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Clusterization of water at a surface of nanosilica A-380*

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Thermodynamic and structural characteristics of water (0.07–1 g per 1 g of silica) bound to nanosilica A-380 ($S_{BET} = 378 \text{ m}^2/\text{g}$, primary particle diameter 7.2 nm) alone or on co-adsorption with chloroform alone or in the mixture with DMSO or acetonitrile were determined using ¹H NMR spectroscopy with layer-by-layer freezing-out of water at 200–273 K and NMR-cryoporometry.

1. INTRODUCTION

One of important trends in surface science deals with features of chemical and physical processes in nano-confined space [1,2]. In such space adsorbed substances can lose homogeneity due to clusterization and strong dependence of the properties on clusters localization and solid surface characteristics. Structural heterogeneity of adsorbates can be especially great for strongly associated liquids such as water. The thickness of a boundary water layer disturbed by surface forces can reach ten or more molecular layers [3,4]. Water in nanoconfined space especially with mosaic hydrophilic/hydrophobic walls has the hydrogen bond network largely different from that of bulk water. Clusters of hexagonal ice with four hydrogen bonds per a molecule can be considered as a structural model of liquid water [5,6]. However, thermal motions of molecules can destroy a portion of the hydrogen bonds, and certain water molecules can be

^{*}This article is dedicated to Professor Roman Leboda on the occasion of his 65^{th} birthday

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in structural voids without the hydrogen bonds with neighboring molecules (interstitial water). This results in greater density of liquid water than that of ice and in decrease of the average number of the hydrogenous bonds per a molecule, despite their coordination number [7,8]. Clustered structure of water confined in narrow pores undergoes strong changes because of inconsistence in the positions of adsorption sites (e.g. surface hydroxyls) and hydroxyls of water molecules in the network characteristic of ice Ih [8]. This results in additional structural and energetic heterogeneity of bound water. Co-adsorbates such as polar and nonpolar organics are additional disturbing factors [9].

Nanosilicas are widely used in industry and medicine as adsorbents, fillers, carriers, etc. [10]. Nonporous primary silica nanoparticles tend to be aggregated more strongly with their decreasing size; i.e. with the increasing specific surface area [9,11]. Aggregates of nanoparticles are characterized by textural porosity. Voids between the adjacent primary particles are the main adsorption places for water molecules. However, the adsorption of water onto nanosilicas from air is relatively low (1-7 wt%) and depends on features of aggregation of nanopartcles. An increase in water amounts wetting nanosilica can lead to significant changes in the structure and characteristics of wetted powder materials or aqueous suspensions [9]. Additionally, the characteristics of water bound to nanosilica can be changed on co-adsorption with organic solvents, lowmolecular organics, polymers, etc. [9]. These effects depend on many factors; therefore, sometimes it is difficult to interpret the observed results. The aim of this work was to study the influence of hydration level and co-adsorption of different organic solvents on the characteristics of water bound to nanosilica A-380 characterized by significant aggregation of primary particles. The measurements were carried out using low-temperature ¹H NMR spectroscopy with layer-by-layer freezing-out of bound water and NMR-cryoporometry to characterize structure of bound water affected by co-adsorbates [9,11-15].

2. MATERIALS AND METHODS

Nanosilica A-380 (pilot plant of the Institute of Surface Chemistry, Kalush, Ukraine, specific surface area $S_{\text{BET}} = 378 \text{ m}^2/\text{g}$) was heated at 673 K for several hours before performing the measurements to remove organic adsorbates and residual HCl. Polar and weakly nonpolar deuterated (D) solvents CD₃CN, (CD₃)₂SO, CDCl₃ (Aldrich, qualification "for NMR spectroscopy" at content of main isotope of 99.5%) soluble or practically insoluble in water were used in the deuterium form to avoid their contribution to the ¹H NMR signal intensity of unfrozen interfacial water at *T* < 273 K. Bidistilled water was used here.

The samples (Table 1) at various hydration h = 0.07-1 gram of water per gram of dry silica and co-adsorbed solvents CDCl₃ (0.5–9 g/g), CD₃CN (1 g/g),

DMSO (0.5–1 g/g) were studied using the NMR method. Total amounts of water and organic solvents were much smaller than the empty volume (V_{em}) in the dry silica powder because the bulk density $\rho_b \approx 0.05$ g/cm³ provides $V_{em} \approx 20$ cm³/g [9]. Therefore, a liquid phase was absent in all studied samples representing wetted powders. Before the measurements the samples were equilibrated at room temperature for 20-60 min.

Low-temperature (77.4 K) nitrogen adsorption-desorption isotherm for A-380 was recorded using a Micromeritics ASAP 2405N adsorption analyzer.

Atomic Force Microscopic (AFM) image of A-380 was obtained using a NanoScope III (Digital Instruments, USA) apparatus with the tapping mode AFM measurement technique.

The ¹H NMR spectra were recorded at 200–280 K using a Varian 400 Mercury spectrometer of high resolution (magnetic field 9.7 T) with 90° probe pulses with a duration of 2 μ s. Relative mean errors were ±10% for ¹H NMR signal intensity and ±1 K for temperature. To prevent supercooling of the studied systems, the measurements of the amounts of unfrozen water were carried out on heating of the samples preliminarily cooled to 200 K and equilibrated for 5–7 min for each temperature. The ¹H NMR spectra recorded here include the signals only of nonfreezable mobile water molecules. The signals of water molecules from ice, as well as protons from hydroxyls of silica surface, do not contribute to the ¹H NMR spectra because of features of the measurement technique and the short duration of transverse relaxation of protons in immobile structures over the used temperature range. Water or other liquids can be frozen in narrower pores at lower temperatures that can be described by the Gibbs-Thomson relation for the freezing point depression [8].

Interfacial water can be divided into four types such as (i) strongly bound water (SBW) with changes in the Gibbs free energy ($\Delta G < -(0.5-0.8)$ kJ/mol, frozen at T < 260-250 K); (ii) weakly bound water (WBW) with $\Delta G > -(0.5-0.8)$ kJ/mol; (iii) strongly associated water (SAW) with the chemical shift of the proton resonance $\delta_{\rm H} = 3-5$ ppm; (iv) weakly associated water (WAW) at $\delta_{\rm H} = 1-2$ ppm [9]. The boundary ΔG value corresponds to a kind of the relationship between ΔG and the amounts of unfrozen water $C_{\rm uw}$ determined from the $\Delta G(T)$ and $C_{\rm uw}(T)$ dependences. The mentioned relationship can be used to estimate the ΔG and $C_{\rm uw}$ values for SBW and WBW and for the first water layer [9]. The module of total changes in the ΔG value for all bound water can be considered as the interfacial energy $\gamma_{\rm S}$ [9]. Applications of the NMR technique for different materials were described in detail previously [9,11-15].

3. RESULTS AND DISCUSSION

Dry powder of A-380 can be characterized by certain structural hierarchy of particles starting with primary particles (5–15 nm in size, average diameter 7.2 nm), aggregates of primary particles (Figure 1, 50–200 nm) and agglomerates of aggregates [9]. Adsorbed water at low amounts (< 20 wt%) localizes mainly in the zone of contacts between adjacent nanoparticles [9]. At higher amounts, adsorbed water can form continuous layers covering whole nanoparticles [9,13]. Consequently, for two samples at h = 0.5 and 1 g/g continuous water layers should be formed but for other samples with h = 0.07, 0.08 and 0.15 g/g island adsorption of water could be to form only partial coverage of the surface.



Fig 1. SEM image of aggregates of primary particles of A-380.

Despite this structural difference, water bound to nanosilica gives a single ¹H NMR signal at $\delta_{\rm H} = 4-5$ ppm (Figure 2a), i.e. it is SAW, whose intensity decreases with the lowering temperature at *T* < 250 K due to partial freezing of water. The $\delta_{\rm H}$ value decreases with the increasing temperature because of the influence of thermal motion of water molecules on the hydrogen bond network structure. There are fractions of SBW and WBW but WAS is absent. The addition of organic solvents to A-380/water (Figure 2) slightly affects the shape and the position of the water signal. A weak signal of the CHD₂ groups of admixtures in CD₃CN and DMSO is observed at $\delta_{\rm H} = 2-2.5$ ppm. Co-adsorbed DMSO (in a mixture with CDCl₃) more strongly affects freezing-out of water since even at 210 K an intensive signal of unfrozen water is observed (Figure 2d).

To study features of the influence of organic solvents on the characteristics of bound water localized in voids between the adjacent silica nanoparticles in their aggregates (Figure 1) on the basis of the temperature dependences of changes in the integral intensities of the signals of unfrozen water, the relationships between changes in the Gibbs free energy on water adsorption and the amounts of unfrozen bound water were determined (Figure 3). At relatively high level of hydration (Figures 3a and 3b) the influence of organic solvents is weaker than that at low hydration (Figures 3c-3e). For the former, there are near vertical (related to SBW) and horizontal (WBW) sections in the $\Delta G(C_{uw})$ graphs.



Fig. 2. ¹H NMR spectra of water bound to nanosilica (a) alone at h = 0.08 g/g and with the addition of (b) CDCl₃ (3 g/g) at h = 0.15 g/g; (c) CD₃CN (1 g/g)+CDCl₃ (1 g/g), h = 0.07 g/g and (d) DMSO (0.5 g/g) +CDCl₃ (1 g/g), h = 0.15 g/g recorded at different temperatures.



Fig. 3. Relationships between the content of unfrozen water and the changes in the Gibbs free energy of unfrozen water in differently hydrated powders of nanosilica A-380 at h = (a) 1, (b) 0.5, (c) 0.15, (d) 0.08 and (c) 0.07 and different amounts of organic solvents.

h	Organics	$C_{\rm SBW}$	$C_{\rm WBW}$	$-\Delta G^{S}$	γ_{s}	S (m^2/g)	S_{mic}	S_{mes} (m^2/g)	S_{mac}	$V_{\rm mic}$	V_{mes}	V_{mac}
1	-	250	750	2.52	30.2	116	14	102	0.4	0.007	0.976	0.007
-	1.0	150	850	2.87	23.0	150	35	115	0.5	0.016	0.966	0.008
	CDCl ₃							-				
	2.0	170	830	2.37	27.0	130	0	130	0.1	0	0.996	0.002
	CDCl ₃											
	6.0	30	970	2.57	21.6	121	6	115	0.3	0.003	0.985	0.005
	CDCl ₃											
0.5	-	125	375	2.84	16.5	87	43	43	0.5	0.020	0.451	0.007
	2.0 CDCl ₃	100	400	2.59	15.8	56	23	32	0.8	0.011	0.449	0.014
	8.0 CDCla	75	425	3.16	15.2	53	19	34	0.7	0.009	0.458	0.011
0.15	-	100	50	2.78	11.1	78	67	11	0.1	0.029	0.117	0.001
0.10	3 CDCl ₃	100	50	2.43	9.3	40	28	12	0.1	0.013	0.134	0.001
	6 CDCl ₃	100	50	2.70	8.8	10	0	10	0.1	0	0.145	0.002
	5											
	0.5	100	50	3.37	14.7	181	177	4	0.4	0.073	0.055	0.006
	DMSO											
	0.5	145	5	3.35	21.4	227	221	6	0	0.094	0.056	0
	DMSO+											
	1.5											
0.00	CDCl ₃	(0)	20	2.40					0.2	0.020	0.040	0.000
0.08	-	60	20	3.48	7.8	75	71	4	0.2	0.029	0.043	0.002
	2.0 CDCI	22	25	2.47	4.6	5	1	4	0.1	0	0.074	0.002
	CDCI ₃	70	10	2.02	12.2	170	177	1	0	0.065	0.012	0
	1.0 DMSO	70	10	5.92	12.5	1/8	1//	1	0	0.065	0.013	0
	1.0	70	10	3 76	10.7	116	114	2	0	0.046	0.020	0
	DMSO+	70	10	5.70	10.7	110	114	2	0	0.040	0.029	0
	2.0											
	CDCl ₃											
0.07	1.0	35	35	2.42	3.3	17	0	17	0	0	0.059	0
	CD ₃ CN											
	+1.0											
	CDCl ₃											
	1.0	35	35	2.32	3.1	15	0	15	0	0	0.054	0
	CD ₃ CN											
	+0.5											
	CDCl ₃											
	1.0	30	40	2.14	2.9	15	0	15	0	0	0.056	0
	CD_3CN											
	+2.0 CDC1											

Tab. 1. Characteristics of bound water in hydrated powders of nanosilica A-380 with the presence of organic solvents.

Note. S, S_{mic} , S_{mes} and S_{mac} are the surface area total, micro- (radius R < 1 nm), meso- (1 < R < 25 nm) and macropores (R > 25 nm), respectively, of silica in contact with the unfrozen water; V_{mic} , V_{mes} , and V_{mac} are the pore volume of micro-, meso-, and macropores, respectively.

The maximal amount of SBW is 250 mg/g which corresponds to approximately third volume of pores (voids between the adjacent primary particles in aggregates) filled by nitrogen at 77.4 K. The addition of chloroform alone or in a

mixture with DMSO leads to stronger changes in the characteristics of bound water at lower hydration (Table 1, Figure 3). The effects of chloroform in a mixture with acetonitrile are smaller than those of CDCl₃+DMSO. These effects could be explained by the difference in the solubility of water in these organics individual and in mixtures. Co-adsorbed chloroform decreases the interfacial energy (γ_s) of bound water at different hydration (Table 1). The interfacial energy normalized to h = 1 g/g as $\gamma_s^* = \gamma_s/h$ increases with the decreasing *h* value (Figure 4) because of a decrease in the amounts of WBW. There is tendency of a decrease in the γ_s^* value with the increasing content of chloroform (Figure 4a).



Fig. 4. Normalized interfacial energy (a) as a function of the content of chloroform at different hydration of silica; (b) on the addition of $CDCl_3$, CD_3CN , DMSO and their mixtures at a fixed hydration h= 0.15 g/g.

This can be explained by the displacement of a portion of water from narrow voids to broader ones, and this effect is stronger at lower hydration (Figure 5) when bound water does not form continuous adsorption layers and co-adsorbed organics can easily contact the silica surface. Such electron-donor solvents as CD_3CN and DMSO are well dissolved in water and chloroform. However, chloroform-DMSO (CD_3CN) mixtures can stratify on the addition of a small quantity of water to form layers enriched by chloroform and an electron-donor. To avoid this effect such quantities of mixtures were added to the silica powder to prevent the formation of a liquid phase. CD_3CN and DMSO differently affect the interaction of water with the silica surface (Table 1, Figures 3–5) since



CD₃CN enhances but DMSO diminishes the interfacial energy value of bound water.

Fig. 5. Size distribution of unfrozen water structures for hydrated A-380 powder at h = (a)1, (b) 0.5, (c) 0.15, (d) 0.08 and (c) 0.07 and different amounts of organic solvents.

Radius (nm)

0.006

0.004 0.002 0.000

(e)

+1g/g CD₃CN

+2g/g CDCl₃

2

10

On the co-adsorption of water and studied organics, there are several factors affecting changes in the structure (clusterization) of bound water. If only weakly polar chloroform is co-adsorbed with water that the phase boundary tends to be minimal. Therefore, if pre-adsorbed water forms a continuous coverage of the silica surface that the effects of chloroform are minimal. These effects increase if the island coverage with pre-adsorbed water is realized (Figure 3). Chloroform in a mixture with polar organics can be mixed with bound water (Figure 6) because DMSO effectively interacting with both polar water and nonpolar chloroform can separate water and chloroform clusters. In other words there is no tendency to decrease the contact area between water and chloroform at the silica surface because they contact only with DMSO and the silica surface. This is well seen from the structural characteristics of bound water (Table 1) since maximal specific surface area (total and of micropores) of unfrozen water structures is observed for the DMSO+CDCl₃ (or DMSO alone). However, even for these cases these values are much smaller than the S_{BET} value of silica A-380 (378 m²/g). Notice that $S < S_{\text{BET}}$ on the adsorption of water alone at h = 1 g/g. This can be explained by structural nonuniformity of bound water (i.e. its clusterization, formation of nanodomains and absence of uniform continuous water layers covering silica nanoparticles) and the absence of contacts between the total surface area of silica particles and the water.



Fig. 6. Displacement of water molecules by chloroform and DMSO from the silica surface (force field optimized geometry).

4. CONCLUSIONS

Water bound to nanosilica does not form uniform layers even at relatively high hydration (1 g of water per 1 g of dry silica). Co-adsorption of water with

weakly polar chloroform alone or in a mixture with polar DMSO or acetonitrile more strongly affects the structure of water bound to nanosilica A-380 at lower hydration when significant portion of silica surface remains uncovered by water. Maximal clusterization of bound water is observed on the co-adsorption with chloroform/DMSO mixture because DMSO can effectively interact with both nonpolar (through dispersion interactions of chloroform with CH₃ groups) and polar (water interaction with S=O) structures.

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