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Equilibrium parameters of a liquid—vapor system and thermodynamic characteristics of adsorption of cyclic and cage hydrocarbons in squalane

S. N. Yashkin

Samara State Technical University,
244 ul. Molodogvardeiskaya, 443100 Samara, Russian Federation.
Fax: +7 (846) 278 4400. E-mail: physchem@samgtu.ru

The thermodynamic characteristics of adsorption of adamantane molecules and its alkyl derivatives, as well as some mono- and bicyclic hydrocarbons $C_{10}H_n$, were studied by equilibrium gas liquid chromatography on a column packed with the stationary liquid phase squalane under the conditions of infinitely low concentrations of the sorbate in the gas phase. The influence of specific features of the molecular structure of sorbates on the regularities of their retention on the column with squalane was shown. For the first time we obtained the limiting activity coefficients and excess thermodynamic functions of mixing, which made it possible to study in detail the thermodynamics of dissolution of cage molecules in the nonpolar liquid bulk. The changes in the molar isobaric heat capacity of sorbates during adsorption were determined by the chromatographic method. For reference compounds, these values agree well with the results of direct calorimetric measurements of the change in the molar standard isobaric heat capacity during vaporization.

Key words: alkyladamantanes, bicycloalkanes, gas liquid chromatography, squalane, liquid—vapor equilibrium, critical parameters, Henry´s constant, enthalpies of dissolution, enthalpies of vaporization, entropy of dissolution, excess thermodynamic functions of mixing, activity coefficients, retention indices.

Modern gas chromatography (GC) is a universal method for physicochemical investigation of various adsorption processes. Potentialities of the GC method make it possible to obtain reliable thermodynamic information on the parameters of the vapor—condensed phase equilibrium during both adsorption on various interfaces (gas adsorption (GAC)[1] and gas liquid solid-phase chromatography (GLSC)[2]) and formation of dilute solutions involving molecules of nonelectrolytes, mesogens, and ionic liquids (gas liquid chromatography (GLC)).[3—5] The theoretical interpretation of thermodynamic values obtained by the GC method has been actively pursued[6]; GC is used for studies of the thermodynamics of phase equilibria and intermolecular interactions in adsorption systems and in solutions, as well as in analysis of nano- and supramolecular systems.[7] The main data on the limiting activity coefficients and liquid—vapor partition constant in dilute solutions of nonelectrolytes were obtained by the GLC method[8]; GLC is widely used for the determination of the saturation vapor pressure, boiling point, enthalpy of vaporization, diffusion coefficients, and other physicochemical characteristics.[3]

Most of published works on the application of GL for studying the physicochemical properties of adamantane and its derivatives deal with the determination of normal boiling points[9—14]; the GC method was used to determine the equilibrium values of the saturation vapor pressure[15,16] for molecules of unsubstituted adamantane and other that sublimate easily compounds (cubane, naphthalene, camphor, *etc.*). The thermodynamic parameters of the solid state—vapor equilibrium for molecules of adamantane and some its oxygen-containing derivatives were studied by GC.[15,17] Available data on chromatographic retention of adamantane and its derivatives mainly concern logarithmic retention indices of stationary liquid phases (SLP).[18—25] Data on the thermodynamic characteristics of adsorption (TCA) (adsorption equilibrium constants, heats and entropy of adsorption, *etc.*) of adamantane derivatives under the GLC conditions are scarce.[26—29] They are important for understanding of the mechanism of chromatographic retention and for studying the character of intermolecular sorbate—sorbent interactions. In addition, they can help to establish a relationship between the retention parameters and specific features of the molecular structure and the physicochemical properties of sorbate molecules, which are manifested during adsorption. It is difficult to use conventional direct methods of investigation of the liquid—vapor equilibrium parameters for adamantane and

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its derivatives, because these compounds sublimate easily and, hence, they should be subjected to deep purification in order to isolate particular compounds from a mixture of isomers with similar properties.[30]

The purpose of the present work is the experimental determination and theoretical analysis of the TCA values of molecules of adamantane and its alkyl derivatives, as well as some other cyclic hydrocarbons $C_{10}H_n$ on columns with the SLP squalane under the equilibrium GLC conditions. It was of interest to use the experimental GC data for the determination of equilibrium values of the saturation vapor pressure, enthalpies of vaporization, limiting activity coefficients, and excess thermodynamic functions of mixing for the formation of infinitely diluted solutions with squalane. It was also important to compare the thermodynamic data obtained by the GLC method with the results of studies of the liquid—vapor equilibrium by alternative methods and in this way to estimate a possibility of further application of GC for the determination of the physicochemical properties of cage hydrocarbons and their derivatives.

Experimental

Selected physicochemical characteristics of the studied compounds are listed in Table 1. Individual hydrocarbons (according to the GC-MS data, the content of the major component was > 95%) and their mixtures were used for the study.

Chromatographic measurements were carried out under the GC conditions on a Kristall-4000 chromatograph in the isothermal regime with a flame-ionization detector. A glass packed column (2.0 m × 3 mm) was filled with the solid support Chromaton N-AW with the particle size 0.125—0.160 mm, which contained 15 wt.% SLP squalane (2,6,10,15,19,23-hexamethyltetracosane, $C_{30}H_{62}$, Chemapol, Czechia). Helium served as a carrier gas (trade mark A, 99.995%). The flow rate of the carrier gas was varied from 20 to 22 mL min^{-1}. Samples of liquid (at normal temperature) compounds were injected at least five times as vapor—air mixtures of dilute solutions in *n*-pentane (benzene was used to dissolve naphthalene). Methane served as a non-sorbable substance. The temperature of the column was changed from 333.15 to 413.15 K with an increment of 5 K. The temperature of the injector port is 20 K higher than that of the column. The chromatogram of separation of the model mixture of some studied hydrocarbons is shown in Fig. 1.

The adsorption equilibrium in a gas phase—SLP solution system was characterized by the distribution constants $K_{c,i}$ and Henry´s constants $K_{H,i}$ (bar) of desorption of sorbates from an SLP solution to the gas phase, which were calculated using the following expressions[34]:

$$\lim_{a_{\text{liq}},c_{\text{gas}}\to 0}\left[\frac{a_{\text{liq}}/a_{\text{liq,st}}}{c_{\text{gas}}/c_{\text{gas,st}}}\right] = K_{c,i} \equiv V_{g,i}^{T}\rho_{L}^{T}, \qquad (1)$$

$$\lim_{x_i\to 0}\left[\frac{p_i{}^*}{x_i}\right] = K_{H,i} \equiv \frac{\Re T_{\text{col}}}{V_{g,i}^{T}M_{L}}, \qquad (2)$$

where $V_{g,i}{}^T$ is the specific retention volume (cm^3 g^{-1}); T_{col} is the temperature of the column (K); $\rho_L{}^T$ is the density of the SLP at the column temperature T_{col} (g cm^{-3}); $\Re$ is the universal gas constant (0.08314 L bar mol^{-1} K^{-1}); M_L is the molecular weight of the SLP (g mol^{-1}); p_i* is the partial pressure of the sorbate in the gas phase (bar); and x_i is the mole fraction of the sorbate in the SLP.

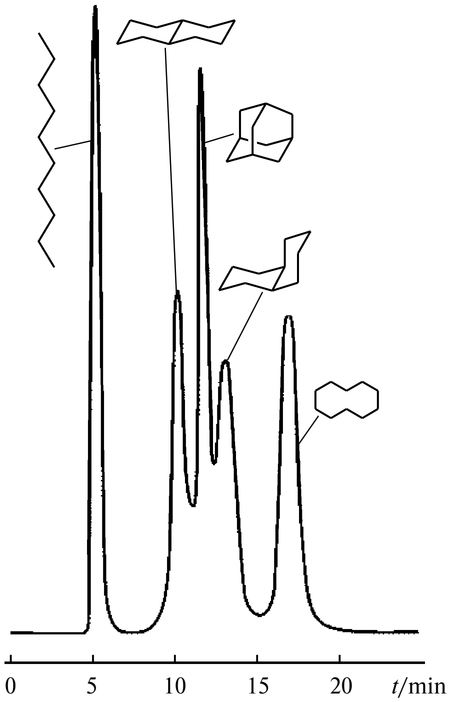

Fig. 1. Chromatogram of separation of a mixture of *n*-decane and saturated carbocyclic hydrocarbons $C_{10}H_n$ on the column with the SLP squalane (T = 373.15 K).

The values of specific retention volumes $V_{g,i}{}^T$ were calculated by the formula[34]

$$V_{g,i}^{T} = \frac{(t_R - t_M)F_{p_aT_a}}{g}\cdot\frac{T_{\text{col}}\cdot 3(p_i/p_a)^2-1}{T_a\cdot 2(p_i/p_a)^3-1}\cdot\frac{p_a-p_w}{p_a}, \qquad (3)$$

where t_R and t_M are the retention times of the sorbate and nonsorbable substance, respectively (min); p_i is the pressure of the carrier gas at the inlet to the column (atm); T_a is ambient temperature (K); p_w is the water vapor pressure at temperature T_a (atm); F_{p_a,T_a} is the flow rate of the carrier gas measured with a foam flow meter at pressure p_a and temperature T_a (cm^3 min^{-1}); and g is the weight of the SLP in the column (g). The error of experimental determination of $V_{g,i}{}^T$ did not exceed 2.5%.

For molecules of bicyclo[*n*.*m*.0]decanes, the values of $V_{g,i}{}^T$ were calculated from the literature data with allowance for logarithmic Kovác retention indices $(I_i{}^T)$[35] using the known expression[36]

$$\ln V_{g,i}^{T} = \left(\frac{I_i^T}{100} - z\right)\left(\ln V_{g,z+1}^{T} - \ln V_{g,z}^{T}\right) + \ln V_{g,z}^{T}, \qquad (4)$$

where $V_{g,z}{}^T$ and $V_{g,z+1}{}^T$ are the specific retention volumes of the corresponding *n*-alkanes between which studied sub-

Table 1. Selected physicochemical characteristics of the studied compounds[a]

Compound	M	T_m	T_b	T_c	P_c /MPa	W	α_M/Å^3		$\ln(p_i^o/\mathrm{Pa}) = A_2 - B_2/(T+C_2)$		
		K					Experiment	Calculation[b]	A_2	B_2	C_2
Adamantane (**1**)	136.2	542.2	467.7[c]	690.7[d]	2.82[d]	96	16.53	16.50	21.216[e]	4015.6[e]	–52.695[e]
1-Methyladamantane (**2**)	150.3	375.2	471.2[c]	695.1[d]	2.64[d]	124	—	18.29	18.367[e]	2464.4[e]	–119.240[e]
2-Methyladamantane (**3**)	150.3	423.0	482.7[c]	698.6[d]	2.54[d]	126	—	18.41	21.394[e]	4208.4[e]	–55.186[e]
1,3-Dimethyladamantane (**4**)	164.3	243.2	474.7[c] 476.5[f]	704.0[f]	2.48[f]	156	20.42	20.25	21.089[e]	4051.6[e]	–49.859[e]
cis-1,4-Dimethyladamantane (**5**)	164.3	—	485.2[c]	701.5[d]	2.40[d]	159	—	20.43	21.256[e]	4187.5[e]	–53.761[e]
trans-1,4-Dimethyladamantane (**6**)	164.3	—	486.2[c]	702.9[d]	2.40[d]	159	—	20.43	21.265[e]	4201.7[e]	–53.685[e]
1,2-Dimethyladamantane (**7**)	164.3	379.2	492.2[c]	711.6[d]	2.40[d]	157	—	20.31	21.319[e]	4288.3[e]	–53.036[e]
1-Ethyladamantane (**8**)	164.3	213.2	492.2[c] 498.8[f]	716.6[d]	2.41[d]	163	20.32	20.68	21.390[e]	4356.1[e]	–53.136[e]
2-Ethyladamantane (**9**)	164.3	249.2	502.2[c]	710.4[d]	2.33[d]	167	—	20.93	21.704[e]	4494.4[e]	–57.330[e]
1,3,5-Trimethyladamantane (**10**)	178.3	—	478.2[c] 483.3[f]	701.0[f]	2.45[f]	192	22.63	22.46	21.241[e]	4166.0[e]	–53.492[e]
1,3,5,7-Tetramethyladamantane (**11**)	192.3	339.2	482.2[c]	709.0[d]	2.21[d]	232	—	24.91	18.050[e]	2464.8[e]	–114.472[e]
1-Ethyl-3-methyladamantane (**12**)	178.3	—	499.2[c]	720.2[d]	2.28[d]	200	—	22.95	21.253[e]	4338.0[e]	–51.724[e]
1-Ethyl-3,5-dimethyladamantane (**13**)	192.3	—	509.9	734.9[d]	2.22[d]	241	—	25.46	20.560[e]	4016.1[e]	–66.636[e]
1-Ethyl-3,5,7-trimethyladamantane (**14**)	206.4	—	512.2	737.5[d]	2.10[d]	286	—	28.22	20.466[e]	4016.0[e]	–64.126[e]
trans-Bicyclo[4.4.0]decane (**15**)	138.3	242.8	460.4	687.2[f]	3.14	109	17.58	17.37	20.693[g]	3611.9[g]	–66.424[g]
cis-Bicyclo[4.4.0]decane (**16**)	138.3	230.0	468.9	702.4[f]	3.20	109	17.42	17.37	20.724[g]	3671.8[g]	–69.735[g]
trans-Bicyclo[7.1.0]decane (**17**)	138.3	—	466.6	687.6[d]	3.49[d]	115	—	17.74	21.555[e]	4016.1[e]	–66.114[e]
cis-Bicyclo[7.1.0]decane (**18**)	138.3	—	471.7	695.1[d]	3.49[d]	115	—	17.74	21.478[e]	4016.2[e]	–68.368[e]
cis-Bicyclo[6.2.0]decane (**19**)	138.3	—	468.0	689.6[d]	3.49[d]	113	—	17.61	21.535[e]	4016.1[e]	–66.775[e]
Cyclodecane (**20**)	140.3	282.8	474.2	697.3[d]	2.99[d]	125	18.16	18.35	20.753[g]	3730.0[g]	–71.254[g]
Tetralin (**21**)	132.2	237.4	480.7	720.0	3.65	89	17.00	—	18.306[g]	2450.0[g]	–131.000[g]
Naphthalene (**22**)	128.2	353.4	491.1	748.4	4.05	72	17.02	—	21.100[g]	4052.6[g]	–67.866[g]
n-Decane (**23**)	142.3	270.5	447.3	617.7	2.11	165	19.24	—	20.914[g]	3464.0[g]	–78.319[g]

[a] T_m, T_b, and T_c are the melting, boiling, and critical temperatures, respectively.

[b] Calculated by the formula $\alpha_M = 0.0613W + 10.688$ ($r = 0.99$; $s = 0.26$).

[c] Calculation by the GLC data.[9]

[d] Calculation by Lydersen's method.[31]

[e] Calculation of p_i^o by the Lee—Kesler method.[31]

[f] Experimental data.[13,32]

[g] Data of Ref. 33.

stance *i* is eluted. The specific retention volumes of *n*-alkanes in a wide temperature range were obtained in this work.

The following standard states of the sorbate were used in determination of the thermodynamic retention characteristics: $c_{gas,st} = 1$ μmol cm^{-3}, $p_{st} = 1$ bar (for the gas phase); and $a_{liq,st} = 1$ μmol cm^{-3} (for the SLP). The density of the SLP squalane at the column temperature T_{col} was calculated by the expression[37]

$$\rho_L{}^T = 0.8228 - 6.014\cdot10^{-4}\cdot(T_{col} - 273.15), \qquad (5)$$

where $\rho_L{}^{293}$ is the SLP density at 293 K.

The differential standard molar Gibbs energies ($\Delta_{sp}\bar{G}^\circ{}_i$, kJ mol^{-1}), enthalpies ($\Delta_{sp}\bar{H}^\circ{}_i$, kJ mol^{-1}), and entropy ($\Delta_{sp}\bar{S}^\circ{}_i$, J mol^{-1} K^{-1}) of adsorption in the SLP were determined by the dependences of $\ln(p_{st}/K_{H,i})$ on $1/T$, taking into account the temperature dependences of $\Delta_{\rm sp}\bar{P}^\circ_i$ and $\Delta_{\rm sp}\bar{S}^\circ_i$ (see Ref. 38)

$$\ln(p_{\rm st}/K_{H,i}) = \frac{-\Delta_{\rm sp}\bar{H}^\circ_i + \Delta_{\rm sp}\bar{C}^\circ_{p,i}T_{\rm av}}{RT} + \frac{\Delta_{\rm sp}\bar{S}^\circ_i - \Delta_{\rm sp}\bar{C}^\circ_{p,i}(1+\ln T_{\rm av})}{R} + \frac{\Delta_{\rm sp}\bar{C}^\circ_{p,i}\ln T}{R} = A_1 + B_1/T + C_1\ln T, \qquad (6)$$

where $\Delta_{\rm sp}\bar{C}^\circ_{p,i} = \bar{C}^\circ_{p,i({\rm sorb})} - \bar{C}^\circ_{p,i({\rm gas})}$ is the change in the standard molar heat capacity of sorbate molecules on going from the gas phase to the state diluted in the SLP (J mol^{-1} K^{-1}); $T_{\rm av}$ is the middle of the studied temperature range (K); R is the universal gas constant (8.314 J mol^{-1} K^{-1}); and $p_{\rm st}$ = 1 bar. Using analogous three-parameter Eq. (6), we determined the values of parameters A_1, B_1, and C_1 for the dependences of $\ln(V_{{\rm g},i}{}^T)$ and $\ln(K_{{\rm c},i})$ on $1/T$ (Table 2). The physical meaning of parameters A_1, B_1, and C_1 calculated from the values of $p_{\rm st}/K_{H,i}$, $K_{{\rm c},i}$, and $V_{{\rm g},i}{}^T$ is different. In particular, parameter B_1 was determined taking into account that the dependence $\ln(V_{{\rm g},i}{}^T) = f(1/T)$ contains the value of $\Delta_{\rm sp}\bar{U}^\circ_i$, which is related to $\Delta_{\rm sp}\bar{H}^\circ_i$ through the relationship $\Delta_{\rm sp}\bar{H}^\circ_i = \Delta_{\rm sp}\bar{U}^\circ_i + RT_{\rm av}$. The detailed theoretical analysis of the relationship of the thermodynamic characteristics of adsorption with the absolute retention values has earlier[39] been published.

The activity coefficients of the sorbate in an indefinitely diluted solution of the SLP (γ_i^∞) were calculated by the formula

$$K_{H,i} = \gamma_i^\infty p_i^\circ, \qquad (7)$$

Table 2. Parameters of the temperature dependences $\ln X = A_1 + B_1/T + C_1\ln T$ for the experimental values $V_{{\rm g},i}{}^T$ (cm^3 g^{-1}), $K_{{\rm c},i}$, and $p_{\rm st}/K_{H,i}$ measured in the temperature range from 333.15 to 413.15 K

Sorbate	X	$-A_1$	B_1	C_1	s	r^2
1	$V_{{\rm g},i}{}^T$	54.606	7822.554	6.950	0.0011	0.999
	$K_{{\rm c},{\rm i}}$	50.171	7669.657	6.223	0.0011	0.999
	$p_{\rm st}/K_{H,i}$	52.980	7822.554	5.950	0.0011	0.999
2	$V_{{\rm g},i}{}^T$	56.492	8027.460	7.201	0.0009	0.999
	$K_{{\rm c},{\rm i}}$	52.057	7874.563	6.474	0.0009	0.999
	$p_{\rm st}/K_{H,i}$	54.866	8027.460	6.201	0.0009	0.999
3	$V_{{\rm g},i}{}^T$	55.557	8345.562	6.973	0.0007	0.999
	$K_{{\rm c},{\rm i}}$	51.122	8192.665	6.246	0.0007	0.999
	$p_{\rm st}/K_{H,i}$	53.931	8345.562	5.973	0.0007	0.999
4	$V_{{\rm g},i}{}^T$	52.060	7911.083	6.530	0.0005	0.999
	$K_{{\rm c},{\rm i}}$	47.624	7758.187	5.803	0.0005	0.999
	$p_{\rm st}/K_{H,i}$	50.434	7911.083	5.530	0.0005	0.999
5	$V_{{\rm g},i}{}^T$	57.630	8449.447	7.287	0.0013	0.999
	$K_{{\rm c},{\rm i}}$	53.194	8296.550	6.560	0.0013	0.999
	$p_{\rm st}/K_{H,i}$	56.004	8449.447	6.287	0.0013	0.999
6	$V_{{\rm g},i}{}^T$	63.740	8881.705	8.134	0.0033	0.999
	$K_{{\rm c},{\rm i}}$	59.305	8728.808	7.407	0.0033	0.999
	$p_{\rm st}/K_{H,i}$	62.114	8881.705	7.134	0.0033	0.999
7	$V_{{\rm g},i}{}^T$	56.367	8543.021	7.070	0.0008	0.999
	$K_{{\rm c},{\rm i}}$	51.932	8390.125	6.343	0.0008	0.999
	$p_{\rm st}/K_{H,i}$	54.741	8543.021	6.070	0.0008	0.999
8	$V_{{\rm g},i}{}^T$	62.325	8991.458	7.903	0.0018	0.999
	$K_{{\rm c},{\rm i}}$	57.889	8838.561	7.176	0.0018	0.999
	$p_{\rm st}/K_{H,i}$	60.699	8991.458	6.903	0.0018	0.999
9	$V_{{\rm g},i}{}^T$	64.090	9259.088	8.108	0.0033	0.999
	$K_{{\rm c},i}$	59.655	9106.191	7.382	0.0033	0.999
	$p_{\rm st}/K_{H,i}$	62.464	9259.088	7.108	0.0033	0.999
10	$V_{{\rm g},i}{}^T$	55.808	8242.501	7.035	0.0002	0.999
	$K_{{\rm c},i}$	51.373	8089.604	6.308	0.0002	0.999
	$p_{\rm st}/K_{H,i}$	54.182	8242.501	6.035	0.0002	0.999
11	$V_{{\rm g},i}{}^T$	59.495	8565.052	7.532	0.0002	0.999
	$K_{{\rm c},i}$	55.060	8412.155	6.805	0.0002	0.999
	$p_{\rm st}/K_{H,i}$	57.867	8565.052	6.532	0.0002	0.999
12	$V_{{\rm g},i}{}^T$	64.720	9205.006	8.229	0.0024	0.999
	$K_{{\rm c},i}$	60.285	9052.109	7.502	0.0024	0.999
	$p_{\rm st}/K_{H,i}$	63.094	9205.006	7.229	0.0024	0.999
13	$V_{{\rm g},i}{}^T$	70.852	9681.521	9.067	0.0042	0.999
	$K_{{\rm c},i}$	66.416	9528.624	8.340	0.0042	0.999
	$p_{\rm st}/K_{H,i}$	69.225	9681.521	8.067	0.0042	0.999
14	$V_{{\rm g},i}{}^T$	65.247	9404.588	8.256	0.0019	0.999
	$K_{{\rm c},i}$	60.812	9251.691	7.530	0.0019	0.999
	$p_{\rm st}/K_{H,i}$	63.621	9404.588	7.256	0.0019	0.999
15	$V_{{\rm g},i}{}^T$	54.038	7801.695	6.841	0.0003	0.999
	$K_{{\rm c},i}$	49.602	7648.798	6.114	0.0003	0.999
	$p_{\rm st}/K_{H,i}$	52.412	7801.695	5.841	0.0003	0.999
16	$V_{{\rm g},i}{}^T$	58.081	8166.611	7.404	0.0004	0.999
	$K_{{\rm c},i}$	53.645	8013.715	6.677	0.0004	0.999
	$p_{\rm st}/K_{H,i}$	56.454	8166.611	6.404	0.0004	0.999
17	$V_{{\rm g},i}{}^T$	60.131	8281.959	7.682	0.0014	0.999
	$K_{{\rm c},i}$	55.696	8129.062	6.955	0.0014	0.999
	$p_{\rm st}/K_{H,i}$	58.505	8281.959	6.682	0.0014	0.999
18	$V_{{\rm g},i}{}^T$	59.567	8342.773	7.584	0.0003	0.999
	$K_{{\rm c},i}$	55.131	8189.876	6.857	0.0004	0.999
	$p_{\rm st}/K_{H,i}$	57.940	8342.773	6.584	0.0003	0.999
19	$V_{{\rm g},i}{}^T$	62.804	8484.879	8.050	0.0003	0.999
	$K_{{\rm c},i}$	58.368	8331.982	7.323	0.0003	0.999
	$p_{\rm st}/K_{H,i}$	61.177	8484.879	7.050	0.0003	0.999
20	$V_{{\rm g},i}{}^T$	68.907	9148.036	8.829	0.0001	0.999
	$K_{{\rm c},i}$	64.472	8995.140	8.102	0.0001	0.999
	$p_{\rm st}/K_{H,i}$	67.281	9148.036	7.829	0.0001	0.999
21	$V_{{\rm g},i}{}^T$	62.008	8645.063	7.890	0.0001	0.999
	$K_{{\rm c},i}$	57.573	8492.166	7.163	0.0001	0.999
	$p_{\rm st}/K_{H,i}$	60.382	8645.063	6.890	0.0001	0.999
22	$V_{{\rm g},i}{}^T$	56.124	8287.496	7.076	0.0001	0.999
	$K_{{\rm c},i}$	51.688	8134.599	6.349	0.0001	0.999
	$p_{\rm st}/K_{H,i}$	54.497	8287.496	6.076	0.0001	0.999
23	$V_{{\rm g},i}{}^T$	69.460	8680.041	8.966	0.0001	0.999
	$K_{{\rm c},i}$	65.025	8527.144	8.239	0.0001	0.999
	$p_{\rm st}/K_{H,i}$	67.834	8680.041	7.966	0.0001	0.999

where p_i^o is the saturation vapor pressure of the sorbate at the column temperature T_{col}. When determining the values of γ_i^∞, we used the symmetric reference system ($\gamma_j \to 1$ at $x_j \to 1$ for both the SLP ($j = 1$) and sorbate ($j = 2$)).

Using the temperature dependences of coefficients γ_i^∞, the excess thermodynamic functions of mixing of the sorbates with the SLP ($\bar{G}_i^{E,\infty}$, $\bar{H}_i^{E,\infty}$ и $\bar{S}_i^{E,\infty}$) were calculated[34]

$$\ln\gamma_i^\infty = \ln\gamma_{H,i}^\infty + \ln\gamma_{S,i}^\infty =$$
$$= \bar{H}_i^{E,\infty}/(RT) - \bar{S}_i^{E,\infty}/R = \bar{G}_i^{E,\infty}/(RT). \quad (8)$$

The values of thermodynamic characteristics of adsorption obtained in the present work are presented in Table 3.

The used values of topological Wiener indices (W) for the studied compounds were calculated by the known procedure.[42]

Results and Discussion

The values of normal boiling points (T_b) presented in Table 1 were determined from the relative retention times (R_t) of alkyladamantanes on squalane and the known values of T_b of some (liquid under normal conditions) alkyladamantanes (1-ethyl-1,3-dimethyl-, 1-ethyl-1,3,5-trimethyl-, 1,2-diethyl-, 1-ethyl-2-propyl-, and 1-ethyl-3-methyladamantane).[9] Using the equation[9] $T_b = 98.8\log R_t - 4$, we calculated T_b for molecules of 1-ethyl-3,5-dimethyl- and 1-ethyl-3,5,7-trimethyladamantanes (see Table 1). The values of T_b for alkyladamantanes reported by various authors can differ noticeably for the following reasons. First, the retention parameters (Kovác indices, relative retention, corrected retention times, *etc.*) are determined for the SLP different in composition and structure. In spite of similarity of the properties of the most part of nonpolar SLP used for these purposes, their chemical structure exerts a significant effect on the values of chromatographic retention parameters and, hence, on the results of the corresponding calculations of T_b. As an example, we can present the values of T_b for a molecule of unsubstituted adamantane calculated from the gas-chromatographic parameters on various SLP.

Table 3. Thermodynamic parameters of adsorption of studied adamantane, alkyladamantanes, bicyclo[*n*.*m*.0]alkanes and other hydrocarbons $C_{10}H_n$ on the SLP squalane in the temperature range 333.15—413.15 K

Sorbate [Hydrocarbon stationary phase (T_{av}/K)]	$K_{c,i}$ [a]	$p_{st}/K_{H,i}$ [a]	I_i [a]	$\Delta_{sp}\bar{H}^\circ_i$ [b]	$\Delta_{sp}\bar{S}^\circ_i$ [c]	$\Delta_{sp}\bar{C}^\circ_{i,p}$ [c]	T_{com} [d]	$\bar{H}_i^{E,\infty}$ [e]	$\bar{S}_i^{E,\infty}$ [c]	γ_i^∞ [a]	p_i^o [a,f]
1 [$C_{30}H_{62}$ (373.15)]	1391.861	25.069	1089	46.58	98.05	49.47	475.1	−1.28	−0.15	0.674	5915
1 [$C_{78}H_{158}$[38] (403.15)]	1278.481	57.233	1112	43.32	82.73	90.90	523.6	—	—	0.295	5915
1 [Apiezon L (483.15)]	—	—	1126[23]	34.3[40]	59.9[40]	—	572.6	—	—	—	5915
1 [$C_\infty H_{2\infty+2}$][g]	—	—	1121[41]	—	—	—	—	—	—	—	5915
2	1614.292	29.075	1110	47.50	99.28	51.56	478.4	−2.85	−3.46	0.607	5774
3	2493.201	44.905	1169	50.86	104.66	49.66	486.0	−2.62	−3.28	0.638	3493
4	1870.082	33.682	1130	48.62	101.05	45.98	481.1	−3.41	−5.05	0.612	5201
5	2666.829	48.032	1178	50.74	103.79	52.27	488.9	−3.19	−4.34	0.604	3447
6	2833.616	51.036	1187	51.71	105.85	59.31	488.5	−4.04	−6.32	0.587	3338
7	3347.869	60.298	1209	52.20	105.80	50.47	493.4	−3.71	−5.70	0.601	2761
8	3988.969	71.845	1233	53.34	107.39	57.39	496.7	−4.08	−6.40	0.583	2386
9	4733.851	85.261	1256	54.93	110.24	59.10	498.3	−2.72	−3.88	0.666	1761
10	2124.019	38.256	1147	49.81	103.18	50.17	482.7	−3.45	−5.98	0.677	3671
11	2394.849	43.133	1164	50.95	105.23	54.30	484.2	−7.96	−15.02	0.470	5022
12	4451.421	80.174	1248	54.10	108.57	60.10	498.3	−5.50	−9.49	0.534	2337
13	4982.235	89.735	1263	55.47	111.31	67.07	498.3	−5.92	−12.23	0.646	1725
14	5286.576	95.216	1271	55.68	111.34	60.33	500.1	−6.93	−14.31	0.601	1748
15	1205.989	21.721	1068	47.17	100.82	51.60	467.9	−2.63	−3.03	0.617	7493
16	1556.295	28.030	1105	48.90	103.34	59.04	473.2	−2.65	−3.41	0.642	5556
17	1448.175	26.083	1095	48.13	101.85	55.56	472.6	1.28	5.27	0.802	4783
18	1674.450	30.158	1115	48.94	102.83	54.74	475.9	1.22	4.86	0.826	4016
19	1518.052	27.341	1101	48.67	102.93	58.61	472.8	0.94	4.36	0.803	4556
20	2028.321	36.532	1141	51.77	108.82	65.09	475.7	−4.32	−7.54	0.617	4437
21	2004.712	36.107	1139	50.50	105.52	57.28	478.6	−1.58	−2.23	0.787	3521
22	2232.384	40.207	1154	50.05	103.42	50.52	483.9	−2.13	−4.50	0.862	2886
23	749.274	13.495	1000	47.45	105.53	66.23	449.6	−1.20	−1.10	0.775	9562

[a] At $T = 373.15$ K.
[b] In kJ mol^{-1}.
[c] In J mol^{-1} K^{-1}.
[d] In K.
[e] In J mol^{-1}.
[f] In Pa.
[g] The data are given for the paraffinic stationary phase with an indefinitely high molecular weight.

SLP	Squalane[9]	DB-1[15]	DB-5[10]	SE-30[13]
T_b/K	467.7	491	463.2	480.3

Second, there is no single universal equation relating the values of T_b with the chromatographic parameters and, therefore, the accuracy of calculation of T_b depends on the form of the used functional dependence $T_b = f(I, R_t, t_R)$ and on the number of reference substances for which this dependence was obtained. Finally, the choice of reference substances based on the principle of structural similarity and taking into account specific features of the studied class of compounds exerts a considerable effect on the accuracy of prediction of the values of T_b. For alkyladamantanes with the nodal and bridging types of substitution and for polysubstituted alkyladamantanes, it is not always possible to construct particular correlation rows because of an insufficient set of reliable experimental data.[13] Figure 2 shows the plot of the values of T_b of alkyladamantanes *vs* values of their molecular polarizability (α_M), which were calculated by the topological Wiener indices (*W*). It is seen that the values of T_b and α_M in the series of alkyladamantanes correlate well only within narrow groups of structural analogs.

Of the set of values of T_b for adamantane and alkyladamantanes, available in the literature in the present work we used the values of T_b determined with allowance for the retention values on squalane, since this SLP is most similar in chemical composition and structure to the structure of the studied compounds[9] and these data were obtained under the same conditions. In addition, the values of T_b determined in Ref. 9 are consistent with the experimental values of T_b for other saturated cyclic hydrocarbons. For example, the value of T_b for an adamantane molecule (467.7 K)[9] turned out to be intermediate between the corresponding values of T_b for isomeric molecules of *trans*- (460.4 K) and *cis*-decalins (468.9 K), which were repeatedly determined by direct precision methods.[33,43] Assuming a direct relationship between the retention values of the considered sorbates on the nonpolar SLP and their boiling points, one may expect that unsubstituted adamantane is eluted between these decalin isomers. The chromatogram of separation of a mixture of hydrocarbons $C_{10}H_n$ (see Fig. 1) shows that adamantane is eluted between isomeric molecules of *trans*/*cis*-decalins and the peaks of adamantane and *cis*-decalin are less efficiently separated than the pair *trans*-decalin/adamantane. This also agrees well with the relative difference in boiling points of the corresponding pairs of compounds. On all nonpolar SLP (including the polymer SLP) this order of elution is retained in the series *trans*-decalin—adamantane—*cis*-decalin.[27,38,44] Therefore, reliable values of T_b for the adamantane molecule can be obtained only from the data on retention on squalane.

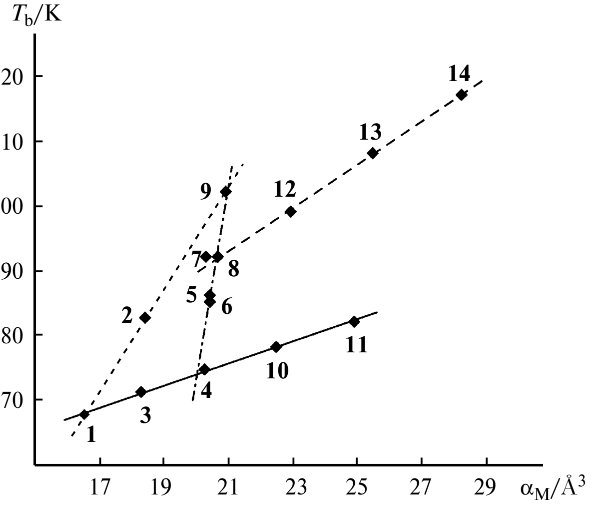

Fig. 2. Dependences of T_b of alkyladamantanes on the molecular polarizability (α_M) (compounds are enumerated in Table 1).

The values of critical temperature (T_c) and pressure (P_c) calculated from the values of T_b, which were determined by GLC and calculated by additive-group Lydersen´s method,[31] are listed in Table 1. Experimental data on the critical parameters of adamantane and its alkyl derivatives are almost lacking from scientific literature, whereas the published experimental values of critical parameters are internally inconsistent. We have earlier[45] shown that Lydersen´s method is applicable to the calculation of critical parameters of alkyladamantanes.

Adamantane and its derivatives sublimate easily and cannot exist in the liquid state under normal conditions. For this reason vapor—liquid equilibrium parameters for the majority of adamantane derivatives, including the most important data on saturation vapor pressure (p_i°) have not been reported earlier. Although the numerical values of saturation vapor pressure for the phase equilibrium solid phase—vapor are known[46] in a wide temperature range, they are inapplicable for the description of the vapor—solution adsorption equilibrium in squalane.[47] Therefore, the determination of the values of saturation vapor pressure for the vapor—liquid system in the alkyladamantane series remains an important and urgent problem.

Equilibrium values of saturation vapor pressure of pure liquids p_i° were calculated by the expansion[31]

$$\ln p_i^{\circ} = f^{(0)}(T_r) + \omega f^{(1)}(T_r). \qquad (9)$$

The functions $f^{(0)}(T_r)$ and $f^{(1)}(T_r)$ were determined using the analytical expression[31]

$$f^{(0)}(T_r) = 5.92714 - 6.09648/T_r - 1.28862\ln T_r + \\ + 0.169347T_r^6, \qquad (10)$$

$$f^{(1)}(T_r) = 15.2518 - 15.6875/T_r - 13.4721\ln T_r + \\ + 0.43577T_r^6, \qquad (11)$$

where $T_r = T/T_c$ is the reduced temperature, and ω is the acentricity factor.

The values of ω were calculated by the equation[31]

$$\omega = D/E \qquad (12)$$

at

$$D = -\ln P_c - 5.92714 + 6.09648\theta^{-1} + 1.28862\ln\theta - 0.169347\theta^6,$$

$$E = 15.2518 - 15.6875\theta^{-1} - 13.4721\ln\theta + 0.43577\theta^6,$$

where P_c is the critical pressure (atm), and $\theta = T_b/T_c$ is the reduced temperature at boiling point T_b.

The values of p_i^o determined by Eq. (9) were approximated using the equation[31]

$$\ln(p_i^o/\mathrm{Pa}) = A_2 + B_2/(T + C_2), \qquad (13)$$

where T is temperature (K). The parameters of Eq. (13) for the temperature range 333.15—413.15 K are presented in Table 1.

The temperature plots of $\ln(p_i^o)$ obtained experimentally and calculated by the method described above are shown in Fig. 3. It can be seen that the experimental and theoretical values of p_i^o agree well in the whole temperature range considered and the relative error of calculation does not exceed 13%. This correspondence is important for alkyl-substituted adamantane derivatives for which the experimental determination of p_i^o (liquid—vapor) was performed only for molecules of 1,3-di- and 1,3,5-trimethyladamantanes.[32] The values of saturation vapor pressure for the vapor—liquid system for adamantane and eleven alkyladamantanes of various structure were calculated for the first time, and good coincidence between the experimental and calculated values of p_i^o for reference compounds additionally indicates that the use of the values of T_b and critical constants (T_c, P_c) is reliable. The found values of p_i^o were used for the determination of the limiting activity coefficients of alkyladamantanes in squalane.

From studies of the effects of specific structure of adamantane and its alkyl derivatives on the parameters of chromatographic retention[9—13,18,20—21,26] a conclusion can be drawn that the adamantane derivatives with nodal and bridging substituents are retained in different manner. The specific features of retention of the adamantane derivatives under the GLC conditions are usually explained by steric shielding of the functional groups by the bulky adamantane radical. This explanation is quite justified if retention of adamantyl-containing substances is compared with that of representatives of other classes of organic compounds.[27] At the same time, similar approach is often inappropriate for a series of positional isomers of adamantane derivatives, since in this case steric shielding of substituents is almost the same. However, these substances differ in several features of the electronic structure, in particular, in the ability to "transfer an electronic effect through the space." [48]. Only nodal carbon atoms of the cage of molecules of adamantane and its derivatives and substituents at these atoms are involved in this non-valence interaction. It was proposed that the appearance of this interaction proves overlapping of the orbitals at the nodal C atoms inside the adamantane cage.[49] However, the quantum chemical calculations showed that similar mechanism of interaction of orbitals is improbable for the adamantane system and, therefore, the concept based on the hyperconjugation mechanism involving the C—C bonds was proposed.[50] Other explanations of the mechanism of electronic effect transfer in adamantane structures are also known.[51] As a whole, we may conclude that for the cage adamantane system the long-range intramolecu-

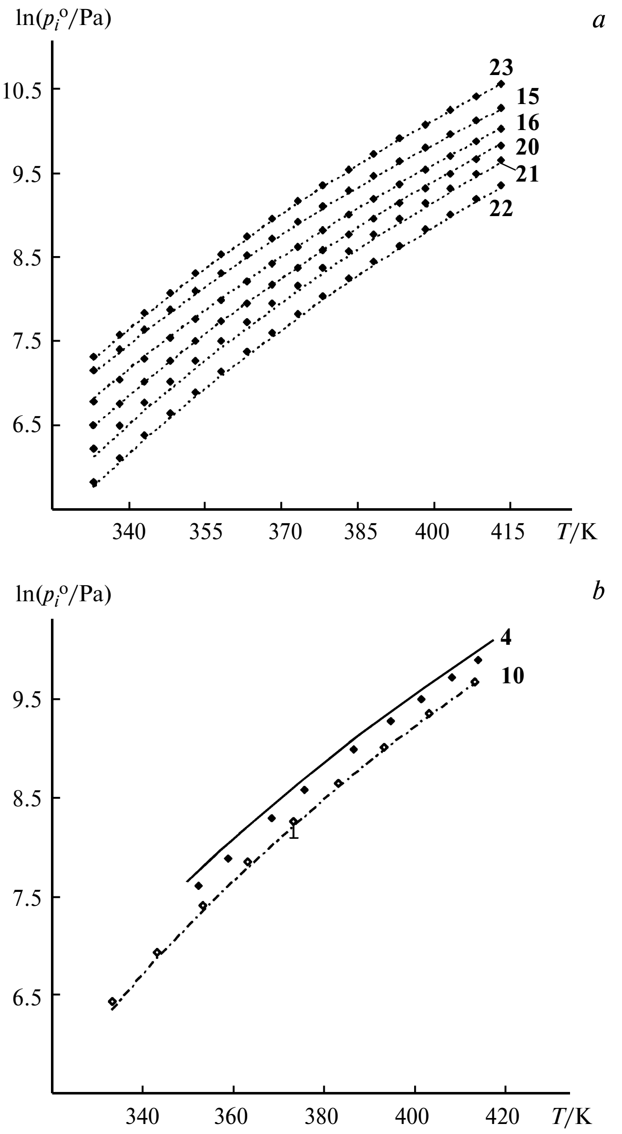

Fig. 3. Temperature plots of the experimental (points) and calculated by the critical parameters (lines) saturation vapor pressures of hydrocarbons $C_{10}H_n$ (*a*) and alkyladamantanes (*b*) in the temperature range 333.15—413.15 K (the compounds are enumerated according to Table 1).

lar interactions are more substantial than standard inductive effect and this intramolecular interaction can exert a noticeable effect on the chromatographic retention of the adamantyl-containing compounds.

A comparison of the values of TCA for adamantane and monomethyladamantane shows that the contribution of the Me group in position 2 of the cage to the values of I_i (373.15 K), $\Delta_{\rm sp}\bar{H}^\circ{}_i$, $\Delta_{\rm sp}\bar{S}^\circ{}_i$ and (80 induction units, 4.28 kJ mol^{-1}, and 6.61 J mol^{-1} K^{-1}, respectively) is comparable to similar values for the Me group in the series of n-alkanes. On the contrary, for the Me group in position 1 of the cage, the contributions to the values of I_i, $\Delta_{\rm sp}\bar{H}^\circ{}_i$, and $\Delta_{\rm sp}\bar{S}^\circ{}_i$ are strongly underestimated (20 induction units, 0.92 kJ mol^{-1}, and 1.23 J mol^{-1} K^{-1}, respectively). Similar pattern is observed in the series of other methyladamantanes with nodal Me groups. As a result, 2-methyladamantane is eluted from the column with squalane after 1,3,5,7-tetramethyladamantane, and the values of $\Delta_{\rm sp}\bar{H}^\circ{}_i$, and $\Delta_{\rm sp}\bar{S}^\circ{}_i$ for these compounds differ insignificantly. In other words, the contribution to the TCA of one Me group in the bridging position of the adamantane cage is comparable with the contribution of four nodal Me groups. No such regularity is observed for any other series of hydrocarbons.

It is known that the Me groups in the nodal positions of the adamantane cage are characterized by a lower value of electron density in the ^{13}C NMR spectra compared to the bridging Me groups (chemical shifts $\delta \approx 31.3$ and 19.1, respectively).[49] As a result, the ability of the nodal Me groups to dispersion intermolecular interaction, whose energy is directly determined by the value of electron polarizability, is lower than that for the bridging Me groups. This feature is characteristic of the nodal Me groups and also for the CH_2 and CH groups in the α-positions to the adamantane core in 1-alkyladamantanes. Therefore, low values of contributions of the nodal Me groups and of the CH_2 group (for example, in 1-ethyladamantane (see Table 3)) to the values of TCA are a consequence of the lower electron density, which is due to specific features of electronic and geometric structures of the bulky high-symmetry adamantane moiety. A similar pattern of changing TCA with the number of Me groups is observed for 1-ethyladamantane, whose nodal positions of the molecule were consecutively substituted by Me groups. In this case, the contribution of the nodal Me groups to the values of TCA is still lower than the contribution of isostructural methyladamantanes with the nodal Me groups (see Table 3). On going from 1-methyladamantane to 1,3,5,7-tetramethyladamantane, the value of I_i increases by 54 induction units, while in the series 1-ethyladamantane—1-ethyl-3,5,7-trimethyladamantane the value of I_i increases only by 38 induction units. It follows from this that long high-performance capillary columns with nonpolar SLP are needed for the separation of alkyladamantanes with nodal Me groups.

The use of nonpolar SLP is due to the fact that with an increase in chromatographic polarity in the series squalane < OV-101 < SP-2250 < SP-2340 the selectivity of sorbents during separation of alkyladamantanes with nodal Me groups decreases sharply, whereas these compounds cannot be separated on the polysiloxane columns with grafted cyanopropyl groups.[29] However, on going to the hydroxyl-containing SLP (for instance, Carbowax 20M), the order of elution of methyladamantanes is inverted.[23] As a result, 1,3,5,7-tetramethyladamantane with high molecular weight and polarizability is eluted from a mixture of alkyladamantanes earlier than unsubstituted adamantane. At the same time, the order of elution of 2-methyladamantane remains unchanged relatively to a molecule of unsubstituted adamantane. A lower adsorption potential of the nodal Me groups compared to the bridging Me groups has been observed earlier[52] when studying adsorption on the graphitized thermal carbon black by gas adsorption chromatography. This confirms the conclusion about the influence of the electronic structure of alkyladamantanes on their chromatographic retention.

The following order of elution from the column with squalane is observed in the series of isomeric alkyladamantanes $C_{12}H_{20}$: 1,3-dimethyl- < *cis*-1,4-dimethyl- < < *trans*-1,4-dimethyl- < 1,2-dimethyl- < 1-ethyl- < 2-ethyl-, which agrees well with the contributions of the nodal and bridging Me groups to the TCA determined above.

The values of TCA of a molecule of unsubstituted adamantane on squalane are well consistent with the data obtained by other authors[38,40,41] for hydrocarbon SLP with high molecular weights. As follows from Table 3, as the molecular weight of the SLP increases, the values of $K_{H,i}$ and I_i increase monotonically, the values of $\Delta_{\rm sp}\bar{S}_i^\circ$ decrease, and $\Delta_{\rm sp}\bar{H}_i^\circ$ remain nearly unchanged. The constant character of $\Delta_{\rm sp}\bar{H}_i^\circ$ can be explained, most likely, by the fact that the energies of intermolecular (in the case, dispersion) interactions ($\Delta_{\rm sp}\bar{H}_i^\circ = \text{const}$) are close to each other and the differences in the values of $K_{{\rm c},i}$, $K_{H,i}$, and I_i are due to the influence of the entropy factor, which depends on the sizes of SLP molecules.

The values of $\Delta_{\rm sp}\bar{C}^\circ{}_{p,i}$, the difference between the molar heat capacities of the sorbate in the dissolved in the SLP ($\bar{C}^\circ{}_{p,i(\rm sorb)}$) and equilibrium gas ($\bar{C}^\circ{}_{p,i(\rm gas)}$) states, are given in Table 3. The values of $\Delta_{\rm sp}\bar{C}^\circ{}_{p,i}$ agree with experimental $\Delta_{\rm vap}\bar{C}^\circ{}_{p,i}$ of pure liquids obtained by direct calorimetric measurements, For instance, the values of $\Delta_{\rm vap}\bar{C}^\circ{}_{p,i}$ for molecules of 1,3-dimethyl- and 1,3,5-trimethyladamantanes at $T = 373.15$ K (corresponding to the middle of the temperature range chromatographically studied in the present work) are −49.83 and −53.32 J mol^{-1} K^{-1},[32] while our corresponding values of $\Delta_{\rm sp}\bar{C}^\circ{}_{p,i}$ are 45.98 and 50.17 J mol^{-1} K^{-1}. Such a similarity is observed for other studied hydrocarbons. It follows from this that the GLC method is quite applicable for the

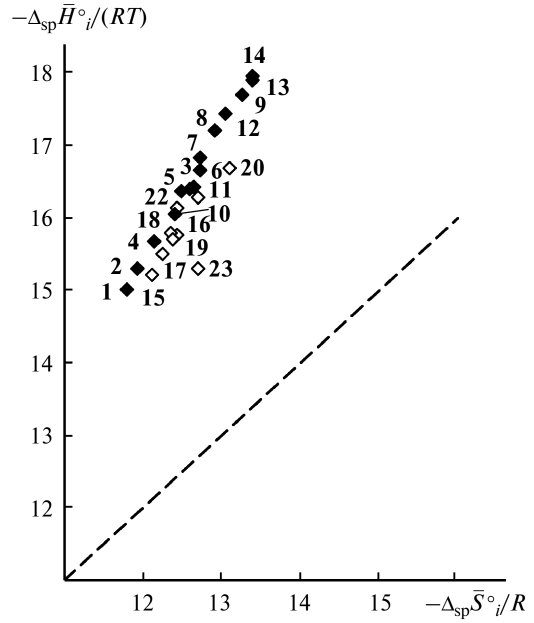

Fig. 4. Correlation between the enthalpy ($\Delta_{sp}\bar{H}^{\circ}_i/(RT)$ at 373.15 K) and entropy ($\Delta_{sp}\bar{S}^{\circ}_i/R$) contribution to the adsorption constant of adamantane and alkyladamantanes (dark designations) and other cyclic hydrocarbons (light designations) on the SLP squalane (dashed line corresponds to the equality of the enthalpy and entropy contributions to the adsorption constant $p_{st}/K_{H,i}$; the compounds are enumerated according to Table 1).

determination of such important parameters as $\Delta_{vap}\bar{C}^{\circ}_{p,i}$, whose direct measurements are still difficult. However, to solve similar problems, it is important to select a suitable temperature range and the SLP close in physicochemical properties to the compounds studied. Squalane is optimal for the determination of $\Delta_{vap}\bar{C}^{\circ}_{p,i}$ in the series of studied adamantane derivatives and other saturated cyclic hydrocarbons.

The enthalpy and entropy contributions to the differential standard molar Gibbs energy of adsorption of various molecules in the SLP ($\Delta_{sp}\bar{G}^{\circ}_i = -RT_{col}\ln(p_{st}/K_{H,i})$) at the fixed temperature of the column T_{col} are compared in Fig. 4. It is seen that at the average value of T_{col} = 373.15 K the adsorption of molecules of different structures on squalane is determined by the enthalpy factor, which indicates the high chemical affinity of sorbate molecules to SLP molecules. The enthalpy contribution to the free energy of adsorption prevails in the whole range of studied temperatures (333.15—413.15 K). The values of temperature(T_{com}/K) at which the enthalpy and entropy factors to the total adsorption energy are equal (in this case, the corresponding value is $\Delta_{sp}\bar{G}^{\circ}_i = 0$ kJ mol^{-1}) are presented in Table 3. The value of T_{com} was defined as the temperature of enthalpy—entropy compensation[53] and can be calculated by the equation $T_{com} = \Delta_{sp}\bar{H}^{\circ}_i/\Delta_{sp}\bar{S}^{\circ}_i$. The physical meaning of T_{com} is that at this temperature the chemical potentials of the sorbate molecules in the gas phase and in the adsorbed state are equal. Since in the boiling point the chemical potentials of the substance in solution and in vapor are also equal, it was of interest to compare the determined values of T_{com} with the values of normal boiling temperatures of the sorbates T_b. The dependences of T_{com} on T_b are shown in Fig. 5, and these plots are almost linear for the series of compounds similar in structure.

As follows from the data in Tables 1 and 3, the values of T_{com} in the series of the studied sorbates differ insignificantly from the corresponding values of T_b. This indicates that the processes of boiling of pure hydrocarbons and their evaporation from solutions in squalane at $T_{col} = T_{com}$ are similar. At the same time, the overestimated values of T_{com} relative to T_b can be explained as follows. First, the values of T_b refer to the standard atmospheric pressure (p_{st} = 1 atm), while in the chromatographic column the pressure is higher than atmospheric, which evidently increases the temperature for the evaporation of the sorbate from a solution in the SLP. Second, the energy of the sorbate—sorbate intermolecular interactions in the pure liquid sorbate usually differs from the sorbate—SLP intermolecular interactions in an SLP solution. This also affects the energy of the transition of sorbate molecules to the equilibrium gas phase. Since in our case $T_{com} > T_b$, the energy of the sorbate—sorbate intermolecular interaction is lower, most likely, than the energy of the sorbate—squalane interaction. Thus, we may conclude that the values of T_{com} can serve as an additional measure in estimating the character of intermolecular interactions in the sorbate—sorbent system and can be used in prediction of T_b for pure sorbates.

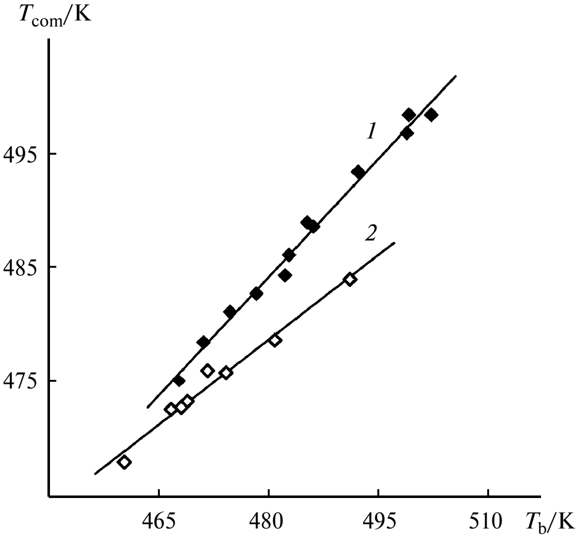

Fig. 5. Correlation between the normal boiling points (T_b) and the temperatures of enthalpy—entropy compensation during adsorption (T_{com}) in the series of studied alkyladamantanes (*1*) and bicyclic hydrocarbons (*2*) on the SLP squalane.

The values of limiting activity coefficients of the sorbates in an SLP solution γ_i^∞ (see Table 3) suggest that solutions of all studied hydrocarbons in squalane are characterized by negative deviations from Raoult's law ($\gamma_i^\infty < 1$). This is well consistent with the assumption about the high affinity of sorbate molecules to SLP molecules. An attempt to find a relationship between the numerical values of γ_i^∞ and specific features of the molecular structure of the sorbates (the number and position of substituents in the molecule, the number of cycles in the molecule, *etc.*) revealed that the values of γ_i^∞ in the series of structurally similar compounds change arbitrarily. However, it turned out that in molecules of strained carbocycles (**17**—**19**) and molecules containing aromatic moieties (**21**, **22**) the values of γ_i^∞ are the highest among the considered compounds. According to Eqs (2) and (7), the molecular weight of the SLP directly affects the numerical values of γ_i^∞, which is easily seen for an adamantane molecule on going from the squalane phase ($C_{30}H_{62}$) to the hydrocarbon phase $C_{78}H_{158}$ (see Table 3).

An analysis of the values of excessive enthalpy $\bar{H}_i^{E,\infty}$ and entropy $\bar{S}_i^{E,\infty}$ of mixing of sorbate—SLP shows that the observed strong negative deviations from ideality are due to the enthalpy contribution to the chemical potential of the sorbate in an infinitely diluted solution in squalane ($\bar{H}_i^{E,\infty} < 0$). The only exception is presented by molecules of strongly strained compounds **17**—**19**, for which the main influence on γ_i^∞ is made by $\bar{S}_i^{E,\infty} > 0$. The negative values of $\bar{H}_i^{E,\infty}$ in the series of cyclic hydrocarbons studied indicate that mixing of molecules of these compounds with Squalane occurs with heat evolution (1.28—6.93 kJ mol^{-1}). It follows from the negative values of $\bar{S}_i^{E,\infty}$ that the obtained real solutions carbocycle—squalane are more ordered than pure liquids due to the bulky structure of conformationally rigid molecules of the sorbates considered. The enthalpy ($\bar{H}_i^{E,\infty}$) and entropy ($T\bar{S}_i^{E,\infty}$) contributions to the partial excess molar Gibbs energy ($\bar{G}_i^{E,\infty}$) in an infinitely diluted solution in squalane for adamantane, alkyladamantanes, and other cyclic hydrocarbons are compared in Fig. 6. The points corresponding to compounds **17**—**19** are closer to the axis $T\bar{S}_i^{E,\infty}$, while the points belonging to other compounds are closer to the axis $\bar{H}_i^{E,\infty}$. The dashed line corresponds to the equality of the contributions of $\bar{H}_i^{E,\infty}$ and $T\bar{S}_i^{E,\infty}$, *i.e.*, to the state of the system when $\gamma_i^\infty = 1$.

Based on the experimental values of $\bar{H}_i^{E,\infty}$ and $\Delta_{\text{sp}}\bar{H}_i^\circ$, we determined the values of the enthalpies of vaporization $\Delta_{\text{vap}}\bar{H}^\circ_{\text{m},i}$, which are related by the equation[4]

$$\Delta_{\text{vap}}H^\circ_{\text{m},i}(\text{GLC}) = \bar{H}_i^{E,\infty} - \Delta_{\text{sp}}\bar{H}^\circ_i. \qquad (14)$$

The values of $\Delta_{\text{vap}}H^\circ_{\text{m},i}(\text{GLC})$ refer to the average temperature of the performed chromatographic experiment ($T = 373.15$ K) at which the values of $\bar{H}_i{}^{E,\infty}{}_i$ and $\Delta_{\text{vap}}H^\circ_i$ were determined. The obtained values of $\Delta_{\text{vap}}H^\circ_{\text{m},i}$ are presented in Table 4.

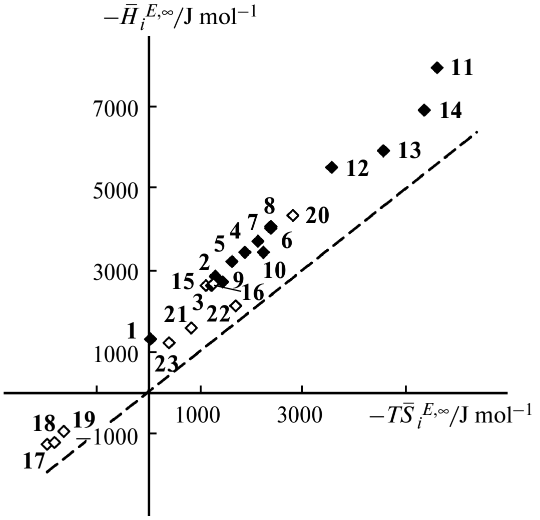

Fig. 6. Correlation between the enthalpy ($\bar{H}_i^{E,\infty}$) and entropy ($T\bar{S}_i^{E,\infty}$) contributions to the partial excess molar Gibbs energy ($\bar{G}_i^{E,\infty}$) of adamantane and alkyladamantanes (dark designations) and other cyclic hydrocarbons (light designations) in an infinitely diluted solution in Squalane at $T = 373.15$ K.

In the present work, we also used alternative methods of estimation of the enthalpy of vaporization. In the first method,[56] the values of $\Delta_{\text{vap}}H^\circ_{\text{m},i}$ at $T = T_\text{b}$ were calculated by the correlation equation

$$\Delta_{\text{vap}}H^\circ_{\text{m},i}(T_\text{b}) = CM^{-m}, \qquad (15)$$

where M is the molecular weight (g mol^{-1}); C and m are constants, whose values depend on the class of studied compounds (in the case of cyclic hydrocarbons, $C = 605$ and $m = 0.44$). The values of $\Delta_{\text{vap}}H^\circ_{\text{m},i}$/cal g^{-1} obtained by this method are given in Table 4.

The calculation of $\Delta_{\text{vap}}H^\circ_{\text{m},i}$ by the second value is based on the additive-group model of determination of the property of a molecule by the sum of contributions of particular fragments

$$\Delta_{\text{vap}}H^\circ_{\text{m},i}(T_\text{b}) = 15.30 + \sum_j^k n_j\delta(\Delta_{\text{vap}}H^\circ_{\text{m},j}), \qquad (16)$$

where $\delta(\Delta_{\text{vap}}H^\circ_{\text{m},j})$ is the contribution of the *j*th structural fragment to the value of $\Delta_{\text{vap}}H^\circ_{\text{m},i}$ (n_j is the number of similar structural fragments), and k is the number of types of structural fragments in the molecule. The values of $\delta(\Delta_{\text{vap}}H^\circ_{\text{m},i})$ were taken from the literature.[57] The values of $\Delta_{\text{vap}}H^\circ_{\text{m},i}$ are also calculated at $T = T_\text{b}$ (see Table 4).

To recalculate $\Delta_{\text{vap}}H^\circ_{\text{m},i}$ to one temperature, we used the widely known method[56] based on the equation

$$\Delta_{\text{vap}}H^\circ_{\text{m},i}(T_2) = \Delta_{\text{vap}}H^\circ_{\text{m},i}(T_1)\left[\frac{1 - T_2/T_\text{c}}{1 - T_1/T_\text{c}}\right]^n, \qquad (17)$$

where T_1 and T_2 are temperatures (K), $\Delta_{\text{vap}}H^\circ_{\text{m},i}(T_1)$ is the known value of the enthalpy of vaporization at T_1,

Table 4. Enthalpies of vaporization ($\Delta_{vap}H^{o}_{m,i}$/kJ mol^{-1}) determined by different methods[a] for the studied compounds

Compound	T_b/T_c	GLC experiment[b]		Calculation				Experiment (literature data)			
				by formula (15)		by formula (16)		(T/K)	373.15 K	T_b	Method[c]
		373.15 K	T_b	373.15 K	T_b	373.15 K	T_b				
1	0.6771	45.30	*39.54*	*45.41*	39.63	*42.92*	37.46	48.19 (298.15)[15]	*44.42*	*38.77*	GC
2	0.6779	44.65	*38.81*	*48.18*	41.88	*44.32*	38.53	—	—	—	—
3	0.6910	48.24	*41.02*	*49.26*	41.88	*46.82*	39.37	—	—	—	—
4	0.6736	45.21	*39.33*	*50.56*	43.98	*45.53*	39.61	49.71 (298.15)[54]	*45.97*	*39.99*	C
5	0.6917	47.55	*40.31*	*51.88*	43.98	*47.72*	40.45	—	—	—	—
6	0.6917	47.67	*40.37*	*51.93*	43.98	*47.76*	40.45	—	—	—	—
7	0.6917	48.49	*40.84*	*52.21*	43.98	*48.02*	40.45	—	—	—	—
8	0.6869	49.26	*41.69*	*51.97*	43.98	*48.17*	40.76	54.96 (298.15)[54]	*50.86*	*43.04*	C
9	0.7069	52.21	*42.90*	*53.52*	43.98	*50.63*	41.60	—	—	—	—
10	0.6894	46.36	*39.45*	*54.16*	46.09	*47.81*	40.68	51.74 (298.15)[54]	*47.70*	*40.59*	C
11	0.6801	42.99	*36.93*	*55.98*	48.08	*48.62*	41.76	—	—	—	—
12	0.6931	48.60	*40.63*	*55.13*	46.09	*50.02*	41.83	—	—	—	—
13	0.6938	49.55	*41.03*	*58.07*	48.08	*51.82*	42.91	—	—	—	—
14	0.6945	48.75	*40.26*	*60.56*	50.02	*53.25*	43.98	—	—	—	—
15	0.6700	44.54	*39.36*	*45.24*	39.98	*43.42*	38.37	44.20 (378.15)[55]	*44.47*	*39.30*	A, MT
16	0.6676	46.25	*40.62*	*45.53*	39.98	*43.69*	38.37	45.50 (386.15)[55]	*46.20*	*40.57*	A, MT
17	0.6786	49.41	*43.12*	*45.81*	39.98	*43.97*	38.37	—	—	—	—
18	0.6786	50.16	*43.56*	*46.04*	39.98	*44.19*	38.37	—	—	—	—
19	0.6787	49.61	*43.23*	*45.88*	39.98	*44.03*	38.37	—	—	—	—
20	0.6801	47.45	*41.06*	*46.57*	40.30	*45.39*	39.28	48.20 (358.15)[55]	*47.35*	*40.98*	EB
21	0.6676	48.92	*42.52*	*44.85*	38.98	*47.40*	41.19	51.10 (326.15)[55]	*48.70*	*42.33*	A
22	0.6562	47.92	*41.68*	*44.04*	38.31	*48.02*	41.77	50.60 (367.15)[55]	*50.30*	*43.76*	A
23	0.7241	46.25	*39.88*	*47.11*	40.62	*43.89*	37.85	51.40 (298.15)[55]	*46.06*	*39.72*	EB, IPM

[a] The values of $\Delta_{vap}H^{o}_{m,i}$ recalculated by the Watson method (see Eq. (17)) to the specified temperature T are italicized.

[b] Data of the present work.

[c] GC is gas chromatography, EB is ebuliometry, IPM is the method with inclined piston manometer, A is the calculation by the values of saturation vapor pressure using the least-squares method, C is calorimetry, and MT is the method of transpiration.

T_c is the critical temperature (K), and n is the parameter determined by the ratio T_b/T_c.

The values of $\Delta(\Delta_{vap}H^{\circ}_{m,i})$ corresponding to the difference between the values of $\Delta_{vap}H^{\circ}_{m,i}$(GLC), determined in this work by Eq. (14), and $\Delta_{vap}H^{\circ}_{m,i}$(method), calculated by Eqs (15) and (16) and taken from reference literature, are presented in Table 5. The data presented show than the highest values of $\Delta(\Delta_{vap}H^{\circ}_{m,i})$ are observed when

Table 5. The values of $\Delta_{vap}H^{o}_{m,i}$/kJ mol^{-1} determined by GLC and other methods at T = 373.15 K

Compound	I[a]	II[b]	III[c]
1	−0.11	2.38	0.88
2	−3.53	0.33	—
3	−1.02	1.42	—
4	−5.35	−0.32	−0.76
5	−4.33	−0.17	—
6	−4.26	−0.09	—
7	−3.72	0.47	—
8	−2.71	1.09	−1.60
9	−1.31	1.58	—
10	−7.80	−1.45	−1.34
11	−12.99	−5.63	—
12	−6.53	−1.42	—
13	−8.52	−2.27	—
14	−11.81	−4.50	—
15	−0.70	1.12	0.07
16	0.72	2.56	0.05
17	3.60	5.44	—
18	4.12	5.97	—
19	3.73	5.58	—
20	0.88	2.06	0.10
21	4.07	1.52	0.22
22	3.88	−0.10	−2.38
23	−0.86	2.36	0.19

[a] Calculated by formula (15).

[b] Calculated by formula (16).

[c] Experimental data.

$\Delta_{\text{vap}}H^\circ{}_{\text{m},i}$ calculated by the first method are used.[56] The lower values of $\Delta(\Delta_{\text{vap}}H^\circ{}_{\text{m},i})$ are obtained when the second method is used; however, for some compounds $\Delta(\Delta_{\text{vap}}H^\circ{}_{\text{m},i})$ is 5—6 kJ mol^{-1}. Obviously, the values of $\Delta_{\text{vap}}H^\circ{}_{\text{m},i}$(GLC) found by Eq. (14) are rather reliable and can be recommended for thermodynamic analysis of liquid—vapor equilibria in the series of studied compounds. Good agreement of the values of $\Delta_{\text{vap}}H^\circ{}_{\text{m},i}$(GLC) with the corresponding literature data indicates reliability of other obtained thermodynamic parameters that characterize the liquid—vapor equilibrium in the series of studied adamantane derivatives and other carbocyclic compounds.

A summary of important conclusions drawn from the present study follows:

— the SLP squalane is the optimal phase for gas-chromatographic determination of parameters of the liquid—vapor equilibrium (normal boiling points, enthalpies and entropies of vaporization, change in the isobaric heat capacity of vaporization) in the series of studied cyclic and cage hydrocarbons, which is confirmed by good agreement of the values obtained in the present study with the results of alternative static measurements in the series of reference compounds;

— a relation between the temperature of enthalpy—entropy compensation of the adsorption process and normal boiling temperatures of the sorbates was established for the first time and the possibility of application of compensation temperatures for the estimation of deviations of the studied sorbate—SLP chromatographic systems from the ideal state was shown;

— the activity coefficients and excess thermodynamic functions of mixing of molecules of cage hydrocarbons with molecules of the hydrocarbon SLP were determined for the first time, which made it possible to perform the detailed thermodynamic analysis of dilute solutions formed by cage molecules;

— large differences were established for contributions of the nodal and bridging Me groups of alkyladamantanes to the values of TCA caused by specific features of the electronic structure of the adamantane moiety, which directly affect the elution order of the studied compounds from the chromatographic column with the SLP squalane.

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