

# Comparative Study on Structure of Solubilized Water in Reversed Micelles. 1. FT-IR Spectroscopic Evidence of Water/AOT/*n*-Heptane and Water/NaDEHP/*n*-Heptane Systems

Quan Li, Shifu Weng, Jinguang Wu,\* and Naifu Zhou

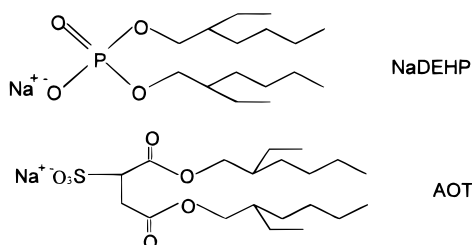
State Key Laboratory of Rare Earth Materials Chemistry and Applications,  
College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Received: July 10, 1997; In Final Form: November 4, 1997

The interactions of water with the polar headgroups in the reversed micelles of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and sodium bis(2-ethylhexyl) phosphate (NaDEHP) have been studied by means of Fourier transform infrared spectroscopy (FT-IR). O–H stretching bands of water in both systems varied with water content ( $W_0$ , the molar ratio of water to surfactant). When  $W_0$  increased from 1 to 20, the O–H stretching frequency shifted from 3493 to 3416  $\text{cm}^{-1}$  in AOT formed reverse micellar system and from 3385 to 3417  $\text{cm}^{-1}$  in NaDEHP system, approaching the frequency of the bulk water. As a response to water solubilization, frequency decreases of sulfonate and phosphate stretching mode in AOT and NaDEHP reverse micellar solutions have also been observed, indicating hydrations of the two surfactants. Results showed that the water molecules encapsulated in reversed micelles are similar to that in the bulk form when  $W_0 > 16$  in AOT system and  $W_0 > 12$  in NaDEHP system. In addition, the splitted peaks of the asymmetric sulfonate stretching band were found shifting to lower frequencies upon hydration, due to the weakening of the sodium–sulfonate interaction after hydration and an associated increase in their spatial separation.

## Introduction

Surfactants such as sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and sodium bis(2-ethylhexyl) phosphate (NaDEHP) can aggregate into reversed micelles and/or W/O microemulsions in nonpolar solvents, showing the capability of encapsulating more or less amounts of water (solubilization) into their hydrophilic micellar cores. This microscopic interfacial process associated with AOT, which is known as a typical reversed micelle and microemulsion-forming surfactant, has been widely studied by employing a great number of physicochemical methods,<sup>1</sup> such as NMR<sup>2,3</sup> and ESR<sup>4</sup> spectroscopies, light scattering,<sup>5</sup> fluorescence,<sup>6–8</sup> DSC<sup>9</sup> and conductivity<sup>10</sup> measurements, and infrared spectroscopy,<sup>11–14</sup> etc. On the other hand, in virtue of practical significance, NaDEHP, which is commonly used as the organophosphorus extractant in hydrometallurgy and the nuclear industry, has received more interest in the field of surface science, and, in particular, water solubilized in such aggregates is thought to mimic the water confined in biological membranes since NaDEHP molecules have a similar phosphate headgroup to that of phospholipids.<sup>15</sup> The structures of the two surfactants are as follows:



Although the structures of AOT and NaDEHP are similar in their hydrocarbon tails, the structures of the two surfactants are

not the same. In NaDEHP, the two hydrocarbon chains are equivalent, while AOT has unequivalent chains forming an asymmetric configuration. The chemical compositions and structures of the headgroups are also different. Thereby, it has been found that the aggregation behavior of the two surfactants differ significantly. In the case of AOT, the reversed micelles are spherical in shape and the size is increased with more water solubilized.<sup>16</sup> However, NaDEHP in *n*-heptane can form very large rodlike reversed micelles, but water can reduce their size tremendously.<sup>17</sup> A more interesting finding is that the water-swollen reverse micellar solution in *n*-heptane can transform to a bicontinuous microemulsion under appropriate conditions.<sup>18</sup>

Unfortunately, the knowledge about the structure and the state of the solubilized water are not at an unambiguous stage. Neuman and Park<sup>19</sup> pointed out that water solubilized in the reversed micelles of  $\text{Ni}(\text{DEHP})_2$  in *n*-heptane behaves differently from that of bulk water. Through the employment of the deconvolution technique to the reverse micellar solutions, efforts were made by some authors to identify the state of water in the core of the reversed micelles. MacDonald et al.<sup>20</sup> reported only two components, i.e., interfacial and bulklike water, while Jain et al.<sup>12</sup> concluded there are free water, bound water, and trapped water in the reversed micelles of AOT. Considering the different effect of polar headgroups and  $\text{Na}^+$  counterion on the water structure in the reversed micelles, we proposed a four-component model on the basis of the two models mentioned above.<sup>21</sup>

The hydration of the surfactants with solubilized water in reversed micelles and microemulsions has been the subject of investigations in this laboratory for decades.<sup>22–24</sup> Results obtained by NMR and FT-IR spectra as well as other physicochemical techniques showed that both cations and anions of the surfactants are hydrated by the water molecules in the core of the aggregates.<sup>23</sup> The hydration has been considered as a

\* To whom correspondence should be addressed.

**TABLE 1: Infrared Frequencies and Assignments of HDEHP, *n*-Heptane as Well as the Related Compounds/Reverse Micellar Solutions of Water/NaDEHP/*n*-Heptane and Water/AOT/*n*-Heptane**

HDEHP	<i>n</i> -heptane	NaDEHP	water/NaDEHP/ <i>n</i> -heptane		AOT	water/AOT/ <i>n</i> -heptane		assignments
			$W_0 = 1$	$W_0 = 20$		$W_0 = 1$	$W_0 = 20$	
			3493	3416		3385	3417	$\nu(\text{H}_2\text{O})$
2960	2959	2959	2959	2958	2958	2959	2959	$\nu_{\text{as}}(\text{CH}_3)$
2932	2925	2927	2926	2924	2929	2927	2928	$\nu_{\text{as}}(\text{CH}_2)$
2873	2873	2874	2874	2873	2873	2873	2874	$\nu_{\text{s}}(\text{CH}_3)$
2861	2858	2859	2859	2866	2860	2860	2861	$\nu_{\text{s}}(\text{CH}_2)$
					1733	1737	1735	$\nu(\text{C}=\text{O})$
				1644			1643	$\delta(\text{H}_2\text{O})$
	1467	1465	1466	1461	1463	1465	1467	$\delta_{\text{as}}(\text{CH}_3)$ , $\text{CH}_2$ sciss
1380	1379	1380	1379		1380	1380	1380	$\delta_{\text{s}}(\text{CH}_3)$ , $\text{CH}_2$ wag
1360					1360	1360		
1341		1341	1341					$\text{CH}_2$ wag
					1215	1219	1219	$\nu_{\text{as}}(-\text{SO}_3^-)$ , $\nu(\text{C}-\text{O})$
1252		1229	1220	1200				$\nu_{\text{as}}(\text{P}=\text{O})$
1114		1114	1110		1092			$\text{CH}_2$ wag, $\text{CH}_2$ twist
1051		1032	1031	1029				$\delta(\text{P}-\text{O}-\text{C})$ , $\nu_{\text{s}}(\text{P}=\text{O})$
					1048	1050	1046	$\nu_{\text{s}}(\text{S}=\text{O})$

main driving force for the solubilization process of water in the reversed micelles and/or microemulsion droplets.

The purpose of this paper is to obtain a definitive picture of how water interacts with surfactants in the core of reversed micelles by the method of FT-IR spectroscopy. The vibrational bands of NaDEHP, AOT, related compounds, and the reversed micelles have been assigned comprehensively. Also, a comparative analysis of the FT-IR spectra of AOT and NaDEHP-reversed micelles and the microstructures and states of the solubilized water molecules are presented. The influence on surfactant polar groups in the two reverse micellar systems has been discussed.

## Experimental Section

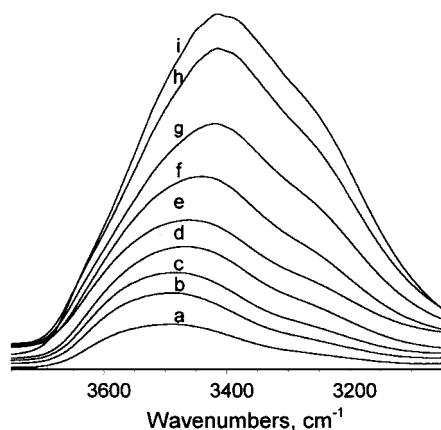
**Materials.** AOT (Fluka product with stated purity of >98%) was purified by the procedure described elsewhere.<sup>25</sup> *n*-Heptane (purity >99.5%) was used as received. Bis(2-ethylhexyl)-phosphoric acid (HDEHP) was purified by copper salt crystallization;<sup>26</sup> the purity of the resultant sample was 98%. Bidistilled water was used to prepare the ternary systems of  $\text{H}_2\text{O}/\text{AOT}/n\text{-heptane}$  and  $\text{H}_2\text{O}/\text{NaDEHP}/n\text{-heptane}$ . Sodium bis(2-ethylhexyl) phosphate (NaDEHP) was obtained by mixing and stirring the solution of 32 mL of HDEHP and excessive 10 mol/L of NaOH for several hours. After the addition of 30 mL of diethyl ether to the mixture in a separating funnel, two phases appeared. The lower phase, which contained an excess of NaOH, was removed. The upper phase, which contained NaDEHP, was washed repeatedly with bidistilled water until the pH value of aqueous phase was near 6.3. The NaDEHP-containing phase was then evaporated to dryness. AOT and NaDEHP were further vacuum desiccated at 60 °C for 48 h to help remove water residual and were stored over  $\text{P}_2\text{O}_5$ . Further analysis on water residual was also performed using FT-IR according to the quantitative relationship between absorbance of O—H stretching vibration of water versus water content. The amount of residual water was found to be 0.1 mol per mole of AOT (i.e.,  $W_0 = 0.1$ ). Such a small residual of water was considered as part of the total water in the mixtures under study.

**Preparation of Reverse Micellar Solutions.** Stock solutions of 1.0 M AOT and NaDEHP in *n*-heptane were prepared at room temperature by weight. Water contents ( $W_0$ ) in the two systems were expressed by the molar ratios of added water to surfactants (AOT and NaDEHP) in both reverse micellar systems. The solutions became transparent after gentle hand-shaking.

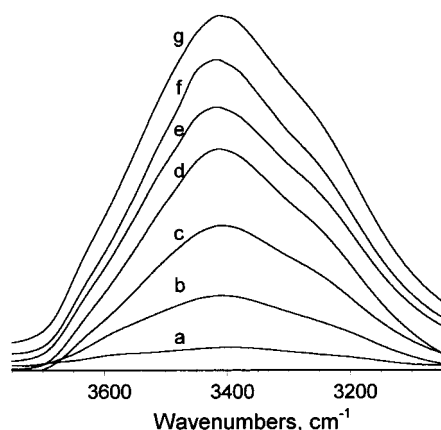
**Spectroscopy.** FT-IR spectra of all samples were recorded in the range of 900–4000  $\text{cm}^{-1}$  with a Nicolet Magna IR 750 spectrometer using  $\text{BaF}_2$  windows. Each sample was recorded with 32 scans at a spectral resolution of 2  $\text{cm}^{-1}$  and was carried out at room temperature ( $\sim 25$  °C). Asymmetric sulfonate stretching bands in the range of 1130–1330  $\text{cm}^{-1}$  were fitted into six subpeaks according to the results of second derivative with the help of the Galactic PeakSolve program.

## Results and Discussion

**IR Assignments of NaDEHP and AOT Formed Reversed Micelles.** Infrared spectra of AOT, NaDEHP, as well as the related compounds and reversed micelles at different water content were recorded in the region of 900–4000  $\text{cm}^{-1}$ . The characteristic frequencies of these solutions along with their assignments are summarized in Table 1. IR bands in the region of 3050–3750  $\text{cm}^{-1}$  were attributed to the O—H stretching vibrations of water in related reverse micellar solutions. Strong peaks around 2959 and 2926  $\text{cm}^{-1}$ , observed for all the investigated solutions, were due to asymmetric C—H stretching modes of methyl and methylene groups while the peaks at ca. 2874 and 2859  $\text{cm}^{-1}$  have their origin in the symmetric C—H stretching modes of methyl and methylene, respectively.<sup>27</sup> The strong bands of 1735  $\text{cm}^{-1}$  in solid AOT and  $\text{H}_2\text{O}/\text{AOT}/n\text{-heptane}$  reverse micellar solutions are attributed to the carbonyl group presented in AOT molecule. The bands around 1644  $\text{cm}^{-1}$ , found in the case of NaDEHP and AOT reverse micellar solutions at  $W_0 = 20$ , were due to the deformation mode of water molecules. Symmetric and asymmetric bending vibrations of methyl occurred around 1380 and 1460  $\text{cm}^{-1}$ , respectively.<sup>27</sup> The methylene group gives rise to four types of bending vibrations: scissoring, rocking, wagging, and twisting, which are listed in Table 1 as the main bands. The peaks around 1465 and 1341  $\text{cm}^{-1}$  arise from the methylene scissoring and wagging modes, respectively. The absorption bands of the succinate backbone as well as the asymmetric stretching bands of sulfonate group have been observed in the region of 1130 to 1330  $\text{cm}^{-1}$ .<sup>28,29</sup> A strong peak near 1252  $\text{cm}^{-1}$ , observed in the case of HDEHP, was assigned to the P=O stretching mode. It shifted to lower frequency (1229  $\text{cm}^{-1}$ ) after HDEHP was saponified. Addition of water to the stock solution shifted the peak to 1220 and 1200  $\text{cm}^{-1}$  when the water contents in  $\text{H}_2\text{O}/\text{NaDEHP}/n\text{-heptane}$  ternary systems were 1 and 20, respectively. The infrared peak at 1051  $\text{cm}^{-1}$  was attributed to the absorption of the P—O—C stretching mode of HDEHP.<sup>30</sup> It shifted to 1032



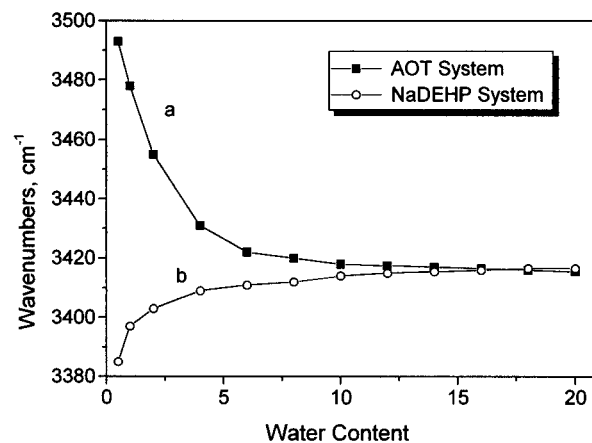
**Figure 1.** O—H stretching band of pure water (i) and water in H<sub>2</sub>O/AOT/*n*-heptane reverse micellar system at selected  $W_0$  values. a, b, c, d, e, f, g, and h represent IR peaks at  $W_0 = 2, 3, 5, 6, 7, 8, 10,$  and  $20$ , respectively.



**Figure 2.** O—H stretching band of pure water (g) and water in H<sub>2</sub>O/NaDEHP/*n*-heptane reverse micellar system at selected values of  $W_0$ . a, b, c, d, e, and f are infrared peaks at  $W_0 = 2, 3, 5, 6, 8,$  and  $20$ , respectively.

$\text{cm}^{-1}$  after HDEHP was saponified and then further shifted to lower frequencies after adding water in the system. It locates at  $1029 \text{ cm}^{-1}$  when the water content in H<sub>2</sub>O/NaDEHP/*n*-heptane reverse micellar system is 20. For the H<sub>2</sub>O/AOT/*n*-heptane system, the  $\nu_s(\text{S}=\text{O})$  varied from ca.  $1051$  to  $1046 \text{ cm}^{-1}$  with the increasing water content.

**O—H Stretching Bands of Water in the Two Reverse Micellar Systems.** O—H stretching bands of water in AOT and NaDEHP formed reverse micellar systems at different water contents; see Figure 1 and Figure 2, respectively. It can be seen from the two figures that the frequencies and shapes of the O—H stretching bands depend on the water content in respective reverse micellar systems. The bands are very broad with asymmetric shapes. Infrared spectra of surfactant-trapped water differ significantly from that of pure water, especially at low  $W_0$  values. It can be seen in Figure 1 that, in H<sub>2</sub>O/AOT/*n*-heptane reversed micelles, the shoulder at ca.  $3550 \text{ cm}^{-1}$  is stronger than that of  $3250 \text{ cm}^{-1}$  at lower  $W_0$  values. There is an increase of the intensity of the high-frequency component of the O—H band with an increase of  $W_0$  value. The intensity of the shoulder at ca.  $3250 \text{ cm}^{-1}$  increased quickly with increasing water content, especially when  $W_0 > 6$ . However, in the H<sub>2</sub>O/NaDEHP/*n*-heptane system, the intensity of the shoulder at ca.  $3250 \text{ cm}^{-1}$  is similar to that of  $\sim 3550 \text{ cm}^{-1}$ . The intensities of the two shoulders increase in parallel with increasing water content.

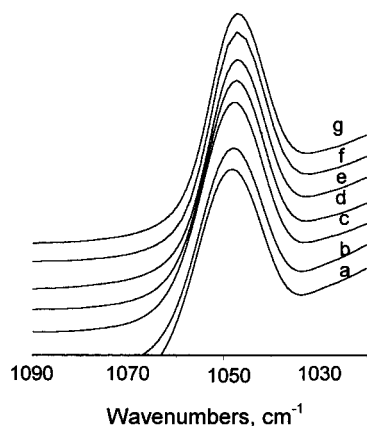


**Figure 3.** Variations of O—H stretching frequencies of water versus water content in the AOT and NaDEHP formed reverse micellar systems.

Compared with the AOT system, in H<sub>2</sub>O/NaDEHP/*n*-heptane reverse micellar solution at lower  $W_0$  values, the shoulders at  $\sim 3325 \text{ cm}^{-1}$  of the O—H stretching bands are much higher, as can be seen in Figure 1 and Figure 2. Apart from the variations in the shape of O—H stretching bands of water solubilized in the two reverse micellar systems, the frequencies of the bands also vary with water content in the respective systems. Variations of O—H stretching frequencies of water with  $W_0$  values in the two reverse micellar systems are depicted in Figure 3.

The significant findings from Figures 1–3 are 2-fold. First, the O—H stretching vibrations of water molecules in the two reverse micellar systems shifted from opposite directions to the same frequency of  $3417 \text{ cm}^{-1}$ , i.e., from  $3385$  to  $3417 \text{ cm}^{-1}$  in the NaDEHP system and  $3493$  to  $3417 \text{ cm}^{-1}$  in the AOT system, respectively. The results of the AOT formed reverse micellar system are consistent with the fitting curves previously reported.<sup>31</sup> Second, the O—H stretching bands of the two reverse micellar systems at higher water contents,  $W_0 > 12$  and  $16$ , respectively for NaDEHP and AOT systems, reveal a similar appearance to that for bulk water, and the maximum frequencies are identical ( $3417 \text{ cm}^{-1}$ ), which is known as that for bulk water. This fact provides evidence for the conclusion that, beyond the above water contents, additional water solubilized in the core behaves like bulk water. The conclusion provided here is based on the general band which is overlapped by various subpeaks. A detailed analysis of the various components of the deconvolution results will be carried out in future works.<sup>32</sup> For the H<sub>2</sub>O/AOT/*n*-heptane reverse micellar system, the greatest shifts are observed for  $W_0 \leq 6$  while no measurable shift occurs when the  $W_0$  values exceed 16. Only minor variation was observed when the water content is in the range of 6 and 16. For the H<sub>2</sub>O/NaDEHP/*n*-heptane reverse micellar system, however, the O—H stretching frequency increases initially with water content until  $W_0 = 12$ , above which it remains practically constant. Peak frequencies quoted in this report are the positions of maximum absorption. After the reversed micelles were fully hydrated, frequencies and shapes of the O—H stretching band of water encapsulated in the core of reversed micelles resemble those of bulk water.

The opposite shift frequency can also be seen from the chemical shifts of proton magnetic resonances of solubilized water in the two reverse micellar systems.<sup>32</sup> The  $W_0$  dependence of O—H stretching bands as well as the chemical shift ( $\delta$ ) of  $^1\text{H}$  NMR can be rationalized by considering the existence of different types of water species which interact with counterions and headgroups in respective reversed micelles. Upon consid-

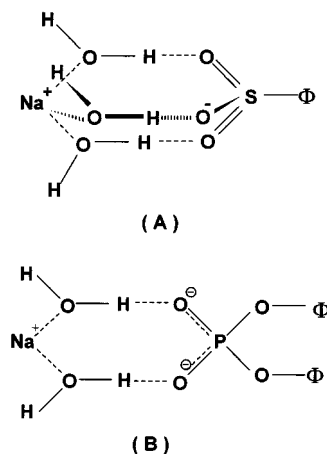


**Figure 4.** Symmetric stretching bands of AOT in H<sub>2</sub>O/AOT/*n*-heptane reverse micellar system, a, b, c, d, e and f represent infrared peaks at  $W_0 = 0.5, 1, 3, 6, 10, 15$ , and  $20$ , respectively.

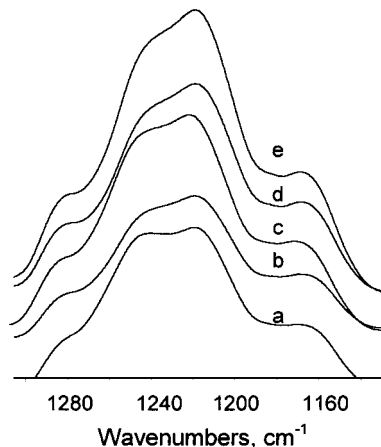
eration of different interactions of water with polar headgroups and sodium counterion, a hydration model is proposed in the following paragraph. The effects of counterion and headgroups on the shifts of O–H stretching bands as well as chemical shifts will be detailed in a subsequent paper.<sup>32</sup>

**Symmetric S=O Stretching Mode.** The infrared spectra of  $\nu_s(\text{S=O})$  in the H<sub>2</sub>O/AOT/*n*-heptane reverse micellar system at various water content are shown in Figure 4. It can be seen from Figure 4 that partial hydration of the reversed micelles in *n*-heptane is accompanied by a shift in the symmetric S=O stretching mode from 1051.4 to 1046.2 cm<sup>-1</sup> when  $W_0$  values increase from 0 to 20. These shifts are due to a weakening of the cation–anion interaction on hydration which results in the removal of the sodium counterion from the sulfonate headgroup.<sup>29</sup> The largest shift in wavenumber of  $\nu_s(\text{S=O})$  mode is observed for  $W_0 \leq 6$ , while the frequency remains practically constant when  $W_0 > 16$ . Only minor variation in peak positions is observed in the  $\nu_s(\text{S=O})$  parameters when the water content is in the range of 6 to 16. This agrees with the conclusion of Onori et al.<sup>13</sup> that part of the added water molecules interact with polar headgroup even at low  $W_0$  values. Our further investigations<sup>32</sup> show that about 43% of the added water molecules bonded with the sulfonate group. First added water tends to interact very strongly with sulfonate group at low water content.

Variations of infrared frequencies reflect the hydration processes of aggregates in reverse micellar systems. Up to  $W_0 = 6$ , the network of water molecules are severely perturbed and bound closely to the sulfonate group as well as Na<sup>+</sup> counterions at the water/organic interface. Beyond this point, there are gradual structural and electronic changes as the water molecules move farther away from the first hydration shell. Lowry et al.<sup>33</sup> observed that the wavenumber shift of the  $\nu_s(\text{SO}_3^-)$  mode upon hydration showed a strong dependence on the alkali metal cation. Other authors have also reported that the metal counterion changes the properties of the AOT reversed micelles, including shape, size, reactivity, and phase behavior et al.<sup>34–37</sup> Moran et al.<sup>29</sup> showed evidence for the hydrogen-bonding between water molecules and the  $-\text{SO}_3^-$  group by complete hydration ( $W_0 = 60$ ) of AOT reversed micelles in isoctane by D<sub>2</sub>O (known to form weaker hydrogen bonds<sup>38</sup>). The symmetric sulfonate stretching mode shifted to 1050 and 1046 cm<sup>-1</sup> in the Raman and infrared spectra, respectively, compared with 1048 and 1045 cm<sup>-1</sup> upon hydration by H<sub>2</sub>O. In the vicinity of the interface, one of the probable coordination structures of water with a sulfonate group and



**Figure 5.** Coordination structures of AOT (A) and NaDEHP (B) with Na<sup>+</sup> counterion by bridging water molecules.

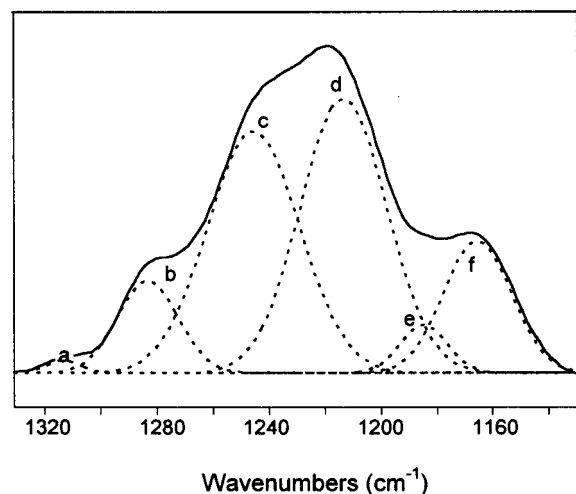


**Figure 6.** Infrared spectra of H<sub>2</sub>O/AOT/*n*-heptane reverse micellar system in the range of 1130 and 1330 cm<sup>-1</sup> at selected values of  $W_0$ . a, b, c, d, and e are peaks at  $W_0 = 0.5, 3, 6, 10$ , and  $20$ , respectively.

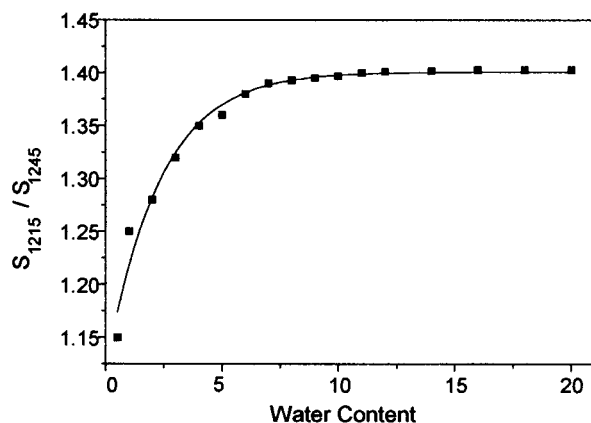
sodium counterion is shown in Figure 5 (A). The interactions of sulfonate groups with water molecules decrease the electric density of S and O atoms which results in weakening of the S=O bond considerably. The strong interactions lead the band of  $\nu_s(\text{S=O})$  to shift to lower frequencies. The strong interactions of water with Na<sup>+</sup> and  $-\text{SO}_3^-$  in AOT formed reversed micelles at low  $W_0$  values have also been studied by NMR,<sup>2,3,39,40</sup> ESR,<sup>5,40</sup> DSC,<sup>39,40</sup> microcalorimetry,<sup>41</sup> thermochemical measurements,<sup>42</sup> and light scattering.<sup>6</sup> Very similar to the results in this study, these investigations have also shown that up to ~10–16 water molecules per headgroup are structurally perturbed. These data suggest that the water molecules are located between the sodium cation and the three sulfonate oxygens, in agreement with previous results.<sup>43</sup>

**Asymmetric S=O Stretching Band.** The solubilized water in the cores of reversed micelles involves interaction with headgroups and counterions initially. The hydration of AOT weakens the interaction of Na<sup>+</sup> with  $-\text{SO}_3^-$ . There is evidence from the asymmetric sulfonate stretching band to verify this conclusion.

Figure 6 shows the infrared spectra of H<sub>2</sub>O/AOT/*n*-heptane reversed micelles at different water contents in the frequency range of 1130 to 1330 cm<sup>-1</sup>. The broad profile consists of the absorbance of the asymmetric S=O stretching mode, the C–O and C–C stretching band of ester linkage, as well as the CH<sub>2</sub> twisting mode.<sup>28,29</sup> An earlier study<sup>44</sup> reported that vibrations of the succinate backbone yield four bands in the region. The

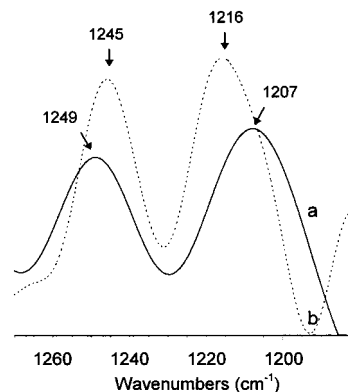


**Figure 7.** Curve-fitted results of infrared spectra of H<sub>2</sub>O/AOT/*n*-heptane reverse micellar solution at  $W_0 = 6$  in the range of 1130 and 1330 cm<sup>-1</sup>: (---) fitted results; (—) the infrared spectrum.



**Figure 8.** Variation of  $S_{1215}/S_{1245}$  as a function of water content in H<sub>2</sub>O/AOT/*n*-heptane reverse micellar system.

strong mode at 1160 cm<sup>-1</sup>, assigned to a combination of C—O and C—C stretching modes of ester linkage [C—C(O)—O], would be expected to contribute significantly to the intensity of the profile.<sup>29</sup> Correlation coupling between two neighboring —SO<sub>3</sub><sup>-</sup> groups yields two symmetric<sup>45</sup> and four asymmetric<sup>29</sup> sulfonate stretching bands. However, the coupling appears to be quite weak in the asymmetric bands, producing a broad profile dominated by two strong peaks at 1215 and 1245 cm<sup>-1</sup>. The infrared spectra change with increasing hydration of reversed micelles. To investigate the changes in the asymmetric S=O stretching bands quantitatively, the broad profiles have been curve-fitted as the sum of subpeaks with the help of the Galactic PeakSolve program according to the result of a second derivative. Figure 7 shows the curve-fitting results of reversed micelles at  $W_0 = 6$ . Two subpeaks at ca. 1215 and 1245 cm<sup>-1</sup> are assigned to the asymmetric S=O stretching mode. Such a doublet indicates that the degeneracy of this vibration is lifted by the nonsymmetric interaction between the sodium cation and the sulfonate group.<sup>29</sup> The formation of reversed micelles leads to a significant change in this profile. It is evident from Figure 6 that the intensity of ca. 1215 cm<sup>-1</sup> increases while the shoulder at ca. 1245 cm<sup>-1</sup> decreases with the increasing water content. The Galactic PeakSolve program also offers the area of each subpeak. Figure 8 shows the variations of area ratio  $S_r$  ( $S_{1215}/S_{1245}$ ) vs water content in the H<sub>2</sub>O/AOT/*n*-heptane reverse micellar system. It can be seen from Figure 8 that the ratio of

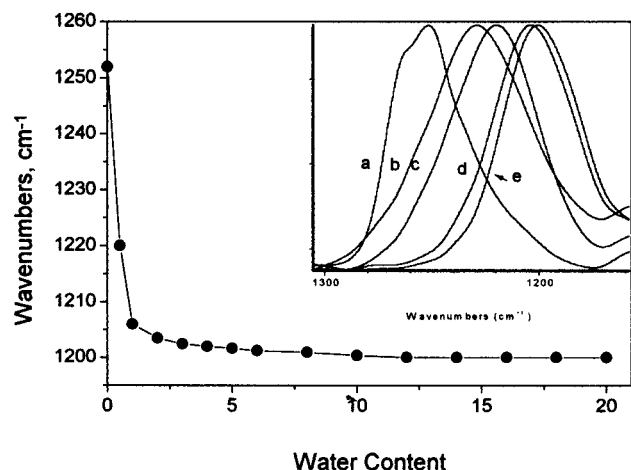


**Figure 9.** Fourier deconvolution results of asymmetric S=O stretching bands of H<sub>2</sub>O/AOT/*n*-heptane reversed micelles at different water contents, a and b are results at  $W_0 = 0$  and 20, respectively.

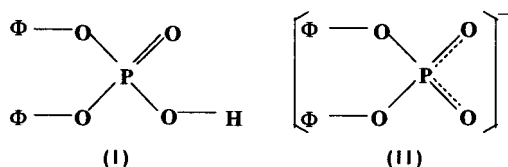
$S_{1215}/S_{1245}$  increases with water content in the system. The data indicate that the greatest variations in the ratio are observed for  $W_0 \leq 6$ , with measurable shifts occurred up to  $W_0 \leq 16$ , but no noticeable changes beyond  $W_0 \geq 16$  (as discussed in the previous section).

For the asymmetric S=O stretching band, the magnitude in wavenumber of the two split peaks reflects the interaction between sodium cation and sulfonate group. The doublet are overlapping and it is difficult to distinguish the two peaks in the profile. However, by employing the Fourier deconvolution technique, the magnitude of the doublet can be identified and measured readily. Figure 9 shows the Fourier deconvolution results of the asymmetric S=O stretching bands in H<sub>2</sub>O/AOT/*n*-heptane reversed micelles at  $W_0 = 0$  (a) and 20 (b). The frequencies of the doublet occur at ca. 1249 and 1207 cm<sup>-1</sup> in stock solution ( $W_0 = 0$ ) and they vary with increasing water content. When the  $W_0$  value reaches 20, the two split peaks locate at 1245 and 1216 cm<sup>-1</sup>, respectively. The magnitude of the band splitting decreases with the increasing water content, reflecting the weakening of the interaction between sodium counterion and the sulfonate group as well as the associated increase in their spatial separation. This observation is consistent with NMR calculations by Maitra, that the average area per headgroup increases upon hydration.<sup>46</sup> As suggested in the previous section, water molecules are located between the sodium counterion and the three sulfonate oxygens, as shown in Figure 5A. The associated charge-dipole and hydrogen-bonding interactions would be expected to disrupt the water hydrogen-bonding network. Even when the water content exceeds 20, two asymmetric sulfonate stretching peaks are still evident, suggesting that some sodium counterions must interact with sulfonate groups under such conditions. This conclusion agrees with those reported previously<sup>3</sup> that more than 70% of the sodium counterions remain associated with the sulfonate groups in fully hydrated reversed micelles.

**Asymmetric P=O Stretching Mode.** Variations of P=O stretching vibrations of HDEHP and the H<sub>2</sub>O/NaDEHP/*n*-heptane reversed micelles with respect to the water content are plotted in Figure 10. Inserted peaks of b, c, d, and e are phosphate stretching vibrations in the reversed micelles at  $W_0 = 0, 0.5, 1$ , and 20, respectively, and peak a is the phosphate stretching band of HDEHP. The band located at 1252 cm<sup>-1</sup> was assigned to the stretching P=O vibration in HDEHP molecules. After saponification, the P=O bond is no longer present in NaDEHP, for the group [O—P—O]<sup>-</sup> is formed due to the electron-cloud delocalization and thus homogenized,<sup>47,48</sup> as illustrated in Figure 11. In the IR spectra, the original



**Figure 10.** The changing position of phosphate stretching band of NaDEHP in  $\text{H}_2\text{O}/\text{NaDEHP}/n$ -heptane reverse micellar system as a function of water content. Inserted peaks b, c, d, and e are phosphate stretching bands at  $W_0 = 0, 0.5, 1$ , and  $20$ , respectively; a is the infrared peak of HDEHP molecule.



**Figure 11.** The structures of the phosphate group in HDEHP and NaDEHP ( $\Phi$  is 2-ethylhexyl group).

frequency (ca.  $1252\text{ cm}^{-1}$ ) for  $\text{P}=\text{O}$  is reasonably displaced by two frequencies, i.e., ca.  $1229\text{ cm}^{-1}$  for the asymmetrical and  $1120\text{--}1050\text{ cm}^{-1}$  for the symmetrical, which is overlapped with the strong absorption band around  $1032\text{ cm}^{-1}$  for the  $\text{P}-\text{O}-\text{C}$  group.

Compared with structure II, there is a considerable strengthening of the  $\text{P}=\text{O}$  bond in the structure I of Figure 11.<sup>49</sup> Addition of water to the stock solution, accompanied by the hydration of the phosphate, results in the variation of  $\nu_{\text{as}}(\text{P}=\text{O})$  to lower frequencies. With increasing water content (from 0 to 20), the  $\text{P}=\text{O}$  stretching vibration shifted from  $1229$  to  $1200\text{ cm}^{-1}$ , due to the strong interaction of water molecules with the polar phosphate group. The most significant variations (from  $1229$  to  $1206\text{ cm}^{-1}$ ) occur when the  $W_0$  value changes from 0 to 5 in the  $\text{H}_2\text{O}/\text{NaDEHP}/n$ -heptane reverse micellar system, as illustrated in Figure 10. Only a minor shift (about  $3\text{ cm}^{-1}$ ) is observed in the  $\nu_{\text{as}}(\text{P}=\text{O})$  parameters when the  $W_0$  values are in the range of 5 and 12 and no observable shift when  $W_0 > 12$ . Similar to the coordination structure of sulfonate groups and sodium counterion with the water molecules, the probable coordination form of water molecules with phosphate group and  $\text{Na}^+$  counterion in  $\text{H}_2\text{O}/\text{NaDEHP}/n$ -heptane reversed micelles is shown in Figure 5B. The interaction weakens the  $\text{P}=\text{O}$  bond and lowers the frequency of the  $\nu_{\text{as}}(\text{P}=\text{O})$  stretching vibration.

## Conclusions

Water molecules encapsulated in reversed micelles exhibit peculiar properties owing to the interaction of water with polar headgroups of surfactants.  $\text{O}-\text{H}$  stretching frequencies of water in  $\text{H}_2\text{O}/\text{AOT}/n$ -heptane and  $\text{H}_2\text{O}/\text{NaDEHP}/n$ -heptane reverse micellar systems shift toward the value of bulk water from the opposite directions with the increasing water content in the respective systems. Meanwhile, hydration of the two reverse

micellar systems results in shifts of the stretching vibrations of headgroups to low frequencies. By detailed examination of the  $\nu_{\text{s}}(\text{S}=\text{O})$  and  $\nu(\text{P}=\text{O})$  bands, it is found that up to  $W_0 \sim 6$  (severely perturbed) water molecules are bound closely to the headgroups and  $\text{Na}^+$  ions at the water/organic interface. The changes in the interactions of water molecules with the ions in AOT and NaDEHP formed reverse micellar systems occurred when the water content is less than 16 and 12, respectively, beyond which, no variations can be observed from the parameters of infrared spectra. It can be concluded that the surfactant molecules can be hydrated to a maximum of 16 and 12 for AOT and NaDEHP formed reverse micellar systems, respectively. Addition of more water does not appear to change the electronic environment, and there is no further frequency shift after the reversed micelles are fully hydrated.

**Acknowledgment.** The authors thank NSF of China and the Climbing Program for financial support.

## References and Notes

- De, T. K.; Maitra, A. *Adv. Colloid Interface Sci.* **1995**, 59, 95.
- Martin, C. A.; Magid, L. J. *J. Phys. Chem.* **1981**, 85, 3938.
- Wong, M.; Thomas, J. K.; Nowak, T. *J. Am. Chem. Soc.* **1977**, 99, 4730.
- Haering, G.; Luisi, P. L.; Hauser, H. *J. Phys. Chem.* **1988**, 92, 3574.
- Zulauf, M.; Eiche, H.-F. *J. Phys. Chem.* **1979**, 83, 480.
- Belletete, M.; Lachapelle, M.; Durocher, G. *J. Phys. Chem.* **1990**, 94, 5337.
- Junquera, E.; Pena, L.; Aicart, E. *Langmuir* **1997**, 13, 219.
- Karukstis, K.; Frazier, A. A.; Martula, D. S. *J. Phys. Chem.* **1996**, 100, 11133.
- Boned, C.; Peyrelasse, J.; Moha-Ouchanne, M. *J. Phys. Chem.* **1986**, 90, 634.
- Nazario, L. M. M.; Hatton, T. A.; Grespo, J. P. S. G. *Langmuir* **1996**, 12, 6326.
- D'Angelo, M.; Onori, G.; Santucci, A. *J. Phys. Chem.* **1994**, 98, 3189.
- Jain, T. K.; Varshney, M.; Maitra, A. *J. Phys. Chem.* **1989**, 93, 7409.
- Onori, G.; Santucci, A. *J. Phys. Chem.* **1993**, 97, 5430.
- Li, Q.; Li, W.-H.; Weng, S.-F., et al. *Acta Phys.-Chim.* **1997**, 13, 438 (in Chinese).
- Li, Q.; Li, Y.; Li, W.-H., et al. *Acta Scientiarum Naturalium Universitatis Pekinensis* **1997**, 33 (4), 409 (in Chinese).
- Ruckenstein, E.; Nagarajan, R. *J. Phys. Chem.* **1980**, 84, 1349.
- Yu, Z.-J.; Neuman, R. D. *Langmuir* **1994**, 10, 2553.
- Yu, Z.-J.; Neuman, R. D. *Langmuir* **1995**, 11, 1081.
- Neuman, R. D.; Park, S. J. *J. Colloid Interface Sci.* **1992**, 152, 41.
- MacDonald, H.; Bedwell, B.; Gulari, E. *Langmuir* **1986**, 2, 704.
- Li, Q.; Weng, S.-F.; Li, Y., et al. *Abstracts of Papers Pittcon'97*, Atlanta, GA, March, 1997; No. 1000.
- Wu, C. K.; Kao, H. C.; Chen, T., et al. *Proceedings of the International Solvent Extraction Conferences (ISEC'80)*, Belgium, 1980; No. 80-23.
- Wu, J.-G.; Shi, N.; Zhou, W.-J., et al. *Progr. Natural Sci.* **1997**, 7, 257.
- Zhou, N.-F.; Wu, J.-G.; Yu, Z.-J., et al. *Sci. China, Ser. B* **1997**, 40, 61.
- Maitra, A. N.; Eicke, H.-F. *J. Phys. Chem.* **1981**, 85, 2687.
- Patridge, J. A.; Johnson, R. C. *J. Inorg. Nucl. Chem.* **1969**, 31, 2587.
- Sheppard, N. *Trans. Faraday Soc.* **1955**, 55, 1465.
- Fowler, R. G.; Smith, R. M. *J. Opt. Soc. Am.* **1953**, 43, 1054.
- Moran, P. D.; Bowmaker, G. A.; Cooney, R. P. *Langmuir* **1995**, 11, 738.
- Zhou, N.-F.; Wu, J.-G.; Sarathy, P. K., et al. *Proceedings of the International Solvent Extraction Conference (ISEC'90)*; (Sekine, T., Ed.; Elsevier Science Publishers) B. V.: Tokyo, 1992; p 165.
- Giammona, A.; Goffredi, F.; Liveri, V. T., et al. *J. Colloid Interface Sci.* **1992**, 154, 411.
- Li, Q.; Weng, S.-F.; Wu, J.-G. *J. Phys. Chem.*, submitted for publication.
- Lowry, S. R.; Mauritz, K. A. *J. Am. Chem. Soc.* **1980**, 102, 4665.
- Eastoe, J.; Tower, T. F.; Robinson, B. H., et al. *J. Phys. Chem.* **1993**, 97, 1459.
- Petit, C.; Lixon, P.; Pileni, M. P. *Langmuir* **1991**, 7, 2620.

- (36) Bardez, E.; Larrey, B.; Zhu, X. X., et al. *Chem. Phys. Lett.* **1990**, 171, 362.
- (37) Leodidis, E. B.; Hatton, T. A. *Langmuir* **1989**, 5, 743.
- (38) Eicke, H.-F.; Christen, H. *Helv. Chim. Acta* **1978**, 61, 2258.
- (39) Quist, P.-O.; Halle, B. *J. Chem. Soc., Faraday Trans. 1* **1988**, 84, 1033.
- (40) Hauser, H.; Haering, G.; Pande, A., et al. *J. Phys. Chem.* **1989**, 93, 7869.
- (41) Haandrikman, G.; Daane, G. J. R.; Kerkhof, F. J. M., et al. *J. Phys. Chem.* **1992**, 96, 9061.
- (42) Goto, A.; Harada, S.; Fujita, T., et al. *Langmuir* **1993**, 9, 86.
- (43) Christopher, D. J.; Yarwood, J.; Belton, P. S.; Hills, B. P. *J. Colloid Interface Sci.* **1992**, 152, 465.
- (44) Moran, P. D.; Bowmaker, G. A.; Cooney, R. P. *J. Mater. Chem.* **1995**, 5, 295.
- (45) Larsson, K. *Chem. Phys. Lipids* **1973**, 10, 165.
- (46) Maitra, A. *J. Phys. Chem.* **1984**, 88, 5122.
- (47) Socrates, G. *Infrared Characteristic Group Frequencies*; John Wiley: New York, 1980; p 66.
- (48) Sato, T.; Nakamura, J. *Inorg. Nucl. Chem.* **1972**, 34, 3721.
- (49) Wu, J.-G.; Shi, N.; Gao, H.-C., et al. *Sci. Sinica, Ser. B* **1984**, 27, 249.