

APPLICATION OF NMR SPECTROSCOPY TO DETERMINE THE THERMODYNAMIC CHARACTERISTICS OF WATER BOUND TO OX-50 NANOSILICA

V. V. Turov,^{a*} V. M. Gun'ko,^a V. E. Gaishun,^b
Ya. A. Kosenok,^b and A. P. Golovan^a

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We have used low-temperature ^1H NMR spectroscopy to determine the thermodynamic characteristics of water bound to OX-50 nanosilica ($S_{\text{BET}} \approx 50 \text{ m}^2/\text{g}$) in different media: aqueous, air, chloroform medium, and gaseous methane. We demonstrate the difference between the hydration parameters of silica OX-50 on going from an aqueous suspension to a hydrated powder. We present the water cluster size distributions in the studied systems, calculated from the Gibbs–Thomson equation. We found that the average water cluster size in suspension is considerably larger than the cluster sizes in hydrated powders.

Key words: highly dispersed silica, ^1H NMR spectroscopy, water clusters, unfrozen water, interfacial energy.

Introduction. Highly dispersed silicas, synthesized by means of high-temperature hydrolysis of silicon tetrachloride in the flame of a hydrogen/oxygen torch, are widely used in many areas of technology as polymer fillers, thixotropic additives, adsorbents effectively binding organic materials of medium and high molecular weight, etc. [1–3]. Highly dispersed silicas have a rather complex structural hierarchy: protoparticles (<1 nm), primary particles (5–100 nm), aggregates of primary particles (<1 μm , secondary particles), agglomerates of aggregates (1–50 μm , tertiary particles), and visible particles. Secondary particles of highly dispersed silica, with high specific surface area, are often rather stable in aqueous medium and cannot be broken down (or reformed) to individual primary particles even with high-intensity sonication [4]. Aggregation of primary particles of highly dispersed silica is responsible for the presence of textured porosity: voids between the primary particles in the aggregates and agglomerates [4–7]. Highly dispersed silica is a hydrophilic material, capable of binding a large amount of water in a liquid medium. The amount of bound water depends on the characteristic features of the interparticle interactions, i.e., on the nature of the textured porosity, the surface charge density on the nanoparticles, the composition of the dispersion medium, and the temperature. If there are significant electrostatic repulsion forces between the particles (at a pH far from the zero charge point), then even concentrated suspensions may not go to the gel-like state and may have a viscosity close to the viscosity of water. However, formation of a three-dimensional network of interparticle bonds (a continuous cluster) at low surface charge density leads to rapid gel formation in the system, in which a significant part of the water is found in the bound state [4, 8]. On the other hand, powders of nanosilicas, not in contact with liquid water, absorb a relatively small amount of water from the air. Under normal conditions (293 K and relative air humidity 70%), the moisture content of silicas is no greater than 2–5%, i.e., interaction of highly dispersed silicas with water is determined not only by the presence of a significant concentration of primary adsorption centers (OH groups) but also by the relative positions of the primary silica particles, their surface roughness, and also the medium in which they are found. Since bound water determines many physicochemical and processing properties of nanosilicas, it is of significant interest to compare the structural and thermodynamic characteristics of water bound to nanosilica found in different media: in air and in an aqueous medium in the presence of liquid and gaseous co-adsorbates, capable of competing with water when they are adsorbed together.

*To whom correspondence should be addressed.

^aA. A. Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, 17 ul. Generala Naumova, Kiev 03164; e-mail: v_turov@ukr.net; ^bF. Skorin Gomel State University, Belarus. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 77, No. 4, pp. 633–640, July–August, 2010. Original article submitted February 5, 2010.

With the aim of minimizing the effect of textured porosity on the properties of bound water, for the investigations we chose pyrogenic silica OX-50 with minimal specific surface area and weak aggregation of the primary particles. The measurements were made by low-temperature ^1H NMR spectroscopy, which allows us to rather exactly calculate the temperature dependence of the bound water concentration and to determine the structural and thermodynamic characteristics of the different types of water [4, 9, 10]. In a study by this method of suspensions and gels of pyrogenic silicas, it was shown in [4] that as the concentration of silica A-380 (C_{SiO_2}) increases from 4.8 to 15.0 wt.%, the interfacial energy (γ_s), defined as the absolute value of the total decrease in free energy of the bound water, has the shape of a curve with minimum $\gamma_s = 142 \text{ mJ/m}^2$ for $C_{\text{SiO}_2} = 6.5\%$ and a maximum $\gamma_s = 258 \text{ mJ/m}^2$ for $C_{\text{SiO}_2} = 15\%$, which is due to concentration-dependent restructuring of the silica aggregates during preparation of the suspensions.

Experimental Section. Materials. We used OX-50 (Degussa, specific surface area determined by the Brunauer–Emmett–Teller method, $S_{\text{BET}} \approx 50 \text{ m}^2/\text{g}$, average diameter of the primary particles $\approx 40 \text{ nm}$), which can form stable aqueous suspensions, the dispersed phase of which consists predominantly of individual primary particles [11]. According to [12], the concentration of hydroxyl groups on the surface of OX-50 is $6 \pm 0.5 \text{ OH/nm}^2$. We used twice-distilled water, chloroform for the NMR measurements, and technical-grade methane.

^1H NMR spectroscopy. The ^1H NMR spectra were recorded on a Varian Mercury 400 high-resolution NMR spectrometer with operating frequency 400 MHz. The temperature was controlled to within $\pm 1 \text{ K}$ using a Bruker VT-1000 temperature controller. The signal intensities were determined within $\pm 10\%$. In order to avoid supercooling the bound water, the ^1H NMR spectra were recorded with heating of samples that had been previously cooled down to a temperature of 200 K. The measurements were made for a suspension with $C_{\text{SiO}_2} = 18 \text{ wt.}\%$ and hydrated powders obtained by drying this suspension at 200°C and then wetting with the required amount of water. As the liquid low-polarity medium, we used deuterated chloroform, and as the gaseous medium we used methane. In order to measure the hydration parameters in methane medium, a silica sample weighing 0.15 g and containing 10% adsorbed water was held in methane medium at room temperature (20°C) for 1 h, and then placed in the probe of the spectrometer, maintaining a connection between the measurement ampul and a methane reservoir at a pressure of 1.1 kg/cm^2 .

The method for determining the characteristics of the interfacial layers of water using ^1H NMR spectroscopy has been discussed in detail earlier in [4, 9, 10]. It is based on the effect of the interface on the temperature of the water–ice phase transition. Owing to the adsorption interactions, the freezing point of bound water is lowered. The free energy of ice varies according to a linear law as the temperature is lowered [13]:

$$\Delta G_i = -0.036 (273 - T), \quad (1)$$

which can be used to estimate the change in free energy of the bound water (ΔG_{UW}), assuming that when it freezes, $\Delta G_{\text{UW}} = \Delta G_i$.

The area under the $\Delta G(\Delta G_{\text{UW}})$ curve determines the magnitude of the interfacial energy (γ_s), which is equal to the absolute value of the total decrease in free energy of water due to the presence of the phase interface:

$$\gamma_s = -K \int_0^{C_{\text{UW}}^{\text{max}}} \Delta G(C_{\text{UW}}) dC_{\text{UW}}, \quad (2)$$

where $C_{\text{UW}}^{\text{max}}$ is the total amount of unfrozen water at $T = 273 \text{ K}$.

On the $\Delta G(C_{\text{UW}})$ curves, usually we observe sections which can be assigned to weakly bound water (freezes at 260–273 K) and strongly bound water (freezes at $T < 260 \text{ K}$). The free energy of the weakly bound water is decreased only a little as a result of interactions with the surface of the adsorbent, in contrast to the strongly bound water, characterized by significantly higher values of $|\Delta G|$ [4]. The quantitative (C_{UW}^{s} and C_{UW}^{w} for strongly bound and weakly bound water) and the energy (ΔC^{s} and ΔC^{w}) characteristics of the layers of bound water can be obtained by extrapolation of the corresponding sections of the $\Delta G(C_{\text{UW}})$ curves to the x and y axes.

The lowering of the freezing point of water in the pores can be described by the Gibbs–Thomson equation [14]:

$$\Delta T_m = T_m(R) - T_{m,\infty} = \frac{2\sigma_{\text{SL}} T_{m,\infty}}{\Delta H_f \rho R} = \frac{k}{R}, \quad (3)$$

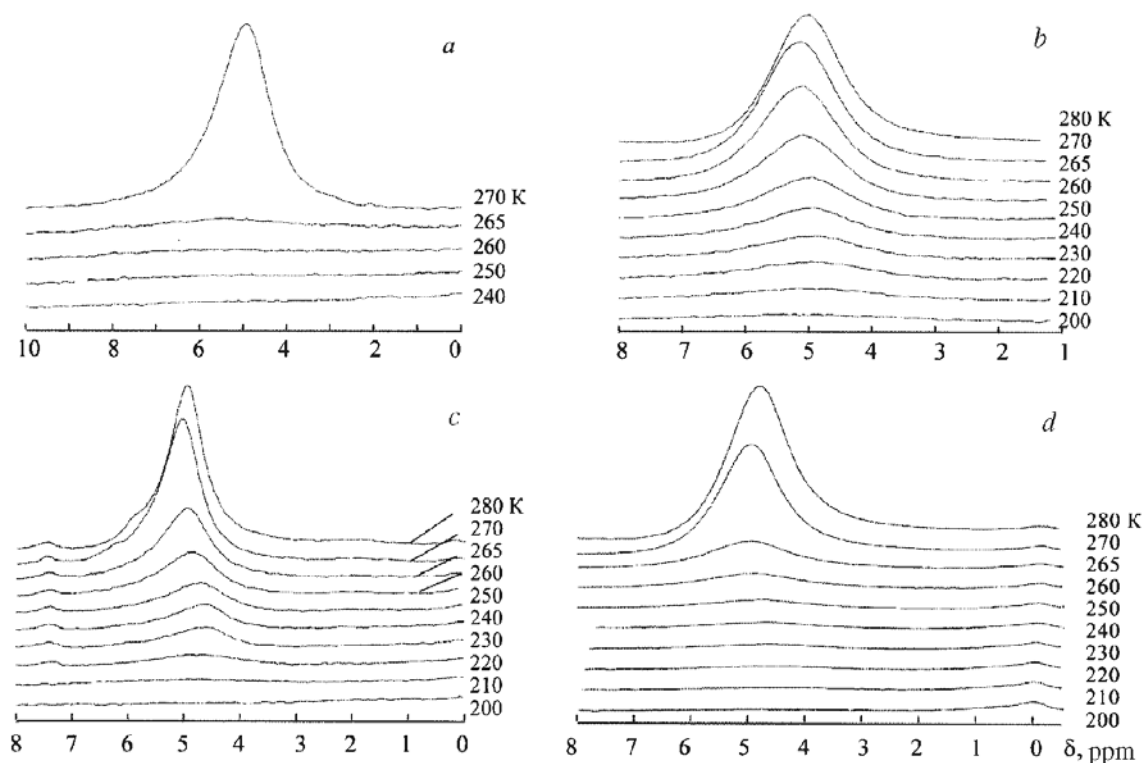


Fig. 1. ^1H NMR spectra of water bound by silica OX-50: a) in 18% aqueous suspension, b, c) in powder containing 2% H_2O , in air (b) and in liquid CDCl_3 medium (c); d) in powder containing 10% H_2O , in a methane atmosphere.

where $T_m(R)$ is the melting point of ice localized in the pores (voids) of radius R ; $T_{m,\infty}$ is the melting point of bulk ice; ρ is the density of the solid phase; σ_{SL} is the energy of interaction between the solid and the liquid (for example, by means of hydrogen bonds); ΔH_f is the bulk enthalpy of melting; k is a constant. This equation is used to calculate the size distributions of pores filled with unfrozen bound water, based on the $C_{\text{UW}}(T)$ curves [4].

Results and Discussion. Figure 1 shows the ^1H NMR spectra of water adsorbed on silica OX-50, recorded at a temperature of 200–280 K. For all the studied samples, the adsorbed water appears as a single signal with proton chemical shift $\delta_{\text{H}} = 4.5\text{--}5.0$ ppm. According to the classification explained earlier [4], it is strongly associated, i.e., its structural properties are close to those for bulk water, which is characterized by approximately the same values of δ_{H} at $T > 273$ K. For an aqueous suspension (Fig. 1a) (the spectra of water have a similar shape for a gel containing 33% SiO_2), the amount of unfrozen water sharply decreases as the temperature is lowered, so that a signal is no longer detected at $T < 240$ K. Consequently a significant portion of the unfrozen water is weakly bound [4]. On the other hand, for hydrated powders, in the spectra a signal is detected from unfrozen water even in the case when the temperature is lowered down to 200 K, i.e., the greater part of the adsorbed water is strongly bound. From the temperature dependences of the water signal, we plot the curves in Gibbs free energy (ΔG) vs. unfrozen water concentration (C_{UW}) coordinates, and also the distributions of clusters of bound water with respect to their radii (Fig. 2). From Eq. (2), we calculated the interfacial energy. The thermodynamic characteristics of the layers of bound water are given in Table 1.

Methane adsorbed on OX-50 hydrated powder appears in the spectra (Fig. 1d) as a single signal with chemical shift $\delta_{\text{H}} \approx 0$ ppm. The intensity of this signal increases as the temperature decreases as a result of admission of additional portions of methane from the reservoir. Despite the high hydrophilicity of silica OX-50 and the absence of micropores, adsorption of methane proved to be quite significant. Adsorption (which was calculated from the intensity ratio of the methane and water signals) increases from 0.43% at 280 K to 1.6% at 200 K. Adsorption of methane led

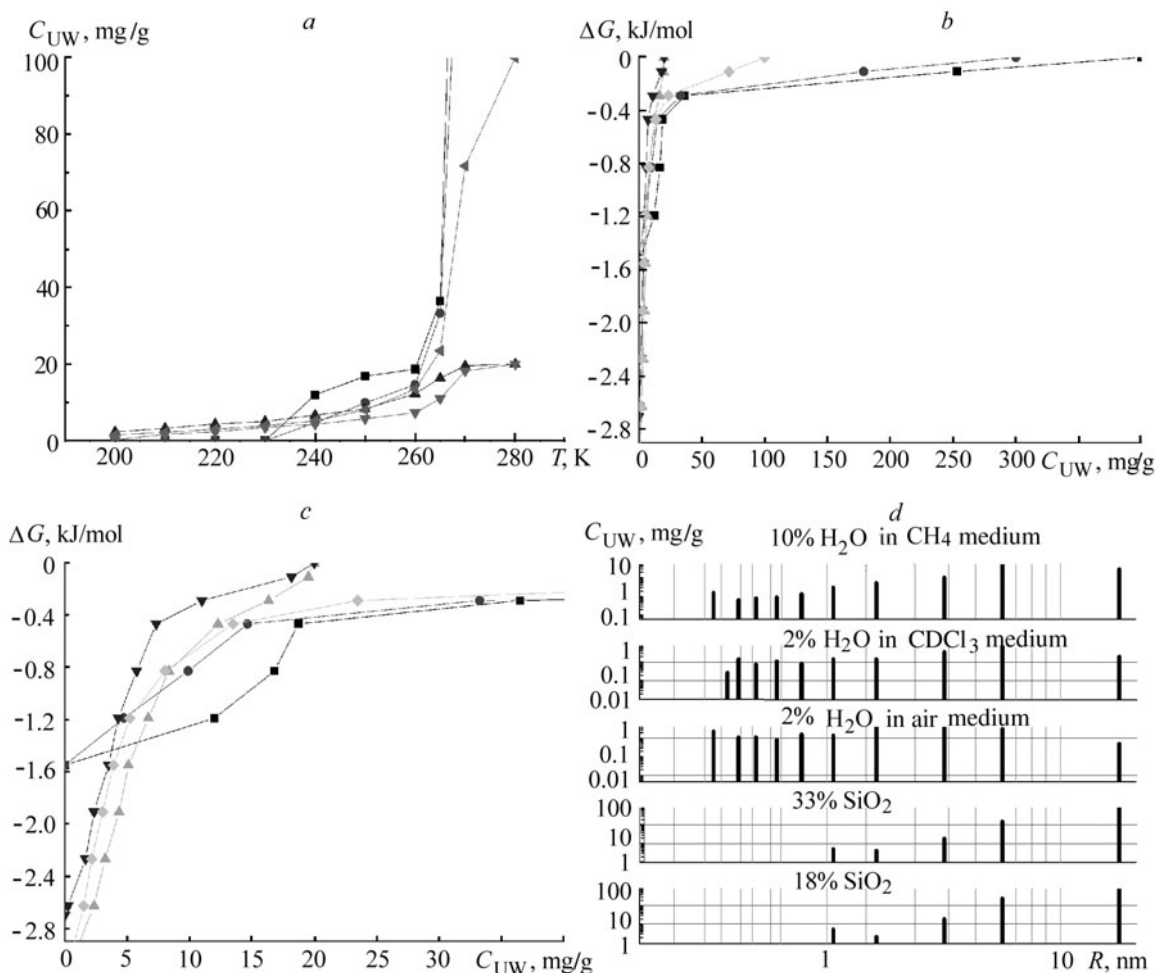


Fig. 2. Concentration of unfrozen water vs. temperature (a), the $\Delta G(C_{UW})$ curves plotted based on the latter dependences (b,c), and the water cluster size distributions in aqueous suspensions and hydrated powders of OX-50 silica (d); (a-c) 18% SiO₂ (■), 33% SiO₂ (●), 2% H₂O (▲), 2% H₂O in CDCl₃ (▼), 10% H₂O in CH₄ medium (◆).

TABLE 1. Thermodynamic Characteristics of Layers of Water Adsorbed on Silica OX-50 in Different Media

Sample	C_{UW}^s , mg/g	C_{UW}^w , mg/g	ΔG^s , kJ/mol	ΔG^w , kJ/mol	γ_s , J/g
18% SiO ₂ (suspension)	17	387	-1.6	-0.6	4.4
33% SiO ₂ (gel)	17	287	-1.6	-0.6	3.2
2% H ₂ O	10.5	9.5	-3.2	-1.2	1.2
2% H ₂ O in CDCl ₃ medium	8	12	-2.7	-0.7	0.8
10% H ₂ O + CH ₄	9	91	-3.2	-0.4	1.8

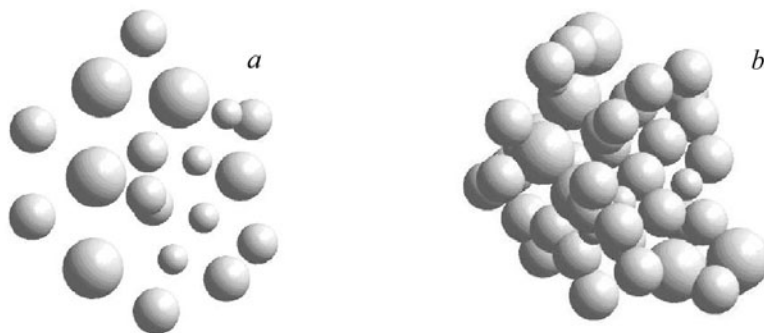


Fig. 3. Schematic drawing of the arrangement of OX-50 silica particles in a concentrated suspension (a) and hydrated powder (b).

to some decrease in the concentration of strongly bound water (Table 1). In Fig. 2c, this effect is apparent as a shift of the $\Delta G(C_{\text{UW}})$ curve to the left. An analogous phenomenon is observed for the sample in a liquid deuteriochloroform medium (Fig. 2c). In this case, the decrease in the value of C_{UW}^{S} proved to be more significant (Table 1).

As follows from Fig. 2c and the data in Table 1, for an aqueous suspension (or gel) of silica, the value of ΔG^{S} is substantially lower than for the hydrated powders. This value reflects the maximum lowering of the free energy of water due to adsorption interactions [4]. The difference between the indicated systems is that in the concentrated gel (stable for several months), the silica particles are mainly in contact during their impacts caused by Brownian motion, while in the powders, there is some packing of nanoparticles differing in the size and number of contact areas with adjacent particles (Fig. 3), which is responsible for the textured porosity.

In a stable suspension of silica OX-50 (Fig. 3a), structured water is bound to the primary particles (OH groups on their surfaces), which form a rather open-work structure with practically no direct contacts between them. We may assume that all the bound water is concentrated in the electrical double layer of the nanoparticles. In the hydrated powders (Fig. 3b), direct contacts between primary particles are preserved (all the way to formation of an insignificant number of siloxane bonds between them) and cluster adsorbed water is localized at the contact points between nanoparticles, since in these regions, the adsorption potential is higher while the geometry of the voids enables formation of clusters and nanodomains of water, which may be considered strongly associated. If the concentration of silanol groups on the silica surface is $10 \mu\text{mol}/\text{m}^2$ (0.5 millimoles/gram) [1], and at least one water molecule interacts on the average with each hydroxyl group (for a uniform distribution of adsorbed water over the surface), then a simple calculation shows that that the hydration of the surface should be 9 mg/g. Of course, water is not distributed over the surface as single molecules even at very low concentrations, but rather is adsorbed as cyclic or 3D clusters, since isolated OH groups of highly dispersed silica appear in IR spectra for an adsorbed water content ≤ 20 wt.%. However, even cluster adsorbed water will be unfrozen all the way down to very low temperatures, since ice formation occurs only from ordered water structures (nuclei of crystallization), the size of which is measured in the single digits or even tens of nanometers [15]. In the studied systems, the onset of the water freezing process is detected at relatively high temperatures (Fig. 2a). Consequently, adsorbed water is found as both clusters and domains, the sizes of which vary over a rather broad range.

Figure 2b shows the size distributions of water clusters in aqueous suspensions and hydrated silica OX-50 powders, calculated from the Gibbs–Thomson equation. As we see, the average size of the water clusters in suspension (or gel) is considerably larger than the sizes of clusters in the hydrated powders. The minimum cluster size in suspension is 1.6 nm, and 0.6 nm in the powders. In a silica suspension (or gel), conditions are provided for which all the silanol groups participate in formation of H bonds with water molecules. Therefore the lack of substantial amounts of unfrozen water at low temperature is evidence for participation of water molecules that are bound to silanol groups in ice formation. Probably during freezing of a suspension, some of the H-bonds between silanol groups and water molecules are preserved, despite the loss of translational mobility by the latter. This can be explained by formation of a layer of amorphous ice near the silica surface. In this case, the unfrozen water, detected as strongly bound (Fig. 2c, Table 1), belongs to the portion of the interfacial water which is localized in voids between particles of both silica and

ice, and the sizes of these voids correspond to the data in Fig. 2d. When the water–silica system goes from a suspension to a gel-like state, the average distance between silica particles decreases, which is apparent in the decrease in the concentration of weakly bound water (Table 1, C_{UW}^w). The difference between the interfacial energies of the suspension and the gel (1.2 J/g, Table 1) determines the difference between the magnitudes of interparticle interactions in the indicated systems. In contrast to gels of pyrogenic silicas with high specific surface area [4], the value of γ_s for an OX-50 suspension proved to be relatively small, which is due to the small value of SBET for OX-50 and therefore the small contribution of unfrozen water, filling the interparticle space in aggregates and agglomerates in the powders or found in the electrical double layer of nanoparticles in suspension.

In hydrated powders of silica OX-50, depending on the dispersion medium, the concentration of strongly bound water is 8.0–10.5 mg/g (Table 1). However, practically all this water freezes when the samples are cooled down to 200 K, and is found in the form of clusters and domains (Fig. 2d), located in the voids between adjacent nanoparticles (Fig. 3b). Considering the relatively low concentration of strongly bound water, we should conclude that the majority of the surface hydroxyl groups remain free, not participating in formation of H-bonds with molecules of cluster adsorbed water. These results agree with data from IR spectral studies in [16], according to which hydrated powders of highly dispersed silica (even for high degree of hydration) contain a significant number of silanol groups not perturbed by interactions with water molecules.

The cluster and domain character of adsorption of water also allows us to explain the effect of the dispersion medium of nonpolar or low-polarity solvents and gases on the interaction between water and the silica surface. Domains of weakly associated water are located in textured mesopores of silica, with a relatively small number of them (compared with the number of H-bonds in the domains) between the domains and the silica surface. In this case, between adjacent water clusters or domains, there may be free sections of surface on which nonpolar molecular may be adsorbed. By adsorbing on these sections, organic molecules may push water away from the surface of the adsorbent, since the energy of H-bonds in bulk water and water bound to the surface of highly dispersed silica is much higher than the interaction energy between nonpolar molecules and water. This also leads to a relative decrease in the concentration of strongly bound water. For chloroform molecules (having higher molar refraction than methane), this effect is more pronounced and accordingly, clusters of adsorbed water in chloroform medium become less strongly bound to the silica surface. The effect described has also been observed in other microporous and mesoporous silica and carbon adsorbents [17–19]. It is probably general for processes involving co-adsorption of water and nonpolar/low-polarity organic substances.

Conclusion. We have shown by low-temperature ^1H NMR spectroscopy that hydration of silica OX-50 nanoparticles and the process of freezing of interfacial water occur differently in stable suspensions (or gels) and hydrated powders, due to structural reorganization of secondary silica particles in suspensions. In the latter, all the silanol groups of highly dispersed silicas can participate in formation of hydrogen bonds with water molecules, and the water phase acts as a single supramolecular system, upon freezing of which at the silica–ice interfaces, the water molecules remain practically unbound to silanol groups and retain their translational mobility. In this case, water with a lowered freezing point is localized in relatively wide gaps between silica particles (weak aggregation of OX-50 particles). In hydrated powders, water is present as clusters and domains of size 0.6–16 nm. The clusters are concentrated in areas of interparticle contacts, having high adsorption potential, while the domains may be found in textured mesopores. Freezing of water in such clusters and domains occurs at different temperatures in the range 200–270 K range. Non-polar and low-polarity co-adsorbates (methane, chloroform) reduce the binding between water and the silica surface, i.e., water is pushed away from the surface and water cluster formation is reduced.

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