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Influence of the chemical nature of siloxanes on the thermodynamic characteristics of sorption for a series of linear and cyclic saturated hydrocarbons

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The thermodynamic characteristics of sorption (Henry´s constants of sorption equilibrium K_{sorp}, heats of sorption q, and standard entropies of sorption $\Delta S°$) were studied by gas chromatography to describe the behavior of linear and cyclic saturated hydrocarbons on phenylmethylsiloxane HP-5, fluoromethylsiloxane OV-210, and methylsiloxane OV-1. The K_{sorp} and q values and, correspondingly, the energy of dispersion interactions decrease in the series HP-5 > OV-1 > OV-210. The difference in structures of adamantane, *trans*-decalin, and decane molecules has almost no effect on the heats of sorption. Henry´s constants increase on going from decane to *trans*-decalin and, further, to adamantane. This effect becomes more pronounced with an increase in the sorbent polarity (OV-1 < HP-5 < OV-210). The entropy factor can play a key role in sorption processes on siloxanes.

Key words: gas chromatography, thermodynamic characteristics of sorption, siloxanes, linear and cyclic hydrocarbons.

Siloxanes are used as stationary phases for gas chromatography.[1—4] The thermodynamic characteristics of sorption (TCS) in systems involving siloxanes are studied in few publications only.

Linear alkanes are testing compounds commonly used for the quantitative estimation of the energy of dispersion interaction with the stationary phase (both liquid and solid).[1,5] Contributions of the specific interaction to the Gibbs energy and heat of sorption are determined on the basis of the sorption values of n-alkanes.[6] Chromatographic data for n-alkanes are necessary to determine the Kovats retention indices and to calculate relative characteristics of sorption in gas chromatography.[1] The latter is one of the main methods for determining linear and cyclic alkanes in various objects, including oil and petroleum refining products.[7,8]

The physicochemical properties of adamantane (AdH) and its derivatives, including sorption behavior, are intensely studied due to the wide use of this class of compounds in medicine, their potential biological activity,[9,10] and, especially, the unique features of the AdH structure.[7,11] The number of publications on the relations of the retention parameters of AdH and its derivatives to the stationary phase nature has substantially increased in recent time.[12—17] Nevertheless, the retention parameters of AdH in a wide temperature range remain virtually unknown and, hence, the TCS of these compounds were not determined.

In this work, we used gas chromatography to study the influence of the chemical nature of siloxanes (methylsiloxane, phenylmethylsiloxane, and fluoromethylsiloxane) on the TCS (constants, heats, and standard entropies) of several linear and cyclic alkanes.

Experimental

Stationary phases were 5% phenylmethylsiloxane HP-5 $—[Si(Ph)_2—O—]_n—[Si(Me)_2—O—]_m—$ (thickness of the grafted phase 0.25 μm; the density of the grafted phase was assumed to be ρ = 1 g mL^{-1}),[2] fluoromethylsiloxane OV-210 $—[(CF_3(CH_2)_2)Si(Me)—O—]_n—$ with the 50% content of trifluoropropyl groups (10% on Chromaton NAW, Russia; particle size 0.16—0.25 mm), and methylsiloxane OV-1 $—[Si(Me)_2—O—]_n—$ (10% on Gas-Chrom Q, USA; particle size 0.16—0.25 mm). Measurements were carried out on a quartz capillary column (30 m×0.32 mm) with HP-5 on an HP-6890 chromatograph (USA) with a flame-ionization detector (FID) and a katharometer and on glass packed columns (120×0.3 cm) with OV-1 and OV-210 on a Tsvet-100 chromatograph (Russia) with a FID. Carrier gases were helium (flow rate

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$\omega(He) = 1$—5 mL min^{-1} for an HP-6890 chromatograph) and nitrogen ($\omega(N_2) = 10$—25 mL min^{-1} for a Tsvet-100 chromatograph).

Some primary data obtained earlier[18] were used for analysis of the results of measurements on the OV-1 phase.

n-Alkanes, AdH (tricyclo[3,3,1,1^{3,7}]decane, $C_{10}H_{16}$), and *trans*- and *cis*-decalins (bicyclo[4,4,0]decane, $C_{10}H_{18}$) (reagent grade, Reakhim, Russia) were used as the main testing compounds. Samples of the substances were injected 3—6 times as dilute steam-and-air mixtures (on OV-1 and OV-210) or dilute solutions in hexane (on HP-5). The "dead" time t_0 was determined by methane.[1]

The procedure of calculation of the retention volumes (V_R (mL)* and V_g (mL g^{-1})) and Kovats retention indices I has been described previously.[19]

The following standard state of the compounds were used to determine the TCS: $c_{st} = 1$ μmol mL^{-1} in the mobile phase and $a_{st} = 1$ μmol g^{-1} in the stationary phase. Since Henry´s constant of sorption equilibrium is determined by

$$K_{sorp} = \lim_{a,c\to 0} \frac{a/a_{st}}{c/c_{st}},$$

then K_{sorp} is numerically equal to V_g.

The sorbent selectivity α toward two compounds (**1** and **2**) was estimated as follows:

$$\alpha = K_{sorp}(\mathbf{1})/K_{sorp}(\mathbf{2}).$$

The initial (Henry´s region) differential molar heats of sorption q (hereinafter, heats of sorption) and the standard entropies $\Delta S°$ were determined from the temperature plot of K_{sorp} in the 343—448 K range using the equation[19]

$$\ln K_{sorp} = q/(RT) + \Delta S°/R + 1.$$

The entropy of the substance in the sorbed state $S°_{sorp}$ was estimated as

$$S°_{sorp} = \Delta S° + S°_{gas},$$

where $S°_{gas}$ is the standard entropy of the substance in the gaseous state, which was calculated from $S°_{gas}$ at the standard pressure $p_{st} = 1$ atm [20,21] using the equation

$$S°_{gas} = S°_{gas}(p_{st}) - R\ln(c_{st}RT/p_{st}).$$

For all testing compounds, the error of experimental determination of the TCS did not exceed 2%.

Results and Discussion

The thermodynamic characteristics of sorption of linear alkanes are presented in Figs 1 and 2.

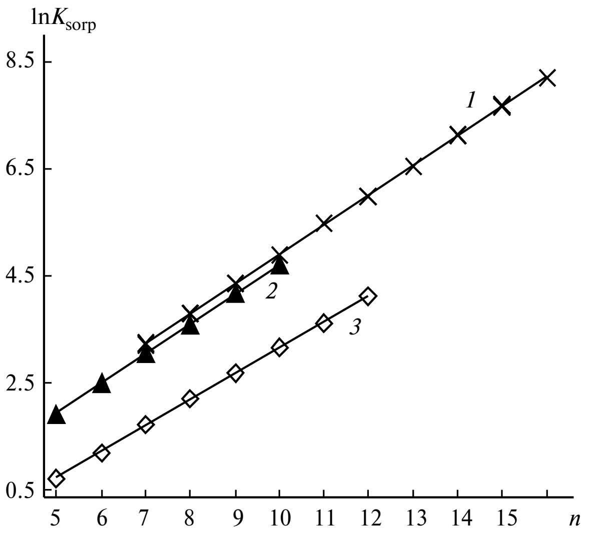

Fig. 1. LnK_{sorp} as a function of the number of carbon atoms n in n-alkane molecules on the stationary phases HP-5 (*1*), OV-1 (*2*), and OV-210 (*3*) at 403 K.

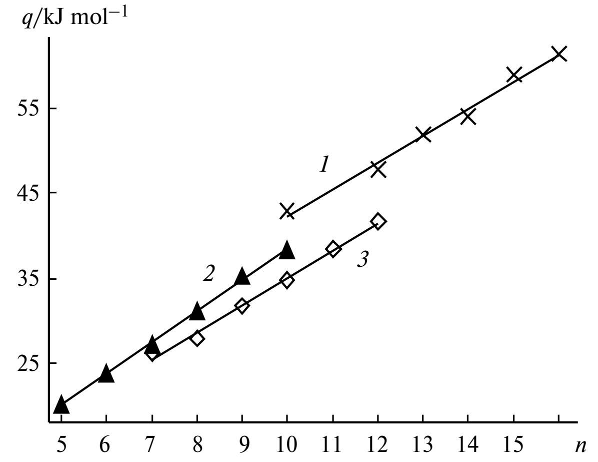

Fig. 2. Heats of sorption q as functions of the number of carbon atoms n in n-alkane molecules on the stationary phases HP-5 (*1*), OV-1 (*2*), and OV-210 (*3*).

The data presented show that Henry´s constants K_{sorp} and the heats of sorption q for the n-alkane series decrease in the order HP-5 > OV-1 > OV-210. Therefore, the lowest energy of dispersion interactions is observed for the fluorine-containing phase OV-210. The decrease in the K_{sorp} values for n-alkanes on going from OV-1 to OV-210 is due to a decrease in the heat and entropy of sorption, while the increase in K_{sorp} on HP-5 over that on OV-1 is caused only by an increase in the heat of sorption, because the standard entropies of sorption on HP-5 are the lowest for all liquid phases under study, for instance, the q and $\Delta S°$ values for decane (Table 1).

The K_{sorp} and q values for both AdH and *trans*-decalin decrease in the same order as the TCS of n-alkanes (in

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* It was established in a series of experiments with the HP-5 sorbent that the use of different detectors exerts almost no effect (within 0.05—0.4%) on the retention volumes V_R. The V_R values are independent (within 0.2%) of the experimental parameters: both a constant pressure of a carrier gas at the inlet of the column (for example for AdH at 120 °C, $V_R = 2.606$ mL) and a constant flow rate of helium ($V_R = 2.603$ mL) can be used.

Table 1. Henry's constants K_{sorp} (403 K), the heats of sorption (q/kJ mol^{-1}), and the standard entropies of sorption ($\Delta S°$/J mol^{-1} K^{-1}) on siloxanes and the standard entropies of the substances in the sorbed ($S°_{sorp}$) and gaseous ($S°_{gas}$) states (J mol^{-1} K^{-1}) at 403 K

Stationary phase	Decane				*trans*-Decalin				Adamantane			
	K_{sorp}	q	$-\Delta S°$	$S°_{sorp}$	K_{sorp}	q	$-\Delta S°$	$S°_{sorp}$	K_{sorp}	q	$-\Delta S°$	$S°_{sorp}$
			($S°_{gas}$ = 653)				($S°_{gas}$ = 464)				($S°_{gas}$ = 405)	
OV-210	22.3	33.8	66.3	586	43.2	33.6	60.4	403	53.4	33.4	58.1	347
OV-1	112	38.4	64.4	588	167	37.2	58.1	405	196	36.8	55.8	349
HP-5	136	42.8	74.6	579	211	41.0	65.2	398	257	40.9	64.0	341

Table 2. Kovats indices at 403 K

Compound	I/abr. units		
	OV-1	HP-5	OV-210
Benzene	672	689	804
Butan-1-ol	597	648	926
cis-Hydrindane*	1004	1015	1066
Adamantane	1103	1113	1190
trans-Decalin	1074	1093	1148

* Data in Ref. 22.

particular, decane (C_{10})), *i.e.*, in the order HP-5 > OV-1 > > OV-210 (see Table 1). These values are determined, primarily, by the energy of dispersion interactions between hydrocarbons and siloxanes. Comparison of q and $\Delta S°$ for AdH and *trans*-decalin suggests that the effect of the entropy of sorption and heat of sorption on K_{sorp} is the same as that for *n*-alkanes. The calculated standard entropies of the substances in the sorbed state $S°_{sorp}$ vary in the same manner as $\Delta S°$.

The Kovats indices I are widely used parameters in chromatographic practice. The indices of cyclic compounds, as well as those of benzene and butan-1-ol (substances that are usually used for the estimation of the stationary phase polarity[1]), are presented in Table 2.

The polarity of the siloxanes under study increases in the series OV-1 < HP-5 < OV-210 (see Table 2), which is completely consistent with the published data.[1,22] The I values for AdH increase with an increase in the polarity of siloxane. The authors[13—17] believe that an increase in I for AdH on going from the nonpolar liquid phase to polar phases can be explained by the specific features of its electronic structure, namely, by the so-called cage effect. However, our results (see Table 2) indicate that although an increase in I with an increase in the stationary phase polarity is a characteristic feature of AdH it is observed also for bicyclic *trans*-decalin and *cis*-hydrindane molecules, and that contradicts the above-mentioned assumption.[12—17]

The retention indices on OV-210 increase compared to the less polar phase OV-1, while the heats of sorption of all cyclic hydrocarbons on fluoromethylsiloxane decrease by 3—4 kJ mol^{-1} (see Table 1).

The data obtained allow us to conclude that the electronic structure of AdH exerts no discernible effect (cage effect) on the energy of its sorption for the studied stationary phases.

The thermodynamics of sorption of AdH, *trans*-decalin, and C_{10} (compounds with the same number of carbon atoms in a molecule and similar molecular weights) show that the substantial distinction in the molecular structures (framework, bicyclic, and linear, respectively) does not virtually affect the heats of sorption for each siloxane (see Table 1). At the same time, the K_{sorp} values increase noticeably on going from C_{10} to *trans*-decalin and, further, to AdH. This is explained by the fact that the determining factor for dissolution in the liquid phase is the saturated vapor pressure of the compounds (for C_{10}, 28 kPa; for *trans*-decalin, 17 kPa; and for AdH, 9 kPa at 403 K), whereas the shape of the molecule is of secondary importance.

The retention selectivities α were determined in a fairly wide temperature range (Figs 3 and 4) to obtain more detailed information on the influence of the chemical nature of siloxane on the order of elution from molecules of the framework (AdH), bicyclic (*trans*-decalin), and linear (C_{10}) structures.

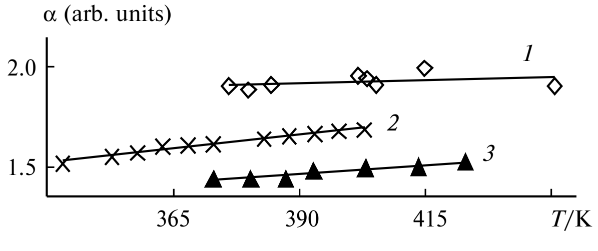

Fig. 3. Temperature plots of the selectivities of sorption α for the *trans*-decalin—decane (C_{10}) pair on the stationary phases OV-210 (*1*, $y = 0.0005x + 1.70$), HP-5 (*2*, $y = 0.0028x + 0.58$), and OV-1 (*3*, $y = 0.0017x + 0.79$); α/arb. units = K_{sorp}(*trans*-decalin)/K_{sorp}(C_{10}).

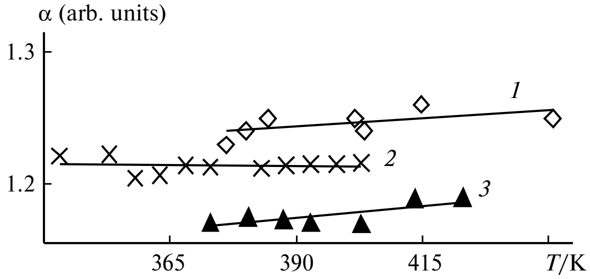

Fig. 4. Temperature plots of the selectivities of sorption α for the adamantane (AdH)—*trans*-decalin pair on the stationary phases OV-210 (*1*, $y = 0.0003x + 1.14$), HP-5 (*2*, $y = -2E - 0.5x + 1.22$), and OV-1 (*3*, $y = 0.0004x + 1.03$); α/arb. units = K_{sorp}(AdH)/K_{sorp}(*trans*-decalin).

The experimental temperature has nearly no effect on α, because the heats of solution of these compounds (C_{10}, *trans*-decalin, and AdH) in each of the liquid phases are almost the same. However, when the siloxane polarity increases (OV-1 < HP-5 < OV-210), K_{sorp} increases in the series C_{10} < *trans*-decalin < AdH. Thus, the entropy factor plays a key role in sorption processes in these systems. It is convenient to use the temperature plots of the selectivity obtained in this work to identify cyclic hydrocarbons without standards.

The study of the temperature plots of K_{sorp} for decalin isomers on HP-5 shows that K_{sorp} for *trans*-decalin is lower than that for the *cis*-isomer. This agrees with a decrease in the vapor pressure (for *cis*-decalin, 13 kPa at 403 K) or an increase in the boiling point of *cis*-decalin. The energy component contributes mainly to the increase in K_{sorp} for the *cis*-isomer compared to *trans*-decalin, because the heat of sorption of *cis*-decalin is higher than that of *trans*-decalin (42.5 and 41.0 kJ mol^{-1}, respectively), whereas the entropy of sorption changes in the opposite direction ($-\Delta S°$ is equal to 67.3 and 65.2 J mol^{-1} K^{-1} for the *cis*- and *trans*-isomers, respectively).

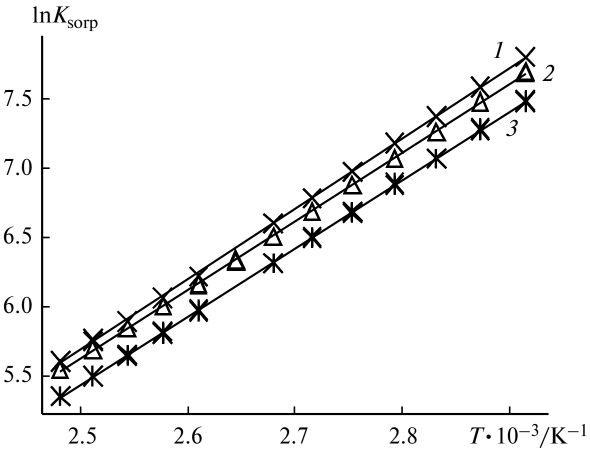

Fig. 5. Temperature plots of lnK_{sorp} for the adamantane and decalin isomers on HP-5: *1* — *cis*-decalin, *2* — adamantane, *3* — *trans*-decalin.

Despite the differences in the heats of sorption and vapor pressures of the compounds, the retention values of AdH and *cis*-decalin on HP-5 differ insignificantly (K_{sorp} at 403 K are 257 and 273 for AdH and *cis*-decalin, respectively).

The data obtained in this work can be used for predicting the retention values of hydrocarbons on siloxanes of different chemical structures and for selecting stationary phases with the optimum (for the solution of specific problems) properties.

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