that for all oxaadamantanes the $I_i$ values vary in the range from 655 to 589.9 (at $T_{av} = 403.15$ K) and the range of changing $I_i$ is only ~65 index units. The latter implies that the peaks of the corresponding oxaadamantanes on the chromatograms should lie between the peaks of *n*-pentane and *n*-heptane and the corresponding compounds are eluted from the chromatographic column as rather narrow group. It follows from this that it is reasonable to use capillary adsorption columns with GTC characterized by the high separation ability for the satisfactory separation of a mixture of

oxaadamantanes considered in this work. On going to thiaadamantanes, the numerical $I_i$ values increase noticeably along with the range of their change, which is 144 index units at $T_{av}$ = 403.15 K. The $I_i$ values obtained show that thiaadamantanes should be eluted between *n*-thiaadamantanes and *n*-nonanes; however, the difference in $I_i$ for isomeric thiaadamantanes is substantially smaller than that for isomeric oxaadamantanes. For example, at $T_{av}$ = 403.15 K the difference in the $I_i$ values for isomeric dioxa- and tetraoxaadamantanes is 17.0 and 13.7 index units, whereas for isomeric dithiaadamantanes it is 6.5 and 2.4 index units, respectively. The range of changing the $I_i$ values for selenaadamantanes at $T_{av}$ = 403.15 K is 259.2 index units, which possibly indicates much better separation of these compounds on the columns with GTC. However, separation will be achieved only between groups of isomers, whereas positional isomers with the equal number of heteroatoms are almost inseparable, because the differences in the $I_i$ values for isomeric di-, tri-, and tetraselenaadamantanes at $T_{av}$ = 403.15 K are 0.6, 2.4, and 09 index units, respectively, which is comparable with the inaccuracy of experimental determination of $I_i$. The $I_i$ values change similarly in the series of the heterocyclic cyclohexane derivatives considered.

Thus, the following conclusions emerge from the results of the present study:

— the introduction of oxygen atoms into the bridging positions of the adamantane framework results in a decrease (and in the case of sulfur and selenium atom, in a monotonic increase) in the TCA values of heteroadamantanes, which is due to differences in the van der Waals sizes and parameters of the potential function of intermolecular interaction with the adsorbent surface for the heteroatoms considered;

— the TCA values calculated by the molecular statistical methods make it possible to extensively describe the adsorbed state of heteroadamantanes on the graphite surface, including the determination of the equilibrium orientation of adsorbate molecules, the character of their motion in the field of adsorption forces, and the energy of intermolecular interaction of the molecule, its various atoms, and atomic groups with the planar graphite-like surface;

— the graphite-like surface is characterized by different sensitivities to specific features of the geometric structure of the positional isomers in the series of di-, tri-, and tetrasubstituted oxa-, thia-, and selenaadamantanes; the difference in the TCA decreases with an increase in the heteroatom size, which can be used in the development of new methods for separation and analytical determination of the compounds considered in complex mixtures under the conditions of equilibrium GAC on columns with GTC.

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