SUPRAMOLECULAR STRUCTURES IN NANOSILICA/MIRAMISTIN HYDRATED COMPOSITE IN A HYDROPHOBIC MEDIUM

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The effect of a hydrophobic medium on the hydrated properties of a powdered nanocomposite based on the cationic surfactant miramistin and silica was studied using low-temperature PMR spectroscopy. The thermodynamic parameters of strongly and weakly bound water layers and the interfacial energy of water in pore cavities of the nanocomposite were determined.

Keywords: PMR spectroscopy, miramistin, silica, weakly bound water, strongly bound water, hydrophobic medium, hydrated properties.

Introduction. Miramistin \{benzyldimethyl[3-(myristoylamino)propyl]ammonium chloride monohydrate\} (MR)

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\begin{align*}
\text{CH}_3 & \quad \text{CH}_2-N-(\text{CH}_2)_3-\text{NH}-\text{C}-(\text{CH}_2)_2-\text{CH}_3 \quad \text{Cl}^- \\
\end{align*}
\]

has recently been widely used as a broad-spectrum antiseptic. The drug has pronounced bactericidal activity against Gram-positive (Staphylococcus spp., Streptococcus spp., Streptococcus pneumoniae, etc.), Gram-negative (Pseudomonas aeruginosa, Escherichia coli, Klebsiella spp., etc.), aerobic and anaerobic bacteria in monocultures, and microbial cocktails including multiply resistant hospital strains. MR is a cationic surfactant (CSA) that is soluble in water, alcohol, and CHCl₃.

Spherical micelles form in water for concentrations \(C_{\text{MR}} > 0.001\) M. One method for increasing the effectiveness of the drug could be immobilization on the surface of nano-sized silica [1, 2]. Thus, the desorption rates and penetration of the bioactive ingredients into skin or mucous membranes can be controlled (especially for composite pastes or gels for external use) by affecting the binding of the removable components to the nano-sized matrix.

The state of water bound to the surface of hydrophilic silica nanoparticles in the presence of a hydrophobic component is of great interest for studying interfacial processes involving MR immobilized on their surface because many medicinal ointments use a fatty (hydrophobic) base. PMR spectroscopy with layer-wise freezing of the liquid phase is the most informative method for examining such systems [3–6]. Weakly associated water (WAW) and strongly associated water (SAW) in clusters can be identified from the chemical shifts of 1–2 ppm for WAW and 4–6 ppm for SAW. Furthermore, freezing points separate weakly bound water (WBW), which freezes at >260 K, from strongly bound water (SBW), which freezes at <260 K. Thus, this method can define the structure of the water H-bonding network in the adsorbed layer using the water chemical shift; the sizes of the adsorbed water clusters and their interaction energy with the surface, from the freezing point depression [4, 7, 8].

The goal of the present work was to study the cluster structure and thermodynamic parameters of water adsorbed to the surface of an SiO₂/MR composite prepared by adsorption of a micellar solution of MR in the presence of hydrophobic media.

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Experimental. The adsorbent was A-300 silica (SiO$_2$, specific surface area 300 m$^2$/g, Kalush Pilot Plant, ISC, NAS of Ukraine) (GOST 14922-77). MR was a white odorless powder (mp = 177°C) that was readily soluble in water, CHCl$_3$, and EtOH. Stock solutions of MR (Infamed) were prepared by dissolving accurately weighed portions of the drug in distilled H$_2$O and dilution to the required concentrations immediately before the experiment. The solution pH values in the range 2–8 were established using phosphate buffers (pH 4.8–7.8) [9] to which HCl or NaOH solutions were added to produce more acidic or basic solutions.

Adsorption of MR from the aqueous solutions onto the silica surface was studied under static conditions. For this, a given volume ($V$, mL) of MR solution of the appropriate concentration ($C_0$, M) was mixed with a weighed portion of adsorbent ($m$, g) in the ratio $V/m = 200$ mL/g until equilibrium was established (~2 h at 20°C). Then, the adsorbent was separated by centrifugation for 15 min at 8,000 rpm and dried in air. The MR concentration in the equilibrium solutions ([C], M) was determined after adsorption from calibration curves that were obtained beforehand for each MR concentration taking into account the actual pH value of the equilibrium solution. The adsorption ($a$, mol/g) was calculated using the equation

$$a = (C_0 - [C])V/1000m.$$  

UV absorption spectra of the solutions were taken on a Specord M-40 spectrophotometer (Carl Zeiss Jena, Germany). Heterochromatic extrapolation at two wavelengths was used to remove the background from the analytical signal ($A$) obtained during measurement of absorption spectra of the test solutions [10]. The solution acidity before and after adsorption was determined using a Hanna Instruments HI 221 pH/mV/°C bench meter with a glass electrode.

NMR studies used powdered silica nanoparticles modified by adsorption of MR to 3.7 mass% ($8 \times 10^{-5}$ mol/g) that were placed into standard 5-mm tubes of height 178 mm. The column of SiO$_2$/MR powder in the tube was 40–45 mm high. The standard for measuring chemical shifts was tetramethylsilane (TMS).

NMR spectra were recorded on a high-resolution Mercury NMR spectrometer (Varian) at operating frequency 400 MHz. We used 90-degree probe pulses of pulse length 3 μs and bandwidth 20 kHz. The temperature in the probe was regulated to ±1°C using a Bruker VT-1000 variable temperature controller. Intensities of resonances were determined by measuring peak areas after deconvoluting the resonance into its components assuming a Gaussian shape and optimizing the baseline and phase. The accuracy was less than ±5% for well resolved resonances and ±10% for overlapping resonances. The water concentration was measured after heating samples that were cooled beforehand to 210 K in order to avoid supercooling of unfrozen water. The procedure for measuring NMR spectra and determining the thermodynamic parameters and bound-water cluster radii was previously described in detail [3–6].

The Gibbs–Thompson equation that relates the radius ($R$) of the pore containing the water to the freezing point depression was used to calculate the geometric dimensions of the adsorbed water clusters [7, 8]:

$$\Delta T_m = T_{m,\infty} - T_m(R) = -2\sigma_{sl}T_{m,\infty}/\Delta H_f \rho R = k_{GT}/R,$$

where $T_m(R)$ is the melting point of ice located in pores of radius $R$; $T_{m,\infty}$, the melting point of bulk ice; $\rho$, the solid-phase density; $\sigma_{sl}$, the interaction energy of the solid with the liquid; $\Delta H_f$, the bulk enthalpy of fusion; and $k_{GT}$, the Gibbs–Thompson equation coefficient [7].

The influence of the solid surface extended into several molecular layers of the liquid [11]. Changes of the Gibbs free energy that were due to effects from the limited space and the nature of the interface corresponded to freezing (thawing) of bound water. The differences from the process in the bulk were less as the distance of the water layer from the surface increased. Water with properties corresponding to those of bulk water froze at 273 K. Water layers situated closer to the surface froze as the temperature was lowered (without accounting for supercooling). The following equation was valid for the free energy change of bound water (ice):

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

where the numerical coefficient is a parameter related to the temperature coefficient for the Gibbs free energy change of ice [12]. The amounts of SBW and WBW and the thermodynamic parameters of these layers could be calculated by determining the temperature dependence of the concentration of unfrozen water $C_{uw}(T)$ from the resonance intensity using the literature method [3–6]. The energy of water at the interface with solid particles or in aqueous solutions was determined as the total reduction of the water free energy that was due to the presence of the interface [3–6] using the equation:

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