Adsorption study of alkyl-silicas and methylsiloxy-silicas

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Abstract

We report the synthesis and adsorption study of the lyophobic porous silicas. Four adsorbents were prepared and tested: (1) octyl-silica, (2) hexadecyl-silica, (3) bis(trimethylsiloxy)-silica, and (4) oligo(dimethylsiloxane)-silica. Octyl- and hexadecyl-silicas were prepared via the reaction of silica with $(CH_3)_2NSi(CH_3)_2C_nH_{2n+1}$ ($n=8$ and 16), the reactions were carried under the optimized conditions yielding high bonding densities of alkyl groups $\sim$2.9–3.0 groups/nm^2 and highly uniform non-polar adsorbents. Bis(trimethylsiloxy)-silica was prepared via the reaction of silica with $ClSi(CH_3)_2(CH_2)_{10}Si(CH_3)[OSi(CH_3)_3]_2$. Oligo(dimethylsiloxane)-silica was prepared via the reaction of silica with $ClSi(CH_3)_2-[OSi(CH_3)_2]_2-Cl$. Adsorption of small organic compounds (*n*-alkanes, alkylbenzene, benzene, diethyl ether) was investigated using two methods, classical static adsorption and gas chromatography. Thermodynamic parameters (heat, Gibbs energy, and entropy) of the adsorption of organic compounds were studied as a function of the nature of adsorbate and of the nature of the bonded layer as well. The results obtained suggest penetration of the adsorbate molecules into the bonded layer and the importance of this process in the retention mechanism in gas chromatography. Energy of the dispersion interactions with the surface decreases in the following order: n-$C_{16}H_{33}(CH_3)_2Si->n$-$C_8H_{17}(CH_3)_2Si->$ $[(CH_3)_3SiO]_2Si(CH_3)-(CH_2)_{10}(CH_3)_2Si->-[\{(CH_3)_2SiO\}_2]_x-(CH_3)_2Si-$. Energy of the electrostatic and hydrogen bonding interactions with the surface, as assessed from the adsorption of benzene and diethyl ether molecules, decreases in the opposite direction, indicating that alkyl-silicas are less polar adsorbents than methylsiloxy-silicas. © 2001 Published by Elsevier Science B.V.

1. Introduction

Chemical modification of surfaces of metal oxides [1–7] by covalent attachment of organosilanes is a versatile technique that can control adhesion, wettability, adsorption, catalytic and other surface properties of solids. The performance of the surface-modified materials in heterogeneous systems is largely determined by the adsorption at solid–liquid or solid–vapor interfaces and the adsorption characterization of such materials is lacking. Although a great number of papers on synthesis and application of the surface modified materials has been published, only in few of them the adsorption of vapors was investigated. In our recent publications we reported syn-

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thesis of well-characterized lyophobic porous silicas with grafted phenylsiloxy [8,9], bromopropyl [10], alkyl and fluoroalkyl [11,12] surface groups and the adsorption study of organic compounds on these adsorbents. In this publication we report the synthesis of new methylsiloxane-silicas and optimized alkyl-silicas with high bonding density and report the results on their adsorption properties by classical static technique and dynamic gas chromatographic method.

2. Experimental

2.1. Silica and other materials

We used Silochrom S-120 as pristine silica adsorbent and as a substrate for the surface modification as well. This silica is a convenient model for the adsorption and surface chemistry study for several reasons: (1) it is very clean chemically, metals content is less than 10 ppb, (2) it has uniform pore size distribution and relatively wide pores, average pore diameter 57 nm, (3) it has been studied by different research groups and these data are available for comparative analysis [9,13–17]. Two batches of Silochrom S-120 were studied in this work: S-120 No. 1 with the average particle size 0.2–0.35 mm and S-120 No. 2 with the average particle size 0.3–0.5 mm. Prior to the study silicas were hydroxylated by boiling in distilled water for 20 h. We note that after hydroxylation the adsorption properties of silicas 1 and 2 become identical for all of test compounds studied in this work within the experimental error (1–8%).

Liquid poly(dimethylsiloxane) phase OV-1 (10% on Gas-Chrom Q, USA, particle size 0.125–0.15 mm) was used as model siloxane sorbent.

2.2. Chemically modified silica adsorbents

Chemical modification of silicas with chlorine-terminated methylsiloxanes was carried out in accordance with the procedure described in Ref. [18], the silica was S-120 (batch 1). Chemical modification of silica with (N,N-dimethylamino)-alkyldimethylsilanes was performed in accordance with the procedure described in Ref. [19], the silica

was S-120 (batch 2). Chemical analysis (% C) of modified silicas was determined using a Carlo Erba 1106 elemental analyzer. Bonding density of the modified silicas was calculated using Eq. (1):

$$\rho \, (\text{group}/\text{nm}^2) = \frac{600\,000 P_C}{(1200n - \text{FW} \cdot P_C)S} \tag{1}$$

where P_C is carbon percentage (by mass) of the silylated silica; n is the number of carbon atoms in molecule of organosilane; FW is molar mass of grafted group; S is the specific surface of initial silica. IR spectra of the modified silicas were recorded on a Perkin-Elmer Spectrum One instrument using a Harrick diffuse reflectance accessory.

2.3. Specific surface areas

Specific surface areas (m^2/g) were determined using: (1) the BET equation and the low temperature nitrogen adsorption isotherms, and (2) the nitrogen thermal desorption method as described in Ref. [20].

2.4. Static adsorption isotherms

Static adsorption isotherms of benzene for bare silicas and chemically modified adsorbents were studied at 298 K using the vacuum McBen–Bakr balance [20]. Prior to the measurements the adsorbents were degassed at 423 K and 1.3 mPa for 20 h.

2.5. Dynamic adsorption studies

Dynamic adsorption studies were performed using the inverse gas chromatography (IGC) techniques. A detailed description of the theory of this technique and its application for the adsorption studies can be found in Refs. [21,22]. Gas chromatography measurements were performed on a Chrom-5 instrument (Czech Republic), with a flame ionization detection (FID) system, carrier gas helium (flow-rate $F = 10$–$20 \, \text{cm}^3/\text{min}$), glass columns. Prior to the measurements, all the adsorbents were equilibrated in the helium flow at 473 K for 30 h. Test compounds were injected in the column in form of diluted vapors via portions of 0.1–0.2 cm^3. Retention volumes V_A were determined as described in Refs. [12,13,20–23]: $V_A =$

$V_N/g \cdot S$, where V_N, g and S are, respectively, net retention volume, mass of an adsorbent in the column and specific surface of an adsorbent. Thermodynamic characteristics of the adsorption were obtained from the chromatographic parameters at zero surface coverage of adsorbate, i.e., from Henry's region of the adsorption isotherm [13,20–23]. The retention volume V_A (cm^3/m^2) was equated with Henry constant $\mathscr{K}$ of the adsorption equilibrium. Concentrations of 1 $\mu mol/cm^3$ and 1 $\mu mol/m^2$ were chosen as standard states for the vapor phase and for the adsorbed phase, respectively [9,13]. The retention volume V_A is obviously related with standard Gibbs energy of the adsorption:

$$\Delta G^0 = -RT \ln \mathscr{K} = -RT \ln V_A \qquad (2)$$

Heat q and standard entropy change ΔS^0 of the adsorption were obtained from the temperature dependence of V_A (measured between 373 and 423 K):

$$\ln V_A = q/RT + (\Delta S^0 + R)/R \qquad (3)$$

assuming that q and ΔS^0 do not depend on temperature. We note, that the values of $\mathscr{K}$, ΔG^0 and ΔS^0 depend on the arbitrary chosen standard states for the vapor phase and for the adsorbed phase, respectively, but q does not [13,22,23]. Adsorption entropies ΔS^0(calc.) were calculated with the assumption that adsorption is accompanied by the loss of one translational degree of freedom (this is equivalent to free motion of adsorbed molecules along the surface) using the equation suggested in Ref. [21]:

$$-\Delta S^0(\text{calc.}) = R[7.85 + \ln(\sqrt{MT})] \qquad (4)$$

where R is the gas constant (8.314 J/mol K), M is the molar mass of the adsorbate (g/mol), T is the temperature (K); the average temperature of measurements was 403 K.

Contributions of methylene groups in a standard Gibbs energy were calculated as follows [13,24,25]:

$$\Delta G^0(CH_2) = -RT \ln[V_A(n+1)/V_A(n)]$$

where $V_A(n+1)$ and $V_A(n)$ are the retention volumes of n-alkanes with $(n+1)$ and (n) carbon atoms, respectively. Specific interactions were estimated by calculating the differences $\Delta(\Delta G^0)$ and Δq for pairs benzene–hexane and diethyl ether–pentane, using the classical method suggested by Kiselev et al. [26]. $\Delta(\Delta G^0)$ are independent of the choice of the standard state and, thus, can be used for characterization of different GC materials including liquid and solid stationary phases.

3. Results

3.1. Synthesis of the adsorbents

Four adsorbents were synthesized by covalent modification of silica surface with organosilanes. Their characteristics are presented in Table 1. Octyl- and hexadecyl-silicas were prepared via the reaction of silica with (N,N-dimethylamino)-dimethylalkylsilanes:
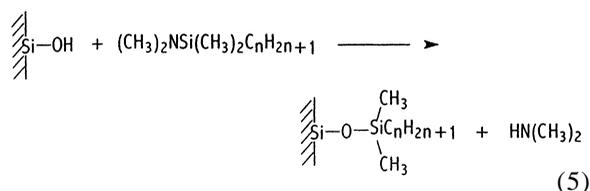
$$\equiv Si-OH + (CH_3)_2NSi(CH_3)_2C_nH_{2n+1} \longrightarrow$$

$$\equiv Si-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}C_nH_{2n+1} + HN(CH_3)_2 \qquad (5)$$

Table 1
Characteristics of bare silicas and the synthesized adsorbents

Surface group	Carbon content (%, w/w)	Bonding density (group/nm^2)	Specific surface area (m^2/g)
Silica, SiO_2 No. 1	<0.1*	–	100
$-[OSi(CH_3)_2]_3-$	1.7	1.53 (4.5**)	95
$-Si(CH_3)_2-(CH_2)_{10}-Si(CH_3)[OSi(CH_3)_3]_2$	5.3	1.55	90
Silica, SiO_2 No. 2	<0.1*	–	93
$-Si(CH_3)_2-C_8H_{17}$	5.18	3.0	87
$-Si(CH_3)_2-C_{16}H_{33}$	8.46	2.9	83

*Detection limit of the method. **Calculated per dimethylsilyl repeat unit.

Bonding densities (Table 1) of alkyl groups were as high as 2.9–3.0 group/nm^2, which corresponds to the closest packing of alkyldimethylsilyl groups on the surface. Bis-trimethylsiloxy-silica was prepared via reaction of silica with 10-bis(trimethylsiloxy-methylsilyl)-decyldimethylchlorosilane:

$$\equiv\!Si\text{–}OH + ClSi(CH_3)_2(CH_2)_{10}Si(CH_3)(OSi(CH_3)_3)_2 \xrightarrow{\ EtN(iPr)_2\ }$$

$$\equiv\!Si\text{–}O\text{–}\underset{\overset{|}{CH_3}}{\overset{\overset{CH_3}{|}}{Si}}(CH_2)_{10}\underset{\overset{|}{CH_3}}{Si}\overset{OSi(CH_3)_3}{\underset{OSi(CH_3)_3}{\diagdown}} + [EtN(iPr)_2]\cdot HCl$$

$$(6)$$

Bonding density for this sample was 1.55 group/ nm^2, which is almost twice as low as for alkyl-silicas. However, taking into consideration relatively high cross-section of bis-trimethylsiloxy groups, this bonding density corresponds to fairly dense packing of grafted molecules.

Oligo(dimethylsiloxane)-silica was prepared via reacting of silica with 1,5-dichlorohexamethyl-trisiloxane:

$$\equiv\!Si\text{–}OH + ClSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2Cl \xrightarrow{\ EtN(iPr)_2\ }$$

[structure of cyclic and linear dimethylsiloxane products]

$$+ [EtN(iPr)_2]\cdot HCl$$

$$(7)$$

Recently, we described [18] the synthesis of oligomeric dimethylsiloxane surfaces by the reaction of low-molecular-mass α,ω-dichloro-poly(dimethyl-siloxanes) with hydrated silicas. According to Fourier transform IR and chemical analysis, Cl[Si(CH$_3$)$_2$O]$_n$–Si(CH$_3$)$_2$Cl ($n = 1$–7) react with silicas covalently yielding cyclic dimethylsiloxane attached to the surface via two Si$_S$–O–Si bonds [18]. Bonding density for the sample studied in this work was ~4.5 dimethylsiloxy groups/nm^2.

All the adsorbents were characterized by IR spectroscopy, spectra are consistent with the structures proposed above (Fig. 1).

3.2. Gas chromatographic study

3.2.1. Adsorbates capable only to dispersive interactions

Thermodynamic parameters of the adsorption of *n*-alkanes (compounds that are capable only to dispersion interactions) on the adsorbents prepared in this work are presented in Table 2 and Fig. 2. The retention volumes V_A of *n*-alkanes decrease in the following order: bare silica≈hexadecyl-silica> octyl - silica > bis(trimethylsiloxy) - silica > oligo (di-methylsiloxy)-silica. This trend is consistent with the carbon percentage in the modified silicas arguing for the interactions of *n*-alkanes with CH$_2$ and CH$_3$ groups of the surface being the principal ones in the adsorption mechanism. This observation also suggests that the interactions of *n*-alkanes with silicon and oxygen in the siloxane chains are substantially weaker than the interactions with alkyl groups.

Table 3 presents $\Delta G^0(CH_2)$ data. We note that $\Delta G^0(CH_2)$ for modified silicas are lower than for non-modified silicas. This is consistent with the weakening of the surface adsorption potential due to chemical modification of silica with liophobic or-ganosilyl groups [13,24,25]. Minimal values of $\Delta G^0(CH_2)$ are observed for bis(trimethylsiloxy)- and oligo(dimethylsiloxy)-silicas. It is noticeable that $\Delta G^0(CH_2)$ for the adsorption of *n*-alkanes are sub-stantially lower than $\Delta G^0(CH_2)$ for the dissolution of *n*-alkanes in liquid poly(dimethylsiloxane) phase OV-1, which is chemically very close to the oligo(dimethylsiloxy)-silica. We note however that, unlike the difference in retention volumes and in $\Delta G^0(CH_2)$, the difference in heats of adsorption (q) of *n*-alkanes on non-modified and on modified silicas are hardly noticeable. This led us to conclude that principal difference in the ΔG^0 of the adsorption on these surfaces is coming from the entropy term. At the same time, heats of adsorption on modified silica are higher than on OV-1 (Table 2), arguing for the more intense interactions with the adsorbates on modified silicas than on liquid phase OV-1. Heats of adsorption are also greater than heats of condensa-tion that are equal 18.7, 23.5, and 25.6 kJ/mol for *n*-pentane, *n*-hexane and benzene at 403 K. En-tropies of the adsorption on bis(trimethylsiloxy)- and oligo(dimethylsiloxy)-silicas are somewhat lower than the entropies of the adsorption on octyl- and
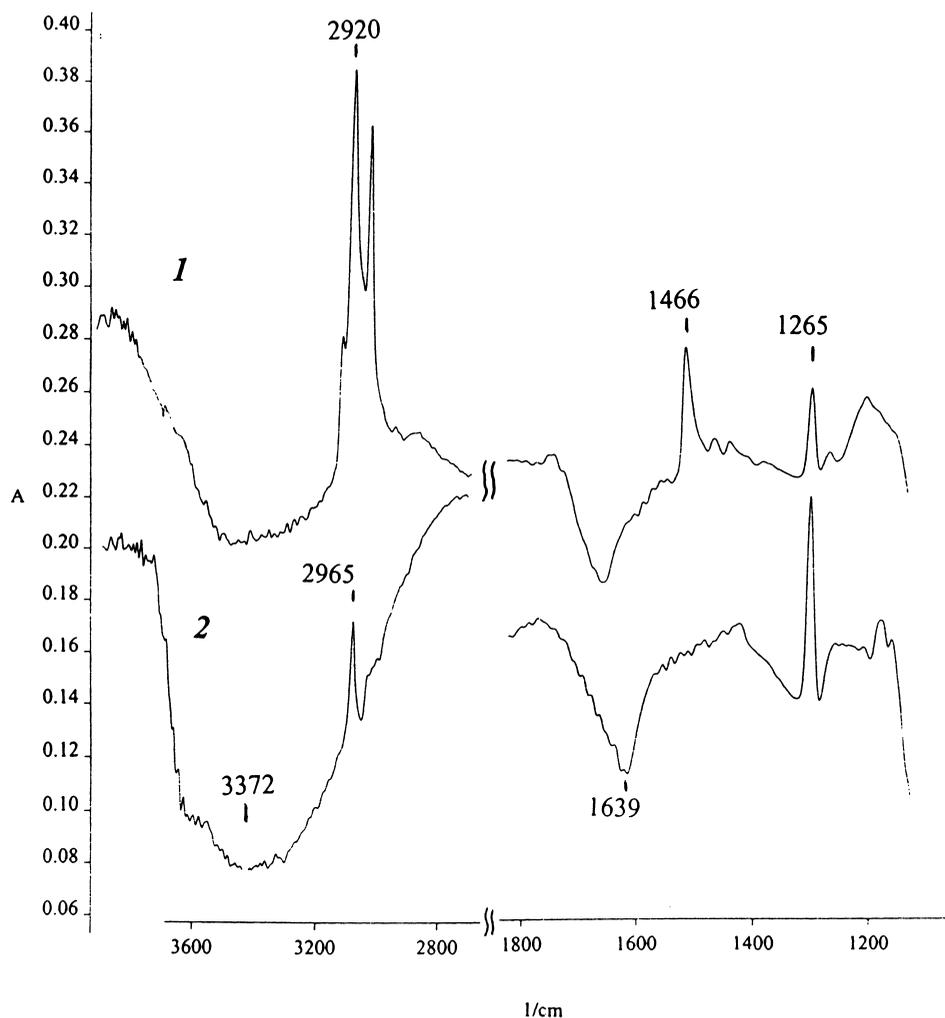
Fig. 1. IR-diffuse reflectance spectra of hexadecyl-silica (1), oligo(dimethylsiloxy)-silica (2).

Table 2
Heats q (kJ/mol) and entropies ΔS^0 (J/mol K) of sorption

Sorbent/surface group	Sorbates						
	Pentane		Hexane		Benzene		Diethyl ether,
	q	$-\Delta S^0$	q	$-\Delta S^0$	q	$-\Delta S^0$	q
SiO_2 No. 1	25	103	30	109	38	121	58
$-Si(CH_3)_2-[OSi(CH_3)_2]_x-$	25	109	30	118	36	130	54
$-Si(CH_3)_2-(CH_2)_{10}-Si(CH_3)[OSi(CH_3)_3]_2$	26	111	29	113	31	115	49
SiO_2 No. 2	27	107	31	112	39	124	60
$-Si(CH_3)_2C_8H_{17}$	25	106	28	109	28	109	44
$-Si(CH_3)_2C_{16}H_{33}$	23	98	29	107	29	106	39
OV-1	20	–	24	–	25	–	21
$-\Delta S^0$(calc.)		108.0		108.7		108.3	
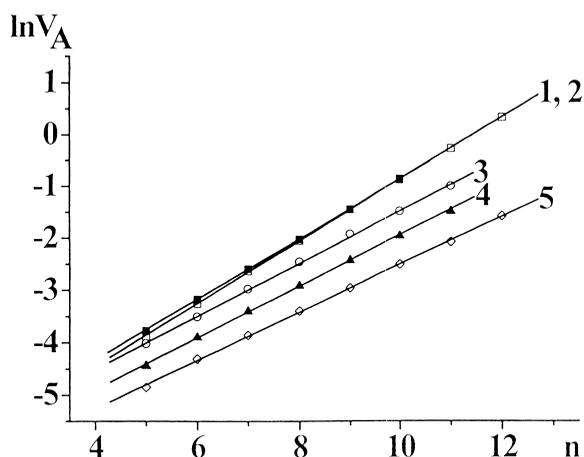
Fig. 2. Dependence of ln V_A vs. number of carbon atoms in *n*-alkanes *n* ($T = 403$ K). (1) Silica, SiO_2 No. 1, (2) $-Si(CH_3)_2-C_{16}H_{33}$, (3) $-Si(CH_3)_2-C_8H_{17}$, (4) $-Si(CH_3)_2-(CH_2)_{10}-Si(CH_3)[OSi(CH_3)_3]_2$, (5) $-Si(CH_3)_2-[OSi(CH_3)_2]_x-$.
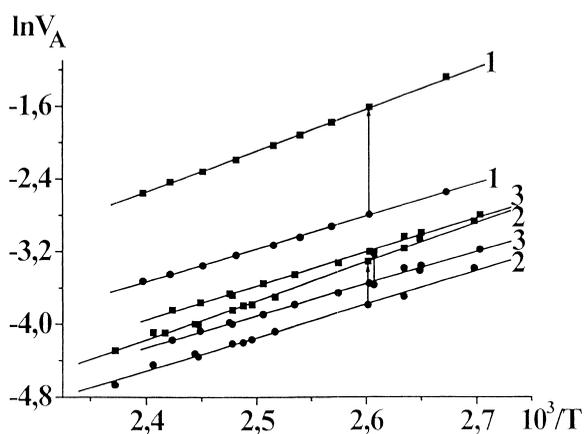

Fig. 3. Dependence of ln V_A vs. temperature for benzene (squares) and for hexane (circles). (1) Silica, SiO_2 No. 1, (2) $-Si(CH_3)_2-[OSi(CH_3)_2]_x-$, (3) $-Si(CH_3)_2-(CH_2)_{10}-Si(CH_3)[OSi(CH_3)_3]_2$.

hexadecyl-silicas. Also, experimental entropies of the adsorption on methylsiloxane-silicas are lower than ΔS^0(calc.), which was calculated in the assumption of losing of only one degree of freedom upon the adsorption, Eq. (4).

The results obtained support the idea of the penetration of an adsorbate into the bonded layer under the conditions of gas chromatography and the significance of these interactions in the retention process. Penetration of the adsorbates into the bonded layer will explain relatively high heats of adsorption due to additional lateral interactions with molecules of the bonded layer. This will also explain the entropy drop due to "the dissolution in the bonded layer". Similar conclusions about the pene-

tration of the adsorbed molecules into the bonded layer were reported in Refs. [27,28], where diffusion of fluorescent and spin probes in the alkyl-silicas were studied by spectral methods.

3.2.2. Adsorbates are polar molecules

Electrostatic interactions and/or hydrogen bonding with residual silanol groups become an issue when the polar molecules, in particular those of small size, adsorb on silica. The contribution of specific interactions can be studied by comparing of the adsorption of pairs of molecules that have close polarizability and Van der Waals sizes, but substantially different electron density distribution, for example: benzene–hexane ($C_6H_6-C_6H_{14}$) and diethyl ether–pentane [$(C_2H_5)_2O-C_5H_{12}$] [13,26,30]. Fig. 3 shows that the

Table 3
Increments of CH_2 groups in Gibbs adsorption energy $\Delta G^0(CH_2)$ for the sorption of *n*-alkanes

Sorbent	$\Delta G^0(CH_2)$	Benzene–hexane		Diethyl ether–pentane	
		$\Delta(\Delta G^0)$	Δq	$\Delta(\Delta G^0)$	Δq
SiO_2 (No. 1)	2.00	3.60	8	13.6	33
$-Si(CH_3)_2-[OSi(CH_3)_2]_x-$	1.54	1.27	6	4.51	29
$-Si(CH_3)_2-(CH_2)_{10}-Si(CH_3)[OSi(CH_3)_3]_2$	1.64	1.06	2	1.88	23
SiO_2 (No. 2)	1.98	3.65	8	13.6	33
$-Si(CH_3)_2C_8H_{17}$	1.71	0.25	0	0.58	19
$-Si(CH_3)_2C_{16}H_{33}$	1.94	0.31	0	0.41	16
OV-1	1.84	1.32	1	-0.09	1

Difference in heats (Δq) and Gibbs energy $\Delta(\Delta G^0)$ of sorption for benzene–hexane and diethyl ether–pentane ($T = 403$ K, all quantities in kJ/mol).

differences in the adsorption of benzene–hexane are substantially greater for non-modified silica than for modified silicas. The differences between modified and non-modified silica are even larger for the adsorption of diethyl ether–pentane (Fig. 4). This is consistent with the fact that diethyl ether forms stronger hydrogen bonds with the surface polar groups than benzene [29]. Indeed, heat of adsorption of diethyl ether on silica is almost 20 kJ/mol larger than that for benzene (Table 2). Quantitatively the specific interactions can be measured as a difference between Gibbs energies of adsorption $[\Delta(\Delta G^0)]$ and the difference between heats of adsorption (Δq) for the pairs benzene–hexane and diethyl ether–pentane. As one can expect, $\Delta(\Delta G^0)$ and Δq decrease substantially for all of the modified silicas, which is in agreement with the substitution of polar silanols with non-polar siloxy groups and shielding of the silica surface due to silanization. Based on these data, the range of surface polarity for the adsorbents studied may be presented as follows:

$$SiO_2 > > -[\{(CH_3)_2SiO\}_2]_x-(CH_3)_2Si-$$
$$> [(CH_3)_3SiO]_2Si(CH_3)-(CH_2)_{10}(CH_3)_2Si-$$
$$> n\text{-}C_8H_{17}(CH_3)_2Si- \geq n\text{-}C_{16}H_{33}(CH_3)_2Si-$$
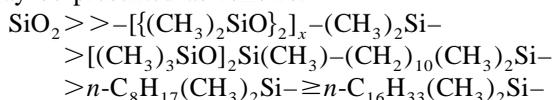
The least polar surfaces are hexadecyl- and octyl-silicas, the adsorbents with the highest bonding density of organic groups. Bis(trimethysiloxy)- and oligo(dimethylsiloxy)-silicas are more polar than alkyl-silicas perhaps because of the greater number
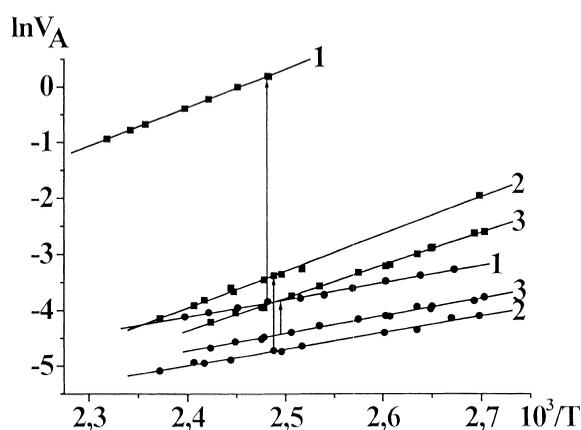
of the accessible silanols on the surfaces (lower bonding density).

Table 3 suggests that thermodynamics parameters of benzene adsorption are less sensitive to the heterogeneity of an adsorbent than those for diethyl ether adsorption. For example, the absolute value of $\Delta(\Delta G^0)$ for the adsorption of benzene on OV-1, which is considered to be one of the least polar siloxane-type liquid stationary phase [31], is greater or almost equal to those obtained for the modified silicas prepared in this work. This led us to conclude that, although benzene may penetrate the bonded layers, the residual silanols remain inaccessible to it. We believe that adsorption of benzene on the modified silicas is primarily controlled by dispersive interactions and not by specific interactions with the residual silanols. Figs. 2 and 5 show that the adsorption energies for benzene, alkylbenzenes, and alkanes change in a similar fashion from sample to sample except for the non-modified silicas.

In summary, benzene does not seem to be a good probe molecule for testing adsorbents for the residual polar groups. Indeed, all of the adsorbents prepared in this work have equally lyophobic and uniform non-polar surfaces as probed by benzene. Diethyl ether is more sensitive to the surface heterogeneity (Table 3) and, therefore, is more appropriate than
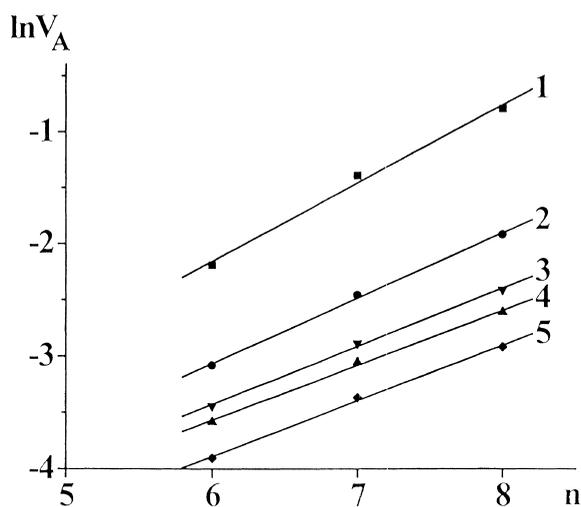

Fig. 4. Dependence of ln V_A vs. temperature for diethyl ether (squares) and for pentane (circles). (1) Silica, SiO_2 No. 1, (2) $-Si(CH_3)_2-[OSi(CH_3)_2]_x-$, (3) $-Si(CH_3)_2-(CH_2)_{10}-Si(CH_3)[OSi(CH_3)_3]_2$.

Fig. 5. Dependence of ln V_A vs. number of carbon atoms in aromatic hydrocarbons n ($T=403$ K). (1) Silica, SiO_2 No. 1, (2) $-Si(CH_3)_2-C_{16}H_{33}$, (3) $-Si(CH_3)_2-C_8H_{17}$, (4) $-Si(CH_3)_2-(CH_2)_{10}-Si(CH_3)[OSi(CH_3)_3]_2$, (5) $-Si(CH_3)_2-[OSi(CH_3)_2]_x-$.

benzene as a test molecule for the studies of surface homogeneity.

3.3. Static adsorption study

Initial regions of the benzene adsorption isotherms for non-modified and modified silicas are shown in Fig. 6. Adsorption isotherms of the modified silicas go substantially lower than these for non-modified silica. The adsorption is consistent with the total concentration of carbon in the sample (Table 1), which is in agreement with the GC retention data and also supports the idea of the principal role of dispersion interactions in the adsorption mechanism on these surfaces. Adsorption on bis(trimethylsiloxy)- and oligo(dimethylsiloxy)-silicas show small difference, which deserves a comment. At very low pressures ($p/p_o < 0.05$) the adsorption on oligo(dimethylsiloxy)-silica is greater than on bis-(trimethylsiloxy)-silica. This is, perhaps, due to the small amount of silanol groups left on the surface of oligo(dimethylsiloxy)-silica. At higher pressures the adsorption on oligo(dimethylsiloxy)-silica is less than on bis(trimethylsiloxy)-silica indicating lower surface energy of the former. We note that at low pressures ($p/p_o < 0.05$) static adsorption method predicts the same order of the adsorbate–surface interactions energy as obtained with the GC, while oligo(dimethylsiloxy)-silica and bis(trimethylsiloxy)-

silica switch their places if the adsorption at moderate pressures is compared. We believe that this example will illustrate the importance of the simultaneous use of the dynamic and static techniques for the adsorption studies. Combination of these techniques enables more complete characterization of the adsorption and the adsorbents.

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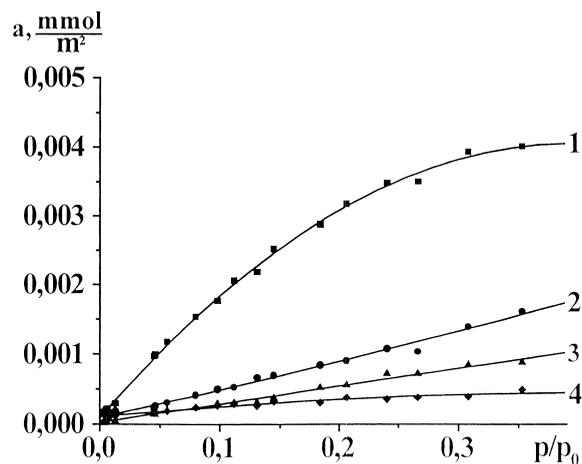
Fig. 6. Adsorption isotherms (298 K) of benzene on: (1) silica, SiO_2 No. 1, (2) $-Si(CH_3)_2-C_{16}H_{33}$, (3) $-Si(CH_3)_2-(CH_2)_{10}-Si(CH_3)[OSi(CH_3)_3]_2$, (4) $-Si(CH_3)_2-[OSi(CH_3)_2]_x-$.

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