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HYDRATION FEATURES OF COMPOSITE SYSTEMS BASED ON HIGH-DISPERSED SILICA AND SUCROSE IN DIFFERENT MEDIA

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The aim of the research was to study the state of water in the hydrated sucrose powder, in its melt, and composite systems containing 3 parts of silica (A-300 or AM1) and 1 part of sucrose in air, low-polar organic solvent-deuteriochloroform and CDCl_3 medium with addition of strong acids by method of low-temperature ^1H NMR spectroscopy. It was demonstrated that at the joint mechanoactivation of sucrose with nano-silica, its amorphization takes place. In this case, the adsorption of water in such a composite is not accompanied by the dissolution process in interfacial water of the sucrose immobilized on the SiO_2 surface. It was found that the effect of sucrose solubility increasing accompanies the placement of the composite in a medium that does not dissolve water and sucrose, an organic solvent-deuteriochloroform. It was suggested that it is due to an increase the contact area of adsorbed water clusters with the sucrose surface. The maximal concentration of sucrose, which dissolves in interfacial water, is about 30% by weight. The replacement of hydrophilic silica A-300 by hydrophobic silica AM1, while maintaining the concentration ratio of components and the amount of adsorbed water, reduces the free energy of water binding in the composite system. The obtained results can be used in development of a new generation of enterosorbents.

Key words: low-temperature ^1H NMR spectroscopy, sucrose, wetting-drying, hydrophilic and hydrophobic silica, composite system.

High-dispersed silica (HDS aerosil, pyrogenic silica) is used in the pharmacopoeia of many countries as an auxiliary substance in the manufacture of dosage forms for more than thirty years. They have a complex of properties that make it possible to use it widely in the food industry, in biotechnology of agriculture, in medicine, pharmacy and laboratory practice. The carried out tests [1] have showed that the HDS exhibits high adsorption properties with respect to toxins of protein nature, can serve as an adaptogenic and immunostimulating agent. It has extremely low toxicity, even at high concentrations, is a source of silicium, which is necessary for the normal functioning of the nervous system and has many other useful properties. The US Food Authority has authorized the use of aerosil as a food additive [2]. Amorphous silicium dioxide has the registration number of food additive E 551.

Most of the properties of silica used in practice are due to the presence of $\equiv\text{SiOH}$ groups on its surface. They determine the high affinity of silica to many biomolecules [3–7]. With the participation of silanol groups, silica particles also interact with water molecules, which form clusters at small concentrations, the radius of which can be from one to several tens of nanometers [8]. With a high content of surface water, the water-silica system turns into a gel.

In recent years, many pharmaceutical companies produce composite systems that, in addition to HDS, contain flavor additives, in particular sucrose, glucose or sorbitol [9–11]. However, depending on the method of sugars administration, hygroscopicity and other physico-chemical properties, such as bulk density, specific surface area, and temperature resistance of the preparation

can vary within wide limits. The basis is the phenomenon of components of the composite system nanostructuring, which can be used to control its parameters. So, in the transition to a nanoscale state, water begins to dissolve poorly many polar molecules, including mineral acids [8, 12–14]. It can be expected that the adsorption of water to the HDS, with sucrose immobilized on its surface, will take place differently than in the case of interaction with sucrose crystals.

The purpose of this work was to study the state of water and the possibility of forming a water-sucrose solution in a cooled melt, high-dispersed powder and nanostructured sucrose immobilized on the surface of hydrophobic and hydrophilic nanosilica, as well as the influence of a weakly polar organic solvent and strong acid additives on this process.

As the main method of investigation, the low-temperature ^1H NMR spectroscopy was used [8, 15, 16], by which the presence of a solution and its concentration can be easily determined by the occurrence the signal of the hydroxyl groups of sucrose in spectra, by the magnitude of the chemical shift of bound water to assess the degree of its association (the number of hydrogen bonds in which each water molecule participates), and by the temperature dependence of the concentration of non-freezing water (C_{uw}) and sucrose — the size of surface clusters calculated in accordance with the Gibbs-Thomson equation [17, 18].

Materials and Methods

Materials. Food sucrose was studied, previously ground by grinding in a porcelain mortar, after which the size of its crystals was reduced to 1–10 microns. Then it was used for the immobilization on the surface of hydrophilic wetting-drying nanosilica of grade A-300 [19] with specific surface area $S = 220 \text{ m}^2/\text{g}$ and of hydrophobic nanosilica of grade AM1 with specific surface area $S = 285 \text{ m}^2/\text{g}$ (Kalush experimental plant of Chuiko Institute of Surface Chemistry). The gritted sucrose powder was mixed in a ratio of 1: 3 with nanosilica and their combined mechanoactivation was performed in a porcelain mortar for 10 min. Then the samples were placed in a 5 mm NMR vials and by 100 mg/g of distilled water were added thereto.

NMR spectroscopy. NMR spectra were recorded on a high-resolution NMR spectrometer (Varian “Mercury”) at an operating frequency of 400 MHz. Eight

60° probing impulses of 1 μs duration with a bandwidth of 20 kHz were used. The temperature in the sensor was controlled by the Bruker VT-1000 thermal attachment with an accuracy of ± 1 degrees. 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 signal format and optimizing the zero line and phase with an accuracy that, for well-resolved signals, was not lower than 5%, and for overlapping signals $\pm 10\%$. To prevent the supercooling of water in the investigated objects, measurements of the concentration of non-freezing water were carried out upon the application of heating the samples previously cooled to a temperature of 210 K.

The value of the chemical shift of protons (δ_{H}) was used as the main parameter determining the structure of the hydrogen bond network of water. It was assumed that the water in which each molecule participates in the formation of four hydrogen bonds (two due to protons and two due to unshared electron pairs of oxygen atoms) has a chemical shift $\delta_{\text{H}} = 7$ ppm (realized for hexagonal ice), and weakly associated water (not involved in the formation of hydrogen bonds as a proton donor) — chemical shift $\delta_{\text{H}} = 1\text{--}1.5$ ppm [8, 15, 16]. To determine the geometric dimensions of clusters of adsorbed water, the Gibbs-Thomson equation was used that relates the radius of spherical or cylindrical water cluster or domain (R) to the value of the freezing point depression [17, 18]:

$$\Delta T_m = T_m(R) - T_{m,\infty} = \frac{2\sigma_s T_{m,\infty}}{\Delta H_f \rho R}, \quad (1)$$

where $T_m(R)$ is the melting point of ice localized in pores of radius R , $T_{m,\infty}$ is the melting point of bulk ice, ρ is the density of the solid phase, σ_s is the interaction energy of solid body with a liquid, and ΔH_f is the volume enthalpy of melting. For practical use the equation (1) can be used in the form $\Delta T_m = (k/R)$, in which the constant k for many heterogeneous systems containing water is close to $50 \text{ deg} \cdot \text{nm}$ [18]. The technique of NMR measurements and methods for determining the radii of clusters of interphase water is described in detail in [8, 15, 16]. With that the clusters can be considered polyassociates, whose radius is $R < 2 \text{ nm}$, and polyassociates of a larger size — domains or nanodrops, since they contain several thousand water molecules [8].

The process of freezing (defrost) of bound water corresponds to changes in the free

Gibbs energy, due to the effects of limited space and the natural phases interface. The difference from the process in the volume is the smaller, the farther from the surface is the layer of water. At $T = 273$ K water freezes, the properties of which correspond to bulk water, and as the temperature decreases (without taking into account the effect of supercooling), the layers of water that are closer to the surface freeze. To change the free energy of bound water (ice), the following relation holds true:

$$\Delta G_{\text{ice}} = -0.036(273.15 - T), \quad (2)$$

where the numerical coefficient is a parameter related to the temperature coefficient of variation of the free Gibbs energy for ice [20]. Determining by the value of the signal intensity the temperature dependence of the concentration of non-freezing water $C_{uw}(T)$ in accordance with the procedure detailed in [8, 15, 16], the amount of strongly and weakly bound water and the thermodynamic characteristics of these layers can be calculated.

The interfacial energy of water at the boundary with solid particles or in its aqueous solutions was determined as the modulus of the total decrease in the free energy of water due to the presence of a phase boundary by the formula:

$$\gamma_s = -K \int_0^{C_{uw}^{\max}} \Delta G(C_{uw}) dC_{uw}, \quad (3)$$

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

Microphotography of composite systems was carried out with a Primo Star microscope (Zeiss, Germany) in reflected and transmitted light, with magnification of x40 and x100.

X-ray diffraction analysis (XRD) was carried out by powder diffractometry with DRON-3M diffractometer ("Burevestnik", Russia) in the Cu $K\alpha$ emission of anode line with a nickel filter in a reflected beam and a Bragg-Brentano survey geometry.

Results and Discussion

The results of the X-ray diffraction analysis of fine-crystalline sucrose and a sample of nanosilica A-300, on whose surface 33 weight % of sucrose is immobilized, are shown in Fig. 1.

As can be seen from the data in Fig. 1, after mechanoactivation the intensity of the peaks

corresponding to the crystalline phase of sucrose decreases substantially. Accordingly, most of the sucrose passes into an amorphous state, in which the size of the crystallites is measured in some units or tens of nanometers (Fig. 2, *a, b*). It can be assumed that as a result of mechanical loads, silica and sucrose form a heterogeneous system in which a significant part of the surface of silica particles is covered with a layer of amorphized sucrose (Fig. 2, *c*).

Fig. 3, *a* shows the ^1H NMR spectra recorded at different temperatures from a sample obtained by sucrose melting in the presence of water (100 mg/g). After cooling, such sample quickly crystallizes and is in the form of a solid polycrystalline system. Three wide signals are fixed in the spectra, two of which with chemical shifts $\delta_H = 6.5$ and 4 ppm refer to the hydroxyl groups of sucrose, and one ($\delta_H = 5-6.5$ ppm) to water that is part of sucrose crystals. Assuming [20] that the chemical shift of tetracoordinated water in hexagonal ice is 7 ppm, and that of nonassociated water (gas phase or solution in nonpolar solvents) is 1.5 ppm, it can be concluded that water in sucrose crystals is present in a strongly associated state. The average number of hydrogen bonds in which each water molecule participates increases from 2.5 at $T = 285$ K to 3.5 at $T = 226$ K.

The signals of CH and OH groups of sucrose dissolved in adsorbed water are recorded in the spectra only at temperatures $T > 260$ K, and adsorbed water at lower temperatures too. The intensity of the water signal at $T > 260$ K practically does not change. Growth in this temperature range of the intensity of sucrose signal indicates an increase in its concentration in the unfrozen phase.

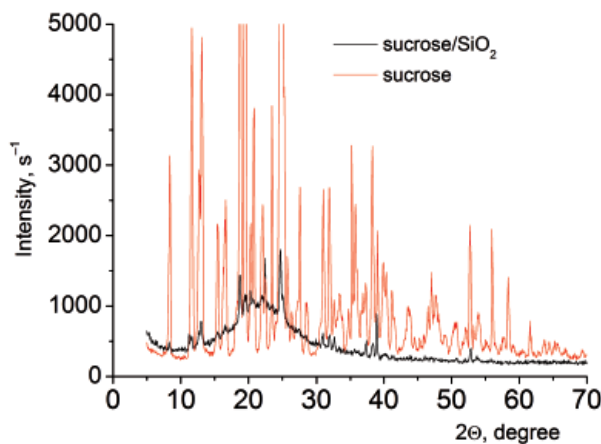


Fig. 1. X-ray diffraction patterns of finely dispersed sucrose and sucrose immobilized on the surface of nanosilica A-300

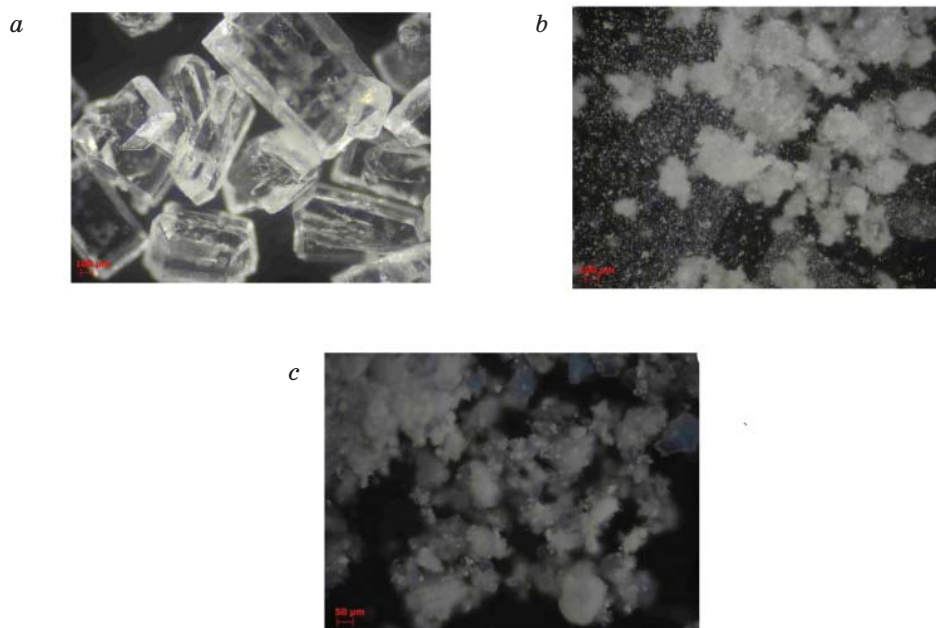


Fig. 2. Microphotographs of: crystalline sucrose (a), ground sucrose (b) and composite sucrose/SiO₂ system (c) taken in reflection modes

For a frozen wet sucrose powder (Fig. 3, b), only one broad signal is observed in the spectra, the intensity of which decreases with a decrease in temperature, and the chemical shift displaces towards weak magnetic fields (larger values of δ_H). The width of the signal is much larger than in the spectra in Fig. 3, a. This makes it difficult to register the signals of dissolved sucrose. It can be assumed that sugar is dissolved in adsorbed on the surface water only near $T = 273$ K or at higher temperatures. Additional heating of the sample up to $T = 340$ K (spectrum at $T = 285$ K) leads to the appearance of a weak signal of dissolved sucrose.

For a sample of sucrose immobilized on the surface of nanosilica (Fig. 3, c), its dissolution in interphase water is not observed in the whole temperature range accessible for measurement. It should be noted that in this sample, the amount of water per mass unit of sucrose is three times higher than that of the sample in Fig. 3, b. So, the transition of sucrose to the amorphous state (Fig. 1) prevents the dissolution of sucrose in adsorbed water.

It could be assumed that the medium of an inert solvent deuteriochloroform, which is capable of dissolving only very small amounts of water and sucrose, will not affect the process of sucrose dissolving by water adsorbed on it. However, it turned out that this is not the case (Fig. 4). In sucrose powder, as well as in sucrose/SiO₂ composite system, the spectra

record the formation of a solution over a wide range of temperatures.

As enterosorbents are used orally, in the stomach they are exposed to gastric juice containing 0.1 N hydrochloric acid solution. Therefore, in Fig. 4 c there are also shown the spectra of aqueous 36% HCl solution at the surface of the sucrose/SiO₂ composite at different temperatures. Three signals are observed in the spectrum, one of which, with a chemical shift $\delta_H = 4$ ppm, can be attributed to protons of sucrose hydroxyl groups, and the other two to an aqueous HCl solution of different concentrations. The second sucrose signal, recorded in Fig. 4, a, b at $\delta_H = 7$ ppm coincides with the intense signal of an aqueous solution of acid and therefore is not observed in the spectra. The appearance of two signals of acid solution is due to the possibility of formation in the adsorption layer of different by structure and size water clusters that have a different solubility in relation to strong acids [12, 13].

To analyze the results obtained, in Fig. 5, a the temperature dependences are given of the change in the concentration of non-freezing water calculated from the change in the intensity of the bound water signal, and in Fig. 5, b, c — calculated distribution of cluster radii (nanodrops) of non-freezing water, in accordance with Fig. 5, a, by equation of Gibbs-Thomson.

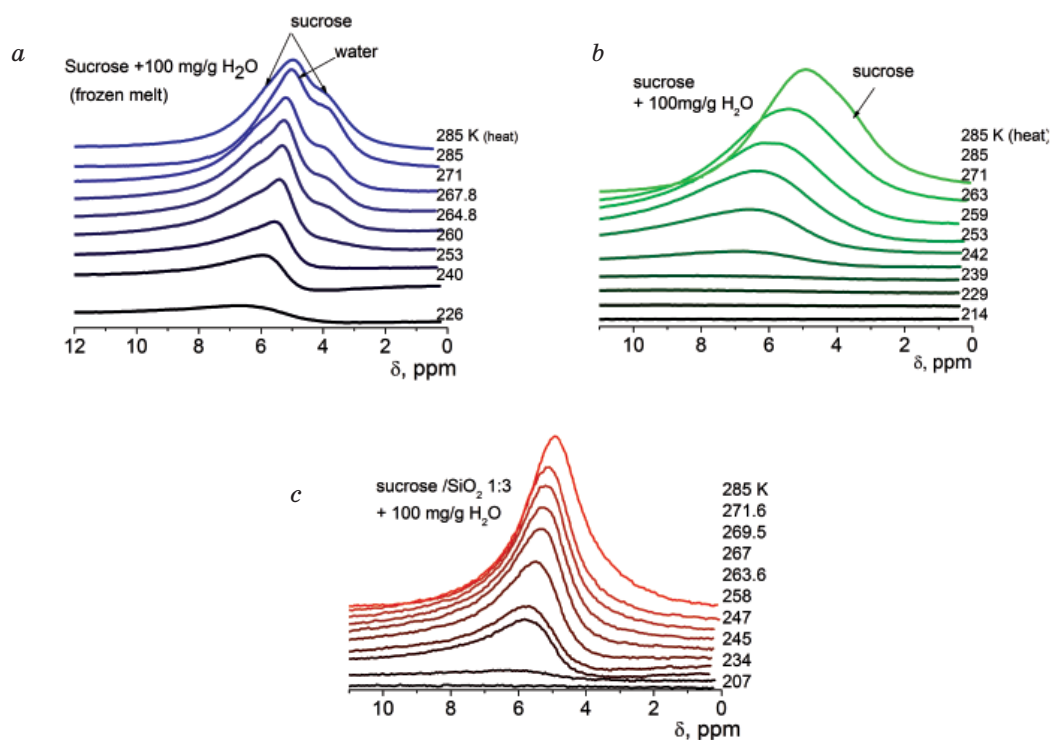


Fig. 3. ^1H NMR spectra of a sample obtained by sucrose melting in: the presence of 100 mg/g of water (a), in finely dispersed sucrose powder (b) and in sucrose/ SiO_2 composite (c) taken at different temperatures

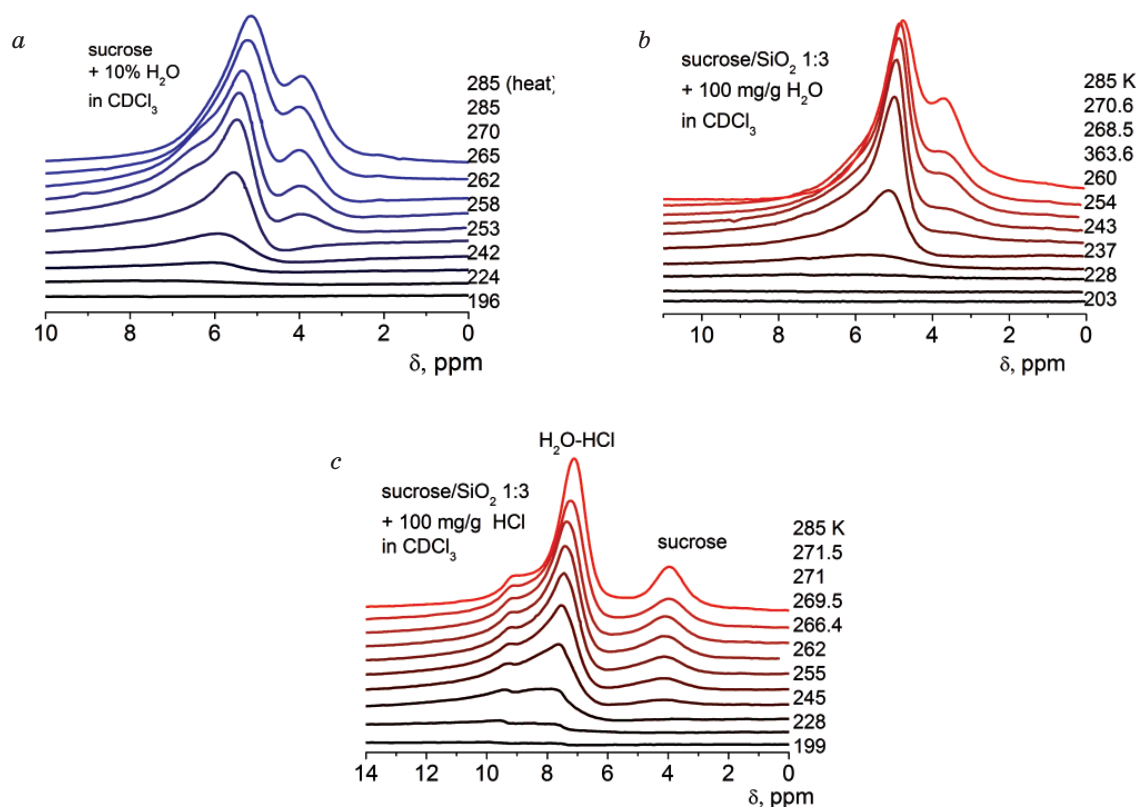


Fig. 4. ^1H NMR spectra of: sucrose wet powder (a), sucrose/ SiO_2 composite (b), and sucrose/ SiO_2 composite containing HCl solution in the CDCl_3 medium instead of water

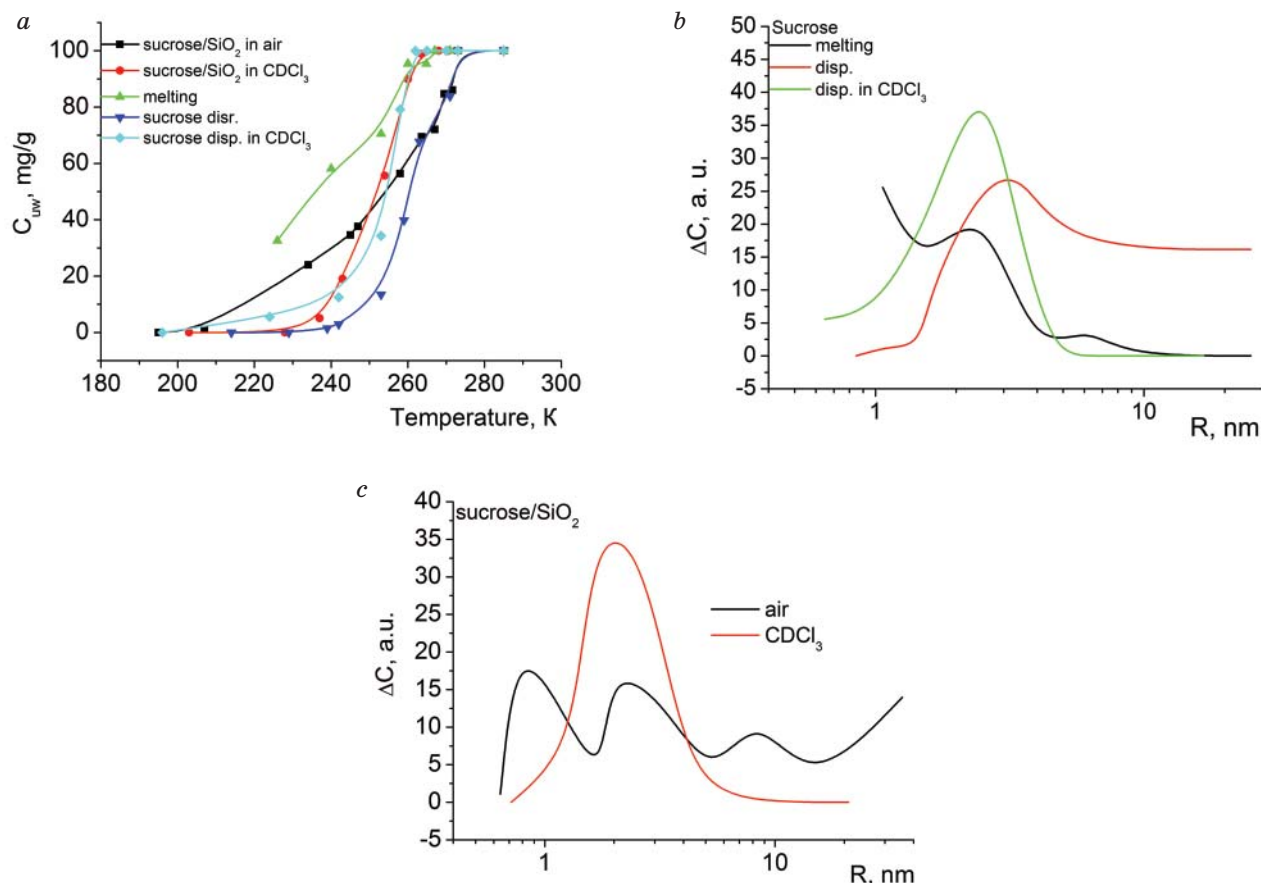


Fig. 5. Temperature dependence of:
the concentration of non-freezing water (a) and radial distribution of adsorbed water clusters in sucrose samples (melt and disperse powder) (b) and in sucrose/SiO₂ composite (c)

In a cooled sucrose melt containing dissolved water, there is a widespread radial distribution of dissolved water clusters, in which there are expressed maxima at $R = 1, 2.5$ and 8 nm. The measurements relate to the range of temperatures in which the water dissolved in the melt is in the form of an individual substance. For wet sucrose powder, a significant amount of water is included in clusters with a radius of 3 nm, but the portion of water absorbed by the sucrose has a radius in the range of 4 – 20 nm. For water adsorbed in sucrose/SiO₂ composite, there are three main peaks on the distribution, corresponding to $R = 0.9, 2.5$ and 9 nm. These values probably correspond to the geometric dimensions of the interparticle gaps in nanostructured silica powders with immobilized sucrose on the surface of the particles.

The deuteriochloroform medium completely changes the form of distributions (Fig. 5, b, c). In a wet powder under the influence of weakly polar medium, relatively large clusters are stabilized, which, apparently, are formed by the fusion of smaller ones. In sucrose/SiO₂

composite system one maximum remains at $R = 1.5$ nm on the distribution. The general property of systems in which the sucrose dissolution in interphase water is recorded (the appearance of sucrose signals in the NMR spectra, Fig. 3, 4) is the presence of a region at $R > 10$ nm, where the value of $\Delta C = 0$ (the change in the intensity of the water signal does not occur, since all the water has already passed into the liquid state, Fig. 5, a)

Possible causes of such a significant effect of the hydrophobic medium on sucrose dissolution may be the partial fusion of surface water clusters and the increase of their contact area with the sucrose surface — water from the almost spherical nanodrops passes into the form of hemispheres wetting the surface. When this happens, the energy of the transition of sucrose from crystals (crystallites) to the dissolved state decreases. Thus, by using inert media or co-adsorbates, methods for controlling the solubility of substances immobilized on the surface of highly dispersed particles can be developed.

The temperature dependences of sucrose concentration in adsorbed water can be calculated from the ratio of water and hydroxyl groups of sucrose concentrations (Fig. 6). As can be seen from the figure, for all systems at $T > 273$ K, sucrose concentration in interphase water is about 30% by weight or about 6 molecules of water per 1 sucrose molecule. As the temperature decreases, the concentration of sucrose decreases rapidly due to its crystallization.

Fig. 7 shows the dependences of the change of free Gibbs energy on the concentration of non-freezing water, calculated from the formula (2), based on the temperature dependences of the change in the concentration of non-freezing water (Fig. 5, a). The thermodynamic parameters of non-freezing water are summarized in Table 1. It was also assumed that the strongly bound water (C_{uw}^S) is that part of the interphase water, which freezes at $T < 265$ K ($\Delta G < -0.5$) [8]. The rest of the water can be classified as weakly bound (C_{uw}^W). The maximum decrease in free energy in the layer of strongly bound water (ΔG^S) characterizes the effectiveness of the surface influence on the part of the water that contacts it. Total decrease of free energy in the entire layer of adsorbed water determined by equation (3) determines the interfacial energy of the surface (γ_S), which depends on the amount of water, the structure of the water clusters, the area of their contact with the surface, the presence of soluble substances, and the medium in which the measurements are made.

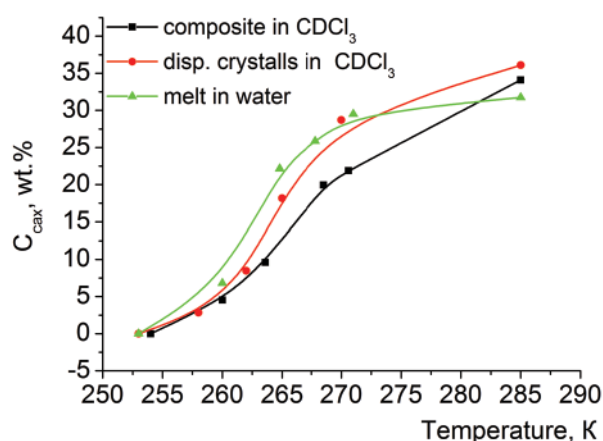


Fig. 6. Temperature dependence of sucrose concentration:
in non-freezing water for its melt,
dispersed crystals and sucrose/SiO₂ composite
in CCl₃ medium

The magnitude of interfacial energy is determined by the ratio of strongly and weakly bound water and the value of ΔG^S . It can be used to analyze the change in free energy when varying the sucrose containing system. Schematically, the changes in the state of interphase water and the associated changes in γ_S are shown in Fig. 8.

The maximum values of the interfacial energy are recorded for a sample obtained by sucrose melting in the presence of a certain amount of water. When the sample is frozen, the water in it is released in the form of nanoscale clusters (Fig. 5), which interact more effectively with the surrounding sucrose. Some contribution to the measured value of γ_S is made also by the partial dissolution of sucrose in the adsorbed water. The interphase energy decreases sharply reaching its minimum value when passing from the melt to the hydrated powder of finely dispersed sucrose. The probable cause is the relatively poor dissolving power of clustered water with respect to sucrose, in conditions of a small contact surface area of dissimilar substances. The difference in the value of γ_S for the melt and dispersed sucrose powder (5.3 J/g) determines the change in the free energy of the water cluster when it moves from the surface to the inside of the sucrose crystal. The hydrophobic medium makes the clustering of interphase water (Fig. 5) and their placement along the surface of crystals (crystallites) of sucrose more thermodynamically advantageous. This increases the area of water contact with the surface of sucrose and facilitates the process of

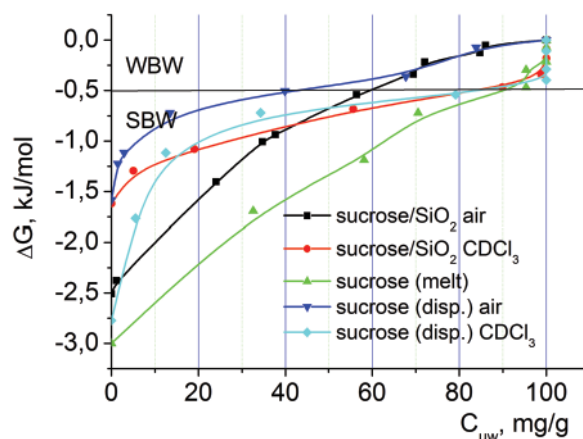
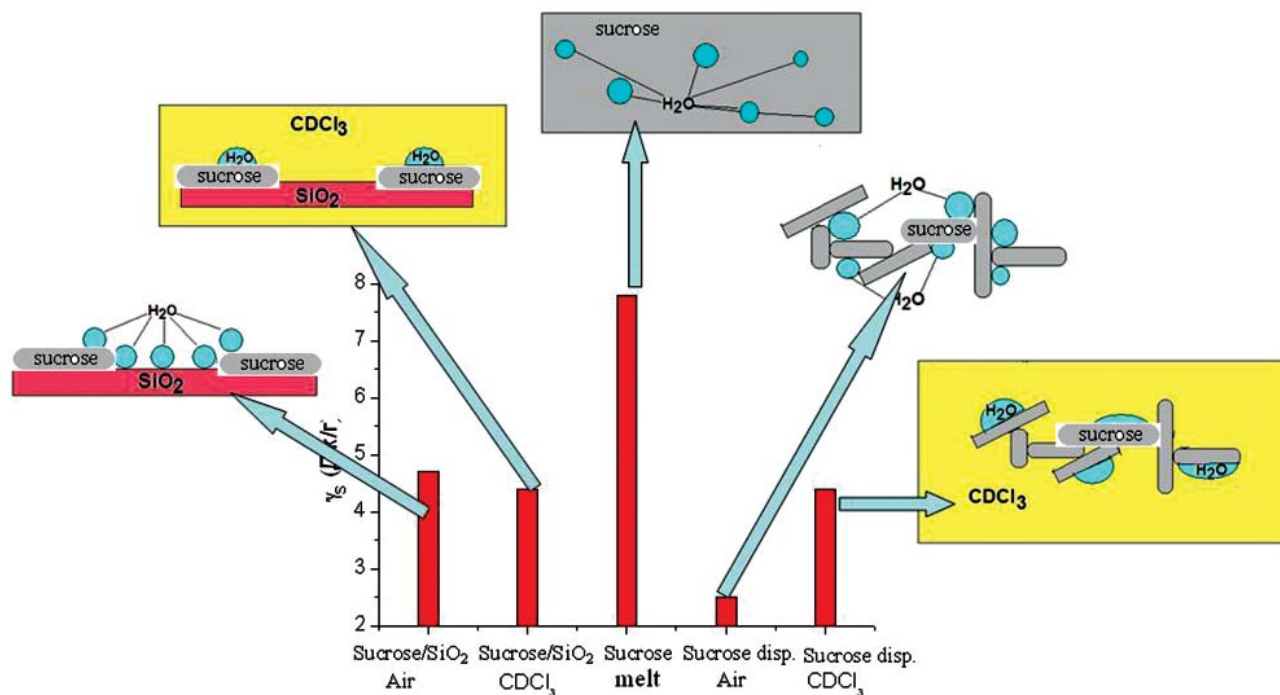


Fig. 7. Dependences of the change of free Gibbs energy on the non-freezing water concentration:
for sucrose samples and sucrose/SiO₂
composite system

Table 1. Characteristics of non-freezing water layers in sucrose samples and sucrose/SiO₂ composite system

Sample	Medium	C_{uw}^S , mg/g	C_{uw}^W , mg/g	ΔG^S , kJ/mol	γ_S , J/g
Sucrose /SiO ₂	Air	60	40	-2.5	4.7
Sucrose /SiO ₂	CDCl ₃	85	15	-1.7	4.4
Sucrose melt		90	10	-3	7.8
Sucrose dispersed	Air	40	60	-1.5	2.5
Sucrose dispersed	CDCl ₃	85	15	-2.7	4.4


 Fig. 8. Schematic changes in the state of interfacial water in sucrose containing samples and in sucrose/SiO₂ composite

partial sucrose dissolution in interfacial water. The resulting free energy gain is 1.9 J/g.

For sucrose/SiO₂ composite system, clusters of adsorbed water can contact both the surface of silica and sucrose. However, the contact area is not sufficient for the essential sucrose solubility, and the small radius of adsorbed water clusters (Fig. 5) makes the dissolution process of sucrose thermodynamically unprofitable. As shown in [8], the chloroform medium is capable of displacing water from the silica surface. In this case, the nanoclusters of water move to silica surface covered with sucrose, where their enlargement takes place (Fig. 5) and the contact area of sucrose-water increases. For water this process turns out to be energetically unprofitable (the value of γ_S decreases by 0.3 J/g), which is probably compensated by

the energy gain due to the high affinity of deuteriochloroform to the silica surface.

By mechanochemical activation, which provides significant mechanical loads, sucrose can also be immobilized on the surface of hydrophobic methyl silica. Thus, when grinding sucrose with methyl silica of grade AM1 in a porcelain mortar, after only 5–10 min a significant compaction of the material is observed (the bulk density increases 3–4 times). Bringing in close contact of sucrose hydrophilic particles with methyl silica surface creates the conditions for the appearance of Van der Waals forces between them that hold particles at atomic distances. In the process, a composite system is formed that has a sufficiently high affinity for adsorbed water.

Fig. 9 shows recorded at different temperatures spectra of water adsorbed by

sucrose/AM1 composite containing sucrose and silica AM1 (in a ratio of 1:3) with addition of 100 mg/g of water in air, deuteriochloroform and CDCl_3 medium with the addition of 15% by weight of deuterotrifluoroacetic acid. From Fig. 9 a we see that even in the air, spectra record the signals of protons of CH and OH. The water signal contains a narrow (observed at $T > 273$ K) and a wide component. It can be assumed that they correspond to different states of interphase water. Since there is practically no adsorption of water on pure methyl silica [15], it is most likely that all water corresponding to a wide component of the ^1H NMR signal can be attributed to water adsorbed on sucrose crystallites forming a mosaic coating on silica aggregates. The narrow component recorded in the spectra at $T = 283$ K (Fig. 9, a) can be associated with submicron drops of water stabilized by hydrophobic silica particles. Due to the presence of a film of hydrophobic powder, nanodrops on the surface, which are not connected with the surface of sucrose, the fusion of water particles dispersed in the heterogeneous system do not occur. In addition, silica particles act as a hydrophobic medium and, similarly to chloroform, promote

the movement of adsorbed water to the surface of sucrose crystallites. As a result, its partial dissolution occurs in the interfacial water.

In the chloroform medium, the narrow component of the water signal in the spectra disappears (Fig. 9, b) and all water concentrates on sucrose crystallites. The solubility of sucrose in adsorbed water rises sharply (the sucrose signal increases). The addition of 15 weight% of trifluoroacetic acid to the dispersion medium results in a shift of the water signal into weak magnetic fields due to the appearance of a contribution from the "acidic" TFA protons (Fig. 9, c). In Fig. 10 for the composite sucrose/AM1 system, the temperature dependences of non-freezing water concentration (a), the sucrose concentration (b), the dependence of the change in Gibbs free energy on the concentration of non-freezing water (c), and radial distribution of non-freezing water clusters are given. The thermodynamic characteristics of the interfacial water layers are summarized in Table 2.

From the data of the table, it follows that, as in the case of dispersed sucrose powder (Table 1), the medium of weakly polar chloroform increases the amount of strongly

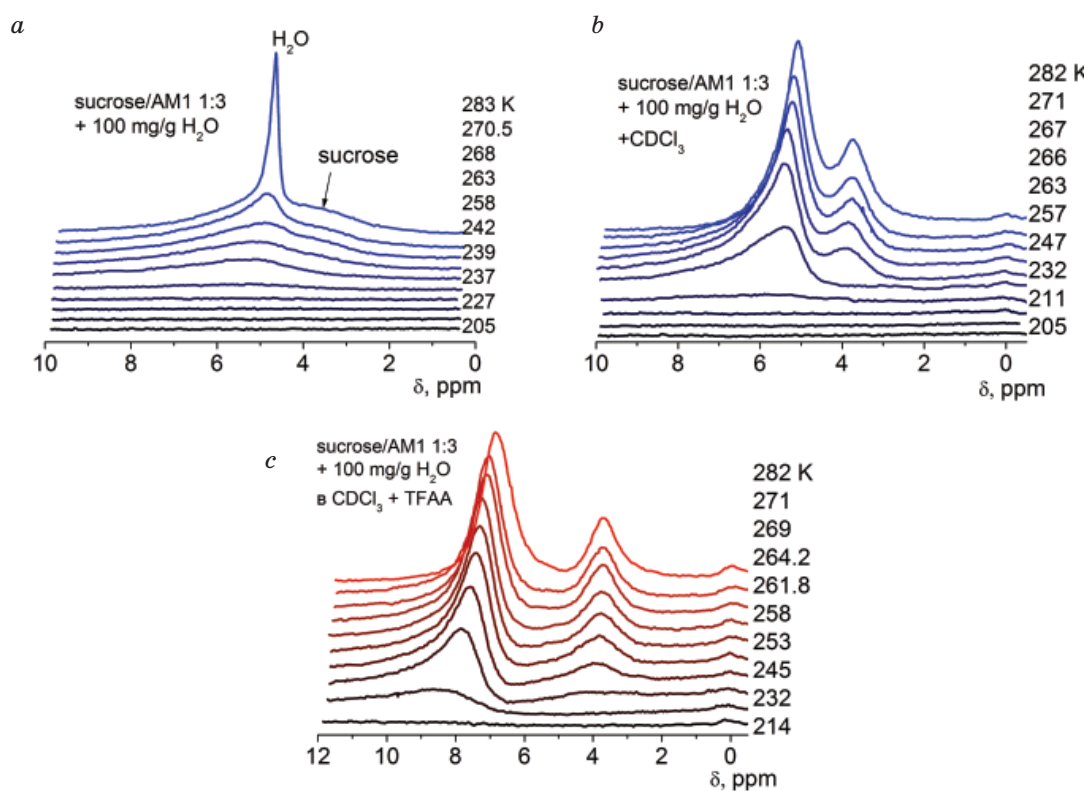


Fig. 9. ^1H NMR spectra of water and sucrose in composite system: sucrose AM1 (1: 3 ratio) in air (a), CDCl_3 medium (b) and CDCl_3 + TFA (c)

Table 2. Characteristics of non-freezing water layers in samples of sucrose/AM1 composite system

Sample	Medium	C_{uw}^S , mg/g	C_{uw}^W , mg/g	ΔG^S , kJ/mol	γ_S , J/g
Sucrose/AM1	Air	45	55	-1.7	2.7
Sucrose/AM1	$CDCl_3$	65	35	-1.5	3.4

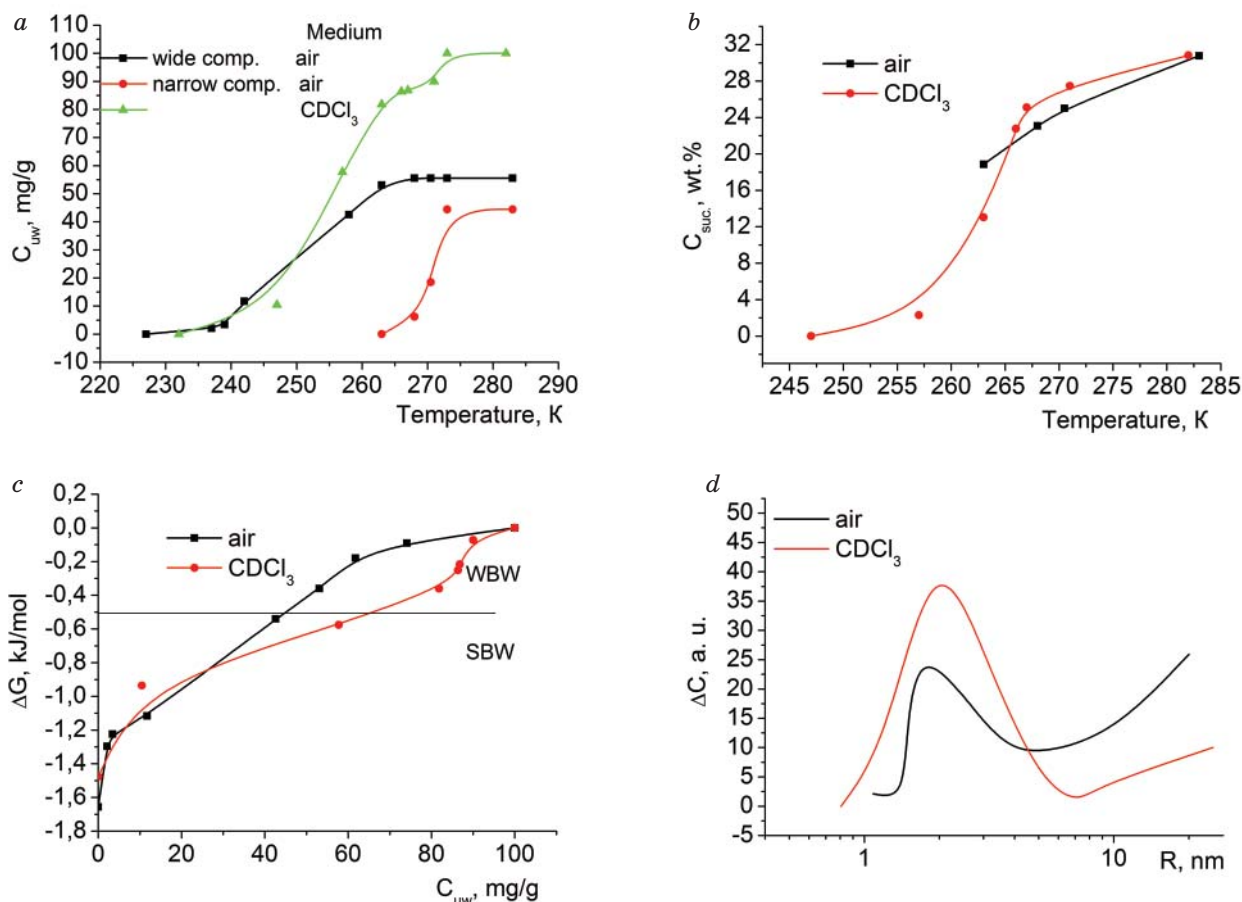


Fig. 10. Temperature dependences of the concentration of:

non-freezing water (a), sucrose concentration (b), the dependence of the change in Gibbs free energy on the concentration of non-freezing water (c), and radial distribution of non-freezing water clusters for sucrose/AM1 composite system

bound water and the value of interfacial energy, which is close in magnitude to that obtained for the dispersed sucrose powder. Consequently, the replacement of hydrophilic silica by hydrophobic silica is accompanied by a significant decrease in the binding of water in the composite system, which confirms the diagram shown in Fig. 7 of water interaction with the components of the composite system. Both in air and in chloroform, a significant part of the adsorbed water is included in clusters with a radius of 2–4 nm. The narrow component of the signal of bound water corresponds to clusters of water with $R > 10$ nm (Fig. 10, a, d). At $T = 282$ K, the sucrose concentration in interfacial water is the same

for the sample in air and in the medium of $CDCl_3$. However, in air, the signal of dissolved sucrose is absent at $T < 263$ K. So, chloroform contributes to the improvement the solubility of sucrose in water at low temperatures.

So, it is shown that sucrose amorphization occurs during the simultaneous mechano-activation of sucrose with nanosilica. The adsorption of water in such a composite is not accompanied by the dissolution process of the sucrose immobilized on the SiO_2 surface in interfacial water. The effect of sucrose solubility increasing upon placing the composite in a medium that does not dissolve water and sucrose, an organic solvent, deuteriochloroform, is caused by an

increase in the contact area of clusters of adsorbed water with the surface of sucrose. The maximal sucrose concentration, which dissolves in interfacial water, is about 30% by weight. While maintaining the ratio of the concentrations of the components and the amount of adsorbed water, replacing the hydrophilic wetting-drying silica (A-300) by hydrophobic (AM1) reduces the free binding

energy of water in the composite system. The obtained results can be used in the development of a new generation of enterosorbents.

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REFERENCES

1. *Medical Chemistry and Clinical Application of Silica* (Eds. A. A. Chuiko). Kyiv: Naukova dumka, 2003. (In Russian).
2. FAO/WHO Codex Alimentarius Commission 1973. List of additives evaluated for their safety-in-use in food. First series. CAC/FAL 1-1973.
3. Tarasevich Ju. I. Surface energy of oxides and silicates. *Teoret. eksperim. khim.* 2006, 42(3), 133–149. (In Russian).
4. Mironyuk I. F., Gun'ko V. M., Turov V. V., Zarko V. I., Leboda R., Skubiszewska-Zięba J. Characterization of fumed silicas and their interaction with water and dissolved proteins. *Colloids Surf. A*. 2001, 180(1–2), 87–101. [https://doi.org/10.1016/S0927-7757\(00\)00764-0](https://doi.org/10.1016/S0927-7757(00)00764-0)
5. Gun'ko V. M., Mironyuk I. F., Zarko V. I., Voronin E. F., Turov V. V. Morphology and surface properties of fumed silicas. *J. Colloid Interf. Sci.* 2005, 289(2), 427–445. doi: 10.1016/j.jcis.2005.05.051
6. Blitz J. P., Gun'ko V. M. (Ed.) *Surface Chemistry in Biomedical and Environmental Science. NATO Sc. Series II: Mathem. Phys. Chem.* V. 228, Dordrecht: Springer, 2006. 444 p.
7. Zarko V. I., Andrijko L. S., Gun'ko V. M., Malysheva M. L., Gackij A. A., Gerashchenko I. I. Structural-absorption characteristics of pyrogenic nanooxides of silica, alumotitanosilicates modified with polyvinyl alcohol and polyethylene glycol. *Himija, fizika i tehnologija poverhnosti.* 2006, V. 11, 225–244. (In Russian).
8. Turov V. V., Gun'ko V. M. Clustered water and ways to use it. K.: Naukova dumka, 2011, 313 p. (In Russian).
9. Smirnov A. N., Markova L. I., Pchelinceva N. V., Krylatova Ja. G., Kosyreva I. V. The main classes of organic compounds. Part IV. Carbohydrates. *Saratov: Izd-vo*, 2010, 59 p. (In Russian).
10. Georgievs'kij V. P. State Formology of Ukraine. *Farmaceutichna enciklopedija.* (In Ukrainian).
11. Gerashchenko I. I. Enterosorbents: Drugs and dietary supplements. Kyiv: Vydavnytstvo Instytutu khimii poverkhni NAN Ukraini, 2014, 248 p. (In Ukrainian).
12. Turov V. V., Gun'ko V. M., Turova A. A., Morozova L. P., Voronin E. F. Interfacial behavior of concentrated HCl solution and water clustered at a surface of nanosilica in weakly polar solvents media. *Colloids Surf. A: Physicochem. Eng. Asp.* 2011, 390(1), 48–55. <https://doi.org/10.1016/j.colsurfa.2011.08.053>.
13. Gun'ko V. M., Turov V. V., Turov A. V. Hydrogen peroxide — water mixture bound to nanostructured silica. *Chem. Phys. Lett.* 2012, V. 531, P. 132–137. <https://doi.org/10.1016/j.cplett.2012.01.090>
14. Gun'ko V. M., Morozova L. P., Turova A. A., Turov A. V., Gaishun V. E., Bogatyrev V. M., Turov V. V. Hydrated phosphorus oxyacid alone and adsorbed on nanosilica. *J. Colloid Interface Sci.* 2012, V. 368, P. 263–272. doi: 10.1016/j.jcis.2011.11.018.
15. Gun'ko V. M., Turov V. V. Nuclear Magnetic Resonance Studies of Interfacial Phenomena. *New York: Taylor & Francis*, 2013, 1070 p.
16. 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, V. 118, P. 125–172. <https://doi.org/10.1016/j.cis.2005.07.003>
17. Aksnes D. W., Kimtys L. Characterization of mesoporous solids by ^1H NMR. *Solid State Nucl. Magn. Reson.* 2004, V. 25, P. 146–163.
18. Petrov O. V., Furo I. NMR cryoporometry: Principles, application and potential. *Progr. In NMR.* 2009, 54(2), 97–122.
19. Krupskaya T. V., Turov V. V., Barvinchenko V. N., Filatova K. O., Suvorova L. A., Kartel M. T. *Method for compressing silica. Ukraine Patent №105151.* March 10, 2016. (In Ukrainian).
20. Thermodynamic properties of infundible substances. Ed. V. P. Glushko, M.: Nauka. 1978, 495 p. (In Russian).

**ОСОБЛИВОСТІ ГІДРАТАЦІЇ
КОМПОЗИТНИХ СИСТЕМ
НА ОСНОВІ ВИСОКОДИСПЕРСНОГО
КРЕМНЕЗЕМУ ТА САХАРОЗИ
У РІЗНИХ СЕРЕДОВИЩАХ**

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Метою роботи було дослідити стан води в гідратованому порошку сахарози, її розплаві та композитних системах, які містять 3 частини кремнезему (А-300 чи АМ1) і 1 частину сахарози в повітряному середовищі, середовищі слабополярного органічного розчинника — дейтерохлороформу та середовищі CDCl_3 з добавками сильних кислот методом низькотемпературної ^1H ЯМР спектроскопії. Показано, що за сумісної механоактивації сахарози з нанокремнеземом відбувається її аморфізація. При цьому адсорбція води в такому композиті не супроводжується процесом розчинення іммобілізованої на поверхні SiO_2 сахарози в міжфазній воді. Виявлено ефект підвищення розчинності сахарози за перенесення композиту в середовище органічного розчинника — дейтерохлороформу, що не розчиняє воду і сахарозу. Висловлено припущення, що цей ефект зумовлений збільшенням площі контакту кластерів адсорбованої води з поверхнею сахарози. Максимальна концентрація сахарози, за якої вона розчиняється в міжфазній воді, становить близько 30 мас.%. За збереження співвідношення концентрацій компонентів та кількості адсорбованої води заміна гідрофільного кремнезему А-300 на гідрофобний АМ1 знижує вільну енергію зв'язування води в композитній системі. Одержані результати можуть бути використані у разі конструювання нового покоління ентеросорбентів.

Ключові слова: ^1H ЯМР спектроскопія, сахароза, гідрощільнений, гідрофільний та гідрофобний кремнезем, композитна система.

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КРЕМНЕЗЕМА И САХАРОЗЫ
В РАЗНЫХ СРЕДАХ**

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Целью работы было изучить состояние воды в гидратированном порошке сахарозы, ее расплаве и композитных системах, содержащих 3 части кремнезема (А-300 или АМ1) и 1 часть сахарозы в воздушной среде, среде слабополярного органического растворителя — дейтерохлороформа и среде CDCl_3 с добавками сильных кислот методом низкотемпературной ^1H ЯМР спектроскопии. Показано, что при совместной механоактивации сахарозы с нанокремнеземом происходит ее аморфизация. При этом адсорбция воды в таком композите не сопровождается процессом растворения иммобилизованной на поверхности SiO_2 сахарозы в межфазной воде. Обнаружен эффект повышения растворимости сахарозы при помещении композита в среду органического растворителя — дейтерохлороформа, не растворяющую воду и сахарозу. Высказано предположение, что этот эффект обусловлен увеличением площади контакта кластеров адсорбированной воды с поверхностью сахарозы. Максимальная концентрация сахарозы, растворяющейся в межфазной воде, составляет около 30 мас.%. При сохранении соотношения концентраций компонентов и количества адсорбированной воды замена гидрофильного кремнезема А-300 на гидрофобный АМ1 снижает свободную энергию связывания воды в композитной системе. Полученные результаты могут быть использованы при разработке нового поколения энтеросорбентов.

Ключевые слова: ^1H ЯМР спектроскопия, сахароза, гидроуплотненный, гидрофильный и гидрофобный кремнезем, композитная система.