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Phase transitions in compressed metil silica with the participation of water and methanol

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Methanol, water, and their mixtures in the interparticle gaps of wetting-drying methyl silica AM-1 were studied using low-temperature 1H NMR spectroscopy. The bulk density of the samples in the wet state was 200-300 mg/cm^3. It is shown that both on dry and on wet samples of methyl silica AM-1, methanol melts up to 280 K, which is 100 degrees higher than the bulk melting temperature. Water is present in the form of nanoscale clusters of strongly and weakly associated water on wet hydrocompacted samples of methylsilica. It is assumed that weakly associated water is a nanoscale analogue of supercritical water. It mixes well with weakly polar chloroform or polar methanol. In the latter case, a concentrated solution of unassociated molecules of water and methanol is formed in the interparticle gaps of methyl silica AM-1. As the temperature decreases, both strongly and weakly associated water freeze and cease to be registered in liquid NMR spectra.

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

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Introduction

The properties of substances at the interphase boundaries of solid bodies with a developed surface differ significantly from those of the bulk [1-3]. This is due to a decrease in the free energy of substances caused by adsorption interactions. Therefore, there is usually a decrease in the freezing point, an increase in the heat of evaporation and boiling point. However, in recent years, when studying the process of thawing molecular liquids in the interparticle space of silica adsorbents, it was established that part of the substance continues to be in a solid state even at temperatures several tens of degrees higher than the bulk freezing temperature [4-6]. In addition, it was established that the hydrophobic surface has a significant effect on the ability of self-associated liquids, which include water in particular, to form a spatial network of hydrogen bonds [7-10].

Nanosized (nanostructured) composite materials created on the basis of chemically and structurally modified silicas can become a promising direction in the creation of a new type of functionalized materials for technical or medical purposes. At the same time, their functionalization can occur by changing the properties of the adsorption layer as a result of phase transitions of adsorbed substances under the influence of surface forces and effects caused by limited space and changes in the hydrophobic-hydrophilic properties of the mineral component of composites. In particular, limitedly hydrated materials are characterized by the formation of a system of nanosized clusters rather than a continuous layer of adsorbed water. The latter, in turn, depending on the type of surface with which they are in contact, can be in different states - strongly associated (the network of hydrogen bonds is similar in structure to the network of hydrogen bonds in liquid water) or weakly associated, when most of the hydrogen bonds are destroyed. This state of water is in many respects close to water in the supercritical state [11-14], which is realized for water at 647 K and a pressure of 217 atm. The simultaneous existence of both strongly and weakly associated water can be considered as a phase transition of the first kind. The physical and chemical properties of such water are very different from the volume properties. Thus, the dielectric constant decreases significantly, the solubility of weakly polar substances increases, the freezing and boiling points may change. Then, by purposefully increasing the amount of weakly associated water in the adsorption layer, it is possible to control the processes of adsorption and desorption of biologically active substances, or the parameters of adsorption interactions.

I. Experimental part

1.1. Materials.

Hydrophobic silica of the AM-1 brand with a specific surface area of S_{BET} = 175 m^2/g (Kalush, Ukraine) was used in the work, which was obtained by chemically modifying the surface of the original nanosilica A-200 with dimethyldichlorosilane. As a result of the reactions, pairs of dimethylsilyl groups cross-linked by siloxane bridges are formed $=Si(CH_3)_2\text{-}O\text{-}Si(CH_3)_2\text{-}$. Wetting of methyl silica powder was carried out by mechanochemical activation in a porcelain mortar in accordance with the method described in [9,15,16]. Samples containing methanol were additionally compacted in a porcelain mortar (T = 290 K, 5 min).

1.2. ^{1}H NMR spectroscopy.

NMR spectra were taken on a high-resolution NMR spectrometer (Varian "Mercury") with an operating frequency of 400 MHz. Eight 60˚ probing pulses with a duration of 1 μs and a bandwidth of 20 kHz were used. The temperature in the sensor was adjusted with an accuracy of ±1 degree. Signal intensities were determined by measuring the peak area using the procedure of decomposing the signal into its components assuming a Gaussian waveform and optimizing the zero line and phase with an accuracy of ± 10 %. To prevent supercooling of water in the studied objects, the measurement of the concentration of non-freezing water was carried out by heating the samples previously cooled to a temperature of 210 K. The temperature dependence of the intensity of the NMR signals was carried out in an automated cycle, when the time of holding the sample at a constant temperature was 9 min, and the measurement time 1 min. NMR measurements were performed in an air environment. The concentration of strongly and weakly associated water (C_{uw}^S and C_{uw}^W, respectively), changes in the Gibbs free energy from the concentration of unfreezing water $\Delta G(C_{uw})$, the value of the interfacial energy (γ_S) and in accordance with the Gibbs-Thomson equation were calculated from the change in the intensity of water signals with temperature – distributions by cluster radii (R) of adsorbed water. A detailed description of the calculation method used is given in [17-20].

By determining the chemical shifts of adsorbed water, it is possible to draw conclusions about the structure of water as a system of molecules participating in the formation of a network of hydrogen bonds. At the same time, they take into account the fact that the maximum number of hydrogen bonds in which a water molecule can participate is four, which is realized for hexagonal ice, in which protons have a chemical shift of δ_H = 7 ppm. [21]. At the same time, unassociated water in the gas phase has a chemical shift δ_H = 0-1 ppm [22]. That is, the average number of hydrogen bonds formed by each water molecule can be calculated from the value of the chemical shift [18-20]. Liquid water is characterized by the chemical shift of protons δ_H = 5 ppm, which indicates the formation of 2-3 hydrogen bonds by each molecule. As the temperature decreases, the chemical shift of adsorbed or liquid water usually increases, which is due to the increase in the orderliness of the network of hydrogen bonds. It can be assumed that in the case when δ_H < 2 ppm water is weakly associated (WAW), and in the case of δ_H > 4 ppm – strongly associated (SAW).

II. Results and discussion

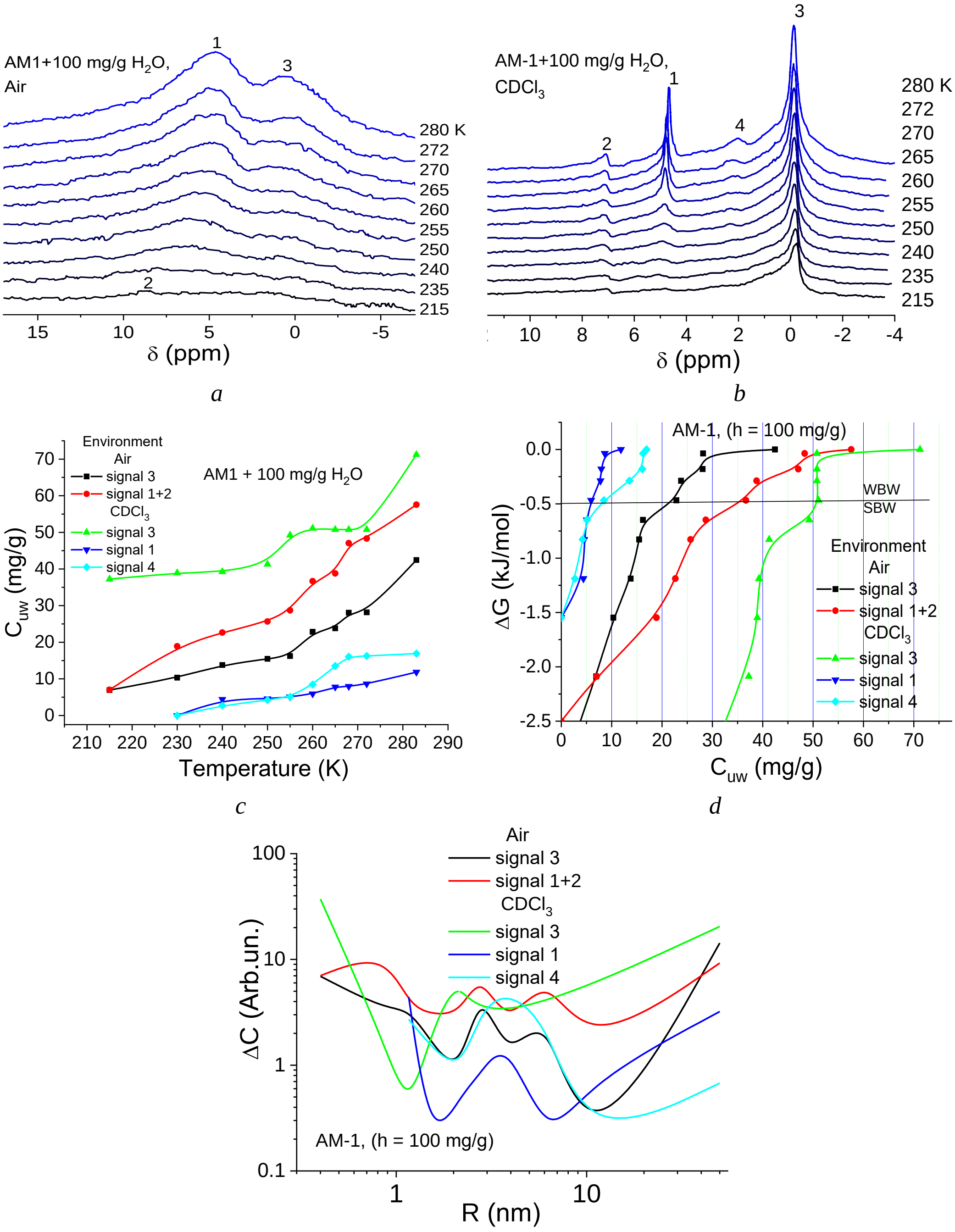
In Fig. 1 shows the 1H NMR spectra of water adsorbed in interparticle gaps of AM-1 in air (*a*) and in $CDCl_3$ (*b*) taken at different temperatures, the temperature dependence of the concentration of various forms of non-freezing water (*c*), the dependence of the change in Gibbs free energy on the concentration of non-freezing water of water (*d*) and size distributions of adsorbed water clusters at h = 100 mg/g.

In the spectra, there are several signals related to different forms of adsorbed water. In the air environment (in addition to water, interparticle gaps contain air, (Fig. 1,*a*) at low temperatures, signals of water with chemical shifts δ_H = 0 and 8 ppm are observed - signals 3 and 2, respectively. With increasing temperature, signal 2 transforms into signal 1 with a chemical shift δ_H = 5-6 ppm. The first of them refers to water that does not form hydrogen bonds (weakly associated water). Signals 1 and 2 - to strongly associated water, and the orderliness of the network of hydrogen bonds the bonds of water responsible for signal 2 can be attributed to tetracoordinated water. Thus, a significant part of the water in wetting-drying methyl silica AM-1 is in a weakly associated state and forms water systems with a destroyed network of hydrogen bonds.

Replacing the air environment with the environment of a weakly polar organic solvent - deuterochloroform (Fig. 1,*b*) stabilizes weakly associated forms of water to an even greater extent. About 75% of the water present in the interparticle gaps can be considered weakly associated. In addition, signal 4 appears in the spectra with a chemical shift δ_H = 2 ppm, which corresponds to a water network with a partially destroyed network of hydrogen bonds. It is likely that a concentrated mixture of weakly associated water and chloroform, stabilized by a hydrophobic surface, is formed in the nano-sized interparticle gaps of AM-1. The possibility of separate observation of several types of adsorbed water clusters indicates their spatial separation when the molecular (proton) exchange between them is slow (on the NMR time scale).

When the amount of interfacial water is doubled, the general appearance of the spectra of adsorbed water does not change (Fig. 2). However, the relative amount of strongly associated water increases (the ratio of the intensities of signals 1 and 3). The total value of the interphase energies, $\Sigma\gamma_S$ when replacing air with chloroform increases from 10.3 to 13.88 J/g, that is, relatively less than when h = 100 mg/g (Table 1.). The appearance of the distributions according to the radii of the adsorbed water clusters is similar to that shown in Fig. 1,*d* and contains several maxima corresponding to the predominant formation of water clusters of a certain size. Thus, by means of structural modification in the process of mechanoactivation with water in the pore space of AM-1 methylsilica, a mixture of clusters of strongly and weakly associated water is formed. In contact with a liquid hydrophobic medium, the amount of weakly associated water increases significantly.

As the temperature decreases, all types of interfacial water freeze, forming ice (Fig. 1,*c*). For SAW, this is a natural process – as a result of freezing, a tetragonal structure of hexagonal ice is formed. However, the formation of ice from WAW and its structure are unknown. It can be assumed that WAW freezes in the form of amorphous ice, since upon thawing (melting) it again passes into a weakly associated state with a destroyed network of hydrogen bonds. Both SAW and WAW are characterized by the presence of not only strongly but also weakly bound water (Fig. 1(2), *d*, Table 1), that is, water in which the change in free energy due to adsorption interactions does not exceed 0.5 kJ/mol. Therefore, the WAW freezing process can be carried out with low energy costs. The total interphase energy ($\Sigma\gamma_S$) in the weakly polar medium of chloroform was twice as large



a *b*

c *d*

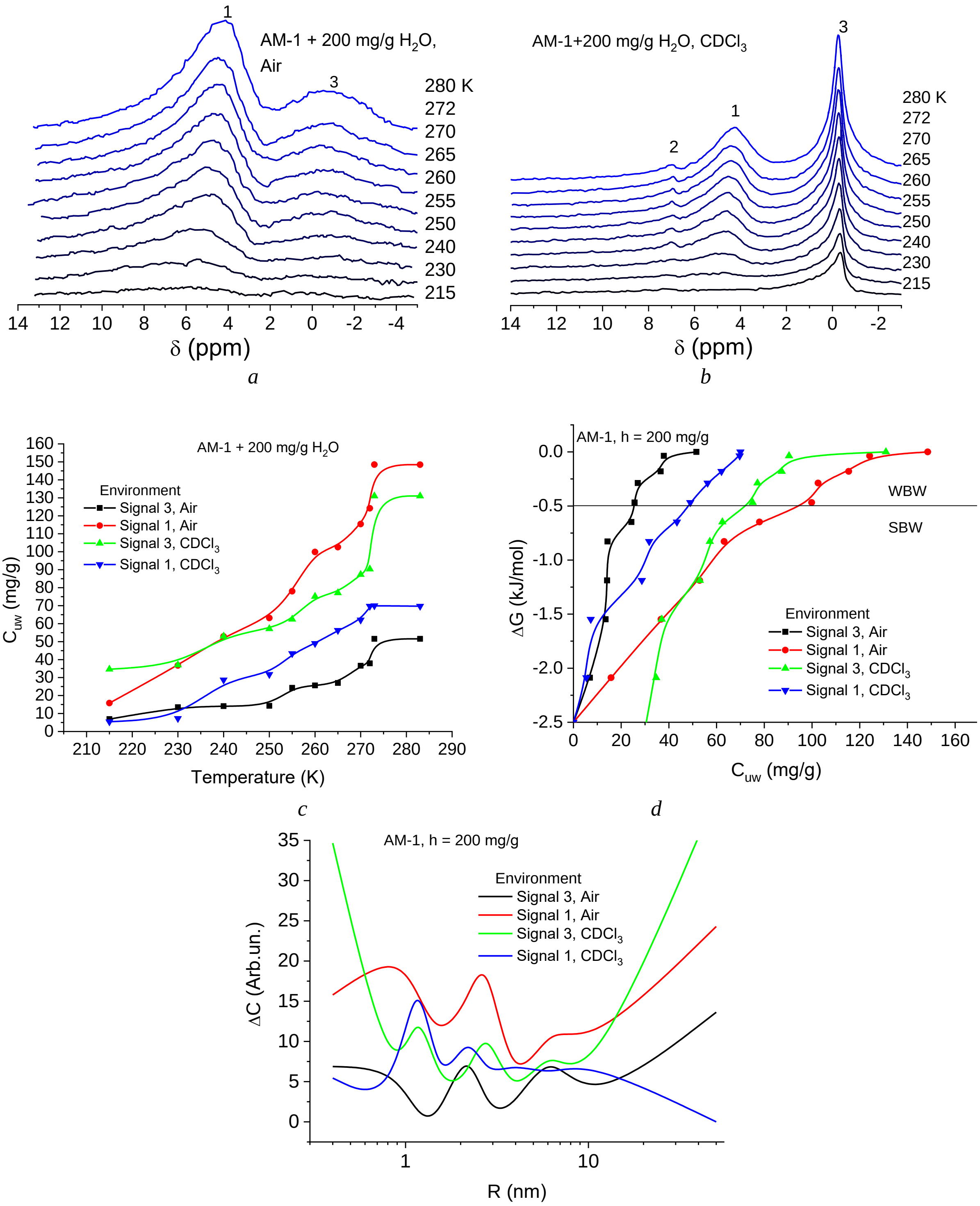
e

Fig. 1. The 1H NMR spectra of water adsorbed by AM-1 in air (*a*) and in $CDCl_3$ medium (*b*), temperature dependences of the concentration of various forms of non-freezing water (*c*), dependences of the change in Gibbs free energy on the concentration of non-freezing water (*d*) and size distributions of adsorbed water clusters at *h* = 100 mg/g (*e*).

as in air (Table 1). That is, chloroform stabilizes the nanoscale state of water clusters in the gaps between hydrophobic AM-1 particles.

It should be noted that unlike the supercritical state, water weakly associated with a stabilized surface exists only in the form of nanosized clusters (Fig. 1 (2), *e*), the radius of which is in the range of 0.5-50 nm. Several maxima are observed in the size distributions of SAW and WAW clusters, but weakly associated water is characterized by the presence of a larger number of small clusters. This is evidenced by smaller values of ΔG^S (signal 3, Table 1), which characterizes the maximum decrease in the free energy of water in the adsorption layer.

Unlike chloroform, methanol is a polar compound. Due to the presence of an alcohol OH group, its molecules are capable of self-association, in which two or three spit molecules can participate. Methanol is a good wetting



a *b*

c *d*

e

Fig. 2. The 1H NMR spectra of water adsorbed by AM-1 in air (*a*) and in CDCl3 medium (*b*), temperature dependences of the concentration of different forms of non-freezing water (*c*), dependences of the change in Gibbs free energy on the concentration of non-freezing water (*d*) and size distributions of adsorbed water clusters at *h* = 200 mg/g.

agent for silica, and therefore can promote its compaction by removing air from the interparticle spaces. 1H NMR spectra of methyl and hydroxyl groups of methanol taken at different temperatures during sample heating from 215 to 280 K for dry AM-1 and AM1 containing 200 mg/g of adsorbed water are shown in Fig. 3,*a*. Pre-wetting of hydrophobic silica with water was carried out by using the process of mechanoactivation with water in a porcelain mortar.

The chemical shift of CH_3 groups is 3.5 ppm, and that of hydroxyl groups is 5-6 ppm. With a decrease in temperature, there is a shift of hydroxyl groups towards weak magnetic fields (the chemical shift increases), which is due to the stabilization of associated forms of alcohol. It should be noted that for methanol monomers one should expect chemical shift values similar to those observed for unassociated forms of water, the weak signal of which is observed in Fig. 3,*a* at $\delta_H = 0$ ppm.

It is known that methanol belongs to cryogenic liquids and freezes at $T_f = 171$ K. However, as can be seen from the data in Fig. 3, and adsorption interactions with the surface of methyl silica do not lower but significantly increase its melting temperature. That is, the hydrophobic surface stabilizes the solid state of organic matter and allows observing the solid phase of methanol up to room temperature (Fig. 3). This effect also persists for hydrated samples, although the range of methanol thawing temperatures changes slightly.

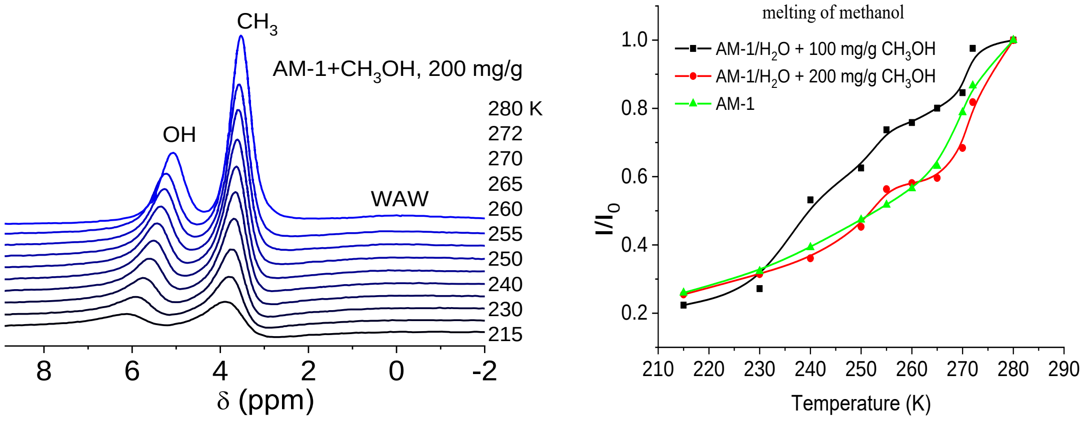
The influence of methanol on the structure of water associates concentrated in the interparticle gaps of methyl silica was also studied. The spectra of the compacted sample AM-1, which contained 200 mg/g of H_2O and 200 mg/g of CH_3OH, taken at different temperatures, are shown in Fig. 4,a. Common signals of strongly associated water and OH groups of methanol (δ_H = 5-6 ppm), CH_3 groups of methanol (δ_H = 3.5 ppm) and weakly associated water (δ_H = 0 ppm) are observed in the spectra. The size distributions of SAW and WAW clusters were calculated using the Gibbs-Thomson equation based on the change with temperature in the concentration of strongly and weakly associated water (Fig. 4,*b*,*c*).

A significant part of WAW is formed by clusters of large size (R > 10 nm). There are also WAW clusters with R = 0.8 and 2 nm. For SAW, the cluster size distribution contains maxima at R = 0.6, 2 and 30 nm. Probably, at

Table 1.

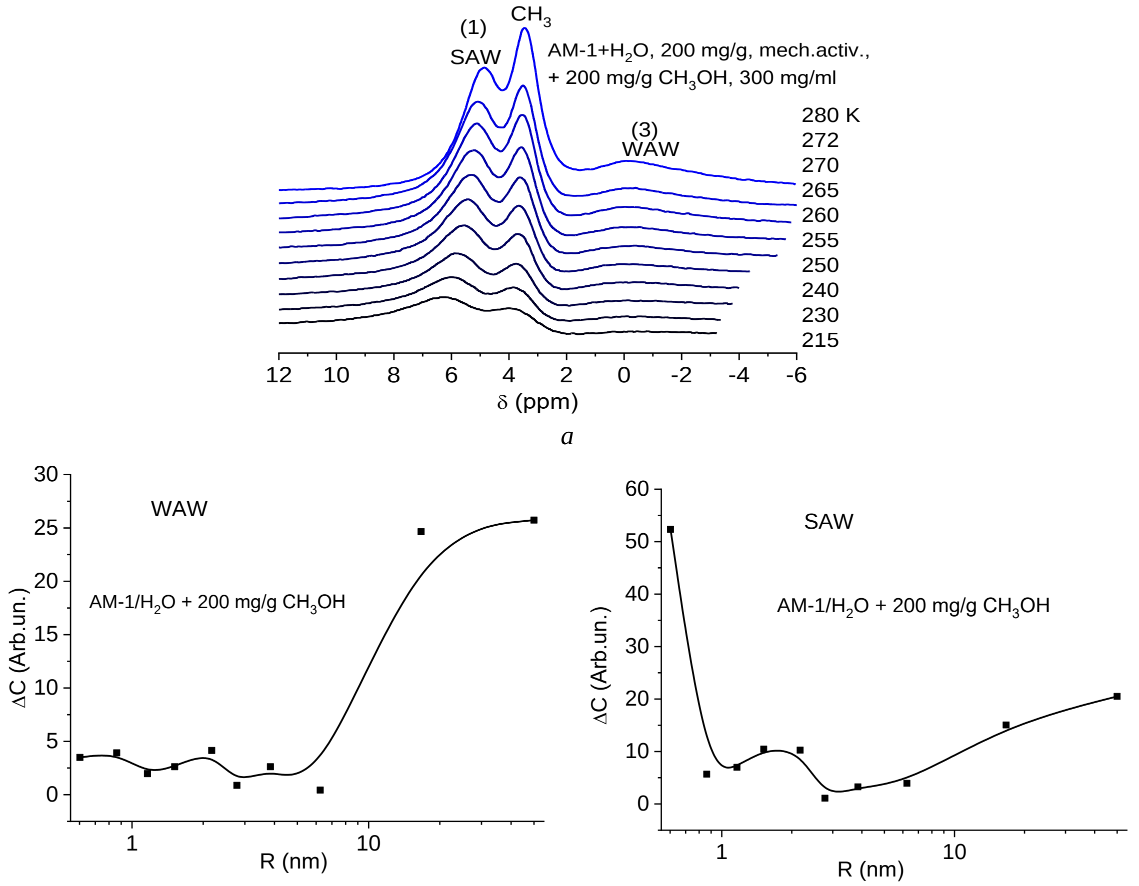
Characteristics of interfacial water in hydrated methyl silica AM-1 and composites with methanol

Sample *h*, mg/g	Environment	Signal	C_{uw}^S, mg/g	C_{uw}^W, mg/g	ΔG^S, kJ/mol	γ_S, J/g
AM-1 Activated with water /100	Air	3	22	18	-3,0	2,00
		1+2	36	19	-2,5	3,10 $\Sigma\gamma_S$ 5,1
	$CDCl_3$	3	51	18	-6,0	9,10
		1	6	6	-1,5	0,44
		4	8	8	-1,5	0,57 $\Sigma\gamma_S$ 10,30
AM-1 Activated with water /200	Air	3	25	25	-2,5	2,23
		1	95	45	-2,5	7,52 Σ9,75
	$CDCl_3$	3	72	45	-6,0	10,28
		1	43	25	-2,5	3,60 $\Sigma\gamma_S$ 13,88
AM-1 Activated with water /200	CH_3OH 200 mg/g	3	20	50	-3,5	2,30
		1	90	40	-6,0	16,40 $\Sigma\gamma_S$ 17,70
	CH_3OH 100 mg/g	3	60	40	-3,5	5,20



a *b*

Fig. 3. The 1H NMR spectra of the methyl and hydroxyl groups of methanol wetting dry AM-1 (*a*) and changes in the relative signal intensity of the methyl groups of methanol and dry and wet samples (*b*) were taken at different temperatures.



a

b *c*

Fig. 4. Spectra of a mixture of water and methanol adsorbed on AM-1 (*a*) and size distributions of clusters of weakly (*b*) and strongly associated (*c*) water taken at different temperatures.

the chosen ratio of concentrations of methanol and water, a solution of strongly associated water and methanol is formed. As the temperature decreases, part of the water freezes, and the concentration of the solution increases, which leads to an increase in the number of small SAW clusters at low temperatures (Fig. 4,*b*).

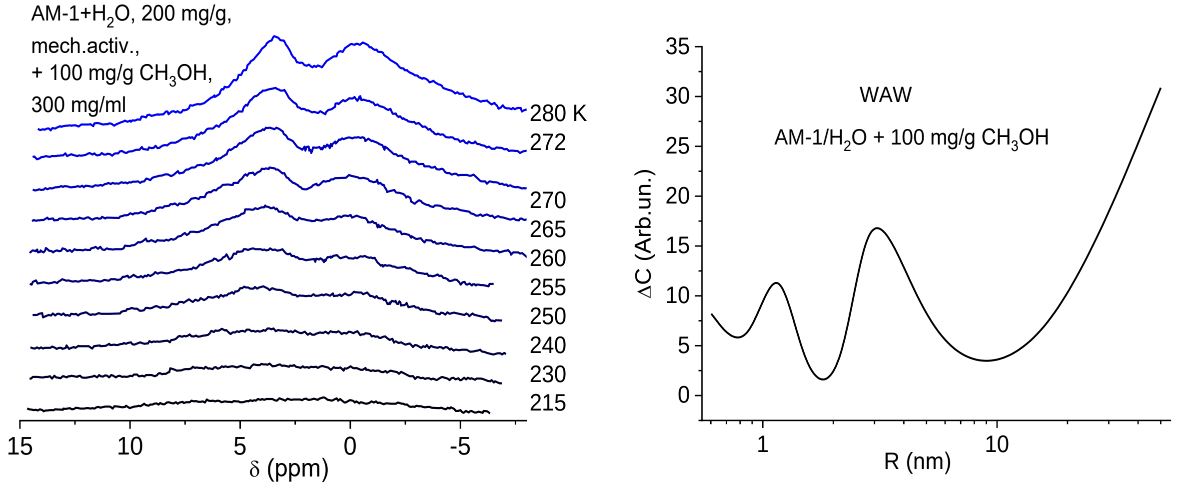
A decrease in the concentration of methanol in the adsorption layer leads to a complete change in the structure of the adsorbed water (Fig. 5,*a*). In the spectra, the signal of strongly associated water completely disappears, instead, the intensity of the signal of weakly associated water increases. The disappearance of the signal of the hydroxyl groups of alcohol indicates that methanol, like water, completely transitions to an unassociated state. Adsorbed water is observed in the form of clusters with R = 1, 3, and 20 nm. With a high degree of probability, it can be assumed that the state of this solution is close to the supercritical state in terms of properties, but it exists only in the form of nano-sized clusters stabilized by the surface of hydrophobic methylsilica particles. Thus, depending on the ratio of components, a water-methanol solution can be formed in the interparticle gaps of AM-1, in which methanol is dissolved in strongly associated water (excess water) or clusters of a mixture of unassociated molecules of water and methanol with certain properties of the supercritical state of substances are formed.

In Fig. 6 shows the temperature dependences of the concentration of different forms of water in the AM-1/H_2O/CH_3OH systems (*a*) and the dependence of the Gibbs free energy change on the concentration of non-freezing water (b) calculated on their basis. Characteristics of bound water layers are contained in table. 1. Since the amount of water in both samples was the same (h = 200 mg/g), it can be concluded that the total binding energy of water to the surface is greater in the case of the simultaneous formation of clusters of strongly and weakly associated water ($\Sigma\gamma_S$ = 17.7 J/d). This is probably due to the exothermic process of methanol dissolution in strongly associated water. On the contrary, during the formation of a non-associated solution of a mixture of water and methanol, the free energy of the system decreases much less (γ_S = 5,2 J/g).

Conclusions

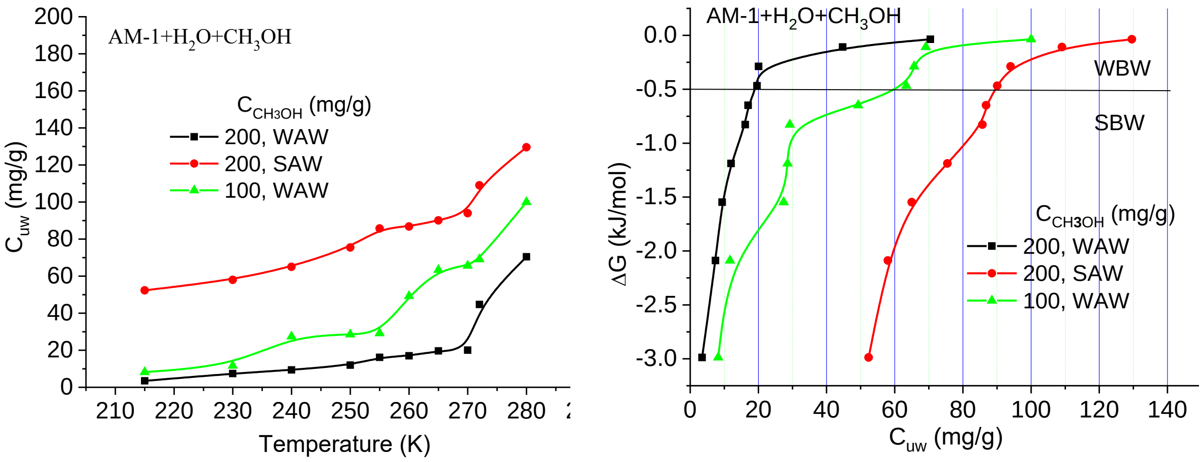
It was established that water in the interparticle gaps of hydrated methylsilica AM-1, obtained by hydraulic compaction using strong mechanical loads, exists in the form of a system of nano-sized clusters of strongly and weakly associated water, which is an analogue of supercritical water.

Such water forms mixtures (solutions) with weakly polar organic solvent - chloroform and polar - methanol. At the same time, depending on the concentration ratio of



a *b*

Fig. 5. 1H NMR spectra of a mixture of water and methanol in a mechanoactivated sample AM-1/H2O taken at different temperatures (*a*) and the size distribution of weakly associated water clusters in this system (*b*).



a *b*

Fig. 6. Temperature dependences of the concentration of different forms of water in the AM-1/H2O/CH3OH systems (*a*) and the dependence of the change in Gibbs free energy on the concentration of non-freezing water calculated on their basis (*b*).

water and methanol, the latter can preferentially dissolve both in strongly associated water (excess water) and in weakly associated water. At the same time, a mixture of unassociated molecules of water and alcohol is formed (similar to a supercritical solution). Energy consumption for the formation of a non-associated solution is three times lower than for a solution of methanol in strongly associated water.

Melting of methanol in the interparticle gaps of methylsilica AM-1 occurs in a wide temperature range, up to room temperatures, which is 100 degrees higher than the bulk melting temperature. This effect is preserved both for dry and wet surface of AM-1.

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Krupska T.V. – Doctor of Chemical Sciences, leading researcher;
Kartel M.T. – academician of the National Academy of Sciences of Ukraine, Professor, Doctor of Science.

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Фазові переходи в ущільненому метилкремнеземі за участю води та метанолу

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Методом низькотемпературної ^{1}H ЯМР-спектроскопії досліджувались метанол, вода та їх суміші в міжчастинкових зазорах гідроущільненого метилкремнезему АМ-1. Насипна густина зразків у вологому стані складала 200-300 мг/см^3. Показано, що як на сухому, так і на вологих зразках метилкремнезему АМ-1, танення метанолу проходить аж до 280 К, що на 100 град вище об’ємної температури плавлення. На вологих гідроущільнених зразках метилкремнезему вода знаходиться у вигляді нанорозмірних кластерів сильно- та слабоасоційованої води. Зроблено припущення, що слабоасоційована вода є нанорозмірним аналогом надкритичної води. Вона добре змішується із слабополярним хлороформом або полярним метанолом. В останньому випадку в міжчастинкових зазорах АМ-1 утворюється концентрований розчин неасоційованих молекул води та метанолу. Зі зниженням температури як сильно- так і слабоасоційована вода замерзають і перестають реєструватись в спектрах рідинного ЯМР.

Keywords: ^{1}H ЯМР спектроскопія, метилкремнезем, метанол, механічні навантаження.