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**Use of microcoagulation effect to control water binding in a  
heterogeneous polymethylsiloxane/silica/water system**

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The binding of water in heterogeneous systems containing polymethylsiloxane (PMS) pyrogenic nanosilica (A-300) water and the surface-active substance decamethoxin (DMT) was studied. Composite systems were created using metered mechanical loads. The low-temperature  $^1\text{H}$  NMR spectroscopy was used to measure the structural and thermodynamic parameters of bound water. It is shown that when filling PMS interparticle gaps with hydrocompaction, the interfacial energy of water in the interparticle gaps of hydrophobic PMS with the same hydration is twice as large as the interfacial energy of water in hydrophilic silica A-300. This is due to the smaller linear dimensions of the interparticle gaps in the ICP compared with the A-300. In the composite system, A-300/PMS/DMT/ $\text{H}_2\text{O}$ , a non-additive growth of water binding energy is observed, which is likely due to the formation under the influence of mechanical load in the presence of water of microheterogeneous sites, consisting mainly of the hydrophobic and hydrophilic components (microcoagulation). Thus, using mechanical loads, the adsorption properties of composite systems can be controlled.

**Keywords:**  $^1\text{H}$  NMR spectroscopy, silica, methylsiloxane, decamethoxin, microcoagulation.

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## **Introduction**

One of the basic principles of formation of stable heterophase liquids is their desire to minimize free energy [1]. In particular, non-miscible liquids (eg, water and oil) exist in the form of spatially separated layers, and their mixing in ultrasound treatment is thermodynamically unprofitable, since it is accompanied not by a decrease but by an increase in free energy. Surfactants having a high affinity for both liquids make it possible to create a stable colloidal system in which the non-miscible phases are separated by a thin molecular layer of surfactants. The increase in free energy due to the dispersion of one of the liquids (formation of a micellar structure) is compensated by its decrease due to the molecular interactions of the surfactants with the hydrophobic and hydrophilic components of the heterogeneous system [2].

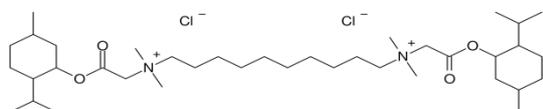
Unlike liquids, solids with different hydrophobic-hydrophilic properties (in the dry state), after mechanical stirring, can form a virtually homogeneous mixture, which is a part of the aggregates and interact with the

help of Van der Waals forces. The difference in the interaction energies of hydrophobic, hydrophilic and mixed particles is small. However, the possibility of their coexistence of heterogeneous particles in the volume can be violated by the addition of a liquid phase (surfactant, water or hydrophobic fluid) [3, 4]. The spontaneous distribution of components in mixtures of powders or viscous liquids (microcoagulation) caused by Brownian motion cannot or is carried out very slowly, however, this process can be significantly accelerated under the influence of mechanical stress applied to the composite system during mixing, especially in the presence of surfactants. Since coagulation reduces the free energy of a multicomponent system, it must lead to an increase in the binding energy of the liquid components to the surface of the dispersed particles.

If a heterogeneous system, based on fine substances, contains water (or other liquid with a known freezing temperature), its melting temperature (freezing) can be reduced by adsorption interactions with the particle surface [5] or the transition to a clustered (nanoscale) state [6]. The freezing point depression is due to clustering and is determined by the Gibbs-Thomson

equation [7, 8]. The lower the melting point, the greater the adsorption interactions or the smaller the radius of nanopapels (clusters) of the liquid. An integral indicator that can be used to judge the free energy reduction in heterogeneous systems containing the same amount of water is the amount of interfacial energy of water, which is determined from the data of low-temperature  $^1\text{H}$  NMR spectroscopy [6, 9-11].

The purpose of this work was to develop methods for managing the binding energy of water in the silica/polymethylsiloxane/water composite system by the addition of surfactant – decamethoxine (DMT) and mechanical loading using a microcoagulation process. Decamethoxine is a synthetic antiseptic and antifungal preparation for topical use, which is at the same time a cationic surfactant having hydrophobic and hydrophilic moieties:



## I. Materials and methods

### 1.1. Materials

Polymethylsiloxane (PMS) adsorbents are hydro- or xerogels of methylsilicic acid, synthesized from methyl trichlorosilane [12-14]. In the first stage, a non-porous polymethylsiloxane is formed in reaction with water, which is then dissolved in a solution of alkali (NaOH or KOH). This produces sodium (or potassium) methyl silicone, which, after addition of the amount of acid (HCl or  $\text{H}_2\text{SO}_4$ ) required to neutralize the alkali, is converted to methyl silica gel. This gel is washed with water from residues of acid and salt, after which it can be used as an enterosorbent in both gel and dried states [15, 16].

The starting material was 6 % methyl silicic acid gel, manufactured by "Creomapharm" (Ukraine), which is commercially available as an enterosorbent for the treatment of digestive disorders. After drying at room temperature, the water content of dry polymethylsiloxane was less than 1 wt. % by weight of dry matter. Conversion to the aqueous medium was carried out according to the procedure described in [17-19] for other hydrophobic materials, by grinding the PMS powder with an equal amount of distilled water to form a homogeneous PMS/water composite, the bulk density of which in the wet state was  $C_d = 500 \text{ g/dm}^3$ . Pyrogenic silica brand A-300 with a specific surface area of BET  $S_{\text{BET}} = 285 \text{ m}^2/\text{g}$  and a bulk density of  $C_d = 60 \text{ g/dm}^3$  (State Enterprise "Kalush Test Experimental Plant of Surface Chemistry Institute of National Academy of Science of Ukraine"). For the preparation of the composite system A-300/PMS/DMT, dry ingredients were taken in the ratio of 30/68/2, and PMS/DMT – 30/2, which were carefully triturated in a porcelain mortar until a homogeneous mixture was formed. Moisture of the sample was performed by adding to the dry powder PMS

or composite equal to the mass of the amount of distilled water. Hydraulic compaction of the material occurred [20, 21] and its bulk density was  $C_d = 200 - 300 \text{ g/cm}^3$ . It was assumed that under the influence of mechanical loading in the sample will be able to form microheterogeneous areas, consisting mainly of hydrophobic or hydrophilic components. The amount of water for all systems studied was equal to  $C_{\text{H}_2\text{O}} = 1000 \text{ mg/g}$  and sufficient to fill the bulk of the interparticle gaps.

### 1.2. $^1\text{H}$ NMR spectroscopy

NMR spectra were obtained on a 400 MHz high resolution NMR spectrometer (Varian "Mercury"). The temperature in the sensor was regulated by a Bruker VT-1000 thermocouple with an accuracy of  $\pm 1$  deg. The signal intensities were determined by measuring the peak area using the signal decomposition procedure into its components in the assumption of a Gaussian line shape, zero line optimization and phase with an accuracy that was not lower than  $\pm 5 \%$  for well separated signals. To prevent water cooling in the studied objects, the measurement of the concentration of non-freezing water was carried out by heating the samples, pre-cooled to 210 K. The NMR technique, the determination of thermodynamic characteristics and the calculation of radius of clusters of interfacial water are described in detail in [9-11].

As the temperature decreases, the intensity of the water signal decreases due to its partial freezing in the interparticle gaps. Then, knowing the total amount of water in the samples ( $C_{\text{H}_2\text{O}} = 1000 \text{ mg/g}$ ), the integral value of the water signal intensity can be used to determine the freezing water concentration ( $C_{\text{uw}} = (I_T/I_{280}) \cdot 1000$ ) for each temperature ( $I_T$ ) and construct the dependences  $C_{\text{uw}}(T)$ . The process of freezing (melting) of interfacial water, localized in a solid porous matrix, occurs in accordance with the changes in the free Gibbs energy caused by the influence of the surface: it is smaller the farther from the surface the water layer is studied. At  $T = 273 \text{ K}$  freezes water, the properties of which do not differ from the volumetric, and as the temperature decreases (without taking into account the effect of hypothermia) freeze the layers of water, which are closer to the surface, and for the interfacial water is fair:

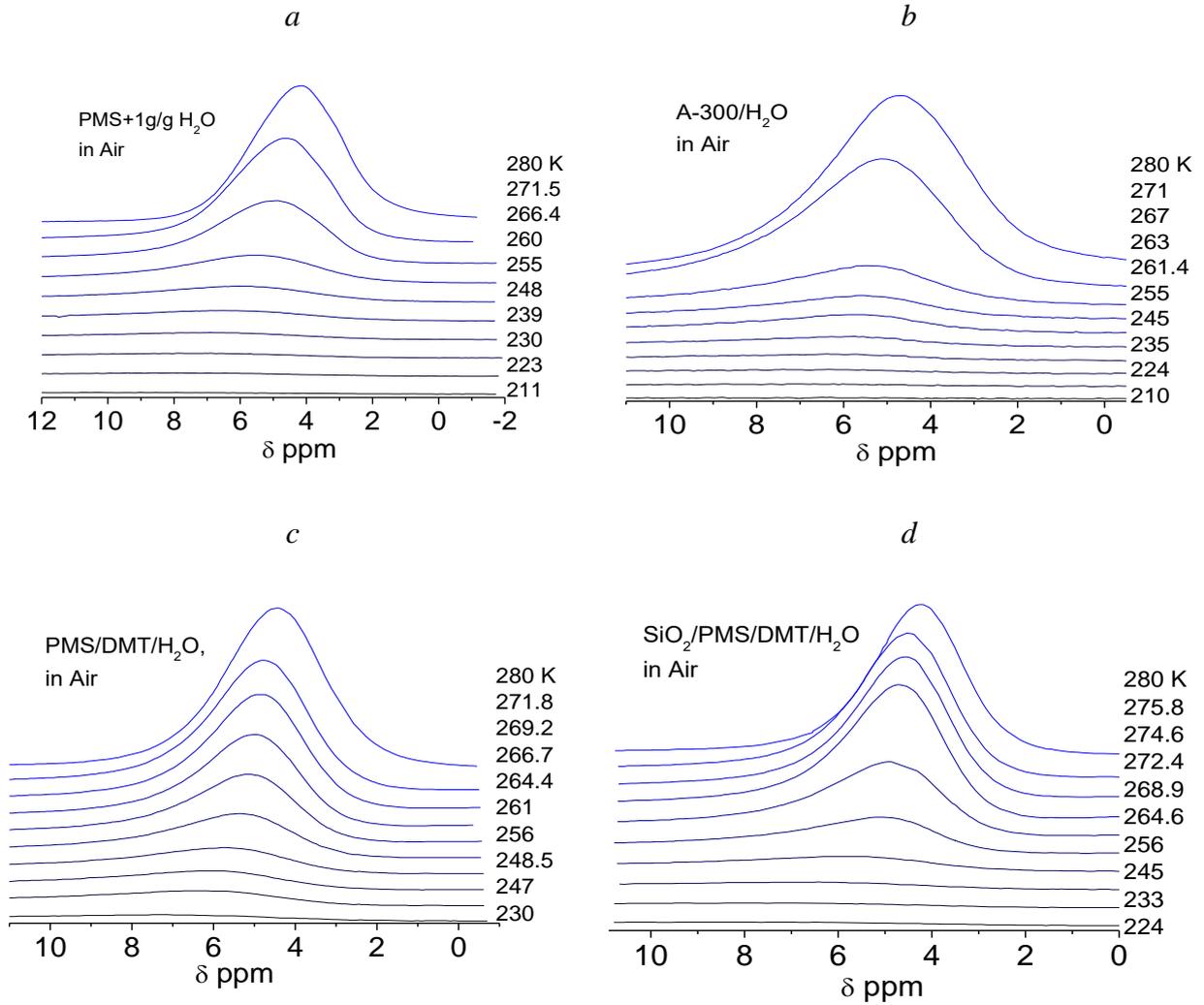
$$\Delta G_{\text{ice}} = -0.036(273.15 - T), \quad (1)$$

where the numerical coefficient is a parameter that is related to the temperature coefficient of change of Gibbs free energy for ice [22].

The interfacial energy of solids or biopolymers was defined as the modulus of the total reduction of free energy of adsorbed water, due to the presence of an internal boundary of the phase-separation of water-polymer by the formula:

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

where is the total amount of freezing water at  $T = 273 \text{ K}$ .



**Fig. 1.** The spectra of  $^1\text{H}$  NMR of water in hydrated PMS powders, A-300 silica and composite systems based on them were taken at different temperatures.

The amount of interfacial energy is a convenient parameter that allows you to compare the binding energy of water in different systems, especially if the amount of water in them is the same.

In this case, the Gibbs-Thomson equation [14, 15] can be used to determine the geometric dimensions of the bounded solid surface of nanoscale fluid aggregates [14, 15], which relates the radius of spherical or cylindrical pores ( $R$ ) to the freezing point depression:

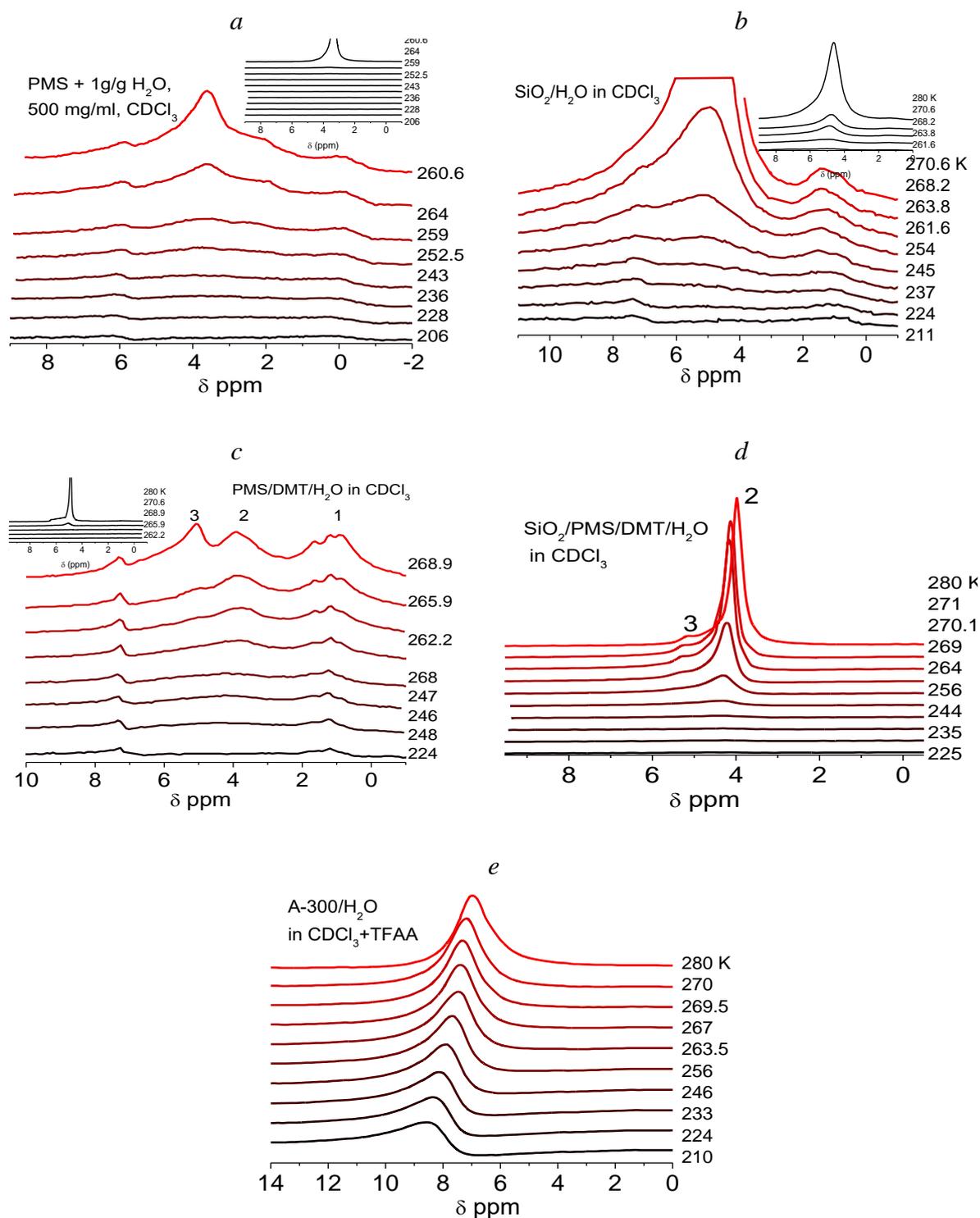
$$\Delta T_m = T_m(R) - T_{m,\infty} = \frac{2\sigma_{sl}T_{m,\infty}}{\Delta H_f \rho R} \quad (3)$$

where  $T_m(R)$  is the melting temperature of the ice localized in the pores with radius  $R$ ,  $T_{m,\infty}$  is the melting temperature of the bulk ice,  $\rho$  is the solid phase density,  $\sigma_{sl}$  is the interaction energy of the solid with the liquid, and  $\Delta H_f$  is the bulk enthalpy of melting. In the case where water fills the entire interparticle space, formula (3) allows to determine the radius distribution of interparticle gaps.

## II. Results and discussion

Taken at different temperatures, in the process of heating the samples from 210 - 230 K to 280 K, the spectra of  $^1\text{H}$  NMR of water in the studied systems in air are shown in Fig. 1, and in the deuterium chloroform medium – in Fig. 2. In the spectra of individual substances and their composites, under conditions of the same hydration ( $C_{H_2O} = 1000$  mg/g) and filling of a large part of the interparticle space with water, one signal of water is observed, the chemical shift of which increases from  $\delta_H = 4 - 4.5$  ppm. at  $T = 280$  K to  $\delta_H = 6.5 - 7$  ppm at  $T = 210 - 230$  K. The signal intensity decreases with decreasing temperature with partial freezing of the interfacial water.

Despite the high hydration of the studied systems, the hydrophobic environment of chloroform significantly affects the appearance of the spectra of the interfacial water (Fig. 2, a-d). Several freezing water signals differ in the spectra, differing in chemical shift value ( $\delta_H$ ). Signal 1 ( $\delta_H = 1$  ppm) can be attributed to water clusters that do not participate in the formation of hydrogen bonds [10, 11] (weakly associated water), signal 2 ( $\delta_H =$



**Fig. 2.** The <sup>1</sup>H NMR spectra of water in hydrated PMS powders, A-300 silica and composite systems based on deuterium chloroform (a-d) and 1/7 CDCl<sub>3</sub>/TFAA (e) mixtures were taken at different temperatures.

3.5 - 4 ppm). ) - to water clusters with partially destroyed hydrogen bonds and signal 3 ( $\delta_H = 5$  ppm) to clusters of highly associated water close in structure to liquid water. In addition, the spectra show signals of the unproteinated component of chloroform (CHCl<sub>3</sub>), and in samples containing DMT also the signals of aliphatic protons of hydrocarbon chains.

The appearance in the spectra of several water

signals indicates a slow proton (or molecular) exchange between water molecules that are part of different clusters of interfacial water in the NMR time scale. In general, it can be stated that the environment of weakly polar chloroform exhibits chaotropic (disordered) influence on water localized in the interparticle gaps [23, 24]. Compared with the samples in the air environment (Fig. 1), the region of strong changes in the signal

intensity is shifted towards high temperatures (near  $T = 273$  K). Therefore, under the influence of chloroform, there is a partial displacement of water from the narrowest interparticle gaps.

Then the exchange processes are accelerated, if 15 wt.% of deuterium trifluoroacetic acid (TFAA) is added to the chloroform medium and in the spectra, a single signal shifted to the region of large chemical shift values ( $\delta_H = 7 - 8.5$  m) is recorded in all available temperature range measurements  $h$ ) (Fig. 2e). The intensity of the proton signal with temperature changes slightly, due to the complication of the freezing process of water from a concentrated solution of strong acid.

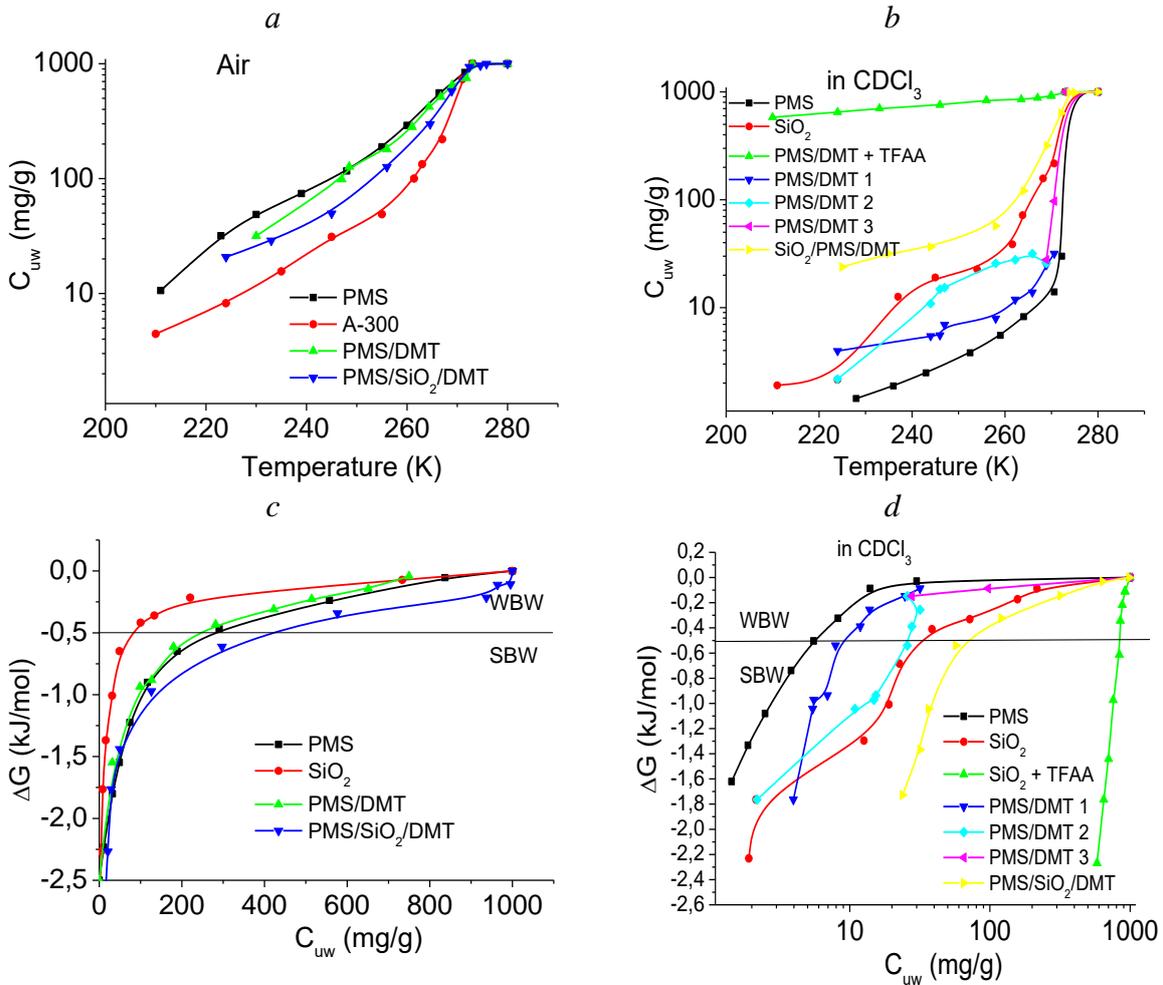
The dependences of the concentration of freezing water on temperature and based on them in accordance with equation (1), the dependence of the Gibbs free energy change on the concentration of freezing water  $\Delta G(C_{uw})$  are shown in Fig. 3. For the PMS/DMT system (Fig. 3b, d), the figure shows the  $C_{uw}(T)$  and  $\Delta G(C_{uw})$  dependencies for all three interfacial water signals observed in the spectra in Fig. 2c.

If one considers that the part of water for which the Gibbs free energy  $\Delta G < -0.5$  kJ/mol is reduced is

strongly bound [10, 11], based on the dependences given in Fig. 3 c, d can be calculated parameters of layers of interfacial water, which are summarized in table 1. In this case,  $\Delta G^S$  is the maximum reduction of free energy in the layer of strongly bound water,  $C_{uw}^S$  and  $C_{uw}^W$  are the concentration of strongly and weakly bound water, respectively, and  $\gamma_S$  is the interphase energy equal to the total free energy reduction of all interphase water, which is determined respectively to equation (2).

In Fig. 4 shows the radius distributions of water clusters localized in the interparticle gaps of the systems studied in air (a) and  $CDCl_3$  (b).

According to the above data, in the air environment the total binding energy of water in the hydrated hydrophobic PMS powder is more than twice the binding energy of water in hydrophilic silica (Table 1). Since the specific surface of the PMS can reach  $500$  m<sup>2</sup>/g, it can be concluded that the binding of water is determined not by the hydrophobic properties of the surface, but by the morphology of the internal interparticle space (Fig. 4a). The maximum on the distribution curve over the radii of water-filled pores (interparticle gaps) in the PMS is  $R = 4$  nm, which is much smaller than in silica ( $R = 10$  nm).



**Fig. 3.** The temperature dependences of the change in the concentration of freezing water and calculated on the basis of the dependence of the change of Gibbs free energy on the concentration of freezing water in the air (a, c) and in the medium  $CDCl_3$  (b, d).

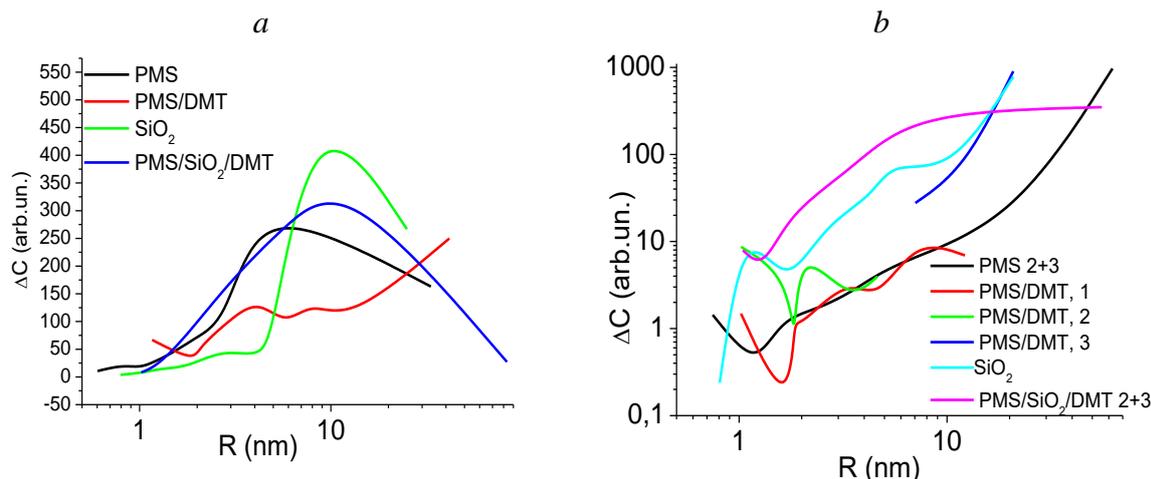


Fig. 4. Distribution over the radii of clusters of adsorbed water in air (a) and in medium  $\text{CDCl}_3$  (b).

Table 1

Characteristics of water layers in hydrated PMS and composite systems based on it containing 1000 mg/g of water

System	Medium $\text{mg}/\text{cm}^3$	$\Delta G^S$ , $\text{kJ}/\text{mol}$	$C_{uw}^S$ , $\text{mg}/\text{g}$	$C_{uw}^W$ , $\text{mg}/\text{g}$	$\gamma_s$ , $\text{J}/\text{g}$
PMS	Air	-2.5	280	720	23.8
	$\text{CDCl}_3$	-2.5	10	990	1.3
$\text{SiO}_2$	Air	-2.2	80	920	11.2
	$\text{CDCl}_3$	-3	35	965	6.2
PMS/DMT	Air	-3	250	750	20.9
	$\text{CDCl}_3$	-3.5(1)* -2.2(2)	9(1) 25(2)	966(3)	5.3
PMS/ $\text{SiO}_2$ /DMT	Air	-3.5	425	575	32.2
	$\text{CDCl}_3$	-2.5	70	930	10.6

\*The values obtained for signals 1, 2 and 3 are indicated in brackets.

As the average radius of the interparticle gaps decreases, the values of the interfacial energy increase (Table 1). The addition of a small amount (2 wt.%) Of the surfactant (DMT) to the PMS results in a significant change in the morphology of the interparticle space and a slight decrease in the interfacial energy up to 20.9 J/h. On the distribution curve  $\Delta C(R)$ , several maxima appear, both in the region of small and large values of  $R$ . However, in a composite system containing surfactants, hydrophilic and hydrophobic components, the value of  $\gamma_s$  increases to 32.2 J/g. This indicates the formation under the influence of mechanical loading of the composite with a minimum amount of free energy. Probably, in the presence of surfactants, aggregates of PMS and A-300 particles aggregate and formation of spatially ordered regions (microcoagulation), which contain interparticle gaps, where much of the water is highly bound (Table 1). The rest of the water fills in the gaps between hydrophobic and hydrophilic aggregates, with the distribution across the radii of the water-filled cavities having one wide maximum at  $R = 10$  nm (Fig. 4a).

The environment of the low-polar organic solvent  $\text{CDCl}_3$  reduces the energy of interaction of water with the surface (Table 1), both for the hydrophobic and

hydrophilic components of the composite system. Most clearly this effect can be seen from the comparison of the quantities of interfacial energy in air and organic environments. The maximum effect is observed for hydrated PMS – the amount of interfacial energy decreases from 23.8 to 1.3 J/h. For other systems, including hydrophilic silica, the value of  $\gamma_s$  decreases by 2-3 times in the  $\text{CDCl}_3$  medium. Comparing the magnitudes of the interphase energies (Table 1) and the distribution across the radii of the water-filled interparticle gaps (Fig. 4b), we can conclude that the decrease in water binding when using the organic medium is manifested in a significant increase in the average size of non-freezing water clusters (Fig. 4b). Most of the water fills the interparticle gaps, whose radius is  $R > 10$  nm, while the narrow pores are filled with chloroform. Chloroform molecules are likely to easily penetrate into the aqueous medium, filling the interparticle gaps of PMS and A-300 aggregates, diffusing over the surface of solids. The result is a change in the morphology of the interparticle space and the redistribution of the aqueous and organic phases.

It can be assumed that in the composite system A-300/PMS/DMT in the air environment, the hydrophobic

part of the surfactant molecules mainly contacts the surface of the PMS, while the hydrophilic end groups form hydrogen bonds with silanol groups or hydroxyl groups of water on the surface of the silica particles. thus providing the minimum free energy values of the system. In a hydrophobic environment, the composite particles easily form a stable suspension, despite the high concentration of interparticle water. In this case, most likely, the hydrophobic regions of the surfactant molecules are in contact with chloroform, and hydrophilic - with water, which is part of the particles of the composite system.

In a composite system containing hydrophobic and hydrophilic components (PMS and A-300) in the presence of the surfactant - decamethoxin, there is an additive increase in the binding energy of water, which is probably due to the formation under the influence of mechanical loading in the presence of water, microheterogene (microcoagulation), consisting mainly of hydrophobic and hydrophilic components. Thus, the mechanical wetting can control the wetting process of hydrophobic powder composites.

## Conclusion

It is shown that when filling the inter-particle gaps of polymethylsiloxane by the method of hydro-sealing, the inter-phase energy of water in the inter-particle gaps of hydrophobic PMS with the same hydration is twice the inter-phase energy of water in hydrophilic silica. This is due to the smaller linear dimensions of the interparticle gaps in the PMS compared to the A-300.

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- [1] M.O. Mchedlov-Petrosyan, V.I. Lebed, O.M. Glazkova, O.V. Lebed, Colloid chemistry (Karazin KhNU, Kharkov, 2012) (in Ukrainian).
- [2] B.D. Deryagin, Success of chemistry, 48(4), 675 (1979) (<https://doi.org/10.1070/RC1979v048n04ABEH002332>) (in Russian).
- [3] V.M. Muller, Colloid chemistry, 58(5), 634 (1996) (in Russian).
- [4] I.F. Efremov, Periodic colloidal structures (Chemistry, Leningrad, 1971) (in Russian).
- [5] Yu. G. Frolov, Colloid chemistry course. Surface phenomena and disperse systems (Chemistry, Moscow, 1982) (in Russian).
- [6] V.M. Gun'ko, V.V. Turov, P.P. Gorbik, Water at the interface (Naukova dumka, Kyiv, 2009) (in Russian).
- [7] D.W. Aksnes, K. Forl, L. Kimtys, Phys. Chem. Chem. Phys., 3, 3203 (2001) (<https://doi.org/10.1039/B103228N>).
- [8] O.V. Petrov, I. Furó, Progr. NMR Spectroscopy 54(2), 97 (2009).
- [9] V.V. Turov, V.M. Gun'ko, Clustered water and ways to use it. (Naukova dumka, Kyiv, 2011). (in Russian).
- [10] V.M. Gun'ko, V.V. Turov, Nuclear Magnetic Resonance Studies of Interfacial Phenomena (CRC Press Boca Raton, 2013).
- [11] V.M. Gun'ko, V.V. Turov, V.M. Bogatyrev, V.I. Zarko, R. Lebeda, E.V. Goncharuk, A.A. Novza, A.V. Turov, A.A. Chuiko, Adv. Colloid Interface Sci. 118, 125 (2005) (<https://doi.org/10.1016/j.cis.2005.07.003>).
- [12] I.B. Slinyakova, T.I. Denisova, Organosilicon adsorbents: production, properties, application, (Naukova dumka, Kyiv, 1988) (in Russian).
- [13] Y.N. Shevchenko, B.M. Dushanin, N.I. Yashina, Silicon for the chemical industry (Norway, Sandefjord, 1996).
- [14] Yu.N. Shevchenko, B.M. Dushanin, A.V. Polyanskiy, N.I. Yashina, Hydrogels of methylsilicic acid as adsorbents of medium molecular metabolites and a method for their preparation (RU Patent 2111979, 1998) (in Russian).
- [15] I.A. Mayev, YU.N. Shevchenko, A.B. Petukhov, The clinical use of Enterogel in patients with pathology of the digestive system. New approaches to therapy (Ministry of Health of the Russian Federation, Moscow, 2000) (in Russian).
- [16] I.A. Volokhonskiy, N.M. Pokrasen, V.V. Turov, Ukr. Chem. Journal, 58(8), 640 (1992) (in Russian).
- [17] V.M. Gun'ko, V.V. Turov, E.V. Pakhlov, T.V. Krupskaya, M.V. Borysenko, M.T. Kartel, B. Charmas, Langmuir 34(40), 12145 (2018) (<https://doi.org/10.1021/acs.langmuir.8b03110>).
- [18] V.M. Gun'ko, V.V. Turov, E.V. Pakhlov, E.M. Matkovsky, T.V. Krupskaya, M.T. Kartel, B. Charmas, J. Non-Crystalline Solids, 500, 351 (2018) (<https://doi.org/10.1016/j.jnoncrysol.2018.08.020>).
- [19] V.V. Turov, V.M. Gun'ko, E.V. Pakhlov, T.V. Krupskaya, M.D. Tsapko, B. Charmas, M.T. Kartel, Colloid and Surf. A, 552, 39 (2018) (<https://doi.org/10.1016/j.colsurfa.2018.05.017>).

- [20] T.V. Krupskaya, V.V. Turov, V.N. Barvinchenko, K.O. Filatova, L.A. Suvorova, G. Iraci, M.T. Kartel, Adsorption Sci. & Technol., 36(1-2), 300 (2017) (<https://doi.org/10.1177/0263617417691768>).
- [21] V.M. Gun'ko, V.V. Turov, E.V. Pakhlov, T.V. Krupskaya, B. Charmas, Applied Surface Sci. 459, 171 (2018) (<https://doi.org/10.1016/j.apsusc.2018.07.213>).
- [22] V.P. Glushkov, Thermodynamic properties of individual substances (Nauka, Moscow, 1978). (in Russian).
- [23] M.F. Chaplin, Biophys. Chem., 83(3), 211 (2000) ([https://doi.org/10.1016/s0301-4622\(99\)00142-8](https://doi.org/10.1016/s0301-4622(99)00142-8)).
- [24] P.M. Wiggins, B.A.E. MacClement, Internat. Rev. Cytol., 108, 249 (1987) ([https://doi.org/10.1016/s0074-7696\(08\)61440-0](https://doi.org/10.1016/s0074-7696(08)61440-0)).

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## Використання ефекту мікрокоагуляції для керування зв'язуванням води у гетерогенній системі поліметилсилоксан/кремнезем/вода

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Вивчено зв'язування води в гетерогенних системах, що містять поліметилсилоксан, високодисперсний аморфний кремнезем, воду і поверхнево-активну речовину – декаметоксин. Композитні системи створювалися при використанні дозованих механічних навантажень. Методом низькотемпературної  $^1\text{H}$  ЯМР-спектроскопії вимірювалися структурні і термодинамічні параметри зв'язаної води. Показано, що при заповненні міжчастинкових зазорів поліметилсилоксану способом гідроущільнення, міжфазна енергія води при однаковій гідратованості вдвічі перевищує міжфазну енергію води в гідрофільному кремнеземі. Це пов'язано з меншими лінійними розмірами міжчастинкових зазорів в поліметилсилоксані порівняно з кремнеземом. В композитній системі, кремнезем/поліметилсилоксан/декаметоксин/вода спостерігається неадитивне зростання енергії зв'язування води, яке, ймовірно, обумовлене формуванням, під впливом механічного навантаження в присутності води, мікрогетерогенних ділянок, що складаються переважно з гідрофобної і гідрофільної компонентів (мікрокоагуляція). Таким чином, за допомогою механічних навантажень можна керувати адсорбційними властивостями композитних систем.

**Ключові слова:**  $^1\text{H}$  ЯМР-спектроскопія, кремнезем, поліметилсилоксан, декаметоксин, мікрокоагуляція, композитна система.