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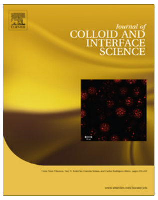

Spectroscopic study of the melting and reconstruction of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles from their frozen states

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ABSTRACT

The confinement of water in organic self-assemblies with nanometer-sized pores is ubiquitous in nature. Water pools in sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles have been intensively studied as a representative model of such confined water. However, the freezing and melting behavior of such water pools is poorly understood owing to their poor structural stability under phase transition. In the present work, the melting of iced water pools accompanied by a reconstruction of AOT reverse micelles was studied with infrared spectroscopy. For all AOT reverse micelles tested (R_w: 1.2–4.4 nm), a characteristic ice–water coexistence phase was observed during melting. The results provide experimental evidence of the previously proposed core–shell structure of the water pool. For larger frozen reverse micelles ($R_w > 2.3$ nm), shifts of the υ(OH) bands were observed. The spectra of the shifted υ(OH) bands were similar to those for the melted water pools in the smaller micelles. The mechanism of the reconstruction of AOT reverse micelles from their frozen states and the corresponding transient changes in the local environments were also discussed.

1. Introduction

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles have nanometer-sized spherical pores formed by self-assembly [1]. AOT reverse micelles are well known and have been widely studied because they have a well-controlled radius with a narrow size distribution [1–12]. Water confined in their spherical pores is referred to as a "water pool". The radius of the water pools (R_w) can be easily controlled by varying the water/surfactant molar ratio ($W_0 = [H_2O]/[AOT]$) [2,3]. Water pools in AOT reverse micelles have received attention as size-controlled microreactors. For example, water pools have been applied as model surfaces of biological membranes and as reaction pockets at activity points in enzymes [11,12]. Furthermore, they have been used as microreactors for the synthesis of colloidal particles [13] and have been applied in new analytical methods for extraction and/or chemical reactions, where the nanometer-sized aqueous phase domains were suspended in an oil phase [14–16].

In terms of the basic science and applications of such confined water at the nanometer scale, it is important to understand its thermal behavior. For studying the phase transition of water pools in self-assembled AOT reverse micelles, the effect of temperature on their structural stability, breakup, and reconstruction is crucial. Although AOT reverse micelles maintain a stable and homogeneous structure at room temperature, collision and fusion often take place. Thus, the exchange of the internal water and external AOT molecules occurs rapidly. When the AOT reverse micelles are cooled without special care, undesired loss of iced water pools often takes place during freezing. This has often hindered the investigation of the freezing behavior of water pools in AOT reverse micelles [17–20]. Consequently, our knowledge of the melting and reconstruction processes of AOT reverse micelles is limited.

Recently, to prevent loss of the internal water in AOT reverse micelles and thereby enable spectroscopic investigation of the phase transition of water pools, we developed a thin optical cell that can be combined with an attenuated total reflection infrared (ATR-IR) spectrometer [21]. Using a cooling rate of ca. -100 K min^{-1} and sample thickness of ca. 50 μm, the crystallization of water pools with large radii ($R_w \leqslant$ ca. 2.1 nm) was successfully achieved. It was revealed that cubic ice can be formed in the

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large, flexible, organic self-assembled AOT reverse micelles, as well as in inorganic and solid materials with a pore radius of ca. 2 nm. In our previous study, we succeeded in the freezing of water pools with radii greater than 1 nm [21]. This report detailed the first successful stable freezing for such large-sized AOT reverse micelles but was not extended to clarify the melting process. In addition, we failed to achieve stable freezing of water pools with radii greater than 2.1 nm, for which we observed the collapse of the micelles. Thus, reconstruction of the collapsed AOT reverse micelles is an interesting process that remains to be understood.

In the present study, melting of iced water pools with radii of 2.1 nm or less, and the reconstruction of collapsed AOT reverse micelles of radii greater than 2.1 nm upon freezing were studied using a custom-made cell combined with an ATR-IR spectrometer. Simultaneous measurements of the IR spectra in the υ(OH) mode provided rich information of the local structural changes in the hydrogen-bonding network of the water pool in the AOT reverse micelles during melting and reconstruction.

2. Materials and methods

2.1. Sample preparation

Sodium bis(2-ethylhexyl)sulfosuccinate (AOT; ⩾96%, Sigma–Aldrich, St. Louis, MO, USA) and *n*-heptane (99%, Sigma–Aldrich) were used without further purification. Water was purified by a Millipore Milli-Q system (Simpli Lab-UV, Merck Millipore, Billerica, MA, USA). The AOT reverse micelle solution was prepared at $W_0 = 5, 10, 15, 20$, and 30 by injecting water into a 0.5 M AOT–heptane solution.

The apparent water pool radius (R_w) of the different AOT reverse micelles was calculated from the difference between the apparent hydrodynamic radius (R_h) determined with dynamic light scattering (DLS) and the length of the AOT molecule (ca. 1 nm) [22]. The DLS apparatus (Nano ZS, Malvern Instruments, Malvern, UK) was equipped with a He–Ne laser operating at 633 nm and at a scattering angle of 90°. The AOT reverse micelle solution was prepared by injecting water into a 0.2 M AOT–heptane solution for DLS. The measurements were performed at 298 K. The DLS spectra and corresponding values of R_w for each W_0 are shown in the Supporting Information (Fig. SI.1). The obtained R_w values [nm] for W_0 are 1.2 ± 0.1 ($W_0 = 5.0$), 1.8 ± 0.1 ($W_0 = 10$), 2.1 ± 0.02 ($W_0 = 15$), 2.3 ± 0.1 ($W_0 = 20$), and 4.4 ± 0.3 ($W_0 = 30$), respectively.

2.2. ATR-IR measurements

All IR spectra were recorded on a Fourier transform infrared (FT-IR) spectrometer (Nicolet 6700, Thermo Fisher Scientific, Waltham, MA, USA) equipped with an ATR accessory, the prism of which comprised a single diamond crystal (Smart Orbit, Thermo Fisher Scientific, Waltham, MA, USA). We constructed a custom-made cooling unit on the ATR prism and cooled the sample solutions with liquid nitrogen via a thin cover glass (Matsunami, 0.12–0.17-mm thickness, C01824, Osaka, Japan). To set the sample thickness to ca. 50 μm, 0.8 μL of the AOT reverse micelle solution was dropped on the ATR prism in the Nicolet 6700 FT-IR spectrometer. The sample solution completely covered the ATR prism. The temperature of the sample solution was monitored in real time with a platinum resistance temperature detector (Netushin, UNR-351-100S-1-0.5-30-1000TF13-A-3-M4YS-3 mm, Saitama, Japan). The maximum cooling rate was estimated to be ca. $-100\ \mathrm{K\ min^{-1}}$ and the lowest temperature was ca. 193 K in the present system. It is worth noting that the sample thickness was only 50 μm, which is approximately one tenth of the typical sample thicknesses used in similar experiments. This significant reduction in sample thickness contributes to greater temperature uniformity in the sample during temperature change.

After confirming the freezing of the water pool by the changes in the shape of the υ(OH) band, the sample solutions were melted by removing the liquid nitrogen reservoir at room temperature (ca. 298 K) (Fig. 1(a)). The temperature rise of the sample solutions was monitored in real time, and the results are shown in Fig. 1(b). During the initial heating stage, the rate of temperature rise was approximately $1.0\ \mathrm{K\ s^{-1}}$. During the most important stage, namely, the onset of melting and the formation of a coexistence phase of ice and water, the rate of temperature rise was approximately $0.5\ \mathrm{K\ s^{-1}}$.

The IR spectra of the sample solutions from ca. 193 K to room temperature (ca. 298 K) were recorded with a resolution of $4\ \mathrm{cm^{-1}}$ and with no accumulation (i.e., single scans). The time resolution of the measurements was 2 s.

Spectral decomposition using curve fitting was performed with the equipped software (OMNIC 7.2a, Thermo Fisher Scientific, Waltham, MA, USA) and commercial software (KaleidaGraph, Ver. 4.00, Synergy Software). The baselines of all spectra were corrected before curve fitting, which was conducted with a combination of Gaussian functions.

3. Results and discussion

3.1. Spectroscopic monitoring of water pool melting

The spectral changes of the water pools for $R_w = 1.2$ nm from the frozen phase to the fully melted phase were first investigated.

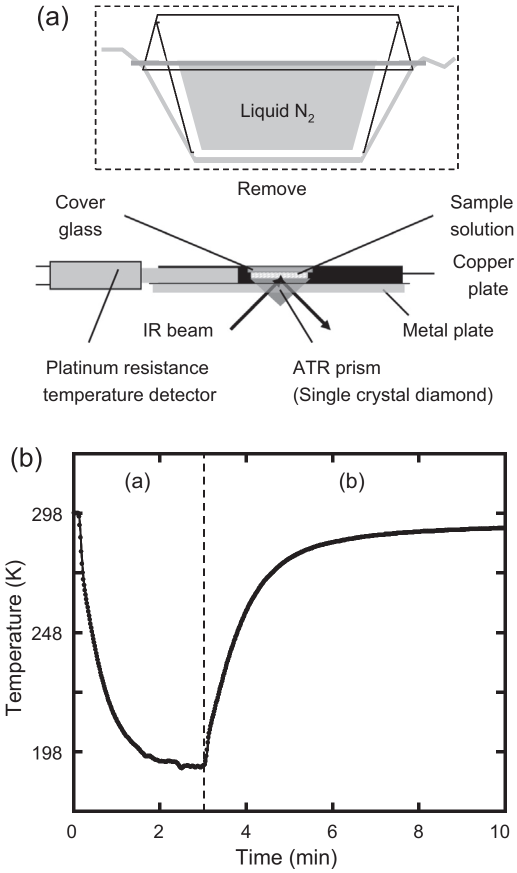

Fig. 1. (a) Schematic illustration of the rapid cooling cell for the ATR-IR measurements. (b) Time evolution of the temperature of the samples under freezing and melting.