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WATER IN A HYDROPHOBIC ENVIRONMENT AND THE EFFECT OF SOME ORGANIC SUBSTANCES ON IT

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The structure of water in the interparticle gaps of methyl silica was investigated using the method of low-temperature ^1H NMR spectroscopy. It is shown that the main part of the interfacial water is in the form of large clusters, or nanodroplets, which freeze at a temperature of about 273 K. After freezing of this water, signals of strongly and weakly associated water are observed in the spectra, which melts at temperatures of 215–368 K. It is likely that the freezing of weakly associated of water occurs through the formation of clusters in which closely spaced water molecules interact not through hydrogen bonds, but through dipole-dipole interactions. In the presence of chloroform, the amount of weakly associated water increases several times. This is explained by the possibility of formation of chloroform hydrates, in which the mobility of water molecules is approximately the same as in strongly associated water clusters. If joint adsorption of chloroform and methane occurs on the hydrated surface of methyl silica, under the influence of CH_4, weakly mobile weakly associated water is transformed into methane hydrates in quasi-liquid and solid states, while only mobile forms of hydrates are recorded in the spectra. DMSO reduces the possibility of formation of weakly associated water, but a certain amount of it is fixed even in the medium of liquid DMSO. At the same time, the freezing of water in systems containing DMSO occurs at much lower temperatures due to solvation of water and DMSO molecules. The difference in interphase energy in air and in organic media determines the solvation energy.

Keywords: hydrated methyl silica, strongly and weakly associated water, hydrates, ^1H NMR spectroscopy

INTRODUCTION

Water belongs to strongly associated substances, as it easily forms hydrogen bonds with neighboring molecules. In the absence of spatial obstacles, the maximum number of such bonds is four, and in two of them the molecule acts as a proton donor, and in the other two - an electron donor. That is, crystals or crystallites of water have a tetragonal crystalline cell at their base, which is the structural basis not only of various forms of ice, but also of liquid water [1–3]. However, in the limited space formed by closely spaced particles of hydrophobic substances, there may be spatial restrictions for the formation of a network of hydrogen bonds of ordered water clusters, and a certain part of water may be in an unassociated state, which is characteristic, in particular, of gaseous water [4–6] or water in supercritical state [7–9]. The properties of such unassociated water must differ significantly from the properties of liquid water both in terms of dielectric constant and parameters of interactions with organic substances. These differences can become especially important in biological systems that stabilize weakly ordered forms of water or when

solid bodies that contain disordered water are in contact with biological objects. The presence of even small amounts of poorly ordered water can play a significant role in important physiological processes at the cellular and subcellular level. Therefore, systems in which the possibility of the coexistence of different forms of water is ensured are of great interest.

When studying the hydration of AM-1 representing nanosilica modified by dimethyldichlorosilane, *i.e.*, the surface silanols replaced by dimethylsilyl functionalities with subsequent lateral cross-linking under conditions of weak surface hydration ($h < 10$ mass. %) by the method of low-temperature ^1H NMR spectroscopy [10–13], it was found that adsorbed in interparticle gaps, water is in the form of a system of clusters, the radius of which does not exceed 50 nm, and the simultaneous existence of clusters of strongly associated water (SAW), in which each water molecule simultaneously participates in the formation of at least two hydrogen bonds, and weakly associated water (WAW) is possible), which practically does not participate in the formation of hydrogen bonds [14–17]. Since the chemical shift of protons (δ_H)

in water depends significantly on the number of hydrogen bonds in which it participates [10], WAW and SAW clusters are observed in different spectral regions $\delta_H = 0$–1 and 4–6 ppm in accordance. The aim of the work was to study the possibility of the formation of weakly associated water in the interparticle gaps of AM-1 under conditions of high hydration of the material ($h = 200$ and 650 mg/g), and the effect on its amount of the presence of certain types of organic molecules – chloroform, methane and dimethyl sulfoxide (DMSO).

EXPERIMENTAL PART

As hydrophobic silica, methyl silica (Kalush, Ukraine) was used, the specific surface of which according to BET was $S_{BET} = 185$ m^2/g. It was produced on the base of the corresponding fumed silica (A-200) by chemical modification with dimethyldichlorosilane. The degree of substitution of silanol groups by methyl groups ≥ 98 %.

Hydrophobic materials are not wetted by water due to the presence of a thin layer of air on their surface, the molecules of which isolate the surface from contact with water. Volumetric air filling of micro- and mesopores can also be carried out in porous bodies. It has been shown that one of the effective methods of replacing air with water in hydrophobic powders is their mechanical treatment with water by grinding with the use of significant mechanical loads [18–20]. In the case when the total volume of water is equal to or greater than the volume of interparticle cavities, entire air can be replaced by water and the hydrophobic powder, as it is processed, sinks into the aqueous medium. However, with a relatively small amount of water, after 10–15 min, a significant part of it evaporates from the samples [16, 17], leaving only 20–30 mg/g of interfacial water. Therefore, for the hydration of hydrophobic materials with water in amounts of 100–600 mg/g, an effective method is their preliminary compaction with water under load (or an organic solvent without load) to a density of 200–300 mg/cm^3, followed by drying and adding the required amount of water to the already compacted material. In the compacted material, the distribution of water in the interparticle gaps is carried out in 30–60 seconds of additional mechanical processing, and the evaporation of water during this time can be neglected.

NMR spectra were recorded 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 area of peaks 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 the water in the studied objects, the measurement of the concentration of non-freezing water was carried out by heating the samples pre-cooled to a temperature of 210 K. The temperature dependence of the NMR signal intensity was carried out in an automated cycle, when the time of holding the sample at a constant temperature was 5 min, and the measurement time 1 min. NMR measurements were performed in an air environment. As an added hydrophobic substance, to prevent the appearance of additional signals in the spectra, deuterochloroform CDCl$_3$ was used, in which the share of the main isotope (deuterium) was 99.9 %.

The effect of methane gas on adsorbed water was studied under isobaric conditions [21, 22], when a 5 mm NMR ampoule containing 0.5 ml of hydrated silica powder was connected to a reservoir with gaseous methane, which was at an excess pressure of 0.1 bar. During the experiment, methane could freely adsorb on the surface or be removed from it.

The process of freezing (melting) of interfacial water localized in the interparticle gaps or in the pores of the adsorbent takes place in accordance with changes in the Gibbs free energy caused by the influence of the surface. It is smaller, the further from the surface of the studied water layer (the larger the size of the interparticle cavities). At $T = 273$ K, water freezes, the properties of which do not differ from bulk water, and as the temperature decreases (without taking into account the effect of supercooling), water that is located closer to the surface freezes, and for interphase water, the ratio is valid:

$$\Delta G_{\text{ice}} = -0.036(273.15 - T), \tag{1}$$

where the numerical coefficient is a parameter related to the temperature coefficient of Gibbs free energy change for ice [26].

The interfacial energy was determined as the modulus of the total decrease in the free energy of absorbed water, due to the presence of the internal boundary of the water-polymer phases according to the formula:

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

where C_{uw}^{max} – the total amount of non-freezing water at $T = 273$ K.

The value of the interfacial energy is a convenient parameter that allows one to compare the binding energy of water in different systems, especially if the amount of water in them is the same. At the same time, the Gibbs-Thomson equation [27–29] can be used to determine the geometric dimensions of nanoscale fluid aggregates limited by a solid surface, which relates the radius of spherical or cylindrical pores (R) to the freezing temperature depression:

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

where $T_m(R)$ is the melting temperature of a frozen liquid in pores of radius R, $T_{m,\infty}$ the bulk melting temperature, ρ the density of the solid, σ_{sl} the energy of solid-liquid interaction, ΔH_f the bulk enthalpy of fusion, k_{GT} is a constant, and for water bound to nanosilica $k_{GT} = 67$ K·nm.

A FEI Nova NanoSEM (5 kV) scanning electron microscope (SEM) was used to study silica samples. The morphology was also analyzed using a Dual Beam Quanta 3D FEG FEI apparatus under conditions of low vacuum at an accelerating voltage of 2–10 kV.

RESULTS AND DISCUSSION

Microscopy images (Fig. 1) show: initial (Fig. 1 *a, b*) and compacted (Fig. 1 *c, d*) methyl silica. Aggregates of methyl silica in the powder are present in the form of micron-sized particles. When the resolution of the microscope is increased, a rough structure is observed on the surface of the particles due to the formation of secondary pores, the size of which is fractions of a micron. In the compacted form of silica, the density increases slightly due to the reduction of mostly large-sized pores.

The data of the study of the hydration of melyl silica by the method of low-temperature ¹H NMR spectroscopy are shown in Figs. 2, 3 for samples containing 200 and 650 mg/g of adsorbed water (Fig. 2 and Fig. 3, respectively). At the same time, hydration was studied in an air environment (Fig. 2 *a, b* and Fig. 3 *a, b*), with the addition of deuterochloroform (Fig. 2 *c–d* and Fig. 3 *c*), with the addition of chloroform in a methane atmosphere (Fig. 2 *e*) and with the addition of dimethyl sulfoxide-D₆ (Fig. 3 *d*).

Water adsorbed in the interparticle gaps of AM-1 (Figs. 2, 3) is observed in the spectra in the form of two signals of strongly and weakly associated water (SAW and WAW) with different values of the chemical shift. This indicates a slow molecular (or proton) exchange between different forms of water. A possible reason may be the spatial separation of SAW and WAW clusters. In particular, clusters (or individual molecules) of weakly associated water can be localized in narrow pores, where the formation of a network of hydrogen bonds is difficult. As the temperature decreases, the intensity of both signals decreases, which indicates the possibility of freezing of both types of water.

For strongly associated water, this is a natural process, as a result of which hexagonal ice is formed in the interparticle gaps [23]. The possibility of freezing of weakly associated water is less obvious. If we assume the existence of WAW in the form of individual molecules adsorbed on the hydrophobic surface of AM-1, for it to freeze even in the form of amorphous ice, water molecules must change their location by moving to pores of a larger radius, where there are already ice nuclei, or gather into clusters, in which the formation of hydrogen bonds between individual water molecules is possible. However, the significant width of the WAW signal in the spectra (Fig. 2 *a, b* and Fig. 3 *a, b*) indicates a low mobility of molecules [24, 25], close to the mobility of molecules in SAW clusters. WAW is probably in the form of some kind of fluid in which the molecules are held together by dipole-dipole interactions, and the hydrophobic surface prevents the formation of hydrogen bonds.
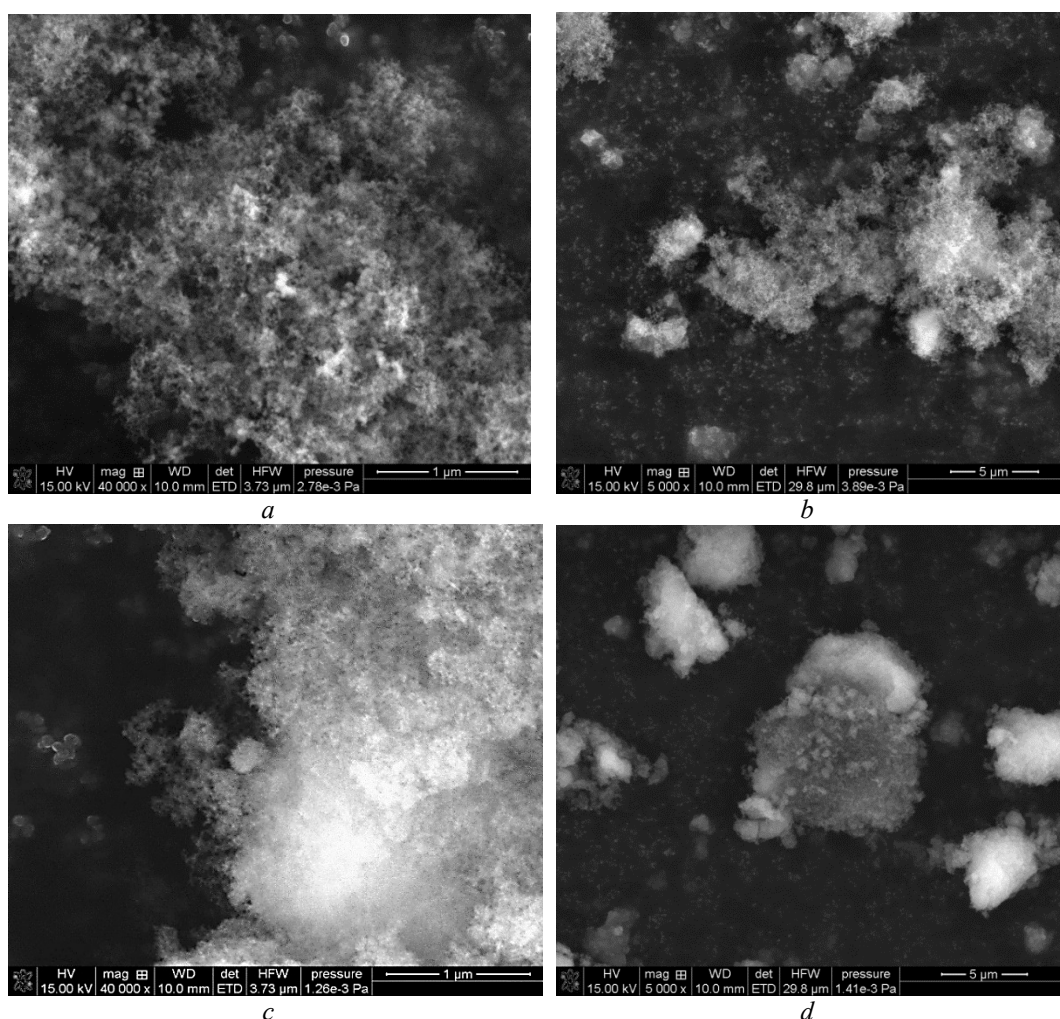
Fig. 1. SEM image of the original (*a*, *b*) and compacted methyl silica (*c*, *d*)

The addition of chloroform helps to increase the amount of weakly associated water (Fig. 2 *c*, *d* and Fig. 3 *c*). At the same time, the width of the WAW signal changes slightly. It can be assumed that in the limited space of narrow interparticle gaps of AM-1 particles, WAW clusters are capable to form chloroform hydrates stabilized by a hydrophobic surface. The use of a methane environment for a sample containing water and chloroform (Fig. 2 *e*) significantly changes the appearance of the spectra. A relatively narrow signal of adsorbed methane ($\delta_H = 0$ ppm) appears in them, while the broad signal of weakly associated water disappears or significantly decreases. Instead, the spectra show a signal with $\delta_H = 1$ ppm, the width of which is comparable to that of the methane signal. That is, the adsorbed methane destroys the sluggish WAW fluid. As can be seen from the data in Fig. 2 *e*, the intensity of the methane signal increases with increasing temperature, which is not characteristic of physical adsorption [26]. The reason may be the simultaneous formation of solid and quasi-liquid. Since solid hydrates are not observed in liquid NMR spectra (due to the very large signal width in solids) [24], it should be assumed that quasi-liquid methane hydrates, similar to chloroform hydrates, stabilize with increasing temperature (Fig. 2 *c*, *d* and Fig. 3 *c*).

If deuterodimethylsulfoxide, which is a strong electron donor, is used as a polar substance as an organic medium, the type of spectra changes slightly (Fig. 3 *d*). The intensity of the WAW signal decreases slightly, and a strong temperature dependence of the chemical shift is observed for the SAW signal. The reason is the partial destruction of strongly associated

water clusters when DMSO molecules are included in their composition. The latter form strong hydrogen bonds with water molecules, in which the chemical shift of water protons is close to 3 ppm. Accordingly, the SAW signal is observed, which is averaged between water clusters containing or not dissolved DMSO. As the temperature increases, the signal of water

protons shifts toward smaller values of the chemical shift due to an increase in the probability of formation of dimers $(CH_3)_2SO...H-O-H$. In the presence of DMSO, water freezes at relatively lower temperatures, since freezing is prevented by solvation of water and DMSO molecules.
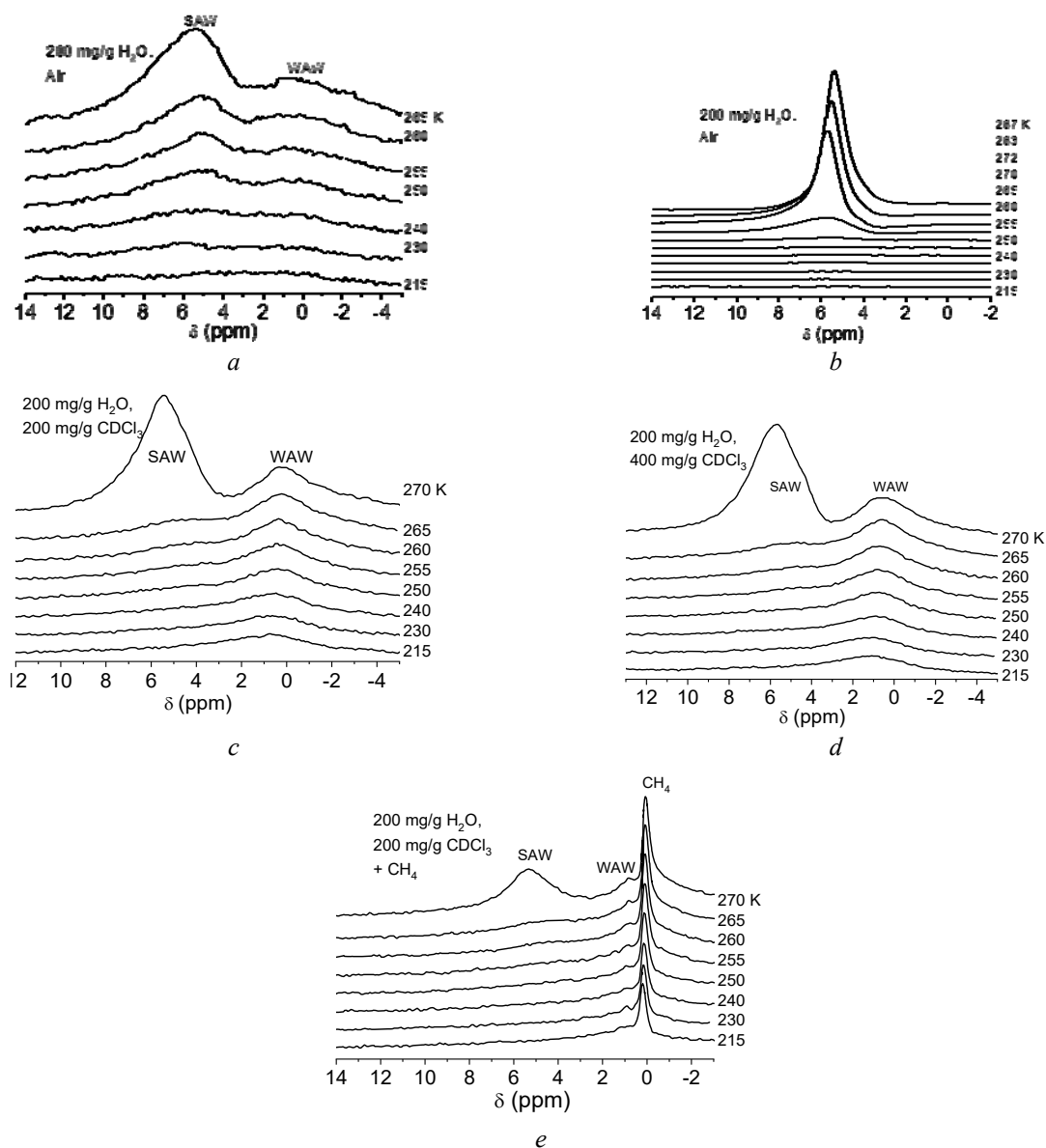

Fig. 2. ^1H NMR spectra of water in the interparticle gaps of AM-1 (h = 200 mg/g) in an air environment (*a*, *b*) with additions of $CDCl_3$ (*c-e*) and methane (*e*) taken at different temperatures

Since the total concentration of water in the samples is known, based on the ratio of water signal intensities before and after freezing, the concentrations of strongly and weakly associated water (C_{uw}) can be calculated. The temperature

dependences of the concentration of weakly and strongly associated water are shown in Fig. 4. Since the possibility of the existence of water in the solid state decreases with increasing temperature, an increase in the amount of both

types of interphase water is observed. However, in the case of the presence of chloroform for WAW, the $C_{uw}(T)$ dependences show areas of decrease in the amount of non-freezing water with increasing temperature. From the data in Fig. 4 *c, d*, it follows that precisely in the same temperature range, the amount of liquid strongly associated water increases significantly. A change in the thermodynamic stability of the system containing WAW, SAW, chloroform hydrates, and ice may be the likely cause. The presence of a significant amount of SAW can stimulate the transition of a part of WAW from chloroform hydrates to the strongly associated form of water.
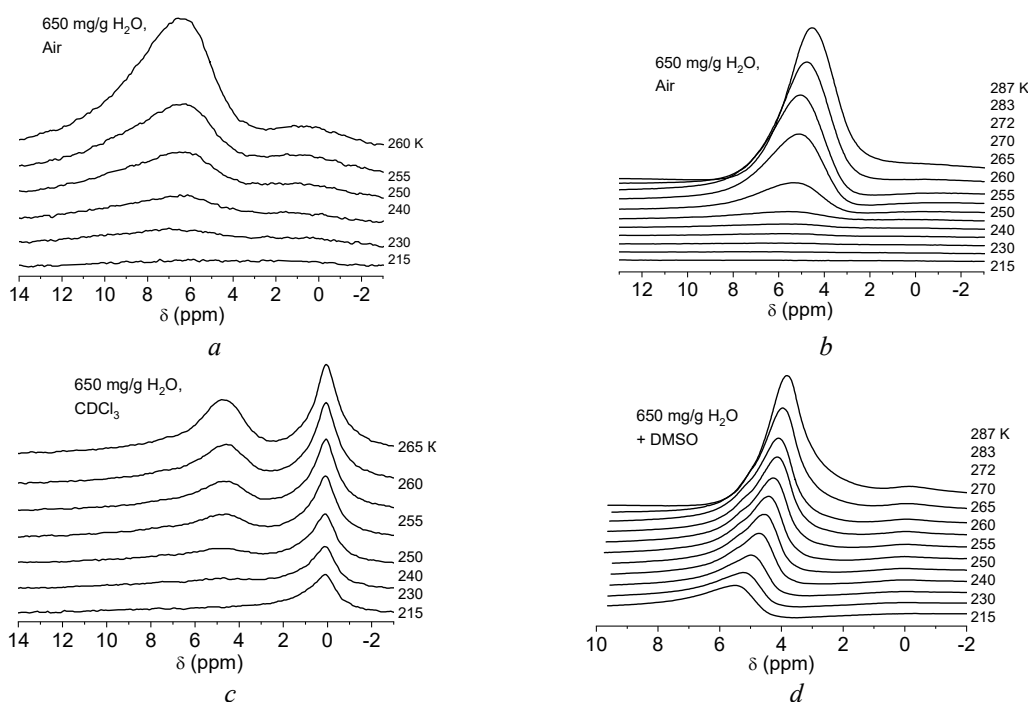

Fig. 3. ¹H NMR spectra of water in the interparticle gaps of methyl silica (*h* = 650 mg/g) in an air environment (*a, b*) with additions of CDCl₃ (*c*) and DMSO (*d*) taken at different temperatures

Determining the temperature dependence of the concentration of non-freezing water $C_{uw}(T)$ by the value of the signal intensity according to the method described in detail in [10–13], the amounts of strongly and weakly bound water (SBW and WBW, respectively), as well as thermodynamic characteristics can be calculated for these layers (Fig. 5 *a, b* and Table).

Usually weakly bound (WBW) water can be considered the part of water that melts at a temperature $T > 265$ K (Fig. 4 *c, d*). For strongly hydrated systems, the WBW part may not differ in its properties from bulk water [12]. Water that melts at lower temperatures is referred to as strongly bound water (SBW).

In the Table values of the amount of strongly and weakly bound water (C_{uw}^S and C_{uw}^W), the interfacial energy (γ_S) and the maximum reduction of the Gibbs free energy in the strongly bound water layer (ΔG^S) for all studied systems are given. The main part of interfacial water is in the form of clusters of strongly associated water, which interacts weakly with the surface. Distributions by radii of water clusters are shown in Fig. 5. Several maxima are observed in these distributions in the region $R = 0.5–10$ nm. A significant part of water is part of clusters with a radius of 50 nm or more. That is, in the process of mechanical processing, water is dispersed and the interparticle cavities are filled with it, and the water is in the form of a separate phase, and the interphase water clusters interact with the surface mainly by the Van der Waals mechanism. Despite the relatively large amount of water in the interparticle gaps, no more than 10 mg/g of interfacial water is strongly bound. It is probably water that is in the form of clusters with a radius $R < 5$ nm.
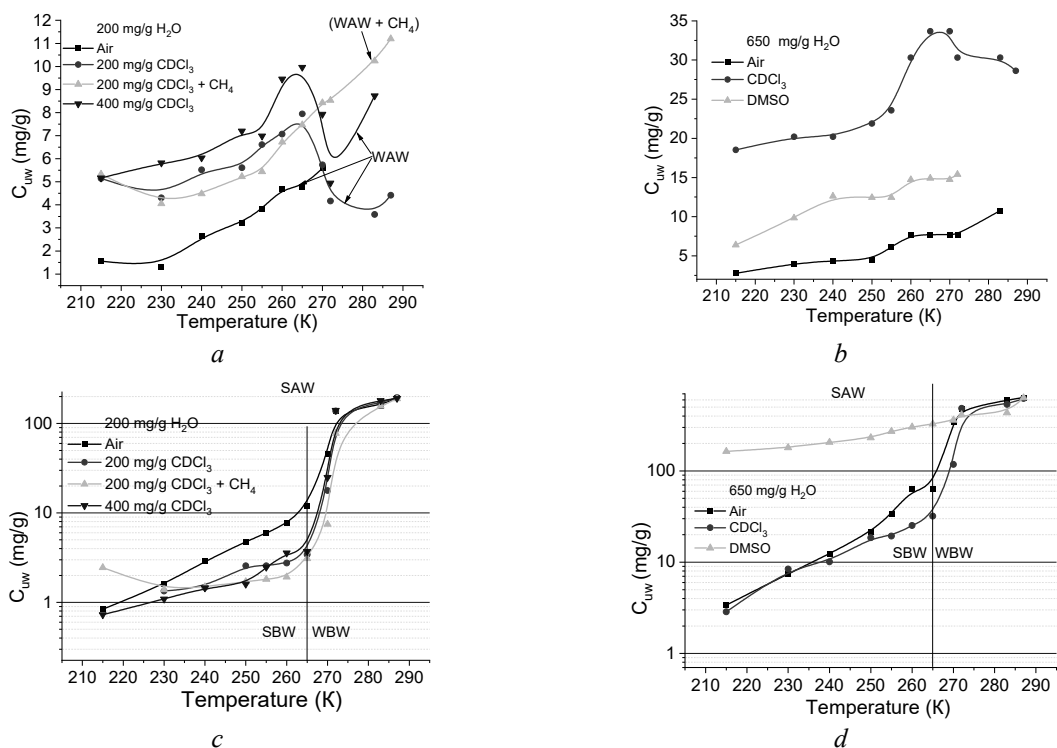
Fig. 4. Temperature dependences of the concentration of weakly (*a*, *b*) and strongly associated (*c*, *d*) water in the interparticle gaps of methyl silica
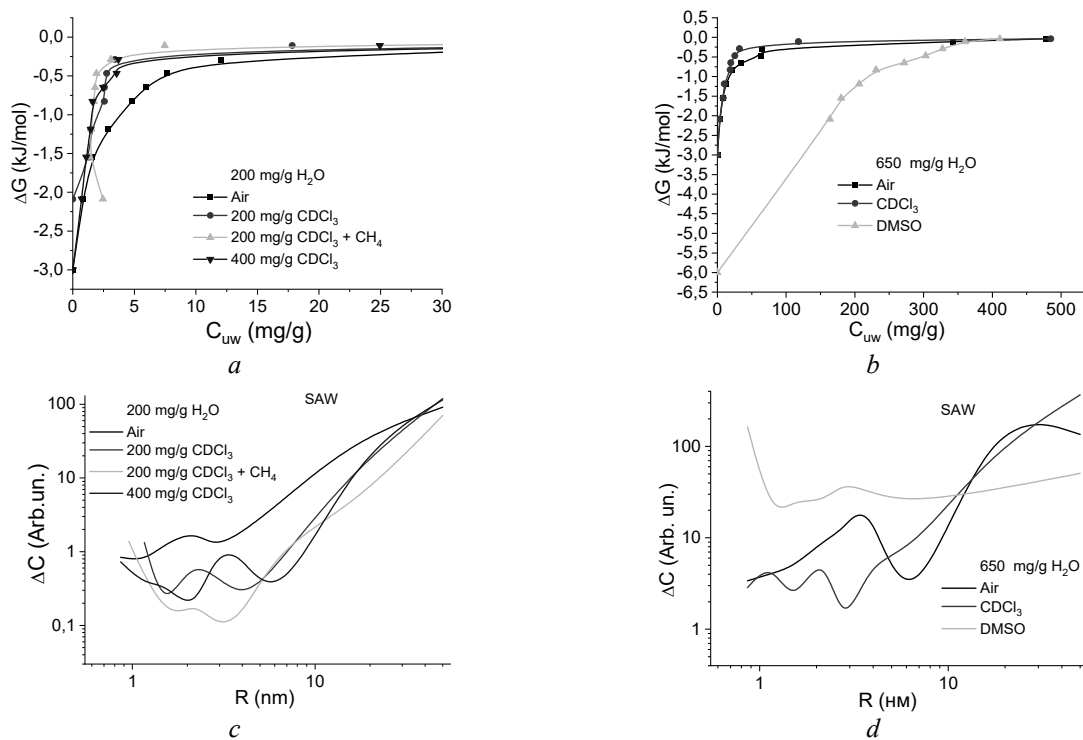

Fig. 5. Dependences of the Gibbs free energy change on the concentration of non-freezing water (*a*, *b*) and the distribution of interphase water cluster radii in hydrated powders of methyl silica and the influence of some organic substances on them (*c*, *d*)

Table. Characteristics of layers of non-freezing water (SAW) in hydrated methyl silica powders in the presence of organic substances

Environment	h, mg/g	C_{uw}^{S}, mg/g	C_{uw}^{W}, mg/g	ΔG^{S}, kJ/mol	γ_{S}, J/g
Air	200	15.0	185.0	-3	1.33
200 мг/г CDCl₃		4.0	196.0	-2	0.87
200 мг/г CDCl₃+CH₄		2.0	198.0	-3	0.27
400 мг/г CDCl₃		3.0	197.0	-3	0.94
Air	650	8.0	642.0	-3	6.80
CDCl₃		2.5	647.5	-3	4.30
DMSO-D₆		320.0	330.0	-6	45.50

It follows from the data in the table that the addition of chloroform significantly reduces the value of the interfacial energy and the amount of strongly bound water. This occurs due to the preferential adsorption on the hydrophobic surface of chloroform and its partial displacement of strongly associated water clusters into gaps of a larger radius [13]. A significant increase in interfacial energy in the presence of DMSO is due to solvation effects. At the same time, the difference in the values of the interfacial energy in air and organic media determines the energy of formation of the water-DMSO solution.

CONCLUSIONS

In pre-compacted methyl silica, under the influence of mechanical loads, the distribution of water in the gaps between particles occurs quickly enough in 20–30 seconds.

The main part of the interfacial water is in the form of large clusters, or nanodroplets, which freeze at a temperature close to 273 K. After freezing of this water, signals of strongly and weakly associated water are observed in the spectra, which melts at temperatures of 215–368 K. It is likely that the freezing of weakly associated water occurs by the formation of clusters in which closely spaced water molecules interact not through hydrogen bonds, but through dipole-dipole interactions.

In the presence of chloroform, the amount of weakly associated water increases several times. This is explained by the possibility of the formation of chloroform hydrates, in which the mobility of water molecules is approximately the same as in strongly associated water clusters. If joint adsorption of chloroform and methane is carried out on the hydrated surface of AM-1, under the influence of CH₄, the weakly mobile WAW is transformed into methane hydrates in quasi-liquid and solid states, while only mobile forms of hydrates are recorded in the spectra.

DMSO reduces the possibility of formation of weakly associated water, but a certain amount of it is fixed even in the medium of liquid DMSO. At the same time, the freezing of water in systems containing DMSO occurs at much lower temperatures, which is due to solvation of water and DMSO molecules. The difference in interphase energy in air and organic media determines the solvation energy.

Вода у гідрофобному оточенні та вплив на неї деяких органічних речовин

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Методом низькотемпературної ^1H ЯМР-спектроскопії досліджено будову води в міжчастинкових проміжках метилкремнезему. Показано, що основна частина міжфазної води знаходиться у вигляді великих кластерів, чи нанокрапель, які замерзають при температурі близько 273 К. Після замерзання цієї води в спектрах спостерігаються сигнали сильно- та слабкоасоційованої води, яка тане при 215–368 К. Ймовірно, замерзання слабкоасоційованої води відбувається шляхом утворення кластерів, в яких близько розташовані молекули води взаємодіють не через водневі зв'язки, а диполь-дипольні взаємодії. В присутності хлороформу кількість слабкоасоційованої води зростає в декілька разів. Це пояснюється можливістю формування гідратів хлороформу, в яких рухливість молекул води приблизно така ж, як і в кластерах сильноасоційованої води. Якщо на гідратованій поверхні метилкремнезему відбувається спільна адсорбція хлороформу та метану, під впливом CH_4 слабкорухлива слабкоасоційована вода трансформується в гідрати метану, що знаходяться в квазірідкому та твердому станах, при цьому в спектрах фіксуються тільки рухливі форми гідратів. ДМСО зменшує можливість формування слабкоасоційованої води, проте певна її кількість фіксується навіть в середовищі рідкого ДМСО. При цьому замерзання води в системах, що містять ДМСО відбувається при значно нижчих температурах, що обумовлено процесами сольватації молекул води та ДМСО. Різниця в величинах міжфазної енергії в повітряному та органічному середовищах визначає енергію сольватації.

Ключові слова: *гідратований метилкремнезем, сильно- і слабкоасоційована вода, гідрати, ^1H ЯМР-спектроскопія*

REFERENCES

1. Dore J. Structural Studies of Water in Confined Geometry by Neutron Diffraction. *Chem. Phys*. 2000. **258**(2–3): 327.
2. Sinitsin V.V., Ponyatovsky E.G., Kolesnikov A.I., Dahlborg U., Calvo-Dahlborg M. Thermodynamic Properties and Structural Futires of Water an Normal and High Pressures. *Solid States Ionics*. 2001. **145**(1–4): 415.
3. Chaplin M.F. A Proposal for Structuring of Water. *Biophys. Chem*. 1999. **83**(3): 211.
4. Mitra R.K., Verma P.K., Pal S.K. Exploration of the Dynamical Evolution and the Associated Energetics of Water Nanoclusters Formed in a Hydrophobic Solvent. *J. Phys. Chem. B*. 2009. **113**(14): 4744.
5. D'Arrigo G., Maisano G., Mallamace F., Migliardo P., Wanderlingh F. Raman Scattering and Structure of Normal and Supercooled Water. *J. Chem. Phys*. 1981. **75**(9): 4264.
6. Ratcliffe C.I., Irish D.E. Vibrational Spectral Studies of Solutions at Elevated Temperatures and Pressures. 5. Raman Studies of Liquid Water up to 300 °C. *J. Phys. Chem*. 1982. **86**(25): 4897.
7. Derjaguin B.V., Rabinovich Y.I., Churaev N.V. Measurement of forces of molecular attraction of crossed fibers as a function of width of air gap. *Nature*. 1977. **265**(5594): 520.
8. Galkin A.A., Lunin V.V. Water in sub- and supercritical states is a universal medium for chemical reactions. *Uspekhi Khimii*. 2005. **74**(1): 24. [in Russian].
9. Marsall W., Jones E. Liquid–vapor critical temperatures of aqueous electrolyte solutions. *J. Inorg. Nucl. Chem*. 1974. **36**(10): 2313.
10. Turov V.V., Gun'ko V.M. *Clustered water and ways to use it*. (Kyiv: Naukova dumka, 2011). [in Russian].
11. Gun'ko V.M., Turov V.V., Gorbyk P.P. *Water at Interface*. (Kyiv: Naukova Dumka, 2009). [in Russian].
12. Gun'ko V.M., Turov V.V. *Nuclear Magnetic Resonance Studies of Interfacial Phenomena*. (New York: Taylor&Francis, 2013).
13. Gun'ko V.M., Turov V.V., Bogatyrev V.M., Zarko V.I., Leboda R., Goncharuk E.V., Novza A.A., Turov A.V., Chuiko A.A. Unusual Properties of Water at Hydrophilic/Hydrophobic Interfaces. *Adv. Colloid Interface Sci*. 2005. **118**(1–3): 125.
14. Gun'ko V.M., Turov V.V., Pakhlov E.M., Krupska T.V., Borysenko M.V., Kartel M.T., Charmas B. Water interactions with hydrophobic versus hydrophilic nanosilica. *Langmuir*. 2018. **34**(40): 12145.

15. Gun'ko V.M., Turov V.V., Pakhlov E.M., Matkovsky A.K., Krupska T.V., Kartel M.T., Charmas B. Blends of amorphous/crystalline nanoalumina and hydrophobic amorphous nanosilica. *J. Non-Cryst. Solids*. 2018. **500**: 351.

16. Gun'ko V.M., Turov V.V., Protsak I., Krupska T.V., Pakhlov E.M., Dong Zh. Interfacial phenomena in composites with nanostructured succinic acid bound to hydrophilic and hydrophobic nanosilicas. *Colloid Interface Sci. Commun.* 2020. **35**: 100251.

17. Turov V.V., Krupska T.V. Influence of Mechanical Loads on the State of Water in the Hydrophobic Environment of Methyl Silica Particles. *Theor. Exp. Chem*. 2022. **58**(1): 48.

18. Krupska T.V., Turov V.V., Gunko V.M., Kartel M.T. Method of transferring a mixture of hydrophilic and hydrophobic silica into an aqueous medium by using high mechanical loads. Utility model patent N 138023, publ. 11.11.2019 N 21, announced on 24.05.2019 [in Ukrainian]

19. Patent 138129. The method of transferring hydrophobic silica into an aqueous environment by using high mechanical loads. Krupska T.V., Turov V.V., Kartel M.T. 2019. [in Ukrainian].

20. Turov V.V., Gun'ko V.M., Krupska T.V., Kartel M.T. Influence of solid and liquid hydrophobic compounds on characteristics of water located in an adsorption layer of a hydrophilic component of the system. *Him. Fiz. Tehnol. Poverhni.* 2018. **9**(4): 341.

21. Gun'ko V.M., Turov V.V., Krupska T.V., Pakhlov E.M. Behavior of water and methane bound to hydrophilic and hydrophobic nanosilikas and their mixture. *Chem. Phys. Lett.* 2017. **690**: 25.

22. Gun'ko V.M., Turov V.V., Krupska T.V. Interfacial behavior of methane and organic solvents with low freezing points upon interaction with hydrophilic and hydrophobic nanosilicas. *Him. Fiz. Tehnol. Poverhni.* 2018. **9**(2): 107. [in Russian].

23. Kinney D.R., Chaung I-S., Maciel G.E. Water and the Silica Surface as Studied by Variable Temperature High Resolution ^{1}H NMR. *J. Am. Chem Soc*. 1993. **115**(15): 6786.

24. Derome E. *Modern NMR methods for chemical research.* (Moscow: Mir, 1992). [in Russian].

25. Abragam A. *The Principles of Nuclear Magnetism.* (UK: Oxford University Press: Oxford, 1961).

26. Iler R.K. *The Chemistry of Silica. Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry.* (Wiley: Chichester, 1979).

27. Glushko V.P. *Thermodynamic Properties of Individual Substances.* (Moscow: Science, 1978). [in Russian].

28. Aksnes D.W., Førland K., Kimtys L. Pore size distribution in mesoporous materials as studied by ^{1}H NMR. *Phys. Chem. Chem. Phys.* 2001. **3**(15): 3203.

29. Petrov O.V., Furó I. NMR cryoporometry: Principles, application and potential. *Prog. Nucl. Magn. Reson. Spectrosc.* 2009. **54**(2): 97.