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Dynamics of water state in nanoconfined environment

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ABSTRACT

To investigate water state in vitro conditions, cetyltrimethylammonium bromide/isooctane 1-hexanol reverse micellar system was used as a model for nanoscale medium. Using Fourier transform infrared spectroscopy and deconvolution technique, the water states in these systems were studied at several water/surfactant molar ratios, w_o, with respect to time. The presence of four sub-peaks in deconvolution of FT-IR absorption spectra of OH stretching band certified four different states of water. The results showed time dependency of water state, especially in those systems having low w_o, that are more dynamic. Also, exchange of water molecules between different states results in approaching each state to a final steady state value. Based on deconvolution results, it was found that mechanism of ionizing surfactant head group can control water bonded to the bromide counter ion. Moreover, more than 50% of water molecules are like frozen water in reverse micelles and they are not available for solubilization of hydrophilic compounds. Based on the results of this study, state and properties of water in nanoscale medium are quite different from bulk scale.

1. Introduction

Soaps, detergents and surface-active agents known as surfactants are amphiphilic molecules which possess both hydrophilic and hydrophobic regions. Reverse micelles form when certain amounts of surfactant dissolve in non-polar solvents. This structure is thermodynamically stable and depends on the amount of water, and its radius typically varies between 0.5 and 5 nm. Reverse micelles are increasingly used in analytical applications such as a suitable medium for hosting enzymatic reactions [1], production of ultrafine particles [2–4], control the pore size of cross-linked polymers [5,6], and selective separation of biological products [7]. Also, reverse micellar systems have been used to model in vitro DNA condensation [8,9]. The key factor for solubilization process inside a reverse micelle is water content, w_o, which identify water–surfactant molar ratio. As shown in Fig. 1, when an ionic surfactant like cetyltrimethylammonium bromide (CTAB), is brought into contact with water in reverse micelles, some parts of bromide dissociate as counter ion and can bond to water in reverse micelles. In addition, water can bond to ionic part of surfactant known as head group. The other site that water molecule can bond is among hydrocarbon chains of surfactants as monomer molecules. Finally, the most proper site is in the core of reverse micelles, where the water state is bulk-like. The behavior of water bonded to counter ions, head groups, and hydrocarbon chains of surfactants is markedly different with the bulk water. Study of water properties in these systems allows one to understand the nature of interactions responsible for significant phenomena such as interface curvature, protein folding, and structure of entrapped biomolecule [1,10–12].

The deconvolution technique has been shown as a promising tool in the study of FT-IR absorption spectra, and it allows one to find the state of water in reverse micelles [13–15]. This technique involves curve fitting of the observed peaks with a number of Gaussian functions, each one representing one characteristic hydroxy stretching band of water molecules. The values of the stretching bands are generally correlated to a particular state of water molecules. Several attempts have been made to distinguish the state of water in reverse micellar systems. In 1997, Ikushima et al. [13] carried out three-region model to find water state in an anionic, sodium bis(2-ethylhexyl) sulfosuccinate (AOT), reverse micellar system. Later on, Temsamani et al. [14] investigated water state in the same system in the presence of cationic species. Some researchers developed water state in AOT reverse micelles at different conditions by using four-region model [15–19]. Besides AOT reverse micelles, this phenomenon was investigated in a few reverse micellar systems which containing nonionic or cationic surfactants such as nonionic fluorocarbon or sodium bis(2-ethylhexyl) phosphate (NaDEHP) [18–20]. In this study, due to the use of CTAB reverse micelles in many applications [21–25], we will investigate the state of water in these nanocompartments. In this way, we will decompose FT-IR absorption spectra of OH stretching by applying deconvolution technique with four Gaussian peaks. Moreover, the dynamics of water will be studied at different w_o values for observing the stability of water in each state.

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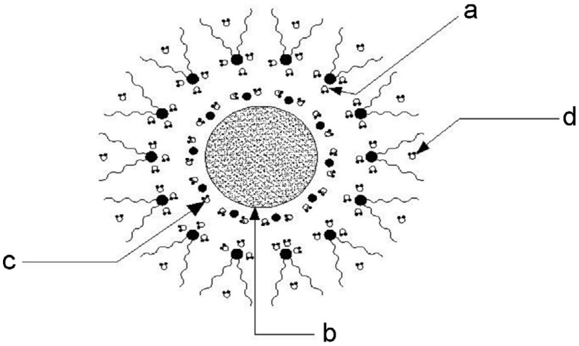

Fig. 1. Different states of water in CTAB/isooctane, 1-hexanol reverse micellar system: (a) water bonded to head group, (b) bulk-like water, (c) water bonded to counter ion, and (d) trapped water.

2. Materials and methods

CTAB, Karl-Fischer solution with titration ratio 5–6 mg H_2O/ml Karl-Fisher, and dried methanol for titration was provided from Fluka. Other chemicals such as solvent and co-solvent were all commercially available reagents of analytical grade. The reverse micellar solutions were prepared by adding CTAB surfactant to the organic solvent, isooctane-1-hexanol, while adding required amount of water using injection method. In all samples, concentration of CTAB and volume percentage of 1-hexanol were 20 (mM) and 10%, respectively. In addition, the required amount of water was calculated by multiplying w_o and surfactant concentration based on unit volume of solution. Then, to obtain a clear phase, the mixture was shaken for 5 min. Water content in the reverse micelles was measured using Karl-Fischer titrator 758 (Metrohm, Ltd., Herisau, Switzerland). Fourier transform infrared (FT-IR) spectroscopy of all samples was recorded in the range of 400–4000 cm^{-1} with a Bruker (Karlsruhe, Germany) model VECTOR 22 spectrophotometer using a fixed path length of 0.05 mm cell equipped with CaF_2 windows at room temperature (25 °C). Each sample was recorded with 32 scans at an effective resolution of 2 cm^{-1} for obtaining a superior quality of the spectra. The hydroxy stretching vibration band (3000–3700 cm^{-1}) fitted using the Levenberg–Marquardt algorithm.

3. Theory

The area of each peak, A_i, is corresponding to the amount of water in each state, and the sum of all areas is equal to the total area, A, which indicates the total amount of water in reverse micelles [17]. Thus, mole fraction of water in each state, X_i, is the ratio of corresponding area to the total area.

$$X_i = \frac{A_i}{A} \tag{1}$$

To obtain mole of water per mole of surfactant in each state, n_i, the mole fraction should be multiplied by w_o:

$$n_i = X_i . w_o \tag{2}$$

4. Results

Fig. 2 shows the OH stretching bands of water in CTAB reverse micelles 3 min after preparation and different values of w_o. As shown in this figure, the intensity of OH stretching band increases with increasing water content, which is in agreement with previous reports [16–18].

Fig. 3 shows deconvolution result based on four-region model for OH stretching spectra of water in reverse micelles using Gaussian functions. The sub-peaks centered at 3237.0 ± 20 cm^{-1} (a), 3416.9 ± 10 cm^{-1} (b), 3536.0 ± 10 cm^{-1} (c), and 3682.1 ± 10 cm^{-1} (d). These peaks are assigned to the OH stretching mode of water bonded to the head group of surfactant [16], bulk-like water [16–18], water bonded to the bromide counter ion [16], and trapped water [13,16–18], respectively. Water bonded to the opposite charges of surfactant is as two symmetric peaks with respect to the bulk-like water peak.

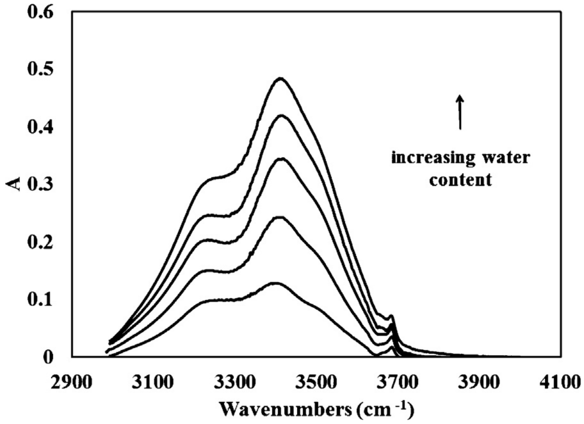

Fig. 2. FT-IR spectra of OH stretching band of water in CTAB/isooctane, 1-hexanol reverse micelles at different w_o values (10, 15, 20, 25, and 30).

Fig. 4 shows the time dependency of OH stretching in water at different values of w_o (10, 20, and 30). The intensity of spectra decreased with time for all w_o values and approach to the final state. We can attribute this time dependency of OH stretching band to the dynamics of water state in reverse micelles and competition of some groups to bond with water molecules.

As can be seen in Fig. 4, this competition is more distinguishable at low w_o, especially for the lowest frequency of OH stretching which is corresponding to the water bonded to head group of surfactant.

5. Discussion

The deconvolution results, based on Eqs. (1) and (2), are shown in Tables 1a and 1b at different w_o values and time. The mole fraction of trapped water is comparable with other states of water in reverse micelles. This behavior is predictable for water at this

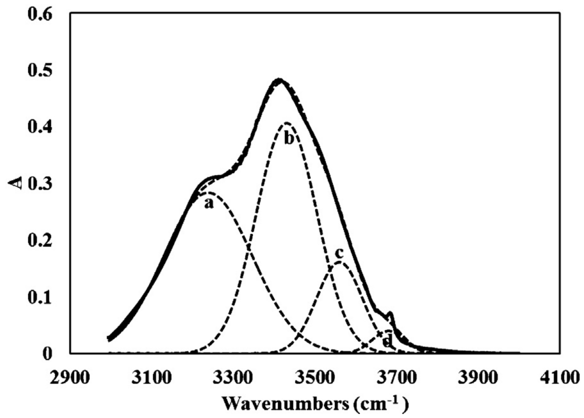

Fig. 3. Curve-fitting results of the OH stretching mode of water in CTAB/isooctane, 1-hexanol reverse micellar system at w_o = 30 and 3 (min) after preparation where a, b, c, and d are assigned to the OH stretching mode of water bonded to the head group of surfactant, bulk-like water, water bonded to the bromide counter ion, and trapped water.