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## Gas chromatography study of retention of organic compounds on silica with an attached layer of hydrophobic groups

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### Abstract

Silica adsorbents with bonded  $C_{16}H_{33}$ ,  $n-C_6F_{13}(CH_2)_3$ , *tert.*- $C_6F_{13}(CH_2)_3$  or  $n-C_3F_7(CH_2)_3$  groups were prepared by the reaction between hydroxylated silica (Silochrome) and corresponding *N*-(organodimethylsilyl)morpholines. These adsorbents, as well as silica with bonded phenylpolysiloxane which was prepared by multilayer attachment of phenyltrichlorosilane, were investigated by means of gas chromatography at zero surface coverage. Thermodynamic functions (Gibbs energies, entropies and heats of adsorption) were shown to change significantly with chemical nature and structure of attached groups. On the basis of the investigation of the adsorption of cyclic compounds we proposed that the mechanism of interaction between non-polar organic compounds and silanized silicas is adsorption to the bonded layer. Dispersive and specific components of intermolecular interaction in adsorption have been estimated by several techniques. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Stationary phases, GC; Thermodynamic parameters; Silica, bonded

### 1. Introduction

Hydrophobized silicas are used in modern science and technology, in particular as adsorbents, fillers, stabilizing additives etc. [1]. Silicas with covalently attached alkyl tails occupy the leading position in modern high-performance liquid chromatography (HPLC) [1,2]. The wide use of alkyl modified silicas in analytical gas chromatography (GC), regardless of a few number of successful examples, is prevented by poor hydrolytical and thermal stability of com-

mercially available stationary phases like Durapak. Also, commercially available silanized silicas have residual silanol groups which cause surface heterogeneity and asymmetry of chromatographic peaks of polar compounds [3]. On the other hand, fluorine-containing compounds, including fluorine-containing stationary phases, have become more and more popular in modern research and technology because of their highly hydrophobic nature, and high chemical and thermal stability [4–7]. Fluorine-containing stationary phases are known to show high selectivity in the separation of halogen-containing compounds; silicas with grafted polyfluoroalkyl groups demonstrated good results in HPLC [3,8–10].

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GC studies of surface modified silicas gives important results concerning the adsorption properties of new stationary phases and on the structure of grafted layer [11–17]. Surface-modified silicas with dense and uniform coverage may be used as a model surface for basic study of intermolecular interactions [11,14–16,18,19]. In GC, stationary phases are tested under the conditions of their use in practice, which permit estimation of their selectivity towards various groups of organic compounds and comparison with the most popular stationary phases [14,15,17].

The goal of the present work was the synthesis of alkyl-, phenyl- and polyfluoroalkylsilicas with the following study of their gas chromatographic and adsorption properties at close to zero surface coverage.

## 2. Experimental

### 2.1. Materials

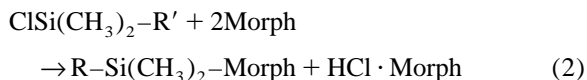
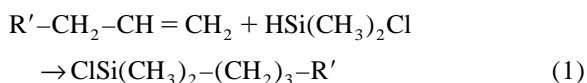
Notation and some characteristics of the samples studied are given in Table 1. Bare silica was Silochrome C-120 (Stavropol, Russia), average particle size 0.3–0.5 mm. Before the surface modification, silica was subjected to hydroxylation (boiling with water for 72 h).

In order to understand the mechanism of adsorption on the modified silicas, the following model adsorbents were also studied: bare silica [15], graphitized thermal carbon black (GTCB) [21–24] and polydimethylsiloxane OV-1 (10% on Gas-Chrom Q, USA, particle size, 0.125–0.15 mm, glass column, 1 m×3.5 mm I.D.).

The test adsorbates used were saturated and aromatic hydrocarbons, oxygen-, chlorine- and nitrogen-containing compounds. These substances were of analytical grade and were purchased from Reakhim, Russia.

### 2.2. Synthesis

(I) Silicas with attached alkyl and polyfluoroalkyl chains of monolayer structure were prepared by using morpholine derivatives. Morpholine derivatives were obtained in accordance with the scheme [20]:



where  $\text{R}' = \text{C}_{16}\text{H}_{33}\text{-}$ ,  $n\text{-C}_6\text{F}_{13}(\text{CH}_2)_3\text{-}$ ,  $\text{tert-C}_6\text{F}_{13}(\text{CH}_2)_3\text{-}$ ,  $n\text{-C}_3\text{F}_7(\text{CH}_2)_3\text{-}$  and Morph = morpholine.

Silica (10 g) was placed in a three-necked flask and covered with 100 ml of toluene containing 1 mmol of modifier:

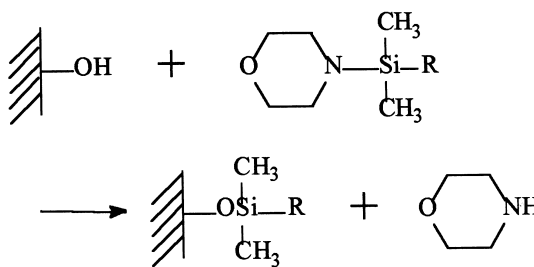
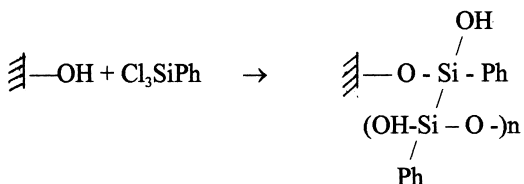


Table 1  
Notations and characteristics of the samples studied

Notations in the text or figures	Group attached to surface	Carbon content (% w/w)	Surface concentration (groups/nm <sup>2</sup> )
SiO <sub>2</sub>	Bare silica	–	–
C16(I)	$n\text{-C}_{16}\text{H}_{33}(\text{CH}_3)_2\text{Si-}$	7.1	2.4
C16(II)	$n\text{-C}_{16}\text{H}_{33}(\text{CH}_3)_2\text{Si-}$	8.5	2.9
nCF	$n\text{-C}_6\text{F}_{13}\text{-(CH}_2)_3\text{-(CH}_3)_2\text{Si-}$	3.8	2.1
tCF	$\text{tert-C}_6\text{F}_{13}\text{-(CH}_2)_3\text{-(CH}_3)_2\text{Si-}$	3.5	1.9
C3F7	$n\text{-C}_3\text{F}_7\text{-(CH}_2)_3\text{-(CH}_3)_2\text{Si-}$	3.3	2.4
PhBS	PhSi≡	8.6	8.8

The mixture was heated and stirred for 20 h at 120°C. The sorbent obtained was subsequently washed on a glass filter with xylene, acetone, ethanol before undergoing treatment with water–ethanol (80:20) for 20 h. Finally, the sorbent obtained was dried at 120°C for 2 h in a vacuum drying box.

(II) Phenyl-bonded silica was obtained using phenyltrichlorosilane in presence of water as described in Ref. [15]:



Due to polycondensation of phenylsiloxane modifier phenyl-bonded silica possessed the cross-linked polymer structure.

### 2.3. Characterization of modified silicas

The efficiency of the surface modification reactions – surface concentration of attached groups – was determined from the chemical analysis of carbon percentage in a sorbent (Table 1). The concentration of attached groups (groups/nm<sup>2</sup>) was calculated as follows [1]:

$$N = N_A (\% C) / 12n_C S$$

$$S = S_0 \left[ 1 - \frac{(\% C)M_r}{1200n_C} \right]$$

where % C is the carbon content (% w/w);  $M_r$  is the molecular mass of the attached group;  $n_C$  is the number of carbon atoms in grafted group;  $S_0$  is the specific surface area of bare silica (93 m<sup>2</sup>/g) and  $N_A$  is the Avogadro constant.

### 2.4. Gas chromatography

GC was performed on a Chrom-5 instrument (Czech Republic) equipped with a flame ionization detection (FID) system. High-purity helium was used as a carrier gas (flow-rate  $F = 10\text{--}20$  ml/min). Glass columns were used (0.5–1.2 m × 2–2.5 mm I.D.). Before any measurements were made, the columns

containing silicas were conditioned at 453 K during 20–30 h under a flow of helium.

Thermodynamic characteristics of adsorption (TCA) of dilute vapors of organic compounds [retention volumes  $V_a$  (ml/m<sup>2</sup>), Gibbs energies  $\Delta G^0$ , entropies  $\Delta S^0$  and heats of adsorption  $q$ ] and Kováts retention indices  $I$  were determined at zero surface coverage. Measurements were performed within the region 373–433 K. Asymmetry coefficients ( $A_s$ ) were calculated at 1/2 of peak height.

## 3. Results and discussion

### 3.1. Mechanism of retention of non-polar compounds

Figs. 1 and 2 and Table 2 show TCA and retention indices of saturated hydrocarbons, which are capable only to dispersion interaction with surface. Among studied hydrophobized silicas, the highest  $q$  and  $V_a$  values are observed on the phenyl silica ( $q$  is almost the same as on the high-energy surface of GTCB [21–23]), they are close for bare silica and C<sub>16</sub> silica, the lowest values obtained on fluorine containing samples (Figs. 1 and 2a). Chain branching (tCF) as well as reduction in chain length (C3F7) is accomplished with the reduction of dispersion interaction. The impact of methylene units on  $\ln V_a$  (at 373 K), which is the measure of dispersion forces, decreases in the following range: C16(I)=C16(II) (0.68) > nCF (0.51) > tCF (0.48) > C3F7 (0.39). A similar behavior of methylene impacts on  $\ln V_a$  at 373 K is observed for the dissolution of  $n$ -alkanes in methylsiloxane OV-1 (0.64) and fluoroalkylsiloxane OV-210 (0.53). It is noticeable that in spite of the adsorption potential of silica surface, C3F7 silica has often lower interaction energy with saturated hydrocarbons than liquid OV-1 (Fig. 2a and Table 2). It is important to add that polyfluoroalkylsilicas also demonstrate relatively low  $V_a$  values for polar molecules with active functionalities. Therefore, silanization of silica with polyfluoroalkylsilanes decreases all types of intermolecular interactions.

Some idea about mobility of adsorbed molecules can be obtained by comparing entropy of adsorption (Fig. 2b). It is known that experimentally determined  $\Delta S^0$  values for  $n$ -alkanes on GTCB are almost equal

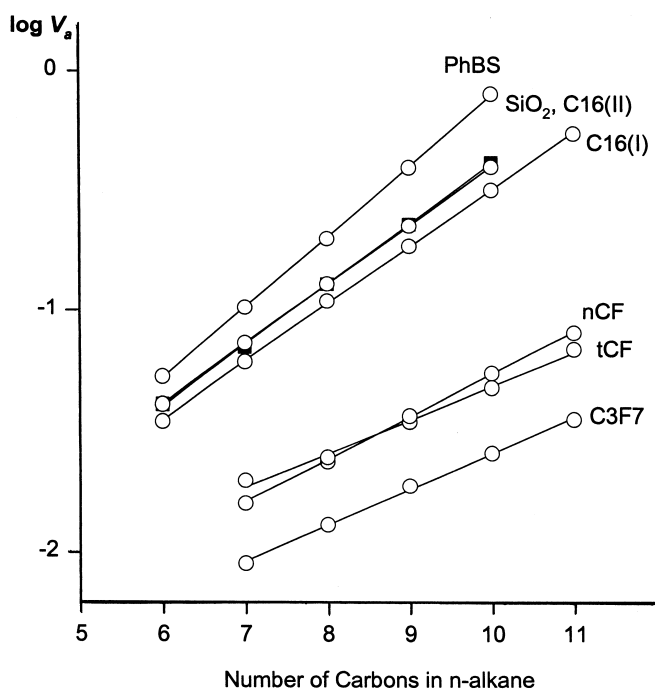


Fig. 1. Dependence of  $\log V_a$  on the number of carbon atoms  $n$  in  $n$ -alkane molecules for the samples studied (adsorbent notations, see Table 1) at 403 K. Horizontal axis: 6=hexane, 7=heptane, 8=octane, 9=nonane, 10=decane, 11=undecane.

to those calculated using the theoretical model which assumes loss of one translation degree of motion, i.e., model of free motion along surface (non-localized adsorption) [22]. In order to understand the reason for the stronger decrease in the entropy of adsorption, especially for phenylsilica, one can assume that the absorption of solutes in the grafted layer along with the adsorption on the surface of the grafted layer lies in the basis of the retention process.

In order to confirm this hypothesis, continuing the ideas of Ref. [15], we studied the adsorption of test molecules which have the same number of carbon atoms but different structure:  $n$ -decane ( $C_{10}$ ), *trans*-decaline (D) and adamantane (Ad) (Table 2). It is common knowledge that cyclic hydrocarbons adsorb more weakly on a flat surface than their linear analogues because of the smaller number of units directly interacting with the surface. For example, D “touches” the surface with five methylene units, Ad with only three, while  $C_{10}$  contacts the surface with all ten carbon atoms. The most suitable example of a flat surface adsorbent is the well studied GTCB, the

surface of which is formed by basic planes of graphite [21]. On GTCB as well on bare silica Ad is retained more weakly than D, D more weakly than  $C_{10}$ , however on  $SiO_2$  the difference in the adsorption energies of these compounds is significantly smaller than on GTCB.

These results, probably, may be explained if the molecular scale roughness of silica surface is considered. In fact, one can assume that the compact rigid molecules of Ad and D match the molecular topography of silica. This assumption, to some extent, is supported by the fact that the entropy of adsorption on  $SiO_2$  is basically smaller than on GTCB (Fig. 2b).

Hydrophobized silicas show quite the opposite elution order: cyclic molecules elute after  $C_{10}$  which is similar to dissolution of solutes in the liquid stationary phase OV-1 (Table 2). Concerning the heats of adsorption, one can mark slight a decrease in  $q$  of cyclic hydrocarbons compared to  $C_{10}$  observed on all sorbents including OV-1. The exception is GTCB, the flat surface of which provides considerable decrease of adsorption heats of Ad and D by

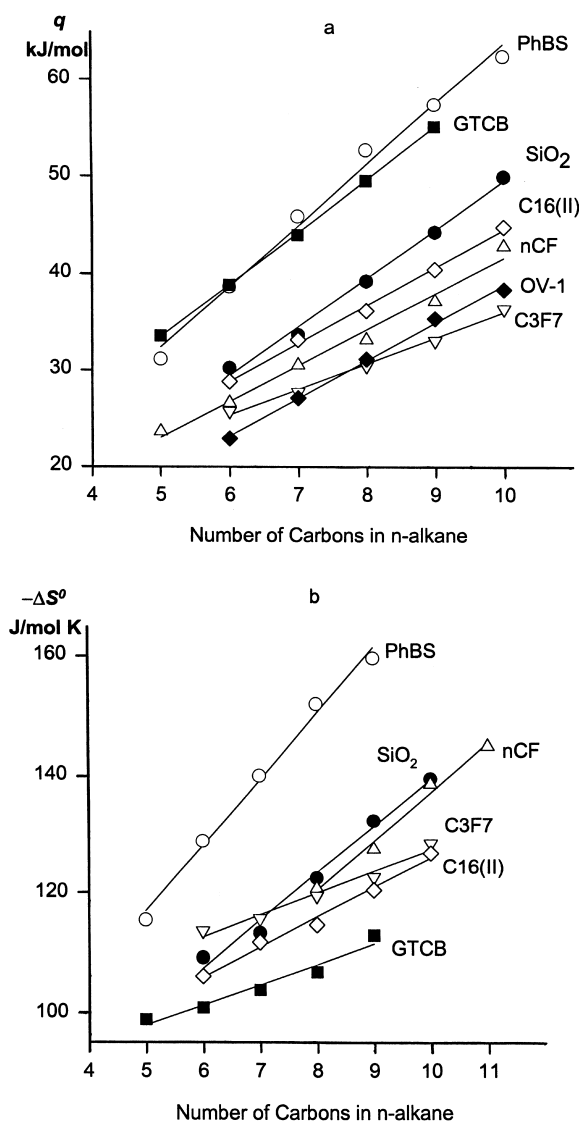


Fig. 2. Dependences of heats of adsorption  $q$  (a) and entropies of adsorption  $-\Delta S^\circ$  (b) on the number of carbon atoms  $n$  in  $n$ -alkane molecules for the samples studied (adsorbent notations, see Table 1), OV-1 and GTCB [22]. Horizontal axis as in Fig. 1.

20 and 10 kJ/mol compared to C<sub>10</sub>, respectively [22,23]. Similar results were obtained for the other cyclic compounds. For example, methylcyclohexane on hydrophobized silicas leaves the column after  $n$ -heptane, as for the liquid stationary phase, while on GTCB after  $n$ -hexane ( $I=606$  [24]). Therefore, one can conclude that non-polar solutes rather pene-

Table 2  
Heats of sorption  $q$  (kJ/mol) and retention indices  $I$  at 403 K on the sorbents studied and GTCB [22,23]

	C <sub>10</sub> $q$	D		Ad	
		$I$	$q$	$I$	$q$
SiO <sub>2</sub>	49.6	975	42.1	969	42.6
C16(I)	–	1034	–	1031	–
C16(II)	44.8	1021	42.1	1016	41.0
nCF	42.6	1065	39.5	1076	–
tCF	–	1018	–	1035	–
C3F7	36.3	1054	35.2	1059	34.3
PhBS	62.4	1030	59.5	1039	58.4
GTCB	60.2	867	50.3	649	39.0
OV-1	38.3	1056	37.2	1103	36.8

trate a surface grafted layer than adsorb on its external surface. Fig. 3 illustrates possible interactions between the decaline and grafted fluoroalkyl layer.

### 3.2. Retention of molecules capable of specific interaction

When studying the adsorption of polar solutes,

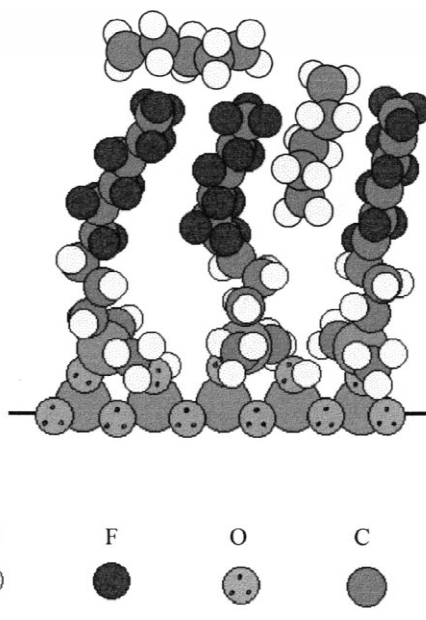


Fig. 3. Drawings of possible interactions between decaline and grafted fluoroalkyl layer (nCF).

especially those of small size, one cannot ignore the detailed structure of the grafted groups and the interaction between solutes and residual surface silanols [1,11,19]. The peak symmetry increases sharply on modified silicas compared with bare silica. For example, the asymmetry coefficient ( $A_s$ ) of aniline at 423 K decreases passing from SiO<sub>2</sub> ( $A_s=3.1$ ) to C16(II) ( $A_s=1.4$ ). At the same time many of the solutes capable of hydrogen bonding (pyridine, phenol, etc.) do not elute from the SiO<sub>2</sub> column at 403 K for an acceptable time (~1 h). However, the most of the polar solutes studied in this work showed symmetric chromatographic peaks on modified silicas at 403 K and higher. This is the main evidence that the surface of silanized silicas is uniform as well as that silane grafting layers are dense enough to shield the silanols fairly well. For example, chromatograms and asymmetry coefficients of some polar compounds are shown in Fig. 4.

In order to study specific interactions between probes and hydrophobic silicas we used several approaches. First, traditional in GC approach, an estimation of the surface polarity by comparison of the retention indices of molecules which have electronic densities localized on definite atoms or bonds (Table 3).

As one can expect, surface silanization reveals a significant decrease of the retention indices for all test solutes which are capable of orientational interaction or hydrogen bond formation. According to this approach, fluoroalkylsilicas are more polar than phenylsilica. The lowest values of  $I$  were obtained for C<sub>16</sub> silicas. Similar trends in polarity behavior were observed for liquid stationary phases: specific interactions increase passing from methylsiloxanes (OV-1, OV-101) to phenylsiloxanes (OV-17, OV-25) and then to fluoroalkylsiloxane (OV-210) [3].

The differences in adsorption on alkyl- and fluoroalkylsilicas can be explained as a result of the non-uniform distribution of electrons in partially fluorinated chains ( $-\text{CH}_2^{+\delta}-\text{CF}_2^{-\delta}-$  [4]) and, therefore, the increase of the total polarity of the layer is due to the appearance of a high dipole momentum which is, probably, close to the dipole momentum of partially fluorinated ethanes ( $\mu \text{CH}_3\text{CHF}_2=2.2-2.3 \text{ D}$ ,  $\mu \text{CH}_3\text{CF}_3=2.3-2.4 \text{ D}$  [25]). However, this explanation is correct if only the degree of shielding of surface silanols is compatible for alkyl- and fluoroalkylsilicas.

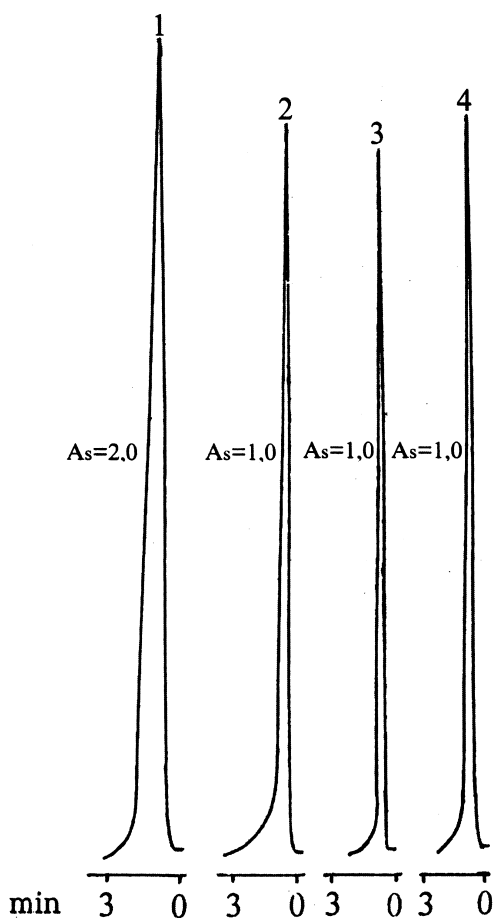


Fig. 4. Chromatograms of pyridine (1), phenol (2), anisol (3) and dioxane (4) on the C16(I) silica at 403 K. Column, 60×0.25 cm I.D.,  $F=11.9 \text{ ml/min}$ .

Concerning fluoroalkylsilicas, one can notice that the retention indices increase on tCF to nCF and increase greatly on C3F7 silica (Table 3). Here, we would like to discuss the factors which affect the polarity of silanized silica. It is known that the specific interaction decreases significantly as the concentration of grafted groups is increased. Increase of grafted chain length decreases the accessibility of the residual silanols, and, therefore, in our case acts in the opposite direction [1,11,14,16,19]. Probably, *tert.*-polyfluoroalkyl groups are more effective in the shielding of surface silanols in spite of the relatively lower surface concentration because of the most volume.

The results on the retention behavior of polar molecules on fluoroalkylsilicas correlate well with

Table 3  
Retention indices *I* on the bare and modified silicas at 403 (\*) and 373 K

	SiO <sub>2</sub> *	PhBS*	C16(II)*	nCF*	C3F7*	C16(I)	C16(II)	tCF	nCF	C3F7
Diethyl ether	1180	583	522	600	700	571	555	–	673	914
Acetone	1246	703	587	853	1078	642	663	892	893	1219
Methyl ethyl ketone	1338	722	634	885	1110	677	694	933	953	1230
Ethyl acetate	1342	699	610	822	986	648	650	879	890	1147
2-Methylpropan-2-ol	945	623	590	730	878	585	660	–	838	1072
Propan-1-ol	–	748	640	826	–	711	729	–	926	1208
Acetonitrile	1115	683	597	887	1109	646	665	876	907	1194
Nitromethane	989	631	570	841	1000	583	617	805	842	1053
Chloroform	665	574	565	624	613	534	570	595	630	615
Tetrachloromethane	648	628	613	673	661	604	605	670	666	644
Benzene	786	641	616	687	671	611	611	660	680	689
<i>n</i> -Butyl acetate	–	854	–	–	–	780	811	1039	1097	1314
Dioxane	–	887	836	1041	1439	807	907	1133	–	–

the wettability of the hydrophobized silicas studied in Refs. [5–7], where tCF was shown to give the most hydrophobic surfaces comparing with linear and/or shorter fluorinated chains.

We would like to discuss the very strong increase of specific interaction for perfluoropropylsilica in detail. One can see that the *I* values of large-dipole-momentum small-size-molecules [e.g., CH<sub>3</sub>CN ( $\mu = 3.9$ ), CH<sub>3</sub>NO<sub>2</sub> ( $\mu = 3.5$ )] reach on C3F7 the corresponding values on bare silica but at the same time the *I* values of the molecules capable of hydrogen bonding (e.g., alcohols) do not. Apparently, the access to the polar part of polyfluoroalkyl groups possessed with quite a large dipole momentum decreases in the sequence of C3F7, nCF, tCF (lengthening of bonded ligand and then branching of bonded ligand). In other words, the role of orientational (dipole–dipole) interaction in the adsorption process decreases in this sequence of fluorinated silicas.

For the last decade, the calculating techniques based on the isolation of impacts of specific interactions  $\Delta G^{\text{sp}}$  into the adsorption Gibbs energy  $\Delta G^0$  have been widely used for the estimation of polarity of various solids, including polymers, fillers, stabilizing agents and adsorbents [11–13,26–28].  $\Delta G^{\text{sp}}$  is calculated by subtracting the change in Gibbs energy due to the adsorption of a hypothetical or real *n*-alkane ( $\Delta G^{\text{d}}$ ), one of physico–chemical properties equal to the compound under study, for example: vapor pressure, boiling point, molar refraction or polarizability ( $\Delta G^{\text{sp}} = \Delta G^0 - \Delta G^{\text{d}}$ , Fig. 5). It was found that the calculation of  $\Delta G^{\text{d}}$ , proposed by

Papirer et al. [11] and based on the application of log *P*, where *P* is the pressure of the saturated vapors, does not work for the alkyl- and phenylsilicas. In these cases, as it may be seen from Fig. 5a, impacts of specific interactions are negative, because the points corresponding to polar solutes are often below the straight line corresponding to *n*-alkanes.

In order to calculate impacts of specific interaction, we followed the approach proposed earlier in the groups of Kiselev and Donnet [21,26,27]. To calculate  $\Delta G^{\text{sp}}$  we used the experimentally obtained dependencies of  $RT \ln V_a$  from the polarizability of test compounds (Fig. 5b). Table 4 shows as an example the results obtained for some silanized silicas. Comparison of *I* and  $\Delta G^{\text{sp}}$  demonstrates that the different approaches used for the estimation of surface polarity may give consistent results (Tables 3 and 4).

$\Delta G^{\text{sp}}$  data obtained by GC measurements on the C<sub>18</sub> bonded silica (Merck, Darmstadt, Germany) are also presented in Table 4. Even though C<sub>18</sub> silica studied in [13] was the best among HPLC stationary phases it was found that the adsorbents presented in our work had more uniform and more dense coverage.

Many publications are trying to differentiate effects caused by the interaction between solutes and acid (acceptor) or basic (donor) centers on the surface of solids. For doing this, the approximate models based on the correlation between the specific interaction and different empirical parameters of solvents: donor and acceptor Gutmann and Schmid numbers, solubility parameters, Dimrot–Reichardt

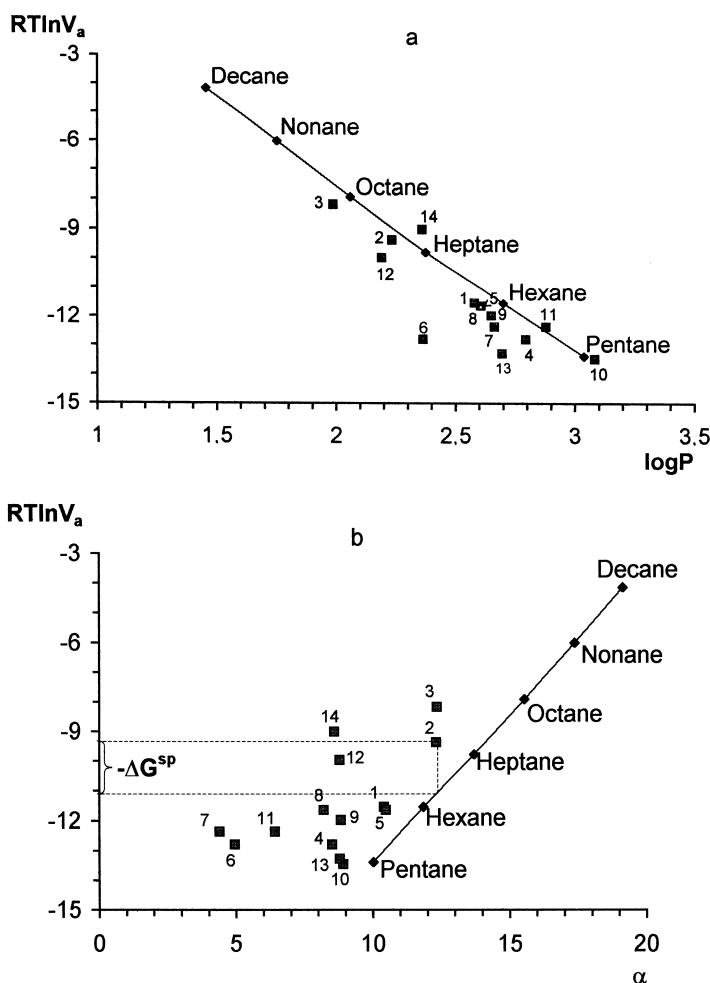


Fig. 5. Variation of  $RT \ln V_a$  as a function of the adsorbate vapor pressure logarithm  $\log P$  (a) and the adsorbate polarizability  $\alpha$  ( $\text{Å}^3$ ) (b) for C16(I) at 403 K. 1=benzene, 2=toluene, 3=chlorobenzene, 4=chloroform, 5=tetrachloromethane, 6=nitromethane, 7=acetonitrile, 8=methyl ethyl ketone, 9=ethyl acetate, 10=diethyl ether, 11=acetone, 12=butan-1-ol, 13=2-methylpropan-2-ol, 14=dioxane.

parameters and others were used [11–13,26–33]. We will discuss only two cases and will show as an illustration two of our attempts to separate the effects of silanols and grafted groups by retention.

The dependence of  $\Delta G^{\text{sp}}$  on the solvent properties may be expressed as follows:

$$-\Delta G^{\text{sp}} = K_1 \delta_a + K_2 \delta_o \quad (1)$$

where  $\delta_a$  and  $\delta_o$  are parameters of solubility, which express the capability of the solvent to act as a proton acceptor (donor of electron) and the capability

toward the orientational interaction, respectively [13,31]. Along with Eq. (1), one can use Eq. (2):

$$-\Delta G^{\text{sp}} = K_1 \text{DN} + K_2 \text{AN} \quad (2)$$

where DN characterizes the capability of the solvent to share its electron pair with suitable acceptor and AN characterizes electrophilicity (Lewis acidity) of the solvent [11,30].  $K_1$ ,  $K_2$  are regression coefficients which are characteristic for the given adsorbent and express the sensitivity of  $\Delta G^{\text{sp}}$  toward two different parameters of solvent polarity.



Table 4  
 $-\Delta G^{sp}$  (kJ/mol) on the samples studied and  $C_{18}$  [13] at 373 K

	C16(I)	C16(II)	tCF	nCF	C3F7	$C_{18}$
Ethyl acetate	4.6	4.7	6.6	7.4	9.1	8.3
Acetone	7.3	7.5	8.7	9.7	11.8	10.6
Methyl ethyl ketone	6.2	6.2	7.8	8.8	10.7	–
Diethyl ether	2.8	2.6	–	3.6	6.1	6.3
Acetonitrile	9.7	9.9	10.1	11.9	12.9	14.4
Nitromethane	7.6	8.3	8.6	10.3	10.7	12.5
Benzene	1.9	1.9	–	2.7	2.2	2.8
Toluene	2.0	2.0	2.1	2.9	2.4	–
Ethylbenzene	1.8	1.7	2.0	2.7	2.2	–
Chlorobenzene	3.2	3.2	3.3	4.3	3.6	–
Chloroform	2.6	3.2	–	3.4	2.6	3.3
2-Methylpropan-2-ol	3.3	4.7	–	6.2	8.2	–

Two-parameter correlation is performed using multiple regression analysis. Coefficient  $K_1$  is believed to be proportional to the concentration of accessible silanols, while  $K_2$ , taking some care, may be assigned to the interaction with grafted groups.

It should be noted that the different solvent parameters contribute with different impact to the total interaction energy, moreover, such parameters often have different dimensions [33]. That is why we decided to use relative values and perform the calculations with regard to the values obtained for bare silica ( $K_1^1, K_2^1$ ) (Fig. 6) or C16(I) silica ( $K_1^2, K_2^2$ ) (Table 5).

Fig. 6 shows a sharp decrease (by 5–40-times,

depending on the chosen equation and sample) of  $K_1^1$  on hydrophobic silicas compared to bare silica which is because of both the substitution and the shielding of silanols with grafted silanes. Changes in  $K_2^1$  are not so remarkable, however there is a trend in the increase of this coefficient as well as  $K_1^1$ , passing from alkyl- to fluoroalkylsilicas. At the same time, the coefficients are pretty close for phenyl- and fluoroalkylsilicas. As one can expect,  $K_1^2$  and  $K_2^2$  calculated according to Ref. [13] are higher for the  $C_{18}$  stationary phase than for the hydrophobized silicas studied in the present work; an exception is C3F7 (Table 5). A decrease in the temperature of the experiment leads to closing of  $K_1^2$  calculated for

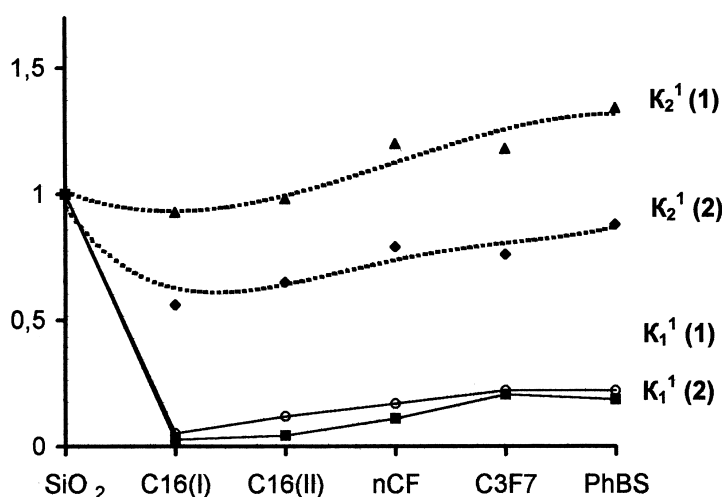


Fig. 6. Coefficients of regression equations  $K_1^1, K_2^1$  calculated from Eqs. (1) and (2) with respect to bare silica for samples studied at 403 K.

Table 5

Coefficients  $K_1^2$  and  $K_2^2$  calculated from Eqs. (1) and (2) with respect to C16(I) on the samples studied and  $C_{18}$  [13] at different temperatures

	$T$ (K)	C16(II)	tCF	nCF	C3F7	$C_{18}$
$K_1^2$ (1)	373	0.9	1.6	1.6	2.5	1.9
$K_1^2$ (1)	403	2.3	–	3.4	4.3	–
$K_1^2$ (2)	373	0.8	1.7	1.4	2.8	2.2
$K_1^2$ (2)	403	1.7	–	4.3	7.9	–
$K_2^2$ (1)	373	1.1	0.9	1.2	1.0	1.4
$K_2^2$ (1)	403	1.1	–	1.3	1.3	–
$K_2^2$ (2)	373	1.1	1.0	1.3	1.2	1.4
$K_2^2$ (2)	403	1.2	–	1.4	1.3	–

different silanized silicas by Eqs. (1) and (2) despite the reasonable growth of  $\Delta G^{sp}$ . The general trend in the change of the coefficients creates the impression that both coefficients reflect specific interactions which are determined by the nature of grafted groups because of chromatographic polarity and, therefore, capability toward donor and acceptor interactions is much higher for phenyl- and fluoroalkylsiloxanes than for methylsiloxanes [3]. A decrease in differences in  $K_1^2$  as the temperature decreases also

indicates that the nature of grafted groups is more important than the non-modified silica surface in the retention process, because the H-bond energy depends more on temperature than the orientational interaction [34]. Unfortunately, the exact conclusions about the role and relative intensity of different types of interactions in adsorption, especially in such a complex object as surface silanized silicas, could hardly be done on the basis of the results obtained in this work, because the regression coefficients, proba-

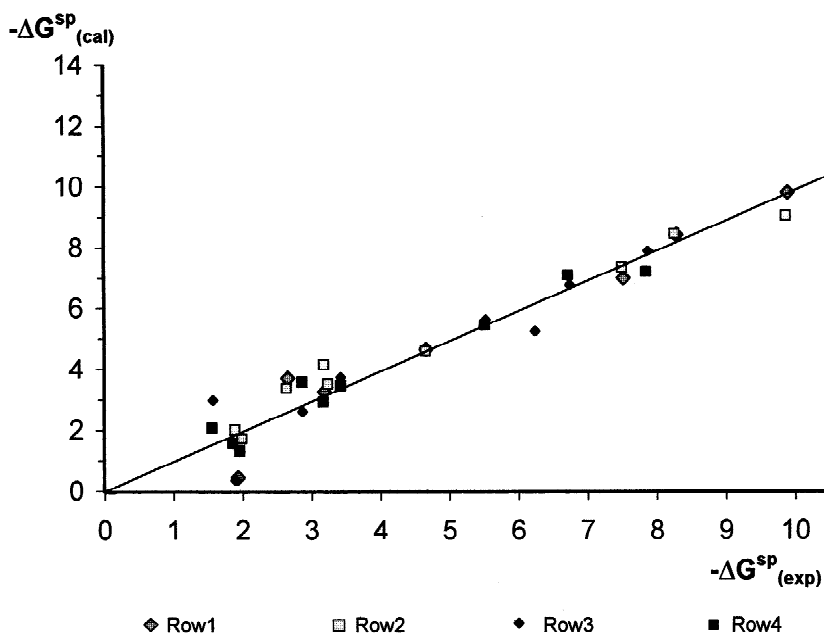


Fig. 7. Comparison of experimental and calculated  $-\Delta G^{sp}$  by means of two techniques for C16(II). Eq. (1): row 1, 373 K; row 3, 403 K. Eq. (2): row 2, 373 K; row 4, 403 K.

bly, are a complex function of the nature and structure of grafted groups and their surface concentration as well.

Nevertheless, good correlation between the calculated and experimental data (Fig. 7) permits one to believe that it is possible to obtain more reliable data about the role of both silanols and grafted groups, if the other solvent parameters, which are more similar to the nature of interactions between solute and modified surface, are used in correlation analysis.

Silicas with a grafted polymeric layer of amino-propyl- or phenylsiloxane were shown to be adsorbents with homogeneous surfaces which are useful in the separation of polar and non-polar compounds [14,15]. In order to compare the selectivities of the sorbents prepared in this work with the polymethylsiloxanes, popular in GC, we determined the retention of alkylbenzenes, alcohols, alkyl acetates and ethers for  $C_{16}$  silica and for OV-1. The results, which are given in Fig. 8, show that  $C_{16}(II)$

silica and OV-1 liquid have properties similar to many oxygen-containing compounds, and benzene derivatives are retained even more weakly than on squalane. Therefore,  $C_{16}$  silicas like polydimethylsiloxanes can be used in the separation of homologous compounds or different oxygen-containing compounds, for example, two chromatograms shown in Fig. 9. Taking into account such advantages of chemically bonded stationary phases as poor volatility, high efficiency, high thermal ( $C_{16}$  stable up to 300–350°C) and hydrolytical stability, one can recommend  $C_{16}$  silicas for wide use in analytical practice. Additional studies are required to evaluate the potential of fluoroalkylsilicas in practical use.

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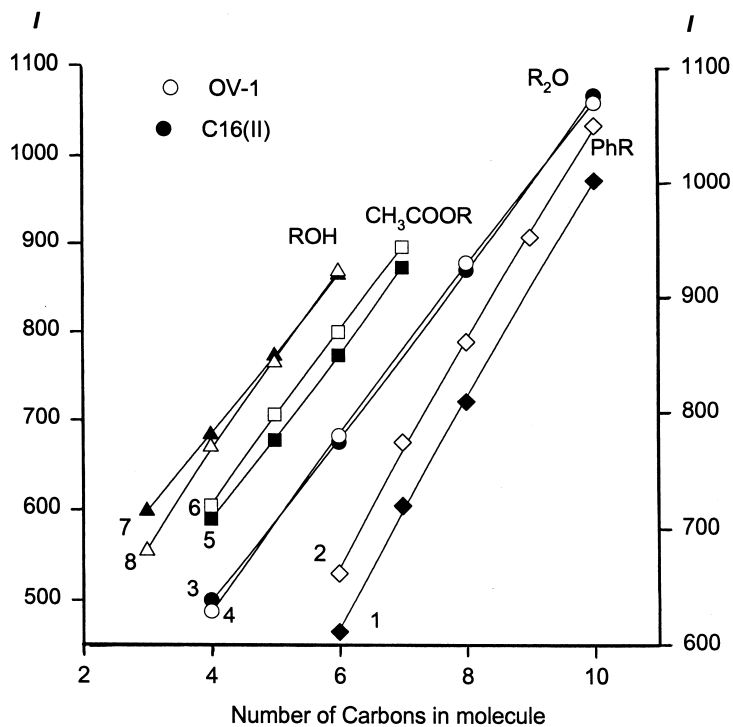


Fig. 8. Dependence of Kováts retention indices  $I$  on the number of carbon atoms  $n$  in the molecules of  $n$ -alkylbenzenes (1, 2), di- $n$ -alkyl ethers (3, 4),  $n$ -alkyl acetates (5, 6),  $n$ -alcohols (7, 8) for  $C_{16}(II)$  (1, 3, 5, 7) and OV-1 (2, 4, 6, 8) at 423 K. The left axis corresponds to 3, 4, 5, 6, 7, 8 dependencies, the right axis to 1, 2 ones.

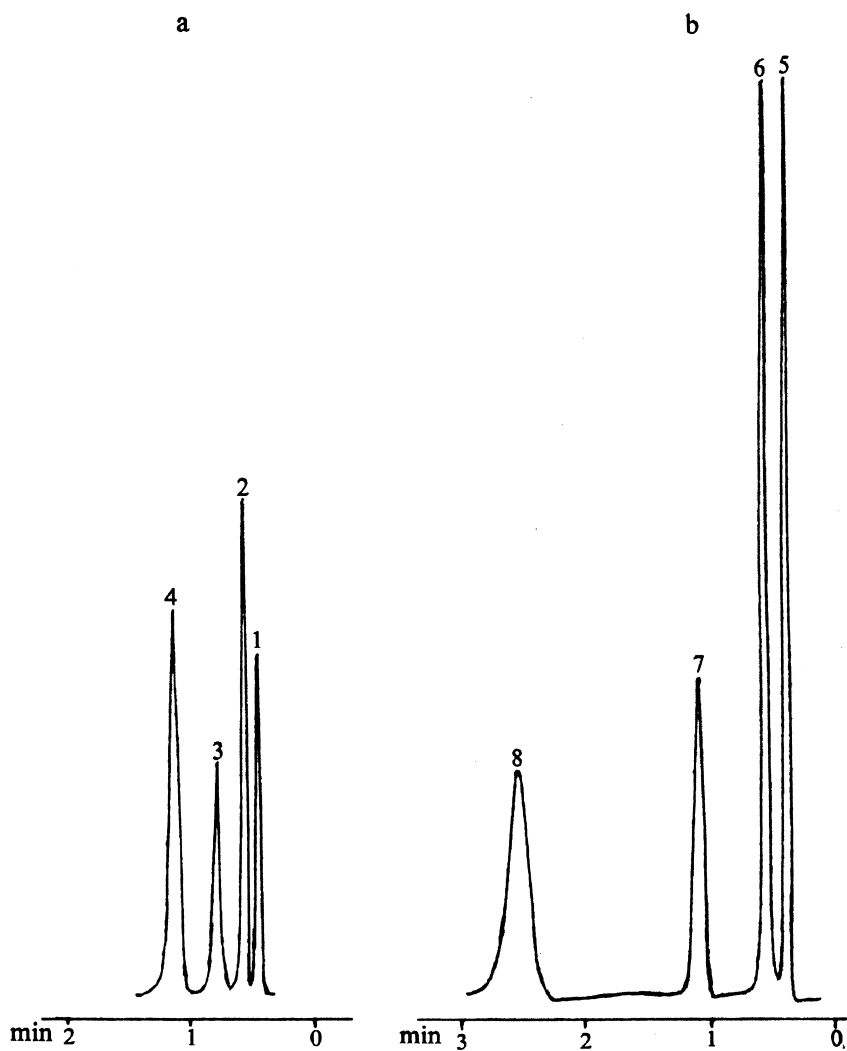


Fig. 9. Chromatograms of esters (a) and ethers (b) on C16(II) silica at 423 K. Column, 120×0.25 cm I.D.,  $F=24.7$  ml/min. 1=Ethyl acetate, 2=*n*-propyl acetate, 3=*n*-butyl acetate, 4=*n*-amyl acetate, 5=diethyl ether, 6=*n*-dipropyl ether, 7=*n*-dibutyl ether, 8=*n*-diamyl ether.

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