



Gas chromatography study of silica modified with polyfluoroalkyl groups[☆]

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Abstract

Silicas with attached polyfluoroalkyl groups were studied by gas chromatography (GC) at zero surface coverage. Organic molecules (*n*-alkanes, ethers, esters, ketones, etc.) were used as test compounds. The contributions of molecule groups to the Gibbs energy of adsorption ΔG_i , and the contributions of specific energy interactions ΔG^{sp} as well as Kováts retention indices were calculated. The strong and weak points of the two approaches (ΔG_i , ΔG^{sp}) were discussed. It was shown on the basis of both approaches that adsorption process on polyfluoroalkyl silicas is to be described by the low contribution of hydrocarbon groups (dispersion interactions) and sufficiently high contribution of groups reinforcing specific interactions. The significant role of entropy in thermodynamic of retention was shown by example of adamantane adsorption.

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1. Introduction

Many modern technology processes such as the preparation of sorbents for ecology needs, the development of new chromatographic stationary phases, and the design of damper and energy saver techniques need both hydrophobic and oleophobic materials. Therefore, fluorine-containing materials including silicas modified with fluorinated groups are attracting the growing attention of researchers [1–4].

Nevertheless, to our knowledge, only some papers [4] including our own [5,6] have reported the thorough investigation of the adsorption properties of new polyfluoroalkyl materials using adsorbates of different classes.

This work is devoted to the study of both the surface chemistry and the nature of adsorption interactions on polyfluoroalkyl silicas by GC at close to zero surface coverage. In order to study adsorption interactions in detail we compared several approaches: calculation of the specific energy contribution to the thermodynamic characteristics of adsorption (TCA), and calculation of the molecule group contributions to the TCA as well as determination of Kováts retention indices.

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2. Experimental

2.1. Materials

Unmodified silica (Silochrome C-120, Stavropol plant, Stavropol, Russia) and silica modified with morpholine derivatives were studied. Synthesis and some adsorption characteristics of modified silicas have been described in Refs. [5,6]. Notation and some characteristics of the samples studied are given in Table 1. Specific surface areas S of modified silicas were calculated as though they are equal to the specific surface area of unmodified silica per 1 g of a modified silica sample. The specific surface area of the unmodified silica was determined by the BET method using nitrogen adsorption isotherms at 77 K. Polymethylsiloxane stationary phase OV-1 (10% on Gas-Chrom Q, Serva, USA), polymethylfluoroalkylsiloxane OV-210 (10% on Chromaton N, Biokhimmak, Moscow, Russia) and Carbo-pack C HT (Supelco, USA) were used as model sorbents.

The test compounds used were hydrocarbons, and oxygen- and nitrogen-containing compounds of analytical grade which were purchased from Reakhim, Russia.

2.2. Gas chromatography

Gas chromatographic analyses were performed using Chrom-5 (Czech Republic) and Tsvet-100 (Russia) instruments with a flame ionization detector and high-purity helium or nitrogen as carrier gases (flow-rate $F=10\text{--}20\text{ cm}^3/\text{min}$). Glass columns were used ($0.5\text{--}1.2\text{ m}\times 2$; 2.5 mm I.D.). All samples were first heated at 473 K for 20–30 h in a helium flow.

2.3. Calculation of thermodynamic characteristics

Thermodynamic characteristics of adsorption (TCA) of organic compounds (retention volumes V_a (cm^3/m^2)= V_g (cm^3/g)/ S (m^2/g), heat of adsorption q (kJ/mol) and standard entropy of adsorption ΔS^0 (J/mol·K)) were determined at a zero surface coverage in the region 373–423 K.

Retention volumes V_a were determined as described in Ref. [7] and were equated with the Henry constant K of the adsorption equilibrium, which is obviously related to the standard Gibbs energy of adsorption:

$$\Delta G^0 = -RT \ln K = -RT \ln V_a \quad (1)$$

q and ΔS^0 were obtained from the temperature dependence of V_a :

$$\ln V_a = q/RT + (\Delta S^0 + R)/R \quad (2)$$

assuming that q and ΔS^0 do not depend on temperature, and q is equal to $-\Delta U^0$ (where ΔU^0 is standard molar change in internal energy of adsorption).

Concentrations of $1\text{ }\mu\text{mol}/\text{cm}^3$ and $1\text{ }\mu\text{mol}/\text{m}^2$ were chosen as standard states for the vapor phase and for the adsorbed phase, respectively [7,8].

2.4. Approaches to quantity assessment of surface properties

In order to calculate the contribution of specific interactions (ΔG^{sp} , q^{sp}) to the standard Gibbs energy of adsorption ΔG^0 or to the heat of adsorption q , we followed the approach proposed earlier by Kiselev and Yashin [9] and Dong et al. [10]. To calculate

Table 1
Notations and characteristics of the studied silicas

Notations of the samples	Group attached to surface	W_c (%)	C (groups/ nm^2)	S (m^2/g)
SiO_2	Bare silica	–	–	93
C_8	$-\text{Si}(\text{CH}_3)_2-(n\text{-C}_8\text{H}_{17})$	5.18	3.0	87
C_3F_7	$-\text{Si}(\text{CH}_3)_2-(\text{CH}_2)_3-(\text{CF}_2)_2-\text{CF}_3$	3.30	2.4	85
C_6F_{13}	$-\text{Si}(\text{CH}_3)_2-(\text{CH}_2)_3-(\text{CF}_2)_5-\text{CF}_3$	3.83	2.1	82

C , surface concentration of grafted groups; S , specific surface area; W_c , carbon content.

ΔG^{sp} (or q^{sp}), we used the experimentally obtained dependencies of $RT \ln V_a$ (or q) on the polarizability of test compounds. ΔG^{sp} was calculated by subtracting the change in Gibbs energy due to adsorption of a hypothetical or real n -alkane (the contribution of dispersion interactions of the test compound, ΔG^{d}), with polarizability equal to that of the compound under study, from the standard Gibbs energy of adsorption (ΔG^0):

$$\Delta G^{\text{sp}} = \Delta G^0 - \Delta G^{\text{d}} \quad (3)$$

An analogous procedure was applied to derive q^{sp} :

$$q^{\text{sp}} = q - q^{\text{d}} \quad (4)$$

where q^{d} is the contribution of dispersion interactions to the heat of adsorption q .

A simple additive scheme was used for calculation of the molecule group contribution to the standard Gibbs energy ΔG^0 of adsorption ($-\Delta G_i = RT \ln V_{ai}$) or to the heat of adsorption (q_i):

$$-\Delta G^0 = RT \ln V_a = \sum n_i RT \ln V_{ai} = -\sum n_i \Delta G_i \quad (5)$$

$$q = \sum n_i q_i \quad (6)$$

where ΔG_i , q_i are the contributions of the group i , and n_i is the number of such groups in the molecule.

The Kováts retention indices I were calculated as follows [11]:

$$I(X) = \frac{\log V_g(X) - \log V_g(n)}{\log V_g(n+1) - \log V_g(n)} \cdot 100 + 100n \quad (7)$$

I values can be also defined as:

$$I(X) = \frac{\ln V_g(X) - \ln V_g(n)}{\ln V_g(n+1) - \ln V_g(n)} \cdot 100 + 100n \quad (8)$$

where $V_g(n)$, $V_g(n+1)$ are the retention volumes of n -alkanes with the number of carbon atoms n and $n+1$, respectively, provided that $V_g(n+1) \geq V_g(X) \geq V_g(n)$.

3. Results and discussion

All the test adsorbates used can be subdivided into n -alkanes, capable only of dispersion interactions,

and other substances, capable of a wide set of intermolecular interactions.

In the case of n -alkanes, the retention volumes (V_a) and the heat of adsorption (q) changed in the sequence: $\text{SiO}_2 > \text{C}_8 > \text{C}_6\text{F}_{13} > \text{C}_3\text{F}_7$ [6]. Polyfluoroalkyl groups attached to the surface produce a much sharper decrease in energy of dispersion interactions than alkyl groups of similar length. The heat of adsorption of n -alkanes on the C_3F_7 sample was so low that the values were close to the heat of n -alkane dissolution in the liquid phases OV-1 and OV-210 (for instance, q values for decane were 36.3 (C_3F_7), 38.3 (OV-1), and 34.8 (OV-210) kJ/mol) and insignificantly exceeded the heat of n -alkane condensation [6]. Taking into account such low adsorption characteristics of n -alkanes, presumably only adsorption on the exterior side of the attached groups and no penetration into the grafted layers takes place in the case of polyfluoroalkyl silicas.

In order to clarify the mechanism of GC retention of non-polar molecules on the samples studied, decane ($\text{C}_{10}\text{H}_{22}$) and cyclic adamantane ($\text{C}_{10}\text{H}_{16}$) were chosen as test compounds. As some links of cyclic molecules are removed from gas–solid interface, adamantane (Ad) eluted from the columns with silica sample or with Carboxpack C HT (the latter is the perfect model of a flat surface [8]) earlier than non-branched hydrocarbon decane (Dec) ($V_{\text{rel}} = V_g(\text{adamantane})/V_g(\text{decane})$; $V_{\text{rel}} < 1$; $\log V_{\text{rel}} < 0$; Fig. 1a). In contrast, for all modified silicas another sequence of retention was found in the pair: adamantane eluted after decane (Fig. 1a). The same order was a characteristic of liquid phases OV-1 and OV-210 where dissolution and therefore pressure of saturated vapors determines retention order ($p_0(\text{Ad}) \approx 9$ kPa, $p_0(\text{Dec}) = 28$ kPa at $T = 403$ K). After calculating the differences in TCA of adamantane and decane ($\Delta(\Delta G)$, $\Delta(\Delta U)$, $\Delta(\Delta S)$), we were able to arrange the samples studied in a row where the difference in the retention of cyclic and linear hydrocarbons was defined from the energy factor (Carboxpack C HT, silica) to the entropy factor (liquid phases; Fig. 1b). As expected, modified silicas, like liquid phases, were found in the upper part of the graph where the entropy factor dominates. Indeed, we propose that the retention mechanism for modified silicas and liquids is fairly similar, and the

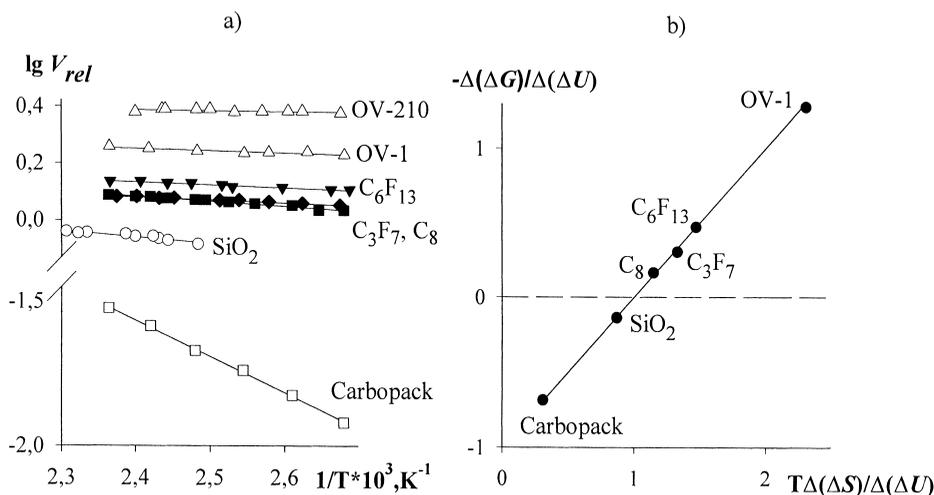


Fig. 1. (a) Dependence of $\lg V_{rel}$ ($V_{rel} = V_g(\text{adamantane})/V_g(\text{decane})$) versus temperature for samples studied. (b) Thermodynamic characteristics of adsorption (TCA) of adamantane and decane in the terms of equation: $-\Delta(\Delta G)/\Delta(\Delta U) = -1 + T\Delta(\Delta S)/\Delta(\Delta U)$. The $\Delta(\Delta G)$, $\Delta(\Delta U)$, $\Delta(\Delta S)$ values are the differences in TCA of adamantane and decane.

only difference is that a grafted layer is much thinner than a liquid film.

Concerning polar molecules, penetration into a grafted layer undoubtedly takes place. Nevertheless, the peak symmetry of polar compounds increased sharply on the modified silicas compared with the initial silica. As shown previously in Ref. [5], peak asymmetry of aniline on modified silicas was twice as small as aniline asymmetry on bare silica. At the same time the peak asymmetry of anisole and phenol was equal to 1 on modified silicas [5]. This is the main evidence that the surface of silanized silicas is uniform. The thermodynamic characteristics of ad-

sorption of polar compounds at lowest surface concentrations are presented in Table 2. One can see that silanisation of the silica surface with alkyl groups (C_8) results in a sharp decrease in the retention volumes and in the heats of adsorption of such compounds. When passing from the alkyl silica sample C_8 to the C_6F_{13} silica sample a further significant decrease in the retention volumes of alcohols and ethers capable of forming sufficiently strong hydrogen bonds was found. The decrease was approximately twice, just a bit smaller than the decrease in the n -alkane volumes [6]. At the same time, the retention volumes of organic compounds

Table 2

Retention volumes V_a (cm^3/m^2) and V_g (cm^3/g) at 403 K and the heat of adsorption q (kJ/mol) for studied silicas and liquid stationary phases OV-1 and OV-210

	SiO_2		C_8		C_6F_{13}		C_3F_7		OV-1, V_g	OV-210, V_g
	V_a	q	V_a	q	V_a	q	V_a	q		
Hexane	0.039	31	0.026	29	0.011	27	0.006	26	1.22	0.33
Diethyl ether	1.21	60	0.019	44	0.011	41	0.009	48	0.665	0.53
Methyl ethyl ketone	2.85	56	0.038	51	0.036	47	0.037	52	1.20	2.25
Ethyl acetate	2.92	61	0.031	47	0.027	46	0.024	51	1.21	1.89
Butan-1-ol	–	–	0.083	58	0.039	54	0.037	58	1.49	1.69
Benzene	0.12	39	0.028	28	0.015	30	0.008	29	1.81	0.93
Acetonitrile	0.82	53	0.030	–	0.036	42	0.037	47	1.03	17.79
Nitromethane	0.39	47	0.023	–	0.030	37	0.025	40	0.94	4.20

capable of participating in the donor–acceptor interactions or in the strong electrostatic interactions (esters, ketones, acetonitrile, nitromethane) do not change significantly between alkyl silica C₈ and polyfluoroalkyl silica C₆F₁₃. Shortening the polyfluoroalkyl chain length (C₃F₇ sample) does not produce any noticeable change in the retention of all such compounds. Surface properties of polyfluoroalkyl silica samples, C₆F₁₃ and C₃F₇, were found to be nearly indistinguishable as regards GC retention of polar compounds.

In order to gain additional information on the influence of both the nature of the grafted group and the residual silanols' presence on the retention volumes, ΔG_i , ΔG_i^{sp} and I were calculated for the samples studied.

First we amended the scheme of the calculation of the end-groups so that the results would not depend on the reference state used (V_a , cm³/m² or V_g , cm³/g). After applying the simple additive scheme, the contributions of the end-groups were modified as follows:

$$-\Delta G_i^* = RT \ln V_{xi} + RT \ln V(-\text{CH}_2-) - RT \ln V_x(-\text{CH}_3) \quad (9)$$

where ΔG_i^* is the corrected increment of the end-group i , $RT \ln V_{xi}$ is the increment of the end-group i defined by the standard state chosen ($V_x = V_a$ or $V_x = V_g$), and $RT \ln V(-\text{CH}_2-)$, $RT \ln V_x(-\text{CH}_3)$ are the increments of methylene and methyl groups, respectively. This amendment allowed us to compare the properties of solid and liquid stationary phases (Table 3). Although the order of the retention volumes for silicas and liquid phases could not be compared (Table 2), the ΔG_i^* values for these materials could be compared (Table 3).

The values of the molecule group increments in the standard Gibbs energy of adsorption (ΔG_i^*) show (Table 3) that the role of all polar groups in retention is substantially lower for alkyl and polyfluoroalkyl silicas than for initial silica. It was found that the contributions of –OH and –O groups for polyfluoroalkyl silicas (C₆F₁₃, C₃F₇) are not less but are sometimes higher than the corresponding values for alkyl silica (C₈). Given this fact, the reduction in the alcohol and ether retention volumes observed in the case of polyfluoroalkyl silicas (Table 2) is merely

Table 3
Molecular group contribution to the standard Gibbs sorption energy ΔG_i , ΔG_i^* (kJ/mol) at 403 K and molecular group contributions to the heat of adsorption q_i (kJ/mol) for studied silicas and liquid phases OV-1 and OV-210

	SiO ₂		C ₈		C ₆ F ₁₃		C ₃ F ₇		OV-1		OV-210		
	– ΔG_i	– ΔG_i^*	q_i	– ΔG_i	– ΔG_i^*	q_i	– ΔG_i	– ΔG_i^*	q_i	– ΔG_i	– ΔG_i^*	– ΔG_i	– ΔG_i^*
–CH ₃	–9.41	1.98	6.0	–9.38	1.71	6.5	–10.48	1.41	6.5	–3.42	1.84	–5.12	1.64
–CH ₂ –	1.98	1.98	4.6	1.71	1.71	4.0	1.41	1.41	3.4	1.84	1.84	1.64	1.64
–O–	15.5	15.5	38	2.1	2.1	22	2.8	2.8	21	1.7	1.7	4.6	4.6
–CN	9.4	20.8	47	–2.4	8.7	–	–0.69	11.2	36	3.4	8.7	14.6	21.4
–NO ₂	6.2	17.6	41	–3.2	7.9	–	–1.4	10.5	31	3.1	8.4	9.74	16.5
–OH	–	–	–	–3.6	7.6	41	–4.5	7.4	37	–0.76	4.5	1.74	8.5

the result of the reduction in the hydrocarbon group contributions and, therefore, the contribution of dispersion interaction, to the retention volumes and, as a result, to the standard Gibbs energy of adsorption.

A sharp increase in the contribution of electron-donor groups or groups reinforcing electrostatic intermolecular interactions is observed in the case of polymethylfluoroalkylsiloxane liquid phase OV-210 compared with the polymethylsiloxane system OV-1 (Table 3). The same results were obtained passing from alkyl silica to polyfluoroalkyl silicas (Table 3). We therefore hypothesised that interaction between the sorbate molecules and the sufficiently polar part of the grafted chain $-\overset{+\delta}{\text{C}}\text{H}_2-\overset{-\delta}{\text{C}}\text{F}_2-$, having the dipole of $\sim 2.2\text{--}2.4$ D, is the important feature of non-dispersion energy interactions on polyfluoroalkyl silicas.

Two approaches—the calculation of the group contributions to the standard Gibbs energy of adsorption (ΔG_i^*) and the calculation of the specific interaction contributions to the Gibbs adsorption energy (ΔG^{sp})—correlate well in the estimation of the properties of chemically modified silica (Tables 3 and 4). Nevertheless, it is not possible to replace one approach by another.

Calculation of the ΔG^{sp} values, unlike calculation of the ΔG_i^* values, results in separation of the contribution of dispersion and specific interactions. However we need to choose one or another molecular parameter for evaluation of the contribution of dispersive interactions to the Gibbs adsorption energy. Some physical parameters are used more often than others, for example: vapor pressure, boiling point, molar refraction or polarizability [10,12]. But every choice of molecular parameter would be a rough approximation and our results

would depend on the parameter chosen and the corresponding reference state. Besides, if the parameter is the polarisability of molecules, it is not possible to apply this approach for studying liquid stationary phases. But, as far as the ΔG_i^* approach is concerned, we only assume the additivity of the Gibbs energy of adsorption or Gibbs energy of dissolution (the mechanism of the process is not important).

Possibly, the easiest and most suitable way to study the surface properties in detail is to calculate the group contribution to the Gibbs energy of adsorption. It should be also noted that, despite the dispersion interaction contribution to every group contribution, there is a good enough correlation between the ΔG_i^* values and ΔG^{sp} values (Tables 3 and 4). We would like also to stress that the correlation does not exist if non-corrected group contributions ΔG_i are taken into account (Table 3). Moreover, there is correlation only between $-\Delta G_i^*$ and q_i , for example with an SiO_2 sample: q_i as well as $-\Delta G_i^*$ change in the sequence of groups $-\text{O}- < -\text{NO}_2 < -\text{CN}$, while $-\Delta G_i$ values change as follows $-\text{NO}_2 < -\text{CN} < -\text{O}-$ (Table 3). Besides, the ΔG_i^* values provide an opportunity to calculate full retention Kováts indices (I) and the ΔG^{sp} values, while it is not possible to calculate ΔG_i^* values from I values.

The group increments and contribution of specific energy interactions to the heat of adsorption, in accordance with heat of adsorption values (Table 2), reduced sharply when passing from initial silica to modified silicas (Tables 3 and 4). But their values, in good agreement with each other, do not change too much in the series of modified silica samples. As the entropy of adsorption is of great importance in the adsorption process on modified silicas, the heat of

Table 4

Contributions of specific interactions to the Gibbs energy of adsorption ΔG^{sp} (kJ/mol) at 403 K and to the heat of adsorption q^{sp} (kJ/mol) for the studied silicas

	SiO ₂		C ₈		C ₆ F ₁₃		C ₃ F ₇	
	$-\Delta G^{\text{sp}}$	q^{sp}	$-\Delta G^{\text{sp}}$	q^{sp}	$-\Delta G^{\text{sp}}$	q^{sp}	$-\Delta G^{\text{sp}}$	q^{sp}
Diethyl ether	14.5	36	1.6	21	2.3	20	3.0	28
Acetonitrile	18.1	42	7.4	–	9.9	30	10.5	35
Nitromethane	15.0	35	6.0	–	8.8	23	9.0	26
Butan-1-ol	–	–	6.7	35	6.8	33	8.0	39

Table 5

Kováts retention indices I at 403 K for the studied silicas and liquid phases OV-1 and OV-210

	SiO ₂	C ₈	C ₆ F ₁₃	C ₃ F ₇	OV-1	OV-210
Diethyl ether	1180	536	600	700	495	689
Methyl ethyl ketone	1338	670	885	1110	597	988
Ethyl acetate	1342	632	822	986	600	904
Butan-1-ol	–	820	912	1128	645	926
Benzene	786	609	687	671	672	804
Acetonitrile	1115	626	887	1109	571	1440
Nitromethane	989	577	841	1000	556	1125

adsorption is a less sensitive characteristic of the nature of intermolecular interactions than the retention volumes.

The Kováts retention indices I are necessary for clarifying the position of the material among other chromatographic stationary phases [11]. However, it should be taken into account that the I values depend on the difference between $\ln V_a$ ($\ln V_g$) of two nearest n -alkanes (Eq. (8)) or, in the case of the additive scheme, on the $\ln V_a(-CH_2-)$ values. Therefore, evaluation of the chromatographic polarity of materials based on the position of the I values as well as evaluation of the polarity from the thermodynamic data (ΔG_i^* , ΔG^{sp}) cannot agree.

The Kováts retention indices I for the initial and modified silicas are presented in Table 5. In accordance with other approaches (ΔG_i^* , ΔG^{sp} ; Tables 3 and 4), an increase in the I values was found for polyfluoroalkyl silica samples compared to alkyl silica sample. But the increase in the I values was much sharper than the increase in the other parameters mentioned above. Therefore, some I values for polyfluoroalkyl silica C₃F₇ are as large as for initial silica (acetonitrile, nitromethane; Table 5). This could be explained by the difference in the $\ln V(-CH_2-)$ values between the silicas under investigation, namely, the sharp decrease in $\ln V(-CH_2-)$ values when passing to polyfluoroalkyl silicas.

Generalization of the data presented in this paper and our previous work [5,6] show that silicas with attached polyfluoroalkyl groups obtained with the help of the new modifiers, morpholine derivatives, are fairly uniform. Their surface properties are described by the low contribution of dispersion

interactions and, at the same time, by the sufficiently high contribution of donor–acceptor or electrostatic interactions. The mechanism of GC retention on such materials includes penetration of the test molecules into the grafted layers; therefore entropy factor is of great importance in such systems.

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