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Water Clusterization in the Interparticle Space of Hydrophobic Nanosilica AM-1

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The processes occurring in hydrated powders and concentrated suspensions of hydrophobic silica were studied by ^{1}H NMR spectroscopy. It is shown that a mixture of methyl silica and water having a hydration of less than 1 g/g is a wet powder, where water is in the form of submicron clusters filling the interparticle voids of nanosilica, and the interfacial energy is directly proportional to the amount of added water. It was found that at high water concentrations there is a spontaneous increase in the size of water structures, which is accompanied by a sharp decrease in interfacial energy, that may reflect the disappearance of narrow interparticle voids or their filling with air. It is shown that aqueous suspensions of AM-1 are easily mixed with a weakly polar organic solvent chloroform, forming a stable suspension with close the amounts both of water and chloroform. It was revealed that the aqueous suspension of methyl silica has high thixotropic properties, which depend on the time and the magnitude of the applied mechanical loads.

Keywords: ^{1}H NMR spectroscopy, hydrophobic silica, thixotropy, mechanical loads.

Introduction

Substances for which the contact angle of a spherical water drop on its surface is equal to or greater than 90º are considered to be hydrophobic ones. It should be take into account that the effect of the gaseous phase (air or saturated vapors of a liquid) is of great importance, which can create gas interlayers or submicron gas bubbles localized at the liquid/solid interface. This process is facilitated by the high (compared to the volume) free energy of the water layer that adjacent to the hydrophobic surface [1-6]. The striving for the minimum value of the enthalpy of a strongly associated aqueous medium can be partially compensated by the appearance of voids on the surface, which are easily filled with air diffusing over the surface or dissolved in the aqueous medium. [7-9]. In the case when a hydrophobic substance is an assemblage of particles with a high specific surface area, interactions at the interface between solid, liquid and gaseous phases can affect the interaction of solid particles with each other, which is reflected in the state of the colloidal system, its viscosity and thixotropic properties [10, 11].

The effect of a hydrophobic surface on the thermodynamic parameters of the water adjacent to it can be studied by investigating a composite system consisting of a highly dispersed hydrophobic substance in which the interparticle voids are filled with water. It was shown the possibility of transferring powderlike hydrophobic substances of different chemical nature into an aqueous medium by grinding them with water in a porcelain or agate mortar [12-15]. In this case, under the influence of a mechanical load, air is removed from the interparticle voids and replaced with water. If the process of mechanical activation is carried out for a long time, then practically all the air is removed from the interparticle voids, and the hydrophobic powder is completely wetted with water provided that the amount of water is greater or equal to than the powder mass. A convenient method for measuring the characteristics of the boundary water layers in concentrated aqueous suspensions or hydrated powders is the method of low-temperature ^{1}H NMR spectroscopy. [16-20]. Using this method, by measuring the depression of the water freezing point, obtained on the basis of the temperature

dependences of the signal intensity of non-freezing water at $T < 273\ K$, changes in the Gibbs free energy (ΔG) of water in the adsorption layer, the concentration of strongly and weakly bound water (C_{uw}^S C_{uw}^W, respectively) and the value of the interfacial energy (γ^S), equal to the total decrease in the water free energy due to interphase interactions. Additional information can be obtained based on the chemical shift of water, which depends primarily on the ordering degree of the hydrogen bond network.

Thus, the aim of this work was to study the processes occurring in hydrated powders and concentrated suspensions of methyl silica with an increase in the water amount of added into the colloidal system by mechanical loads.

I. Materials and methods

1.1. Materials.

For measurements methylsilica AM-1 was used, obtained by modifying highly dispersed nanosilica A-300 by chemical grafting to the surface of dimethylchlorosilane (Kalush, Ukraine). The silica was moistened by adding water to the sample AM-1 (0.5 g). The mixture was stirring until the formation of a homogeneous powder containing no liquid water phase. The homogenization time increased with increasing water content and ranged from 3 min for $h = 0.33$ g/g to 15 min for $h = 1$ g/g. The samples containing $h = 2$ and 3 g/g of water were prepared based on the sample having $h = 1$ g/g of water. At the same time, concentrated suspensions of AM1 in water were formed.

1.2. ^{1}H NMR spectroscopy.

^{1}H NMR spectra were recorded using a Varian 400 Mercury spectrometer of high resolution with an operating frequency of 400 MHz. Eight probing 60° impulses of 1 μs duration were used with a bandwidth of 20 kHz. The temperature was controlled by means of a Bruker VT-1000 device with an accuracy of ± 1 deg. The signal intensities were determined by measuring the area of the peaks using the procedure for decomposing the signal into its components under the assumption of a Gaussian form of signal and optimizing of the zero line and phase with an accuracy that was not less than 5 % for well-resolved signals and ± 10 % for overlapping signals. To prevent supercooling of the studied systems, the measurements of the amounts of unfrozen water were carried out on heating of samples preliminarily cooled to 210 K. The temperature dependences of the NMR signals intensity were carried out in an automated cycle, when the holding time of the sample at a constant temperature was 9 min, and the measurement time was 1 min. The measurement of the chemical shift of adsorbed water was fulfilled with respect to the adsorbed methane signal, which was used as a gaseous medium.

Since the concentration of water in the samples is known, from the intensities of the water signal (I), the concentration values of unfrozen water (C_{uw}) can be calculated at any temperature: $C_{uw} = I_T/I_{T>273} \cdot h$ (mg/g). The process of freezing (melting) of interfacial water localized in a solid porous matrix proceeds in accordance

with changes in the Gibbs free energy caused by the influence of the surface. It is the less, the further from the surface the studied layer of water is. At $T = 273\ K$ water freezes, the properties of which do not differ from ones of bulk water, and as the temperature decreasing (without taking into account the effect of supercooling), the water layers, that are located closer to the surface, freeze. Thus, for interface water the ratio is valid:

$$\Delta G_{ice} = -0{,}036(273{,}15 - T), \tag{1}$$

where the numerical coefficient is a parameter, associated with the temperature coefficient of variation of the Gibbs free energy for ice [21]. Then in accordance with the technique detailed in [15-19], the amount of strongly and weakly bound water (SBW and WBW, respectively) and the thermodynamic characteristics of these layers can be calculated.

If in a colloidal system the total water content significantly exceeds the total pore volume (interparticle gaps or voids), then part of the water can be in a free state when water molecules do not "feel" the disturbing effect from the surface of the particles. It is difficult to accurately determine the amount of "bulk" water, therefore we will consider that part of the water corresponding to the ratio $h > 1500$ mg/g is the bulk water.

The interfacial energy of solids or biopolymers was determined as a modulus of the total decrease in the free energy of absorbed water, due to the presence of an internal water-polymer interface by the formula:

$$\gamma_S = -K \int_0^{C_{uw}^{max}} \Delta G(C_{uw}) dC_{uw}, \tag{2}$$

where $C_{uw}^{max} = 1500$ mg/g.

The magnitude of interfacial energy is a convenient parameter that allows comparing the binding water energy in different systems, especially for the same the amount of water in them.

Herewith, to determine the geometrical dimensions of nanoscale aggregates of liquid limited by solid surface, the Gibbs – Thomson relation [22,23] can be used, connecting radius of spherical or cylindrical pores (R) with the value for the freezing point depression:

$$\Delta T_m = T_m(R) - T_{m,\infty} = \frac{2\sigma_{sl}T_{m,\infty}}{\Delta H_f \rho R}, \tag{3}$$

where $T_m(R)$ is the melting temperature of ice in cylindrical pores of radius R, $T_{m,\infty}$ the bulk melting temperature, ΔH_f the bulk enthalpy of fusion, ρ the density of the solid, σ_{sl} the energy of solid−liquid interaction.

II. Results and discussion

Hydrophobic nanosilica is a finely dispersed powder, the particles of which are aggregated into micron-sized

T.V. Krupskaya, V.M. Gun'ko, L.S. Andriyko, N.V. Yelahina, V.V. Turov
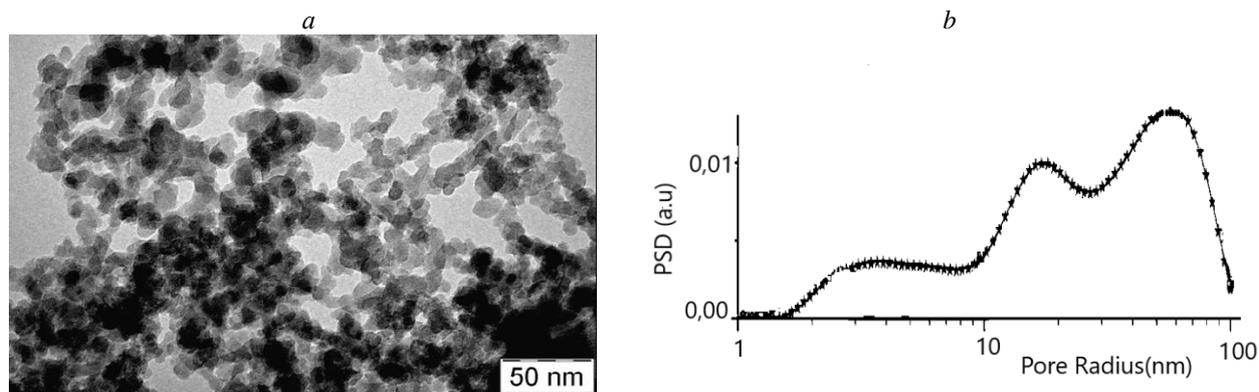
Fig. 1. TEM images (*a*) and pore size distribution (b) for initial (without hydro-compacting) methylsilica AM-1.
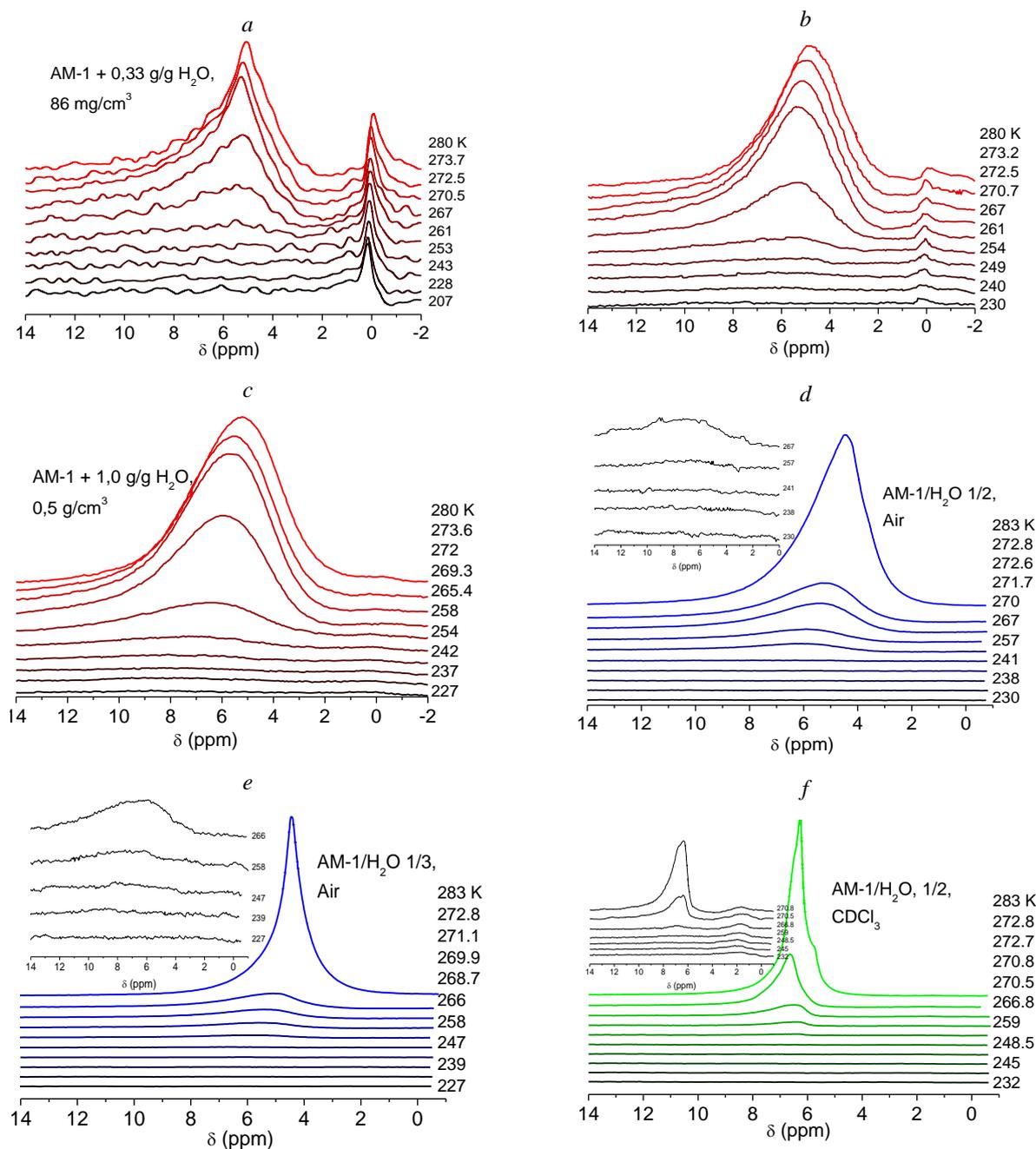
Fig. 2. ^{1}H NMR spectra of water located in interpartical voids of methylsilica AM-1 taken at different temperatures.

agglomerates. Its nanostructure is manifested in TEM

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images (Fig. 1*a*). Primary particles with a radius of 10 - 20 nm serve as the basis. Due to strong interparticle interactions, they form aggregates, the voids between which form a secondary porous structure. Low-temperature nitrogen adsorption data allow us to obtain the size distribution (radius) of secondary pores (interparticle voids) of hydrophobic nanosilica (Fig. 1*b*). Air, organic substances can be adsorbed in these voids, and, under the influence of mechanochemical activation, aqueous polyassociates, which are in the form of nanoscaled clusters or completely fill the interparticle spaces. Three maxima are observed on the pore size distribution curves corresponding to pores of R = 3.5, 10.5, and 60 nm. The pores with R = 60 nm have the largest volume.

Fig. 2 shows taken at different temperatures the ^{1}H NMR spectra of water located in the interparticle voids of AM-1 methylsilica at different surface hydration. To more accurately determine the value of the chemical shift of interfacial water, measurements were carried out in a medium of gaseous methane. This was observed in the spectra at δ_H = 0 ppm. The chemical shift of water bound in interparticle voids of AM1 is 5 - 6 ppm, that indicates the formation of ordered clusters, in which each water molecule takes part in the formation of, on average, three hydrogen bonds with its neighbors [15-18]. With decreasing temperature, the chemical shift of water increases, due to associated with an increase in the ordering of the hydrogen bond network.

For a sample containing 2 g/g of water, measurements were also carried out in a deuterochloroform medium (Fig. 2*f*). The purpose of this experiment was to find out to what extent a weakly polar organic solvent can penetrate into an aqueous suspension of AM-1 and affect the binding parameters of water. At the same time, in addition to the main signal of strongly associated water (SAW) with a chemical shift of δ_H = 6.5 ppm in the spectra of water, a weak signal of weakly associated water (WAW) was recorded with a chemical shift of δ_H = 1.5 ppm, the intensity of which weakly changes with temperature. As shown in [15-18], this type of interfacial water is due to the appearance of a chloroform layer near the dispersed particles surface with an increased dissolving power in relation to water. Such water is weakly associated and practically does not form hydrogen bonds with other molecules.

A decrease in temperature causes partial freezing of interfacial water, and practically all water freezes at temperatures T > 240 K. The chemical shift of such water does not exceed δ_H = 7 ppm. The temperature dependences of the chemical shift of water in samples differing in water content are shown in Fig. 3. For samples with different h values, the form of dependences is somewhat different. The smallest changes in the chemical shift are observed for a sample of hydrated silica containing h = 0.33 g/g water. Other dependences show areas with a high (δ_H > 7 ppm) value of the chemical shift. There is very little amount of water responsible for water with such high values of chemical shift and it is observed only at high sensitivity of the NMR spectrometer at low temperatures. In accordance with the results of the chemical shift investigation the of

hexagonal ice [24] for tetracorodinated water, the value of the chemical shift is δ_H = 7 ppm. Therefore, an insignificant part of the interfacial water in frozen AM1/water composites can be attributed to water that is part of small clusters containing solvated protons [25]. Probably, such clusters are localized near the residual hydroxyl groups, which turned out to be inaccessible to dimethyldichlorosilane in the chemical modification process.
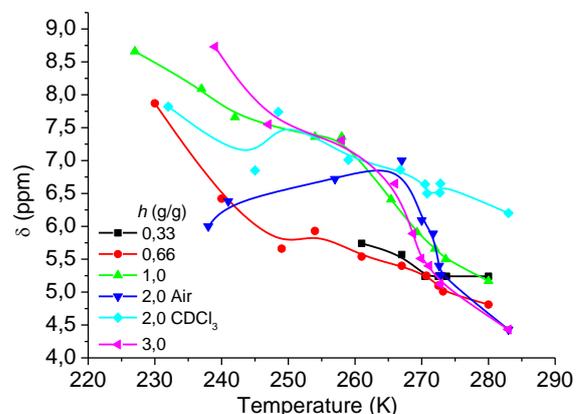
Fig. 3. Temperature dependences of the chemical shift of adsorbed water for hydrated hydrophobic silicas AM-1, differing in the water concentration in the interparticle voids.

Fig. 4 shows the temperature dependences of the unfrozen water concentration (*a*), built on their basis of the dependence of the change in the Gibbs free energy *vs* unfrozen water concentration (*b*) the dependence of the change in the interfacial energy *vs* the adsorbed water amount (*c*) and the size distribution of adsorbed water clusters over the radii for hydrated powders and concentrated aqueous suspensions of methyl silica AM-1, and in Table 1 – characteristics of interfacial water layers. In the case when the hydration of the samples is $h \leq 1$ g/g, the system is a hydrated powder of AM-1, but at high water concentrations it is an aqueous suspension.

As follows from the obtained results, the characteristics of bound water layers for hydrated powders ($h \leq 1$ g/g) differ greatly from the characteristics of aqueous suspensions. For hydrated AM-1 powders, with an increase in water content, the concentration of strongly and weakly bound water, interfacial energy, and the maximum decrease in Gibbs free energy in the layer of strongly bound water (ΔG^S) increase. The bulk density of hydrated methyl silica powder also increases (Table 1) and the proportion of water included in the composition of clusters with a radius R > 20 nm (Fig. 4*d*). These processes can be explained by the transformation of water from a volumetric to a thermodynamically unstable cluster state under the influence of mechanical load. The expenditures of mechanical energy are spent on crushing the initially continuous aqueous medium into a set of submicron drops localized in the interparticle space of methylsilica and surrounded by a hydrophobic shell consisting of solid particles that prevent them from being combined into more extended water structures.

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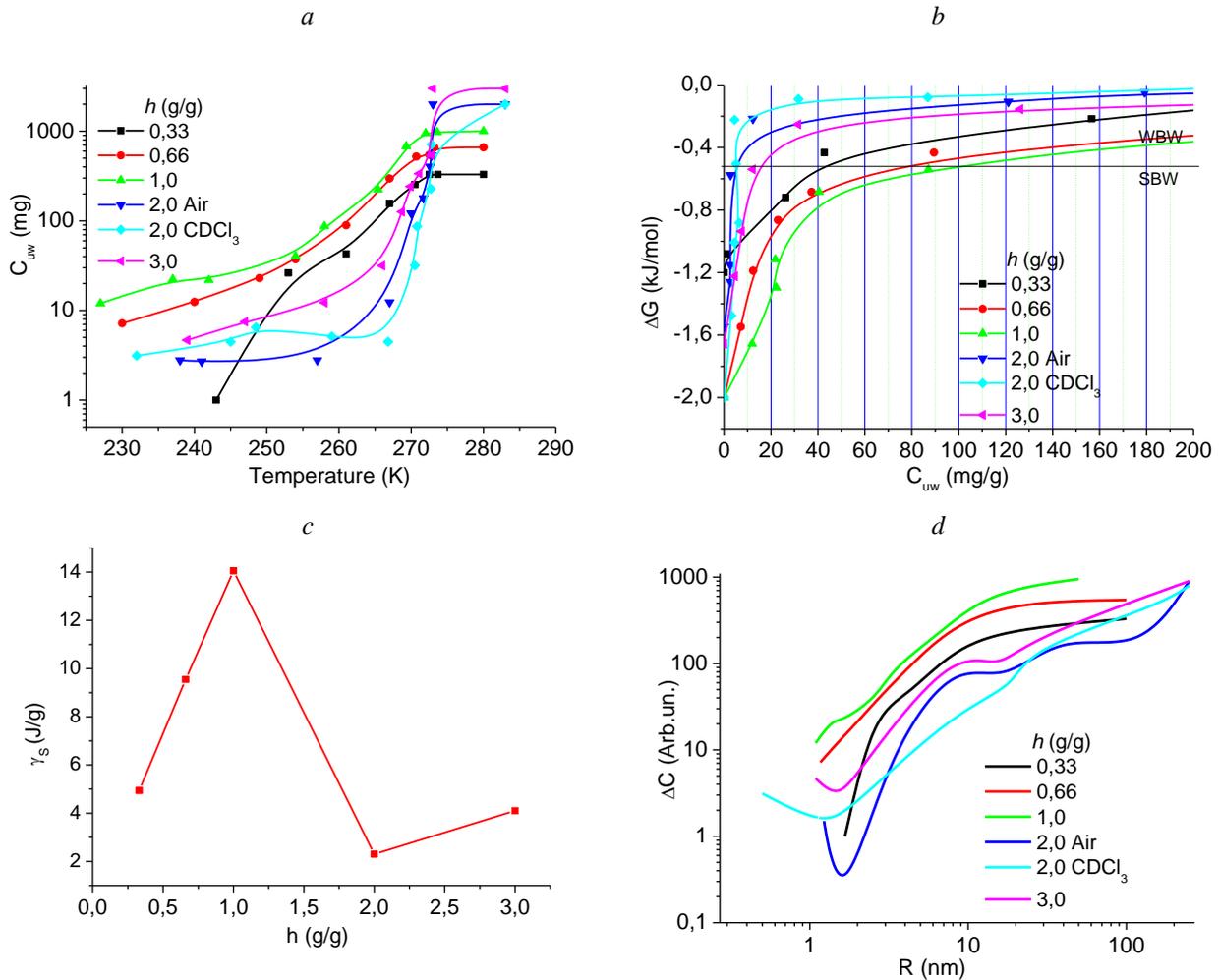
Fig. 4. The temperature dependences of the unfrozen water concentration (*a*), built on their basis of the dependence of the change in the Gibbs free energy *vs* unfrozen water concentration (*b*) the dependence of the change in the interfacial energy *vs* the adsorbed water amount (*c*) and the size distribution of adsorbed water clusters over the radii for hydrated powders and concentrated aqueous suspensions of methylsilica AM-1 (*d*).

Table 1

Characteristics of unfrozen water layers in hydrated powders of methylsilica AM-1 at different water content

h, g/g	C_d, mg/cm^3	C_{uw}^S, mg/g	C_{uw}^W, mg/g	ΔG^S, kJ/mol	γ^S, J/g
0.33	320	50	280	-1.2	5
0.66	540	80	580	-2.0	9.6
1.0	1000	110	890	-2.0	14
2.,0		8	1492	-1.5	2.3
2.0(CDCl$_3$)		9	1491	-2	1.7
3.0		15	1485	-1.7	4.2

In passing to aqueous suspensions ($h> 1$ g/g), the amount of strongly bound water and interfacial energy sharply decreases (Table 1, Fig. 4*c*). Accordingly, the proportion of water in small clusters decreases too (Fig. 4*d*). This may be due to a change in the phase state of the colloidal system. If water in hydrated powders is in the form of clusters separated by hydrophobic particles, then with an increase in the water amount, it becomes possible to form an extended aqueous phase, which serves as a dispersion medium for hydrophobic silica particles. In this case, a spontaneous decrease in the free water energy occurs due to a decrease in its surface – the

assemblage of submicron clusters passes into the state of microdrops or a continuous aqueous medium. Then the voids between nanoscaled silica particles can again be filled with air, or the configuration of the interparticle space changes in such a way as to ensure maximum contact between hydrophobic particles due to van der Waals interactions.

An aqueous suspension containing 2 g/g of water and representing a thick paste, nevertheless, is mixed well with weakly polar, poorly soluble in water chloroform. In this case, the paste liquefies, but does not delaminate and exists in the form of a suspension containing close
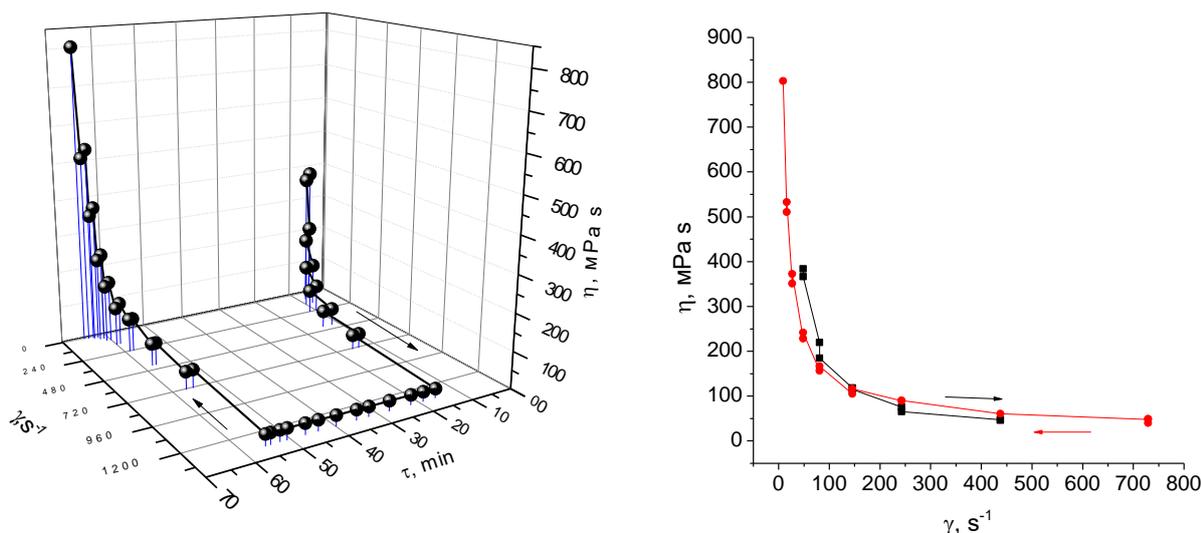
Fig. 5. Change in the viscosity of 15 % suspension of methylsilica AM-1 under the influence of mechanical load.

amounts both of chloroform and water. In accordance with the data table. 1, the chloroform addition led to a significant (from 2.3 to 1.7 J/g) decrease in the interfacial water energy which indicates that chloroform replaced some number of interparticle voids previously occupied by water.

An aqueous suspension of hydrophobic silica is a complex non-equilibrium system, which either itself or under the influence of external loads can change its phase state. These processes can be recorded by measuring the suspension viscosity under the influence of mechanical loads created in the cylindrical measuring cell of the dynamic rotational viscometer Rheotest 2.1 (cylinder system S/N) at a shear rate of 9-1312.2 s^{-1}. To determine the thixotropic properties of the suspensions, the rheological measurements were performed with stepwise increasing shear rate and exposure at maximal shear rate (1312 s^{-1}) up to a constant viscosity, and finally stepwise decreasing shear rate. The results are shown as 3D graphs of the effective viscosity *vs* shear rate and time. Fig. 5 shows the curves of viscosity change with time depending on the rotation speed of the working cylinder. The measurements were carried out on a sample of AM-1 suspension containing 15 % of the solid phase.

The initial viscosity of the suspension is 380 mPa s at a low speed of the rotating cylinder. As the load increases (speed 1200 s^{-1}), the dynamic viscosity decreases to 70 mPa s. Further, over time, the viscosity of the suspension does not change while maintaining rotation speed of the working cylinder. A decrease in the load to the initial value is accompanied by an increase in viscosity, which can be twice the initial viscosity of the suspension. Thus, the aquous suspension of hydrophobic silica has high thixotropic properties, which depend on the time and the magnitude of the applied mechanical load. The basis of the effect is the possibility of reorganizing the interparticle aggregates structure, which strives to ensure the minimum value of the free energy of the heterogeneous system.

Conclusions

Under the influence of mechanical loads, a mixture consisting of a hydrophobic powder of methylsilica AM-1 and water ($h \leq 1$ g/g) can be transformed into a wet powder, in which water is localized in the form of submicron clusters filling the interparticle voids of silica. In this case, the interfacial energy is directly proportional to the amount of added water.

At high water concentrations, a spontaneous increase in the size of water structures occurs, which is accompanied by a sharp decrease in the interfacial energy, and may indicate the collapse of narrow interparticle voids or their filling with air.

Aqueous suspensions of AM-1 are easily mixed with a weakly polar organic solvent – chloroform, forming a stable suspension in which the water and chloroform amount can be close.

Aqueous suspension of methylsilica has high thixotropic properties, depending on the time and the magnitude of the applied mechanical loads.

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Кластеризація води в міжчастинковому просторі гідрофобного нанокремнезему АМ-1

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Методом [1]Н ЯМР спектроскопії було досліджено процеси, що відбуваються в гідратованих порошках і концентрованих суспензіях гідрофобного кремнезему. Показано, що суміш метилкремнезему та води при гідратованості менше 1 г/г являє собою вологий порошок, де вода знаходиться у вигляді субмікронних кластерів, що заповнюють міжчастинкові проміжки нанокремнезему, а міжфазна енергія прямопропорційна кількості води, що додається. Виявлено, що при великих концентраціях води відбувається спонтанне збільшення розміру водних структур, яке супроводжується різким зменшенням міжфазної енергії, що може відображати зникнення вузьких міжчастинкових зазорів або заповнення їх повітрям. В роботі показано, що водні суспензії АМ-1 легко змішуються із слабополярним органічним розчинником хлороформом, формуючи стійку суспензію, де кількість води та хлороформу може бути близьким. Виявлено, що водна суспензія метилкремнезему має високі тиксотропні властивості, які залежать від часу та від величини прикладених механічних навантажень.

Ключові слова: [1]Н ЯМР-спектроскопія, гідрофобний кремнезем, тиксотропія, механічні навантаження.