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Retention and heats of adsorption of *n*-alkanes, aromatic hydrocarbons, aliphatic alcohols and ketones on macroporous silicas

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ABSTRACT

   Adsorption of molecules of *n*-alkanes, aromatic hydrocarbons, alcohols and ketones on the hydroxylated surface of S-80, S-120, and SX-3 silochromes was studied by gas chromatography in the temperature range 80–200°C. The retention volumes and initial differential heats of adsorption were calculated. The contribution of the specific interaction of aromatic compounds with the silica surface in the course of adsorption was evaluated. The properties of the surfaces of the silicas under study were compared on the basis of the chromatographic data.

INTRODUCTION

   In recent years, macroporous silica silochromes have been widely used as stationary phases in analytical gas chromatography [1–5]. Silochromes in the form of microspheres or granules are prepared by hydrothermal treatment in autoclaves [2]. Depending on the purity of the initial reagents and the reaction conditions, the content of impurities in silochromes may be no more than 10^{-4}% [3]. Chemical purity of the surface is very important for the application of silicas as sorbents and supports in chromatography, as the presence of impurity centres may be responsible for peak asymmetry and lead to chemosorption. Qualitative and quantitative characteristics of the state of the silica surface depending on the conditions of preparation and treatment can be derived from the values of V_A, the retention volumes of small doses of the adsorbate, and $-(\Delta \bar{U})$, the differential heats of adsorption of model organic compounds determined by gas adsorption chromatography.

   To evaluate the parameters of adsorption interaction between molecules with different chemical structures and the silochrome surface, we studied the adsorption of *n*-alkanes, aromatic hydrocarbons, alcohols and ketones by gas chromatography and assessed the chromatographic properties of the surfaces of the samples under consideration.

EXPERIMENTAL

Samples of macroporous S-80, S-120 and SX-3 silica silochromes (Khimreactiv, U.S.S.R.) were studied and their characteristics are given in Table I. The specific surface area, s, was determined by thermal desorption of nitrogen. The average pore diameter, d_s, corresponded to the maximum on the differential curve of the size distribution of pore volume calculated by mercury porosimetry, the pore volume v_s being found by titration with water.

TABLE I

STRUCTURAL CHARACTERISTICS OF SILOCHROMES

Silochrome	Specific surface area, s (m^2/g)	Average pore diameter, d_s (nm)	Pore volume, v_s (cm^3/g)
S-120	145	45	1.3
S-80	115	55	1.4
SX-3	100	66	1.5

Adsorption on silochromes was investigated on a Tswet-102 chromatograph with a 20 cm × 3 mm I.D. column and a flame ionization detector. The mass of the sample in the column was *ca.* 0.5 g (0.25–0.5 mm fraction). Helium was used as the carrier gas at a flow-rate of 30 cm^3/min.

Prior to the experiment each silochrome sample was dried in the column with a flow of carrier gas at 220°C for 3 h.

To obtain reproducible results for the retention of each adsorbate, different doses of the vapours were repeatedly introduced into the column. Generally, the relative standard deviation did not exceed 1%. The retention times of each hydrocarbon in the chromatographic column were determined at 80–220°C. The retention volumes were calculated from the retention times found experimentally:

$$V'_R = (t_R - t_0)w \qquad (1)$$

where t_R is the retention time of the hydrocarbon sample, t_0 is the retention time of methane accepted as a non-sorbing substance and w is the flow-rate of the carrier gas passing through the chromatographic column reduced to a zero pressure drop in the column. The mean V'_R values were calculated for small doses of hydrocarbons. The retention time did not depend on the dose.

RESULTS AND DISCUSSION

Under the conditions of equilibrium chromatography, the retention volume V_A of a small sample of the given substance referred to the adsorbent surface in the column

TABLE II

VALUES OF V_A (cm^3/m^2) AT 100°C AND OF $-\Delta\bar{U}$ (kJ/mol) AT 100–150°C FOR ADSORPTION OF n-ALKANES AND AROMATIC HYDROCARBONS ON SILOCHROMES

Adsorbate	S-120		S-80		SX-3		S-120: $\Delta(-\Delta\bar{U})$
	V_A	$-\Delta\bar{U}$	V_A	$-\Delta\bar{U}$	V_A	$-\Delta\bar{U}$	
n-Hexane	0.11	37.3	0.10	37.4	0.09	37.2	—
n-Heptane	0.20	41.1	0.21	41.3	0.19	41.1	—
n-Nonane	0.82	48.8	0.89	49.0	0.84	49.4	—
n-Decane	1.70	53.1	1.79	53.7	2.1	53.5	—
Benzene	0.17	41.1	0.17	40.6	0.19	40.4	6.7
Toluene	0.53	45.5	0.52	45.2	0.53	45.4	7.1
Ethylbenzene	1.09	49.3	0.95	49.9	1.05	49.8	7.1
m-Xylene	1.28	48.5	1.21	49.2	1.24	48.0	5.9
p-Xylene	1.31	48.7	1.29	52.1	1.29	48.0	6.1
o-Xylene	1.31	49.5	1.39	52.1	1.41	50.0	7.1

equals the Henry constant K of the adsorption equilibrium [3–6]. The V'_R values measured experimentally refer to the total surface area of the adsorbent in the column:

$$K = V_A = V'_R/ms = Vm/s \qquad (2)$$

where m is the mass of adsorbent in the column.

If the structure (phase and chemical composition) of the adsorbent is constant, the V_A values are reproduced fairly accurately and represent physico-chemical constants which correspond to the determination of Gibbs thermodynamic values.

Table II gives the values of V_A calculated by eqn. 2 and of $\Delta\bar{U}$, the differential heats of adsorption of hydrocarbons on the three silochromes for zero surface coverages. The differential heats of adsorption were determined from the dependence of log V'_R/T on $1/T$ (Fig. 1) according to the equation

$$-\Delta\bar{U} = Rd \ln (V'_R/T)/d(1/T) \qquad (3)$$

As can be seen from Table II, the V_A and $-\Delta\bar{U}$ values of the corresponding n-alkanes and aromatic hydrocarbons on all three silochromes are close, which points to the similarity of the adsorption properties of the surface of these macroporous silicas.

Inhomogeneity of the surface typical of hydroxylated silicas during the adsorption of molecules of n-alkanes (C_6–C_{10}) and aromatic compounds was apparently not manifested under the experimental conditions.

In homologous series of n-alkanes and aromatic hydrocarbons V_A and $-\Delta\bar{U}$ values increase with increasing number of hydrocarbon atoms in the molecule. The dependences of the heat of adsorption on the polarizability of the molecules, which characterizes the energy of non-specific interactions, are straight lines (Fig. 2). A comparison of the thermodynamic characteristics of n-alkanes and aromatic compounds shows that V_A and $-\Delta\bar{U}$ values for aromatic hydrocarbons are higher

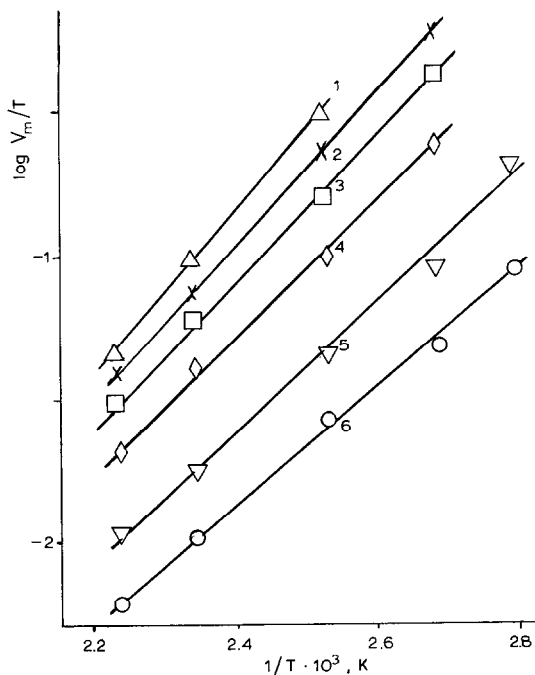Fig. 1. Plots of log (V_m/T) versus $1/T$ for (1) n-decane, (2) ethylbenzene, (3) n-nonane, (4) toluene, (5) n-heptane and (6) n-hexane on S-120.

than those for n-alkanes with a similar molecular mass and the same number of carbon atoms in the molecule. For instance, for benzene and n-hexane and for toluene and n-heptane the V_A values differ almost 2-fold; $-\Delta \bar{U}$ for benzene and toluene is higher than for n-hexane and n-heptane. In the molecules of aromatic compounds the electron
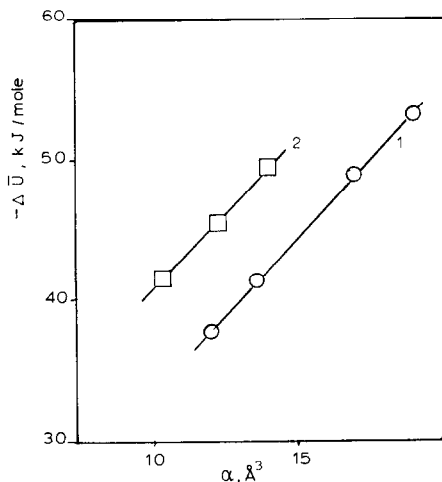

Fig. 2. Heat of adsorption $(-\Delta \bar{U})$ as a function of molecule polarizability (α) for (1) n-alkanes and (2) benzene and monoalkylbenzenes on S-120.

density is localized on the π-bonds of the aromatic ring; therefore, together with non-specific dispersion interactions, aromatic hydrocarbons may also reveal specific intermolecular interactions in the course of adsorption. The presence of hydroxyl groups on the surface of silicas determined the specificity of these adsorbents with respect to organic compounds of different structure owing to the interaction with partially protonated hydrogen atoms in silica hydroxyl groups.

The contribution of the energy of the specific interaction of aromatic hydro-carbons with the hydroxylated surface of silicas to the total heat of adsorption was evaluated by comparing the dependence of heats of adsorption on the polarizability of molecules for n-alkanes and aromatic compounds (Fig. 2). The $\Delta(-\Delta\bar{U})$ values are the differences between the differential heats of adsorption for aromatic compounds and n-alkanes at the corresponding interpolated polarizability values α. The calculated values of $\Delta(-\Delta\bar{U})$ are given in Table II. It is of interest that $\Delta(-\Delta\bar{U})$ for monoalkylbenzenes is higher than that for polyalkylbenzenes, which may be due to the influence of geometric factors during adsorption. The energy of interaction depends on the distance between the adsorbent surface and force centres of the units of the adsorbed molecule, as the benzene ring atoms in xylene molecules are, on average, at greater distances from the adsorbent surface than the atoms of the benzene or ethylbenzene molecules. Probaby because of this fact both the total and the specific energy of interaction on adsorption of xylenes is lower than that for monoalkyl-benzenes.

From the rough dependences of log V_A and $-(\Delta\bar{U})$ on the number of carbon atoms in the molecule (Fig. 3) described by the equations log $V_A = a + bn$ and $-(\Delta\bar{U}) = \bar{a} + bn$, one can evaluate the contributions of the specific interaction and the increment due to the CH_2 group to the retention and heat of adsorption of hydrocarbons of homologous series. These correlation dependences allow one to predict the retention and $-\Delta\bar{U}$ values for individual members of the homologous series. Table III gives the values of the coefficients in the equations for n-alkanes and
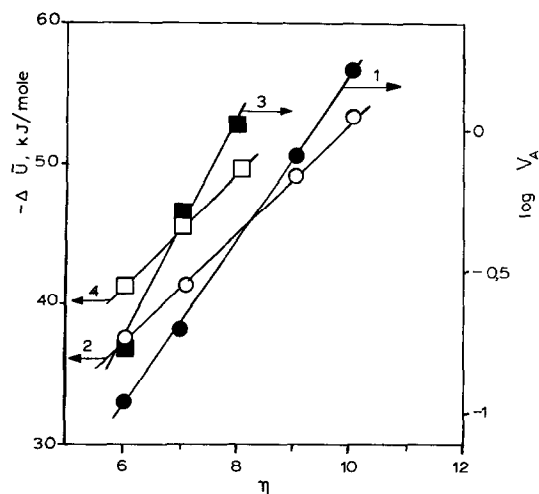

Fig. 3. Plots of log V_A and $-\Delta\bar{U}$ as functions of the number of carbon atoms (n) for (1,2) n-alkanes and (3,4) monoalkylbenzenes.

TABLE III

VALUES OF COEFFICIENTS a, $\bar{a}$, b AND $\bar{b}$ ADSORPTION OF n-ALKANES AND AROMATIC COMPOUNDS ON SILICAS

Adsorbate	Ref.	Column temperature (°C)	$\log V_A = a + bn$			$-\Delta\bar{U} = \bar{a} + \bar{b}n$		
			a	a'	b	$\bar{a}$	$\bar{a}'$	$\bar{b}$
n-Alkanes	This work	100	−2.85	−2.83	0.31	13.7	21.6	3.9
	3	150	−2.88	—	0.21	—	—	—
Aromatic hydrocarbons	This work	100	−2.95	−0.73	0.37	16.1	41.0	4.5
	3	150	−2.34	—	0.21	—	—	—

aromatic compounds. It can be seen that increments in $-\Delta\bar{U}$ of the energy of non-specific interaction by a CH_2 group are 3.9 kJ/mol in the homologous series of n-alkanes and 4.5 kJ/mol in the homologous series of aromatic hydrocarbons. The published values [3] of $\Delta(-\Delta\bar{U})$ per CH_2 group of 4.19 kJ/mol for S-80 silochrome and $a = -2.88$ for n-alkanes at 150°C are close, which indicates that our calculations are correct. However, in our opinion, the coefficients a, $\bar{a}$, b and $\bar{b}$ may alter with a change in the type of homologous series and the chemistry of the surface of the adsorbents.

Table III also lists the values of the coefficients in the equations $\log V_A = a' + bn_1$ and $(-\Delta\bar{U}) = \bar{a}' + \bar{b}n_1$, where n_1 corresponds to the number of CH_2 groups in molecules of n-alkanes and n-alkylbenzenes. In these equations the coefficients a' and $\bar{a}'$ have strict physical meaning: they are $\log V_A$ and the heat of adsorption of ethane for the n-alkane series and benzene for the n-alkylbenzene series. The difference between a' and $\bar{a}'$ mainly characterizes the contribution of the energy of interaction of π-bonds in the aromatic ring with the hydroxylated surface of silica to the total energy of the adsorption interaction of n-alkylbenzene molecules. The evaluation of the contribution of specific interactions calculated as the difference between the heats of adsorption of n-alkylbenzenes and n-alkanes for the same n gives 2.4 kJ/mol, which is almost 50% lower than the values calculated from the plot in Fig. 2. Such underestimated values of $\Delta(-\Delta\bar{U})$ are due to different procedures of calculating the contributions of specific interactions. The procedure proposed in refs. 8 and 9 is apparently more correct, as the polarizability of the molecules is the main parameter of the force constant in calculating the adsorption potential.

Fig. 4 illustrates the temperature dependences of the retention volumes, V_m (ml/g), for methanol, ethanol, propanol, acetone, methyl ethyl ketone and diethyl ether. It is noteworthy that for the ether and ketones, just as for n-alkanes and aromatic hydrocarbons, these dependences within the temperature range studied are virtually straight lines. For the n-alkanols they are clearly non-linear with two straight-line sections with inflection points in the temperature region 150–170°C. The bends on the $\log V_m$ versus $1/T$ plots were observed earlier by Hradil and Švec [10] when studying the chromatography of n-alkanes and n-alkanols on porous sorbent in the range 50–200°C. They assigned the bending of the plot of $\log V_m/T$ versus $1/T$ to the processes of dissolution of these sorbats in the polymeric matrix with increasing temperature. In our case, the appearance of the bend on the $\log V_m$ versus $1/T$ plot can be attributed to the rupture of the hydrogen bonds between alcohol molecules and silanol groups of the
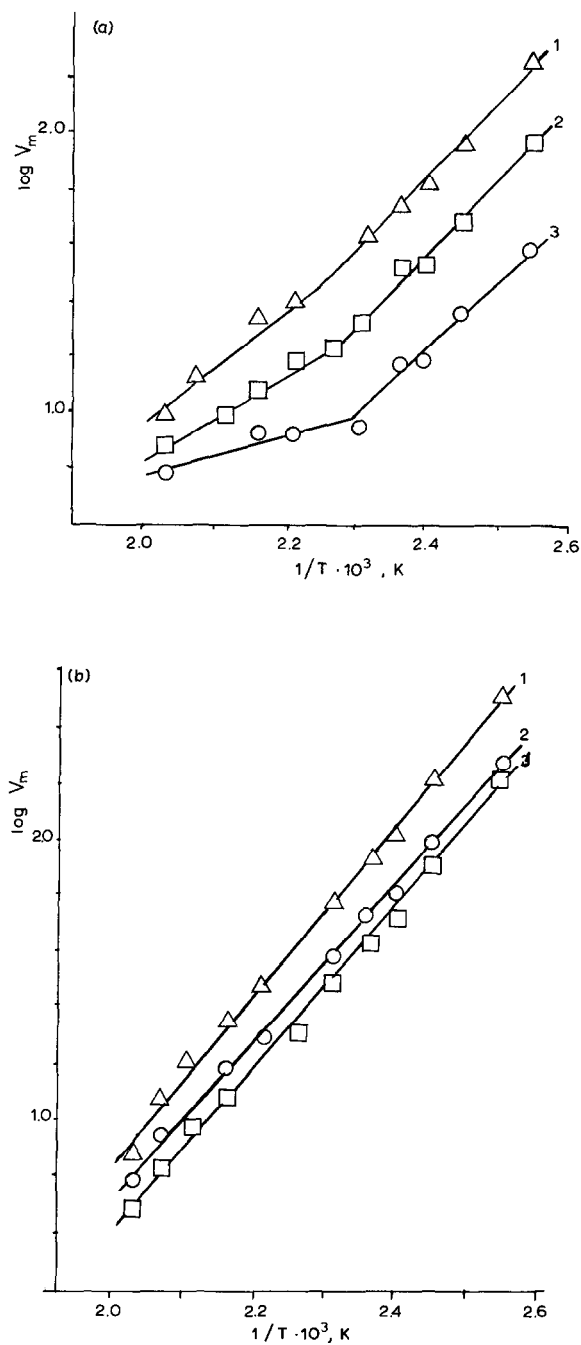
Fig. 4. Plots of log V_m *versus* $1/T$ for (a) (1) *n*-propanol, (2) ethanol and (3) methanol and (b) (1) methyl ethyl ketone, (2) acetone and (3) diethyl ether on S-80.

TABLE IV

VALUES OF $-\Delta\bar{U}$ AND $\Delta(-\Delta\bar{U})$ (kJ/mol) ON S-80

Adsorbate	$-\Delta\bar{U}$			$\Delta(-\Delta\bar{U})$		
	120–150°C	150–220°C	120–220°C	120–150°C	150–220°C	120–220°C
Methanol	46	15.1		45.9	15.1	
Ethanol	50.1	26.1		46.0	21.0	
n-Propanol	54.9	35.4		45.0	25.0	
Acetone			50.6			40.9
Methyl ethyl ketone			54.7			42.1
Diethyl ether			56.9			40.7

silica surface, the bend being more pronounced for lower alcohols (methanol and ethanol). Proceeding from this, we calculated differential heats of adsorption for n-alkanols. Table IV lists the values of $-\Delta\bar{U}$ and $\Delta(-\Delta\bar{U})$ calculated for ketones and n-alkanols with respect to n-alkanes from the dependence on polarizability α [11]. It follows that at 120–150°C the alcohol molecules, when interacting with silanol OH groups on the silica surface, form hydrogen bonds with an energy of 45–46 kJ/mol. A further temperature rise sharply decreases the strength of the hydrogen bonds in alcohol molecules, which is seen from the enthalpy of the specific interaction of these alcohols of 15–20 kJ/mol at 170–220°C.

The behaviour of ketone and diethyl ether molecules apparently remains unchanged over a wide temperature range, from 120 to 220°C, and the energy of the specific interaction between carbonyl groups of the ketone molecules and silanol groups of the silochrome surface is 41–42 kJ/mol. Approximately the same value of the adsorption bond energy is observed for diethyl ether.

Hence the dependences obtained in this paper can be used for elucidation and optimization of separation processes and for physico-chemical investigations.

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