

# Adsorption of Organic Vapor on Trimethylsilylated Silicas

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**Abstract**—Adsorption of various classes of organic compounds has been studied on silicas chemically modified by silanes that contain a trimethylsilyl group:  $(\text{CH}_3)_3\text{SiI}$  (TMS) and  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3(\text{CH}_3)_2\text{SiCl}$  (C3TMS). The effect caused by the nature of the adsorbate and grafted groups on the thermodynamic parameters of adsorption has been studied. Surface modifying is shown to dramatically decrease the Henry constants of *n*-alkane adsorption equilibrium relative to the unmodified matrix. The contribution of specific interactions to adsorption, estimated by different methods, in the TMS-silica sample is higher than in the C3TMS-silica sample.

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Poly(methylsiloxanes) are among the most abundant modifiers, used for solving a broad range of applied problems in making surfaces lyophobic and inadhesive. Silicas bearing chemically grafted trimethylsilyl groups are widely used as sorbents for high-performance liquid chromatography, separation, and concentration [1]. To provide the ultimate lyophobicity and chemical homogeneity of the surface, the modifier should be grafted with the highest density and should shield the remnant silanol groups of the matrix as efficiently as possible.

Improved techniques have been developed for the synthesis of chemically modified silicas (CMSs) with a trimethylsilyl layer; it was also shown that gas chromatography is an efficient tool for quantifying the surface properties of lyophobic silicas [3–7].

The goals of this work were to study, using gas chromatography, the adsorption of vapors of different classes of organic compounds on silicas chemically modified by silanes containing trimethylsilyl groups and to quantify the effect of the hydrophilic sites of the matrix on the thermodynamic parameters of adsorption.

The adsorbates used were from a standard test kit intended to determine whether specific interactions are possible on solid surfaces [8, 9], namely, hydrocarbons and oxygenated and nitrogenated organic compounds.

## EXPERIMENTAL

The objects of our study were silica samples modified with silanes of compositions  $(\text{CH}_3)_3\text{SiI}$  and  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3(\text{CH}_3)_2\text{SiCl}$  with near-theoretical grafting densities (2.8 and 2.1 nm<sup>-2</sup>, respectively). The starting matrix used was silochrom S-120 (from the Stavropol Chemical Plant). Table 1 displays the notations and characteristics of the test samples, the intact matrix [6], and hydrophobic silica modified with octylsilane (C8) [8].

Experiments were performed on Tsvet 500 and Chrom 5 chromatographs equipped with flame-ionization detectors using high-purity nitrogen as carrier gas and glass columns 100 cm long with an inner diameter of 0.3 cm. The adsorbent-conditioning time in flowing nitrogen at 443 K was 20 h. The adsorbent fraction was 0.02–0.035 cm. Test samples were injected as 2- to 20-fold dilute vapors; the sample size was 0.1 mL.

Adsorbate–adsorbent intermolecular interactions are reflected by the following thermodynamic parameters:

**retention volume**,  $V_A$  (cm<sup>3</sup>/m<sup>2</sup>) =  $V_g$  (cm<sup>3</sup>/g)/ $S_{sp}$  (m<sup>2</sup>/g); and

**heat of adsorption**  $q$  (kJ/mol).

From equations reported in [8], these parameters were determined for pentane, hexane, and benzene at 373–423 K and for diethyl ether at 393–433 K, because below 393 K the diethyl ether peak is skewed.

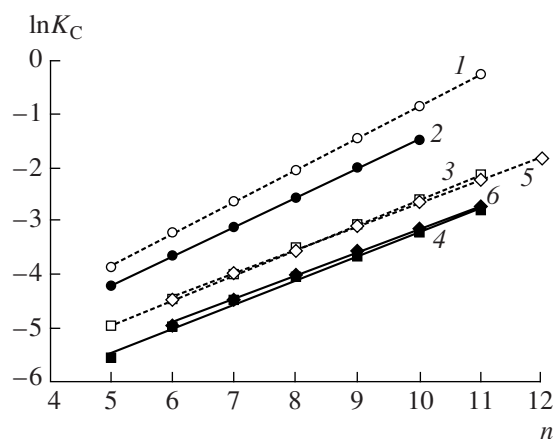
The  $V_A$  value, equal to the Henry constant of adsorption equilibrium ( $K_C$ ), is related to the standard Gibbs energy of adsorption ( $\Delta G^0$ ) through

$$\Delta G^0 = -RT \ln K_C = -RT \ln \{ V_A (c_{st}/a_{st}) \}.$$

The following concentrations were chosen to be the standard state: 1 μmol/mL in the mobile phase ( $c_{st}$ ) and 1 μmol/m<sup>2</sup> in the stationary phase ( $a_{st}$ ).

**Table 1.** Notations and characteristics of test samples: the carbon concentration  $W_C$ , wt %; grafting density  $C$ , nm<sup>-2</sup>; and specific surface area  $S_{sp}$ , m<sup>2</sup>/g

Sample	Grafted group	$W_C$	$C$	$S_{sp}$
SiO <sub>2</sub>	–	–	–	100
TMS	$(\text{CH}_3)_3\text{Si}$ –	1.6	2.8	97
C3TMS	$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3(\text{CH}_3)_2\text{Si}$ –	3.2	2.1	94
C8	<i>n</i> -C <sub>8</sub> H <sub>17</sub> (CH <sub>3</sub> ) <sub>2</sub> Si–	5.18	3.0	85



**Fig. 1.**  $\ln K_C$  vs. the number of carbon atoms  $n$  in the  $n$ -alkane molecule at (1, 3, 5) 403 K and (2, 4, 6) 423 K on (1, 2)  $\text{SiO}_2$ , (3, 4) TMS-silica, and (5, 6) C3TMS-silica.

The heat of adsorption  $q$ , equal to  $-\Delta U^0$  (where  $\Delta U^0$  is the standard internal energy), was calculated from the  $V_A$  versus temperature dependence (on the assumption that  $q$  is temperature independent):

$$\ln V_A = q/RT + A,$$

where  $A$  is a constant for the given adsorbate–adsorbent system.

The determination error for the retention volume and the heat of adsorption for all test compounds was not higher than 5 and 10%, respectively.

The specific-interaction term  $\Delta G^{\text{sp}}$  of the standard Gibbs energy of adsorption was estimated using the Kiselev's method [10]:

$$\Delta G^{\text{sp}} = \Delta G^0 - \Delta G^d,$$

where  $\Delta G^d$  is the dispersion contribution to the total Gibbs energy of adsorption for the given compound. This contribution is determined on the assumption that  $\Delta G^d = \Delta G_A^0$ , where  $\Delta G_A^0$  is the standard Gibbs energy of adsorption for a real or hypothetical  $n$ -alkane whose polarizability is identical to that of the test compound.

**Table 2.** Parameters of equation  $\ln K_C = a + bn$  as functions of  $n$ , the number of carbon atoms in the molecule, for  $n$ -alkanes on the unmodified and modified silica samples at 403 and 423 K

Sample	$T$ , K	$-a$	$\pm\delta a$	$b$	$\pm\delta b$
SiO <sub>2</sub>	403	6.82	0.01	0.596	0.001
	423	6.96	0.01	0.550	0.001
TMS	403	7.256	0.025	0.463	0.003
	423	7.499	0.008	0.427	0.007
C3TMS	403	7.243	0.006	0.447	0.007
	423	7.521	0.069	0.437	0.008

The Kovatz retention indices  $I$  were calculated from the equation found in [10].

## RESULTS AND DISCUSSION

Figure 1 and Tables 2 and 3 display the thermodynamic parameters of adsorption for  $n$ -alkanes (these compounds are capable only of dispersion interactions with the surface virtually regardless of its chemical nature).

It is clear that modified surfaces dramatically decrease the Henry constants  $K_C$  of  $n$ -alkanes compared to the unmodified silica. The  $K_C$  of hydrocarbons is only weakly affected by the nature of the modifier and by the noticeably different carbon concentrations in the TMS-silica and C3TMS-silica samples. This is a reflection of the close oleophobicities of the grafted layers.

In this respect, octylsilyl layers are far exceeded by trimethylsilyl layers; for example,  $K_C$  for hexane and nonane on C8 at 403 K is 0.026 and 0.123, respectively [6]. The  $K_C$  on C3TMS-silica is more than two times lower (0.011 and 0.041, respectively).

In the additive scheme for  $n$ -alkanes, for which the additivity holds with a high accuracy,  $\ln K_C$  is expressed as a function of  $n$ , the number of carbon atoms in the molecule:  $\ln K_C = a + bn$ , where  $b$  equals the contribution of the methylene unit to the Henry constant ( $b = \ln K_C(\text{CH}_2)$ ). According to the data displayed in Table 2, the  $\ln K_C(\text{CH}_2)$  values (which are usually used to estimate the energy of dispersion interactions [9, 11]) on modified surfaces are lower than on the intact matrix, while the parameters  $a$  and  $b$  on TMS-silica and C3TMS-silica are virtually identical.

We should note that it is not always possible to conclude uniquely how the nature of the grafted layer affects the surface properties proceeding from the heats of adsorption: the  $q$  scatter for saturated hydrocarbons on modified silicas and on the unmodified matrix fall within the experimental error (Table 3).

Next, we studied the adsorption of molecules that are capable of sufficiently strong electrostatic and donor–acceptor interactions and capable of H-bonding, including oxygenated and nitrogenated compounds.

Figure 2 displays the  $K_C$  versus temperature curves for benzene and diethyl ether on modified samples and the unmodified matrix. These curves imply that the modification is accompanied by a substantial decrease in  $K_C$ . For benzene and diethyl ether, unlike for linear alkanes, a perceptible differentiation in  $K_C$  is observed for modified samples: the uptake on C3TMS-silica is lower than on TMS-silica, especially for diethyl ether. Evidently, the thermodynamic parameters of benzene adsorption are less sensitive to remnant hydrophilic surface sites than those of diethyl ether adsorption because of the higher energy of H-bonding between diethyl ether and silanol groups [12]. Indeed, the heat of adsorption of diethyl ether is 20 kJ/mol higher than the heat of adsorption of benzene on Silochrom. On pass-

ing from the intact matrix to trimethylsilyl-modified silicas,  $q$  decreases by 4–9 kJ/mol for benzene and 5–10 kJ/mol for diethyl ether (Table 3). On the C3TMS-silica sample,  $q$  approaches the values observed for C8.

Quantifying the role of specific interactions in adsorption in the ordinary way [8, 10], i.e., comparing the adsorption uptakes for the molecules having relatively similar polarizabilities and van-der-Waals dimensions but differing in their electron-density distributions (namely, benzene–hexane and diethyl ether–pentane pairs), we arrived at the following conclusions. The differences between the Gibbs energies ( $-\Delta(\Delta G^0)$ ) and the heats  $\Delta q$  for the aforementioned pairs of compounds decreased significantly after surface modification, due to the substitution and shielding of surface silanol groups by apolar grafted groups (Table 4). The lowest values of  $-\Delta(\Delta G^0)$  and  $\Delta q$  were observed for the octyl phase C8, with the highest, near-theoretical grafting density (Table 1). The higher polarity of C3TMS-silica relative to C8 correlates with the greater density of remnant silanol groups on C3TMS-silica (the groups that have not reacted with the modifier). With the higher grafting density on TMS-silica, on C3TMS-silica the existence of branched and long chains with trimethylsilyl groups (against the short grafted radicals on TMS-silica) decreases more strongly the spatial accessibility of remnant silanol groups to the adsorption of benzene and diethyl ether.

The specific-interaction terms of the Gibbs energy  $\Delta G^{\text{sp}}$  in the test samples are shown by Fig. 3. As expected, modified silica surfaces appreciably decrease  $-\Delta G^{\text{sp}}$  for the compounds capable of electrostatic inter-

**Table 3.** Heats of adsorption  $q$ , kJ/mol

Compound	SiO <sub>2</sub>	TMS	C3TMS	C8
Pentane	25	23	25	25
Hexane	30	28	27	28
Benzene	38	34	29	28
Diethyl ether	58	53	48	44

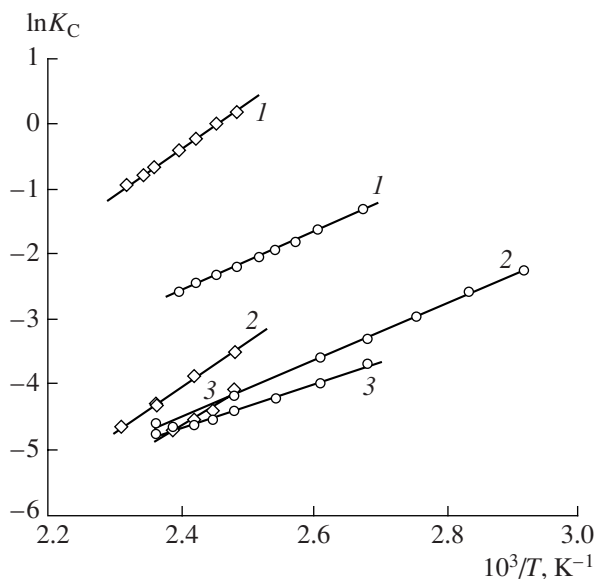
**Table 4.** Differences between the Gibbs energies of adsorption  $\Delta(\Delta G^0)$  (403 K) and the heats of adsorption  $\Delta q$  for benzene and hexane and for diethyl ether and pentane (all quantities are expressed in kJ/mol)

Adsorbate	Benzene–hexane		Diethyl ether–pentane	
	$\Delta(\Delta G^0)$	$\Delta q$	$\Delta(\Delta G^0)$	$\Delta q$
SiO <sub>2</sub>	3.6	8	14	33
TMS	1.4	6	5	30
C3TMS	0.46	2	3.2	23
C8	0.25	0	0.58	19

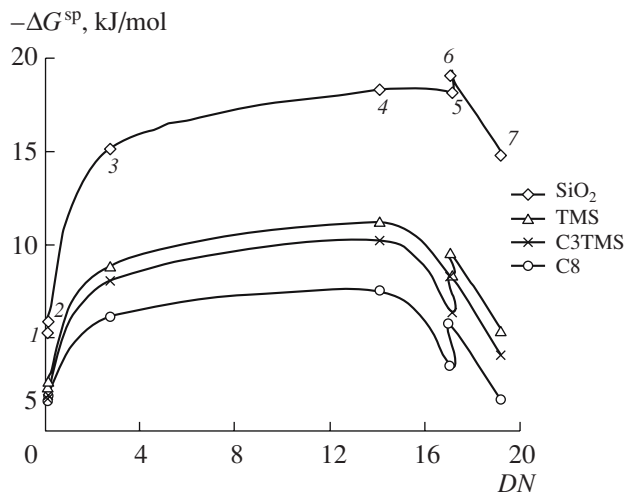
actions and of H-bonding; the role of the specific interactions in adsorption decreases in the order

$$\text{SiO}_2 \gg \text{TMS} > \text{C3TMS} > \text{C8}.$$

This order matches the polarity of the samples, which was estimated by comparing the differences between the heats of chemisorption for benzene–hexane and diethyl ether–pentane pairs. For example, for acetonitrile,  $-\Delta G^{\text{sp}}$  decreases from 18 to 11 and 10 kJ/mol in passing from SiO<sub>2</sub> to TMS-silica and then



**Fig. 2.**  $\ln K_C$  vs. reciprocal temperature for diethyl ether (rhombi) and benzene (circles) on (1) SiO<sub>2</sub>, (2) TMS-silica, and (3) C3TMS-silica.



**Fig. 3.** Contribution from specific interactions to adsorption ( $\Delta G^{\text{sp}}$ ) at 403 K vs. donor number (DN) [13] for the test samples and adsorbates: (1) benzene, (2) toluene, (3) nitromethane, (4) acetonitrile, (5) ethyl acetate, (6) acetone, and (7) diethyl ether.

**Table 5.** Kovatz indices  $I$  at 403 and 423 K and their increments  $\Delta = I(423 \text{ K}) - I(403 \text{ K})$  on TMS-silica and C3TMS-silica samples

Adsorbate	TMS			C3TMS		
	403	423	$-\Delta$	403	423	$-\Delta$
Benzene	689	674	15	627	623	4
Toluene	798	783	15	732	745	-13
Ethylbenzene	899	888	11	830	841	-11
Diethyl ether	817	735	82	697	601	96
2-Methylpropanol-2	1028	982	46	909	780	129
Ethyl acetate	1001	920	81	858	751	107
Acetone	987	886	101	861	747	114
Methyl ethyl ketone	1031	962	69	883	782	101
Acetonitrile	936	892	44	861	796	65

to C3TMS-silica, respectively; on C8, its value is 7 kJ/mol.

In this work the specific interaction terms  $\Delta G^{\text{sp}}$  are analyzed as a function of the donor numbers ( $DN$ ) of solvents (in our case, test compounds), empirical parameters that were introduced by Gutmann [13] to characterize the donating ability of the solvent. For all modified samples, the tendencies in  $\Delta G^{\text{sp}}$  variation as a function of  $DN$  were similar to the unmodified silica. We think this reflects the involvement of the remnant surface silanol groups of CMSs in adsorption. The specific interaction term for adsorption on TMS-silica is higher than on C3TMS-silica, although being far lower than on the unmodified matrix. On the whole, our data imply that the long-chain octyl groups on the C8 sample noticeably decrease the accessibility of remnant hydrophilic sites to adsorption compared to that on TMS-silica samples (Fig. 3). Of the nitrogenated and oxygenated compounds, the lowest  $-\Delta G^{\text{sp}}$  was observed for diethyl ether, despite its high  $DN$ . This observation can be explained as follows: the molecular dipole moment, which determines the energy of orientational interactions, for diethyl ether ( $\mu = 1.1 \text{ D}$ ) is far lower than for the other test compounds (e.g.,  $\mu$  ( $\text{CH}_3\text{CN}$ ) = 3.9 D). Therefore, the decrease in the adsorption energy on account of a decrease in the orientational interaction term cancels out the rise in the adsorption energy on account of the strong H-bonds formed by the ether oxygen atom with silanol groups. Because the Kovatz retention indices are one of the most ordinary ways to ascertain the conventional polarity of stationary phases [14, 15], we calculated them for TMS-silicas at 403 and 423 K in this work (Table 5).

In full agreement with the above data,  $I$  decreases on passing from TMS-silica to C3TMS-silica. An increase in the measurement temperature decreases  $I$  for all adsorbates, except for toluene and ethylbenzene on C3TMS-silica, regardless of the nature of the grafted

layer, because the hydrogen-bond energy always decreases with rising temperature [16]. The decrease in  $I$  on C3TMS-silica is greater than on TMS-silica. Presumably, the conformational mobility of flexible and relatively long grafted groups on the C3TMS-silica sample increases with rising temperature, which favors the efficient shielding of remnant silanol groups.

Thus, despite the lower density of grafted groups in the C3TMS-silica sample compared to TMS-silica, the appearance of two more methyl group in the modifier molecule and the lengthening of the grafted chain result in a coating that more efficiently shields the remnant silanol groups of silica.

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