Influence of the Partial Hydrophobization of Fumed Silica by Hexamethyldisilazane on Interactions with Water

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Received March 26, 2003. In Final Form: July 23, 2003

Fumed silicas unmodified (SBET = 378 m²/g) and modified (379–285 m²/g) by hexamethyldisilazane reacting with silanols (concentration of grafted trimethylsilyl groups CTMS = 0.09–0.79 mmol/g) were studied by means of the NMR, IR, differential thermogravimetry, atomic force microscopy, microcalorimetry, adsorption, and theoretical methods. Variation in the surface composition and changes in the structural characteristics of primary and secondary particles lead to the nonlinear dependence of the Gibbs free energy of interfacial water, the heat of immersion of silicas in water, and the chemical shift δH(T) of water adsorbed from air on CTMS, despite a nearly linear decrease in water adsorption (at p/p0 ≈ 0.8 for 24–72 h) with CTMS. An increase in CTMS causes alterations in the structure of the hydrogen bond network in the interfacial water and other properties of water strongly (700–300 mg/g silica) and weakly (1400–500 mg/g) bound to the silica surfaces.

Introduction

Chemical modification of silica by alkylsilanes or other organosilicon compounds (OSCs) is widely used to change the surface properties1–10 important in interaction with polar and nonpolar substances.1,3,10,11 This modification (hydrophobilization) results in the diminution of the surface affinity to water or other polar compounds, but for nonpolar organics, the opposite effect may be observed. However, the nitrogen (which is nonpolar) adsorption energy and adsorption potentials of the silica gel and fumed silica surfaces modified by different OSCs decrease with increasing amounts of grafted functionalities or growing of their CH chains.11 Aromatic hydrophobic properties of silylated glass particles appear (in the floating rate and the contact angle) at a surface coverage (θ) between 0.5 and 0.6. The heat of immersion of silylated Aerosil A-380 in water significantly reduces from approximately 50 J/g at low θ values to 10 J/g at high θ values.8a Nevertheless, the infrared (IR) and 2H NMR spectroscopy data show that significant amounts of adsorbed water are observed on similar materials.12,13 It has been shown12 that water adsorbed on a surface of mesoporous glasses (modified by hexamethyldisilazane, HMDS) from air is in pores in the form of small clusters with an average number of molecules close to 2. These clusters are linked to residual silanols locating between trimethylsilyl (TMS) groups. Silylation of a surface of both porous (e.g., silica gel) and nonporous (e.g., fumed silica) silicas by different OSCs has been investigated intensively by means of IR and NMR spectroscopies and other methods showing changes in the reactivity of residual silanols and in the properties of the modified surface as a whole depending on the content of the grafted functionalities.1–12 Initially, the reaction of HMDS with silica results in a random distribution of well-separated TMS groups.2 One can assume that a portion of the silanols remaining after silica modification by OSC in contact zones between adjacent primary particles or in narrow pores are difficult to access for OSC molecules; however, these surface patches can be easily accessible for water molecules with the size significantly smaller than that of OSC. Therefore, the 2H NMR spectroscopy


10.1021/la0301238 CCC: $25.00 © 2003 American Chemical Society
Published on Web 11/22/2003
investigations show that a similar surface can disturb a relatively thick interfacial water layer (unfrozen at T < 273 K), and its thickness can exceed that of a similar layer at a hydrophilic surface.13,14 One of the possible reasons of the observed effects is polarization of the heterogeneous surface with different charging of the hydrophobic and hydrophilic patches13 and changes in the structure of the water layers near totally hydrophobic and hydrophilic surfaces.6 Besides, the nonuniform electrostatic field of the oxide surface can reorient dipoles of water molecules, which results in the enhancement of their rotational mobility and disordering of the hydrogen bond network in the interfacial water,6 especially near hydrophilic/hydrophobic surface patches. Therefore, the boundary water remains unfrozen at T < 273 K. In the case of totally hydrophobic surfaces, the number of hydrogen bonds between water molecules in the first interfacial layers becomes greater.6 Consequently, one can expect the essential dependence of the structure of the interfacial water on amounts of grafted hydrophobic TMS functionalities. The use of the 1H NMR spectroscopy in combination with freezing out of bulk water and level-to-level freezing out of the interfacial water allows one to determine the thickness of the water layers disturbed differently by the surface and frozen at different temperatures, changes in the Gibbs free energy of these layers, radial dependences of interaction forces between the surface and the aqueous medium, and amounts of strongly and weakly bound waters.13–18

Despite published results of the investigations of the surface chemical properties of modified silicas and the corresponding interfacial water layers,1–18 many questions related to the relationships between the structural characteristics of modified oxides and the properties of bound water remain unclear. Therefore, the aim of this work was to study the relationships between the characteristics of the fumed silica surface partially modified by HMDS at different TMS loadings (C<sub>TMS</sub>) and the properties of the interfacial water layers in different media (air, liquid and frozen water, and weakly polar chloroform) at different temperatures by means of adsorption, desorption, spectroscopic, and theoretical methods.

Materials and Techniques

Materials. Controlled hydrophobization of fumed silica (A-380, Pilot plant at the Institute of Surface Chemistry, Kalush, Ukraine) was carried out by HMDS ("Siliconpolymer", Zaporozye, Ukraine) reacting with silanols

\[ 2\text{Si(OH)} + [(\text{CH}_3)_3\text{Si}]_2\text{NH} \rightarrow 2\text{SiOSi(\text{CH}_3)}_3 + \text{NH}_3 \]

Before reaction, HMDS was purified by distillation, and fumed silica was heated at 723 K for 2 h to remove adsorbed compounds. HMDS chemisorption occurred in a reactor (Figure 1) with IR-spectroscopy monitoring of the synthesis. Before HMDS chemisorption, the silica powder and plate were heated in the reactor in air at 673–693 K for 1.5 h. Then, the sample was degassed for 10–15 min and cooled to ambient temperature. HMDS vapor (dosed in dependence on a desirable level of surface modification) interacted with the silica for 15–18 h (such a long time of adsorption was caused by the necessity to diminish the difference in the HMDS reaction with silica powder and pressed silica samples) at ambient temperature, and then the sample was heated and degassed at T = 723 K for 2 h. The carbon contents (C<sub>C</sub>) in modified samples SM1–SM6 (Table 1) were determined by chemical analysis. The C<sub>C</sub> values were used to estimate the amounts of grafted TMS groups (C<sub>TMS</sub>).

IR Spectroscopy. IR-spectroscopy monitoring was realized at all modification stages (silica drying, HMDS adsorption, reaction, degassing, and water adsorption from air) by means of a Specord M-80 (Karl Zeiss, Jena) spectrophotometer. The concentration of TMS functionalities grafted on the silica surface was also estimated from the intensity of an IR band of CH<sub>3</sub> groups at \(\nu = 3088\) cm<sup>-1</sup> (Figure 2). This band overlaps with a broad \(\nu_{\text{OH}}\) band of adsorbed water and disturbed (residual) \(\text{SiOH}\) groups that leads to diminution of the exactness of definition of the corresponding baseline. Comparison of the IR spectra of modified samples before (in a vacuum) and after (in air) hydration reveals (Figure 2) that the water adsorption results in the reduction of the intensity of the \(\nu_{\text{OH}}\) band. Because both the IR

<table>
<thead>
<tr>
<th>sample</th>
<th>C&lt;sub&gt;C&lt;/sub&gt;, wt %</th>
<th>C&lt;sub&gt;SiO&lt;/sub&gt;, mmol/g</th>
<th>D&lt;sub&gt;CH&lt;/sub&gt; at 2964 cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>S&lt;sub&gt;BET&lt;/sub&gt;, m&lt;sup&gt;2&lt;/sup&gt;/g</th>
<th>S&lt;sub&gt;SR&lt;/sub&gt;, m&lt;sup&gt;2&lt;/sup&gt;/g</th>
<th>S&lt;sub&gt;OS&lt;/sub&gt;, m&lt;sup&gt;2&lt;/sup&gt;/g</th>
<th>V&lt;sub&gt;D&lt;/sub&gt;, cm&lt;sup&gt;3&lt;/sup&gt;/g</th>
<th>V&lt;sub&gt;D&lt;/sub&gt;, cm&lt;sup&gt;3&lt;/sup&gt;/g</th>
<th>V&lt;sub&gt;DS&lt;/sub&gt;, cm&lt;sup&gt;3&lt;/sup&gt;/g</th>
<th>V&lt;sub&gt;DS&lt;/sub&gt;, cm&lt;sup&gt;3&lt;/sup&gt;/g</th>
<th>V&lt;sub&gt;OS&lt;/sub&gt;, cm&lt;sup&gt;3&lt;/sup&gt;/g</th>
<th>D&lt;sub&gt;44&lt;/sub&gt;</th>
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</thead>
<tbody>
<tr>
<td>A-380</td>
<td>0</td>
<td>1</td>
<td>227</td>
<td>494</td>
<td>385</td>
<td>225</td>
<td>0.77</td>
<td>0.97</td>
<td>0.13</td>
<td>2.03</td>
<td>2.58</td>
<td>3.00</td>
</tr>
<tr>
<td>SM1</td>
<td>0.33</td>
<td>0.09</td>
<td>0.18</td>
<td>378</td>
<td>316</td>
<td>34</td>
<td>0.77</td>
<td>0.97</td>
<td>0.13</td>
<td>2.03</td>
<td>2.58</td>
<td>3.00</td>
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<td>0.52</td>
<td>0.14</td>
<td>0.55</td>
<td>362</td>
<td>327</td>
<td>17</td>
<td>0.85</td>
<td>1.39</td>
<td>0.16</td>
<td>2.14</td>
<td>2.58</td>
<td>3.00</td>
</tr>
<tr>
<td>SM3</td>
<td>0.44</td>
<td>0.12</td>
<td>0.46</td>
<td>372</td>
<td>312</td>
<td>20</td>
<td>0.77</td>
<td>0.96</td>
<td>0.12</td>
<td>2.06</td>
<td>2.58</td>
<td>3.00</td>
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<td>SM4</td>
<td>0.83</td>
<td>0.23</td>
<td>0.12</td>
<td>345</td>
<td>299</td>
<td>7</td>
<td>0.72</td>
<td>0.90</td>
<td>0.11</td>
<td>2.14</td>
<td>2.54</td>
<td>3.00</td>
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<tr>
<td>SM5</td>
<td>1.52</td>
<td>0.42</td>
<td>0.241</td>
<td>330</td>
<td>310</td>
<td>1</td>
<td>0.71</td>
<td>0.98</td>
<td>0.09</td>
<td>2.29</td>
<td>2.57</td>
<td>3.00</td>
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<tr>
<td>SM6</td>
<td>2.84</td>
<td>0.79</td>
<td>0.688</td>
<td>285</td>
<td>300</td>
<td>0</td>
<td>0.678</td>
<td>0.794</td>
<td>0.063</td>
<td>2.58</td>
<td>2.490</td>
<td>2.00</td>
</tr>
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</table>
absorption intensity and the baseline slope depend on the concentration of adsorbed water, a special procedure used to define the intensity of a given band for the unmodified sample \( I_0 \) was also applied to determine the optical density of the chosen band for modified samples as follows:

\[
D_{CH} = \log(I/I_0)
\]  

(1)

The \( D_{CH} \) values (Table 1) were determined with consideration for the difference in the sample weights recalculated to 20 mg using experiments for several samples of 13–35 mg.

**Differential Thermogravimetry.** Differential thermogravimetry (DTG) analysis and thermogravimetry (TG) were carried out by means of a Q-1500D (Paulik, Paulik & Erdey, MOM, Budapest) DTG apparatus. Oxide samples (pressed at 180 MPa and milled) were placed (without additional treatment) in a corundum crucible at room temperature and heated to 1280 K in air at a controlled heating rate (10 K/min) (Figure 3). To control the adsorptive ability of modified silicas with respect to water, samples SM1–SM6 (120–250 mg, heated at 453 K for 4 h, initial silica was heated at 673 K for 2.5 h) were hydrated at a relative water vapor pressure \( p/p_0 \approx 0.8 \) for 24, 48, and 72 h before TG measurements (Figure 4).

**Microcalorimetry.** A study of unmodified and modified samples was carried out by means of a DAC 1.1A (EPSE, Chernogolovka, Russia) differential automatic calorimeter. Before measurements of the heat of immersion \( \Delta H_{im} \), samples (25–50 mg) were degassed at 393 K and 0.01 Pa for 2 h. Used amounts of samples were 50 mg/3 mL of distilled water exposed.
for several hours. The average errors of the $\Delta H_{in}$ measurements were ±3%. Similar investigations of different silicas and other materials were described in detail in the literature.\textsuperscript{12,19}

**$^{3}$H NMR Spectroscopy.** For recording the $^{3}$H NMR spectra of water bound to the silica surface in the gas or liquid media, a high-resolution WP-100 SY (Bruker) NMR spectrometer with a bandwidth of 50 kHz was used. Relative mean errors were ±10% for the signal intensity and ±1 K for the temperature.

The amounts of interfacial unfrozen water ($C_{uw}$) in the suspensions of silica samples frozen at 200 < $T$ < 273 K were estimated by comparison of an integral intensity ($I_{uw}$) of a $^{3}$H NMR signal of the frozen water with that ($I_{f}$) of water adsorbed on silica powder from the gas phase using a calibrated function $I_{uw} = f(C_{uw})$, assuming $C_{uw} = 1C_{uw}f(C_{uw})$. The signals of silanols and the water molecules from ice were not detected because of features of the measurement technique and the short time (~10$^{-2}$ s) of the cross-relaxation of protons in solids. Changes in the Gibbs free energy on water adsorption ($\gamma_{S}$ in mJ/m² or J/g) were calculated (with relative mean error ±13%) using the known (tabulated) dependence of changes in the Gibbs free energy of ice [$\Delta G(T)$] on temperature.\textsuperscript{15,16} One can assume that water is frozen (T < 273 K) at the interfaces when $G = G_{b}$; that is, $\Delta G = G - G_{b}$ is equal to $\Delta G_{i} = G_{i}(T) - G_{i}(T=273 K)$, and it corresponds to a decrease in the Gibbs free energy of the interfacial water due to its interactions with the solid surfaces ($G_{i}$ refers to the Gibbs free energy of the bulk undisturbed water). The $^{3}$H NMR technique applied with freezing-out of the bulk water was described in detail elsewhere.\textsuperscript{15,18} Using this approach, one can calculate the amounts of strongly ($C_{uw}^{s}$) and weakly ($C_{uw}^{w}$) bound unfrozen waters (because they are frozen at different temperatures), a maximal decrease in the Gibbs free energy of strongly ($\Delta G^{s}$) and weakly ($\Delta G^{w}$) bound waters, and the Gibbs free energy of water adsorption ($\gamma_{S}$) corresponding to the total changes in the Gibbs free energy of the interfacial water disturbed by the adsorbent at $T = 273 K$ per m$^{2}$ of the oxide surfaces

$$\gamma_{S} = K \int_{0}^{C_{uw}^{max}} \Delta G \, dC_{uw} \quad (2)$$

where K is a constant dependent on the units of $\gamma_{S}$ and $\Delta G$ and $C_{uw}$ is the total amount of unfrozen water at T = 273 K (Table 2, Figure 5). The $\gamma_{S}$ can also be calculated per gram of unfrozen water ($\gamma_{uw}$).

$\Delta G$ in eq 2 is equal numerically to the differential work of adhesion $\Delta G = -W_{uw}$. Besides, $\gamma_{S}$ is equal to the total work of adhesion and defines the integral change in the Gibbs free energy of the system, consisting of the adsorbate and a dispersed medium and a dispersed medium, stipulated by the presence of the phase boundary. The magnitude of the adhesion force can be calculated from the ratio $F = \Delta G/X$, where X is the thickness of a bound water layer. Graphs of the radial dependences of the adhesion forces for initial and modified silicas are shown in Figure 6. The characteristics of the water layers bound to a surface of explored adsorbents are shown in Table 2 for aqueous 5 wt % suspensions.

**Adsortion.** The specific surface area $S_{BET}$ calculated according to the standard BET method\textsuperscript{20,21} and the pore volume $V_{p}$ (estimated at p/p$_{0}$ ≈ 0.98, where p and p$_{0}$ denote the equilibrium and saturation pressures of nitrogen, respectively), converting the adsorbed amount $a_{0.98}$ (in cm$^{3}$ STP of gaseous nitrogen/g of

**Table 2. Characteristics of Interfacial Water Layer in Aqueous Suspensions of Initial and Modified Fumed Silica**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$-\Delta G^{s}$</th>
<th>$-\Delta G^{w}$</th>
<th>$C_{uw}^{s}$</th>
<th>$C_{uw}^{w}$</th>
<th>$V_{uw}$</th>
<th>$\gamma_{S}^{a}$</th>
<th>$\gamma_{uw}^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-380</td>
<td>2.3</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
<td>1.7</td>
<td>32.7</td>
<td>150</td>
</tr>
<tr>
<td>SM1</td>
<td>3.0</td>
<td>0.7</td>
<td>0.1</td>
<td>0.1</td>
<td>0.9</td>
<td>29.2</td>
<td>120</td>
</tr>
<tr>
<td>SM2</td>
<td>3.3</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>1.5</td>
<td>33.9</td>
<td>140</td>
</tr>
<tr>
<td>SM3</td>
<td>2.6</td>
<td>0.6</td>
<td>0.3</td>
<td>0.2</td>
<td>1.2</td>
<td>42.4</td>
<td>135</td>
</tr>
<tr>
<td>SM4</td>
<td>2.5</td>
<td>0.4</td>
<td>0.3</td>
<td>0.2</td>
<td>1.1</td>
<td>39.1</td>
<td>125</td>
</tr>
<tr>
<td>SM5</td>
<td>3.0</td>
<td>0.7</td>
<td>0.3</td>
<td>0.2</td>
<td>1.2</td>
<td>59.6</td>
<td>160</td>
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</tbody>
</table>

$^{a} \gamma_{S}$ denotes the total changes in the Gibbs free energy of unfrozen water at T = 273 K. $^{b} \gamma_{uw}$ is the total change in the Gibbs free energy per unit of surface area of oxide.
and agglomerates), respectively; \( w = 1 \) for slitlike pores and 2 for cylindrical pores; \( r_s(p) \) is determined by the modified Kelvin equation

\[
r_s(p) = \frac{a_m}{2} + t(p, R_p) + \frac{W_{T_m} \cos \theta}{R_y T \ln(p/p_0)}
\]

and \( t(p, R_p) \) can be computed using the modified BET equation

\[
t(p, R_p) = t_m \frac{CZ}{(1 - Z) \exp((-Z(\beta - 1)n + \gamma)/T)}
\]

\( t_m = a_m R_{BET} - b \exp(\Delta \varepsilon/R_y T); \Delta \varepsilon \) is the excess of the evaporation heat as a result of the interference of the layering on the opposite particle surface or wall of pores \( (\Delta \varepsilon \approx 2.2 \text{ kJ/mol});^{25} t(p, R_p) \) is the statistical thickness of the adsorbed layer; \( a_m \) is the BET monolayer capacity; \( c = c_b \exp(Q_s - R_y T); c_b \) is the BET coefficient for adsorption on the flat surface; \( Q_s \) and \( Q_r \) are the adsorption heats on the flat surface and in pores, respectively; \( Z = pR_p; n \) is the number (noninteger) of statistical monolayers of adsorbate molecules, and its maximal value for a given \( R_p \) (or pore half-width \( x \)) is equal to \( (R_p - \alpha x)/t_m \), and \( \alpha \) is the collision diameter of surface atoms.\(^{25}\) Desorption data were utilized to compute the \( f(R_p) \) distributions with eq 3 and a modified regularization procedure\(^{26}\) under the nonnegativity condition [\( f(R_p) = 0 \) at a fixed regularization parameter \( \alpha = 0.01 \) using a model of cylindrical pores at \( R_p > 0.7 \text{ nm} \) and slitlike pores (gaps between adjacent primary particles) at \( 0.2 < R_p < 0.7 \text{ nm} \). This hybrid model of pores gives the PSDs closest to that calculated for a model of gaps between spherical particles.\(^{27}\) The \( f(R_p) \) functions were renormalized in comparison with that calculated according to\(^{23,28,29}\)

\[
f(R_p) = \frac{R_p f(R_p) V_p}{\int R_p f(R_p) \, dR_p}
\]

to produce the PSDs closest to being dependent on the pore volume increment on \( R_p \). Notice that the PSDs calculated using the density functional theory (DFT) and the modified CONTIN procedure with eqs 3–6 (based on the combination of the modified Kelvin equation and the statistical adsorbed film thickness) are closely related over the 0.2–100-nm range for such adsorbents as fumed silica, silica gel, and active carbons.\(^{9,30}\) Additionally, this approach gives the PSDs for silica close to those computed using nonlocal DFT (NL DFT).\(^{31}\) Notice that certain parameters for silica surface potentials of interaction with nitrogen and the corresponding equations were the same in NLDFT and on computation using eqs 3–6.


To compute the nitrogen adsorption energy distributions (AED), one can use the regularization procedure applied to the equation

$$\theta(T, p) = \int_{0}^{\infty} \theta_i(T, p, x) f(x) \, dx \quad (7)$$

with the Fowler–Guggenheim equation as the kernel (local isotherm $\theta_i$) describing the local monolayer adsorption with lateral interaction as follows:

$$\theta_i(p, E) = \frac{K_p \exp(\omega E/kT)}{1 + K_p \exp(\omega E/kT)} \quad (8)$$

In this case, $K_p$ is the Langmuir constant for adsorption on monoenergetic sites, and the preexponential factor $K_p$ is expressed in terms of the partition function $Z$ of the isolated gas and a surface phase. The nitrogen pressure is denoted by $p$, $Z$ is the number of nearest neighbors of an adsorbate molecule, $w$ is the interaction energy between a pair of nearest neighbors, $k$ is the Boltzmann constant, and $\omega = 380 \, K$. A maximal $p/\omega$ value on the $f(E)$ computation corresponds to coverage $\theta = a \alpha_m = 0.99$, where $a$ is the adsorption and $\alpha_m$ is the BET monolayer capacity.

Cumulative pore volume distributions $f_{PV}(V)$ were calculated versus the pore size and the adsorption energy of nitrogen filling the corresponding pores

$$f_{PV}(V) = \int_{V_{min}}^{V} f(Z) \, dZ \quad (9)$$

where $Z$ denotes the pore size or the adsorption energy [$f(E)$ is normalized by $V_p$ as well as $f(R_p)$]. One can assume that a higher adsorption energy corresponds to adsorption in narrower pores. This assumption allows one to define a connection between $f(E)$ and $f(R_p)$ and to calculate the cumulative PSD as a function of $E$.

A similar procedure was also applied to $\Delta G$ calculations of the silica clusters using the GAMESS program packages. The magnitudes of the NMR shielding were used to calculate the corresponding pores.

Quantum Chemical Calculations. Silica clusters with four or eight SiO$_4$ tetrahedrons and four or eight SiOH groups for the unmodified “surface” (Figure 9) were calculated using the GAMESS program package. The magnitudes of the NMR shielding were calculated by the GIAO method with BLYP/6-31G(d,p) and Gaussian 94 program packages.

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between the adsorbate (one or a few molecules) with a solid surface\textsuperscript{18,40} as well as for consideration of the solvation effects\textsuperscript{18,38} which give quite appropriate results for many energetic and structural parameters.

### Results and Discussion

An increase in the concentration of TMS groups (Table 1, C\textsubscript{TMS}, C\textsubscript{v}, and D\textsubscript{CH}, and Figure 2) leads to changes in the interaction with water (Figures 3–6). These changes are clearly seen in the TG and DTG curves at T lower than 473 K (Figure 3). The first maximum observed on the DTG curves (Figure 3) corresponds to the desorption of water at T < 520 K, but the second one at 650–720 K (marked only for SM4–SM6) is linked to the destruction of TMS groups. An increase in C\textsubscript{TMS} for SM5 and SM6 leads to diminution of the first maximum because surface modification reduces the amounts of silanols, which are adsorption centers for water. For SM1–SM4, diminution of the amounts of water adsorbed in air is not observed (Figure 3). However, in the case of water adsorption on additionally heated samples at a fixed water vapor pressure p/p\textsubscript{0} = 0.8 for 24–72 h, amounts of adsorbed water depend stronger (nonlinearly for SM1–SM3) on C\textsubscript{TMS} (Figure 4). These changes can be connected not only with increased hydrophobicity but also with changes in the spatial structure of the silica surface.

An increase in C\textsubscript{TMS} leads to reduction of the specific surface area (S\textsubscript{BET}). The contribution of micropores (S\textsubscript{DS}) depends on C\textsubscript{TMS} stronger than that for mesopores (S\textsubscript{m}) as well as a decrease in V\textsubscript{DS} that exceeds that for V\textsubscript{p} (Figure 7b). Notice that small relative changes in S\textsubscript{m} and V\textsubscript{DS} versus C\textsubscript{TMS} are closely related in contrast to greater alterations of S\textsubscript{BET}, S\textsubscript{DS}, and V\textsubscript{DS} (Figure 7b). These changes are connected to features of the morphology of nonporous primary and “porous” secondary particles of fumed silica.\textsuperscript{41}

The contact zone (narrow gaps) between adjacent primary particles in aggregates [with the bulk density p\textsubscript{ab} close to 30\% of the true density (p\textsubscript{0}) of silica] becomes less accessible for nitrogen molecules (or other adsorbates, e.g., water) after deposition of TMS groups, which are significantly larger than substituted H atoms in ≡SiOH groups. Relative changes in the pore volume V\textsubscript{p} are lower than that for S\textsubscript{BET} (Figure 7b) because V\textsubscript{p} corresponds only to a minor portion of the empty volume (V\textsubscript{em}) of fumed silica powder (because the bulk density of the powder is p\textsubscript{b} = 0.03–0.05 g/cm\textsuperscript{3} and V\textsubscript{em} = 1/p\textsubscript{b} − 1/p\textsubscript{0}), and chemical modification leads not only to a reduction of the accessible surface area but also to a rearrangement of secondary particles (aggregates and agglomerates).\textsuperscript{17} This is also seen in the f(R) graphs (Figure 8). The contribution of “micropores” (i.e., narrow gaps between adjacent primary particles) at R\textsubscript{p} < 1 nm decreases (see also A\textsubscript{DS}/S\textsubscript{DS} and ΔV\textsubscript{DS}/V\textsubscript{DS} versus C\textsubscript{TMS}) but the contribution of narrow “mesopores” at R\textsubscript{p} < 10 nm (as well as larger pores) increases for some samples.

Only a minor portion of the large gaps between primary particles in secondary ones can be entirely filled by nitrogen even at p/p\textsubscript{0} → 1 (Figures 7a, 8, and 11) because V\textsubscript{p} ≪ V\textsubscript{em}. However, the filling of large pores gives a marked contribution to total adsorption because the volume V\textsubscript{BjHa} determined for pores at R\textsubscript{p} over the 0.85–150-nm range

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Figure 11. Cumulative pore volume distributions versus (a) nitrogen adsorption energy and (b) pore size and (c) nitrogen AEDs for the initial silica and SM6.
is significantly larger than $V_p$. This difference is the largest for SM2, as $V_{BjH} - V_p = 0.545 \text{cm}^3/\text{g}$ (Table 1). SM2 is also characterized by maximal alterations in $f(R_p)$, and a shoulder (absent for other samples) is observed at $R_p \approx 55 \text{ nm}$ (Figure 8). Silylation of silica leads to a reduction of the nitrogen adsorption potential because a high-energy AED peak at $11–12 \text{ kJ/mol}$ decreases (Figure 11). The contribution of the first monolayer (providing the second, and siloxane bonds is equal to approximately $3 \text{ kJ/mol}$, the interaction energy of a nitrogen molecule with silanol complexes by using B3LYP/6-31G(d,p), the difference in the binding of water molecules to the initial silica and modified silicas may be greater than that for nitrogen molecule binding to the pristine silica surface. However, the interaction energy between unmodified silica patches (which have been inaccessible, between adjacent primary particles, for HMDS molecules upon surface modification but are accessible for water molecules because of their smaller size and the mentioned rearrangement of secondary particles in the suspension) and water can be great and gives a significant contribution to $\Delta H_{im}$ or $\gamma_S$ for the modified samples (Figure 12 and Table 2). Notice that the shape of the $\Delta H_{im}(C_{TMS})$ graphs differ from that described previously.\(^{88}\) The magnitudes of the Gibbs free energy of the interfacial water $\gamma_S$ (calculated from the data shown in Table 2) per a mass unit of adsorbent and the values of the heat of immersion $\Delta H_{im}$ measured for the same samples by the microcalorimetry method show consistent changes with $C_{TMS}$ for practically all samples except SM6 because of a greater contribution of changes in enthalpy as opposed to entropy on water interaction with these solids. A small $\Delta H_{im}$ value for SM6 is caused by its poor wetting on calorimetric measurements, but in the NMR experiments, it has been suspended using alcohol/water followed by decanting. Notice that the maximal $\gamma_S$ values were typically observed for complex

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**Figure 12.** Comparison of the heat of immersion ofsilicas in liquid water at room temperature and changes in the Gibbs free energy of interfacial water (in J/g of oxide) at $T = 273 \text{ K}$. **Figure 13.** Particle size distributions in a sonicated aqueous suspension of initial fumed silica at a concentration of 3 wt% with respect to the intensity of the scattered light, particle volume, and particle number measured by the photon correlation spectroscopy method.
adsorbents with a low amount (0.5–3 wt %) of the second oxide or pyrocarbon grafted on the oxide matrix.18 Consequently, a maximum of the ΔH_{im} and γ_{S} values for SM1 corresponds to a general regularity observed for the interfacial water at the surfaces of heterogeneous adsorbents, and one can assume that these materials possess a maximal surface nonuniformity at low amounts of grafted (second) material.

To elucidate changes in the properties of the interfacial water versus C_{TMS}, we have calculated the ΔG_s values for the silica cluster with varied amounts of OH and CH_{3} groups (n_{OH} + m_{CH_{3}} = 4 at n_{OH} and m_{CH_{3}} varied from 4 to 0) using different methods (Figure 10). There is a difference in –ΔG_s (Figure 10) and ΔH_{im} or γ_{S} (Table 2 and Figure 12) that may be caused by too great a ratio between the “surface” and the “volume” of the used cluster in comparison with primary particles because their average diameter for A-380 is approximately 7.2 nm, and the first water monolayer (which gives the lion’s share to ΔG_{im}) corresponds to approximately 12 wt.% silica. Consequently, ΔH_{im} (or γ_{S}) can be lower by 1 order of magnitude than –ΔG_s calculated for the small cluster having only “surface” atoms. With consideration for this difference, the –ΔG_s value is in agreement with the ΔH_{im} and γ_{S} values (recalculated to kJ/mol of the interfacial water). Calculations of ΔG_s with [SM5.42R/B3LYP/6-31G(d) and IEF-PCM/B3LYP/6-31G(d,p)] or without [SM5.42R/HF/6-31G(d)] consideration for the electron correlation effects show that ΔG_s is a linear function of the substitution degree (calculated as m_{CH_{3}}/4; Figure 10). Consideration for the electron correlation effects leads to a slightly steeper lowering of –ΔG_s with an increasing concentration of CH_{3} groups. These results are also in agreement with the experimental data.80 Thus, for the same texture of an adsorbent, one can anticipate a linear decrease in the amounts of disturbed adsorbed (bound) water (unfrozen at T < 273 K) with an increasing C_{TMS} value. Deviation from a similar linear dependence (e.g., nonlinear dependence of amounts of adsorbed water on C_{TMS} < 0.2 mmol/g observed in Figure 4) can be caused by the textural nonuniformity of modified silicas, which can be characterized, for example, by the fractal dimension D_{f} (as well as other structural characteristics) dependent nonlinearly on C_{TMS} (Table 1, Figure 7b).

Both the long-range [corresponding to the small slope of F(X) curves at X > 1 nm] and the short-range (greater slope at X < 1 nm) components of the surface forces appear in the aqueous suspensions (5 wt %) of all samples, which is clearly seen from the obtained results (Figures 5, 6, and 14 and Table 2). The average thickness of a strongly bound water layer is 0.8–1.2 nm (corresponding to the short-range forces), and the total thickness of the disturbed water layer can exceed 3 nm (Figures 6 and 14). The amounts of strongly bound water diminish with C_{TMS}, while for weakly bound water, such a correlation is not revealed (Table 2) because of rearrangement of secondary particles and the nonuniformity of partially modified surfaces. The difference in the dependence of F on X (Figure 6) and ΔG on R_{p} (Figure 14) is caused by a difference in the models of interfacial water layers used on the calculations of F(X) and ΔG(R_{p}). F(X) corresponds to the pure radial dependence for the spherical water layers around individual primary particles, but ΔG(R_{p}) corresponds to the structure of gaps and their volume between primary particles packed in aggregates and agglomerates, and the interfacial water fills these gaps by nonspherical layers. A significant portion of the interfacial water unfrozen at T = 273 K (Table 2, C_{uw} = C_{uw}^S + C_{uw}^W, V_{uw}, γ_{S}, and ΔH_{im} are maximal for SM1) fills the “pore” volume in aggregates (which is close to the empty inner volume in the aggregates plus the volume of the adsorbate monolayer on the outer surface of these aggregates); however, V_{p} is smaller than the volume of unfrozen water V_{uw} (but V_{Bj} is close to V_{uw}). This difference is caused by a stronger interaction of the silica surface with polar water than nonpolar nitrogen molecules. Consequently, a portion of the disturbed water partially fills the gaps in the agglomerates because the total empty volume in the agglomerates is greater than 10 cm^{3}/g because of low bulk density of 0.06–0.07 g/cm^{3}, which is close to that of fumed silica powder (0.03–0.05 g/cm^{3}) than to that of aggregates (ρ_{p} = 0.6–0.7 g/cm^{3}). Hence, the unfrozen interfacial water (with different thicknesses) is nonuniformly distributed in narrow mesopores in aggregates due to confinement of their size and at the outer surfaces of these aggregates, where the opposite “pore walls” are too distant.

Despite diminution of the concentration of silanols (main surface centers for water adsorption) for modified silicas by several times (e.g., if a maximal concentration of SiOH groups on a fumed silica surface is approximately 2.5 μmol/m^{2},1,3,41 i.e., 9.4 mmol/g, for SM6, the residual amount of SiOH groups is approximately 16% of their initial content, and the IR band ν_{OH} at 3750 cm^{-1} is not yet observed; Figure 2c), changes in the Gibbs free energy of the interfacial water layer in the aqueous medium are less 20%. This result is in agreement with previous data obtained for aqueous suspensions of modified fumed silicas.17,18 A great nonuniformity of partially modified surfaces causes disorder of several monolayers of interfacial water (Figures 6 and 14) and enhances the rotational mobility of water molecules that leads to reduction of the freezing temperature (T_{f}) of bound water.

![Figure 14. Relationships between changes in the Gibbs free energy of interfacial water layers and the (a) pore volume and (b) pore radius.](image-url)
Notice that an increase in the electrical conductivity for an alternating current (increase in bound charges, e.g., dipoles of molecules) and its decrease for a constant current (mobile charges, e.g., protons and other ions) were observed for the suspensions of a blend of hydrophilic and hydrophobic (silylated) fumed silicas. Consequently, changes in polarization of interfacial water (enhancement of bound charges) can affect its free energy because of the influence of the electrostatic field of the surface on the rotational mobility of the water molecules (i.e., bound charges—dipoles of molecules) and the hydrogen bond network as a whole.

In the case of contact of a hydrated silica surface with air (water vapor), the structure of adsorbed water is determined not only by the adsorbent surface (i.e., phase boundary of silica/water) but also by the phase boundary of water/air. The appearance of these phase boundaries leads to a reduction of the free energy of the interfacial water accompanied by a lowering of its freezing temperature. The information on a structure of the adsorption complexes at a surface of oxide adsorbents can be obtained from temperature dependences of the chemical shift of protons ($\Delta H$) of interfacial water molecules. It is necessary to take into consideration that $\Delta H$ is defined by the strength of the hydrogen bonds between the water molecule and the active surface sites and depends on the amounts of hydrogen bonds per water molecule.

The chemical shift of protons in water molecules that are not participating in hydrogen binding is 1.5–1.7 ppm. If water molecules form icelike polyassociates in which the volume of each molecule forms four hydrogen bonds (two of them are formed by hydrogen atoms and the two remaining are formed with the participation of the lone electron pair of the oxygen atom), $\Delta H = 7$ ppm. Besides, it is necessary to take into consideration that the binding of $H_2O \cdots \cdot H-OSi\equiv$ influences the $\Delta H$ of the water molecule weaker than that for $H\cdots OX$. The formation of the later hydrogen bonds enhance the $\Delta H$ value by 2.7 ppm.

The $\Delta H$ NMR spectra of the hydrated powders of SM4–SM6 (in chloroform) are shown at different temperatures (Figure 15). For SM1–SM3 (which are not shown in Figure 15), the $\Delta H(T)$ graphs are akin to that for SM4. Because chloroform is a poor proton donor, its molecules are not capable of competing with water molecules upon interaction with residual silanols on modified samples to form the complexes $SiO(H)\cdots H\cdots X$. Therefore, one can assume that, chloroform weakly affects the structure of the water clusters adsorbed on the hydrophilic surfaces. On the other hand, chloroform hampers the proton exchanging between the water molecules interacting with different active surface sites and allows us to specify the $\Delta H$ values in adsorbed water.

For samples SM1–SM4, adsorbed water gives the signal with a minimal width at $T = 240$ K. The signal intensity decreases at low temperatures because of layer-by-layer freezing out of the interfacial water. An increase of the signal width with lowering temperature is caused by reduction of the molecular motility of adsorbed water.
A linear portion of the $\delta_H(T)$ plots can be found for all the samples at any $C_{H_2O}$. Prolongation of these lines to lower temperatures gives their crossing at 115 K at a point corresponding to $\delta_H = 7$ ppm characteristic for molecules possessing four hydrogen bonds, that is, in the icelike structure. It is possible that this temperature corresponds to an ordered structure of adsorbed water akin to that of free ice, which, however, is not observed in our experiments because of features of the used measurement technique.

A small $\delta_H$ value at T close to 320 K testifies to changes in the structure of water clusters adsorbed on the surface of modified silica in comparison with that observed at lower temperatures in consequence of the diminution of the average number of hydrogen bonds per molecule with elevating temperature and because of the enlargement of the hydrogen bonds with T, which results in the reduction of $\delta_H$. A similar picture was observed earlier for the initial silica. So, small $\delta_H$ values for water molecules taking part in the hydrogen bonds with the surface hydroxyls can be also explained by their participation in complexes $\equiv SiO-H \cdots H-H \cdots OH$ as an electron donor; that is, a marked portion of protons of adsorbed water molecules (forming small clusters with only several molecules) do not participate in the hydrogen bonds. Additionally, water interaction with siloxane bonds ($\equiv SiO \cdots H \cdots OH \cdots H \cdots OH$ results in lower $\delta_H$ values than that for $\equiv SiOH \cdots H \cdots OH$ (Figure 9).

Therefore, small water clusters located under “umbrellas” of TMS groups near siloxane bonds can be characterized by relatively small $\delta_H$ values.

Calculations of two types of the adsorbed water clusters around a TMS group (Figure 9c) and “under” this group (Figure 9d) give lower potential energy for the second structure ($\Delta E_{total} = -61$ kJ/mol), which indicates a greater probability of the formation of similar complexes. Localization of a water droplet near a siloxane bond results in the diminution of $\delta_H$ (Figure 9d). Notice that the $\delta_H$ value for H from silandons participating in the hydrogen bonds $\equiv SiO-H \cdots OH$ is greater (> 7 ppm) than that for water molecules $HO-H \cdots OH$ (4–5 ppm). Similar $\delta_H$ values of about 7 ppm were also observed in the NMR spectra of silica. Thus, the “downtake” of the water droplets to the siloxane bonds under “umbrellas” of TMS groups (part d akin to part c of Figure 9) may lead to the diminution of the $\delta_H$ values in comparison with that for the initial silica because of a decrease in the number of water molecules in these clusters in confined spaces between and under TMS groups, diminution of the polarization influence of modified surface on the electronic structure of adsorbed molecules, and low ability of the siloxane bonds to form the hydrogen bonds.

Thus, the $\delta_H$ diminution is observed in the experimental $^1H$ NMR spectra of modified silicas in comparison with that for the initial silica. A similar effect of the $\delta_H$ diminution is observed in the experimental $^1H$ NMR spectra of modified silicas (Figures 15 and 17). It should be noted that the $\delta_H$ dependence on a charge value of H atoms ($q_H$) is nonlinear (Figure 18) because $\delta_H$ depends also on the surroundings of the H atom(s), and $\delta_H(q_H)$ for the water molecules ($\delta_H$ only for H in the hydrogen bonds) differs significantly from that for the $\equiv SiOH$ groups (free and bonded to water molecules; Figure 18). One can assume that water adsorbed in large pores of hydrophobic materials or in large gaps between primary particles in secondary ones tend to form larger droplets in larger pores to reduce the surface area of contacts between water and hydrophobic surfaces. Therefore, partially or totally hydrophobic and porous materials with large pores possess a greater ice-forming ability in comparison with microporous hy-
drophobic materials. This circumstance can be important for adsorption processes occurring (in the atmosphere) on industrial nanoscaled aerosol particles with the participation of water.

Conclusions

Fumed silicas partially modified by HMDS and containing different amounts of TMS groups (from 0.09 to 0.79 mmol/g) are characterized by the nonlinear dependences of changes in the structural, adsorptive, and other parameters such as the specific surface area, the pore volume (total and micro- and mesoporous), the PSDs, the concentrations of weakly and strongly bound water, the Gibbs free energy of these waters, the heat of immersion in liquid water, and the chemical shift $\delta_H(T)$ of water adsorbed from air. Upon water adsorption on modified silicas from air, the size of the water droplets (located between aggregates of primary particles in agglomerates) increases with amounts of grafted TMS groups, and for SM 6 maximum hydrophilic, the main $^1H$ NMR signal of adsorbed water becomes close to that for fluid water.

Figure 17. Temperature dependences of $\delta_H$ for (a) SM 1, (b) SM 2, (c) SM 3, (d) SM 4, and (e) SM 5 at different amounts of adsorbed water and (f) different modified samples.

Partial Hydrophobization of Fumed Silica

Enhancement of the intensity of the IR band $\nu_{OH}$ at 3660 cm$^{-1}$ (corresponding to silanols difficult of access for water and other adsorbates) occurs with increasing $C_{TMS}$. The formation of small water clusters between grafted TMS groups causes the appearance of the $^1H$ NMR signal with the low chemical shift of $^1H$ (in adsorbed water molecules) because of the formation of the ($\equiv Si\equiv O\cdots H\cdots OH$ complexes (characterized by smaller $\delta_H$ in comparison with that for HO\cdots H\cdots OH or $\equiv SiO(H)\cdots H\cdots OH$) and as a result of a smaller number of hydrogen bonds per water molecule in the small water clusters in comparison with that in larger water droplets on maximum hydrophobic silica.

**Acknowledgment.** This research was supported by STCU (Grant 1946). R.L. is grateful to the Foundation for Polish Science for financial support. V.M.G. is grateful to Dr. T. L. Petrenko for the use of the Gaussian 94 program package.

LA0301238
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