

A Proton Magnetic Resonance Study of the System: Di-(2-Ethylhexyl)Sodium Sulfosuccinate– Water–*n*-Octane

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Proton magnetic resonance (pmr) has proved to be a useful technique for following the behavior of water in the complex equilibria produced when water is added to solutions of di-(2-ethylhexyl)sodium sulfosuccinate, (Aerosol OT), in *n*-octane. This system passes through several clear and turbid phase transitions as water content is increased. On the basis of the appearance and location of water proton peaks in the various phases as compared to bulk water, it was possible to differentiate between solubilized and separated water and to draw some conclusions as to the participation of water in these phase transitions.

INTRODUCTION

During the course of an investigation of the system, di-(2-ethylhexyl) sodium sulfosuccinate (Aerosol OT)–water–*n*-octane, it was noted that several phase transitions occurred as the proportion of water increased. For example, water added to a 2% w/w solution of Aerosol OT (AOT) in *n*-octane is solubilized up to a water-to-surfactant molar ratio of 18. At this point a gray-white turbidity is produced, which separates upon standing into two clear phases. With increasing water content, the volume of the lower aqueous layer increases, reaching a maximum, and then decreases until a one-phase blue translucent region occurs. This transition is observed at about 125 moles of water per mole of AOT. This second one-phase region continues to persist with increasing water content until about 145 moles of water per mole of AOT, where another turbid system is produced. Upon standing phase separation occurs, but this

differs from that seen in the first turbid region in that virtually all the water and AOT are now in the lower aqueous layer rather than being distributed between the two phases as in the first case.

The proton magnetic resonance (pmr) technique has been used to investigate changes in the structure of water in the presence of surface-active molecules (1, 2), and in particular to differentiate between solubilized and emulsified water found in water-in-oil emulsions (3). Since the phase transitions observed in the present study appeared to be dependent on the proportion and state of water present, and were believed to involve equilibria between micellar solubilized and emulsified water, it was decided to apply this technique. Of particular interest was the state and location of water in the two-phase, "first turbid region," which appears and disappears merely by increasing the proportion of water present.

EXPERIMENTAL

Materials. Di-(2-ethylhexyl)sodium sulfosuccinate was synthesized according to a procedure described previously (4). Surface

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tension measurements in distilled water at 25°C indicated a critical micelle concentration (c.m.c.) of $2.45 \times 10^{-3} M$, in general agreement with other reported values (4, 5). The absence of a minimum at the c.m.c. indicated a high degree of purity. The *n*-octane (Aldrich Chemical Co.) was treated according to the method of Gillap *et al.* (6). Twice distilled water was used in all experiments.

Instrumentation. Proton magnetic resonance spectra were obtained with a Varian A60 spectrometer. The temperature was maintained at $25^\circ \pm 1^\circ C$, the temperature setting being determined by the chemical shift of the hydroxyl protons of methanol relative to tetramethylsilane (TMS).

Procedure. Water was added with an Agla micrometer syringe (Burroughs-Wellcome and Co.) to 10 ml. portions of a 2% w/w solution of AOT in *n*-octane. The amount of water added was sufficient to give a molar ratio of water to AOT which produces each of the regions described above. This concentration of AOT was selected to provide amounts of water solubilized which could be detected in the spectrometer; however, the various phase transitions were also observed at concentrations down to 0.1% w/w AOT. Samples, contained in 20 ml. Pyrex culture tubes with Teflon-lined screw caps, were equilibrated for 24 hours at 25°C prior to the pmr determinations. These were placed in an instrument room at $25^\circ \pm 2^\circ C$, shaken for one minute, and then pipetted into standard pmr sample tubes. The tubes were securely stoppered, shaken, and placed in the rotator.

To confirm the identity of the peaks due to water, deuterium oxide (Matheson, Coleman and Bell), 99.5 mole % minimum, was substituted for the water, the absence of such a peak being expected in the case of deuterium oxide. Water is soluble in *n*-octane to the extent of 0.014 gm per 100 gm and was not detectable in the pmr spectra (7).

RESULTS AND DISCUSSION

As seen in Fig. 1, a 2% w/w solution of AOT in *n*-octane shows pmr absorption due to the protons of the methyl, methylene, and methyne groups of AOT and the methyl

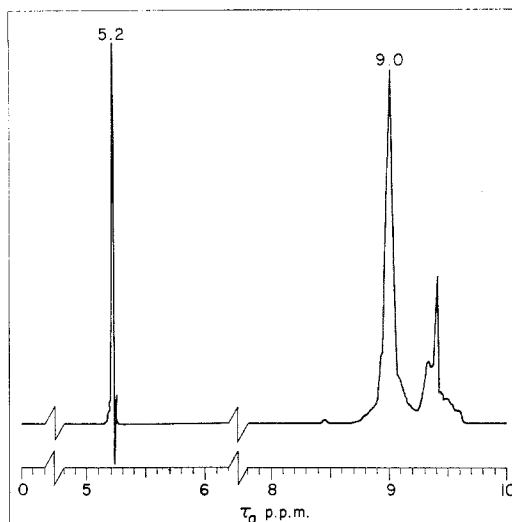


FIG. 1. Proton magnetic resonance spectrum of 2% w/w Aerosol OT in *n*-octane at 25°C, with a capillary tube containing water. $\tau_a = 9.0$ ppm assigned to methylene peak and $\tau_a = 5.2$ for the water peak.

and methylene groups of *n*-octane. For all spectra the methylene peak, set at an arbitrary scale value, $\tau_a = 9.00$ ppm, was chosen as the internal standard since materials such as TMS might have been solubilized or otherwise interfere with micellar structure. In order to determine the location of the "free" water peak, a capillary tube containing water was enclosed in a pmr sample tube filled with 2% w/w AOT in *n*-octane. This peak appeared at $\tau_a = 5.20$ ppm (Fig. 1). It should be kept in mind, however, that water in a capillary tube may give a 0.1 to 0.5 ppm difference in chemical shift from free water in a sample so that this value is only a close approximation to that of actual free water.

As tabulated in Table I and shown with examples in Fig. 2, the addition of water produces new peaks in the region between $\tau_a = 5.20$ and 9.00 ppm, but, apparently because of a lack in instrument sensitivity, these are not detected until 6.98 moles of water per mole of AOT have been added. That the new peak is due to solubilized water is seen when deuterium oxide is used instead of water (Fig. 2), since even at a very high instrument amplification no peak

TABLE I
PEAK LOCATION AND RELATIVE PEAK AREA FOR
SOLUBILIZED AND EMULSIFIED WATER

Moles H ₂ O Mole AOT	Solubilized water		Emulsified water (separated phase)	
	Peak location (τ_a)	Integra- tion curve height ^a	Peak location (τ_a)	Integra- tion curve height ^a
6.98	6.00	0.25	—	—
17.5	5.74	1.0	—	—
31.4	5.68	2.0	5.46	0.25
52.5	5.62	3.5	5.25	1.2
69.8	5.60	4.0	5.28	2.0
87.5	5.58	5.0	5.30	2.1
104.7	5.56	6.5	5.31	1.5
113.5	5.54	8.3	5.31	1.0
122.3	5.53	8.5	—	—
125.8	5.53	8.8	—	—
131.1	5.53	9.0	—	—
139.6	5.53	10.0	—	—
148.4	5.42	13.6	—	—

^a Arbitrary units based on number of grid boxes from base line to curve height.

is observed. An increase in the quantity of water to a molar ratio of 17.5 (still a one-phase system) produces a peak of greater area along with a shift in the τ_a value (Table I). The increase in area due to a greater amount of solubilized water is seen from an increase in the height of the integration curve for each peak, as expressed in arbitrary units of grid boxes (Table I). These values represent relative changes in the area under each peak and hence the change in the number of protons contributing to that peak.

An increase in water content to values ranging from 31.4 to 113.5 moles of water per mole of AOT (Fig. 2 and Table I) gives two peaks, one apparently due to solubilized water as seen at lower molar ratios, and the other due to separated "bulk" or emulsified water. Again, the use of deuterium oxide confirms that these are water peaks. Differences in the two peaks should be noted. As the molar ratio of water increases the solubilized water peak increases and migrates towards the "free" water peak as 5.20 ppm, whereas that due to separated phase first increases in area, migrates in the same direction, but then reverses direction with a concurrent decrease in area. The changes in

peak area would indicate that water added beyond the first turbidity point continues to partition between the separated water and the *n*-octane, first favoring separation and then returning to be solubilized in the *n*-octane. That the AOT micelle in *n*-octane is capable of further water solubilization, despite being in equilibrium with separated water, seems to suggest that with each increment of water the micelle undergoes reorganization as well as an increase in size. Any number of micellar structures, from spherical to laminar, may exist, each with different solubility characteristics. In all cases the location of the solubilized water peaks shows that water solubilized in the micelle appears different from "free" water,

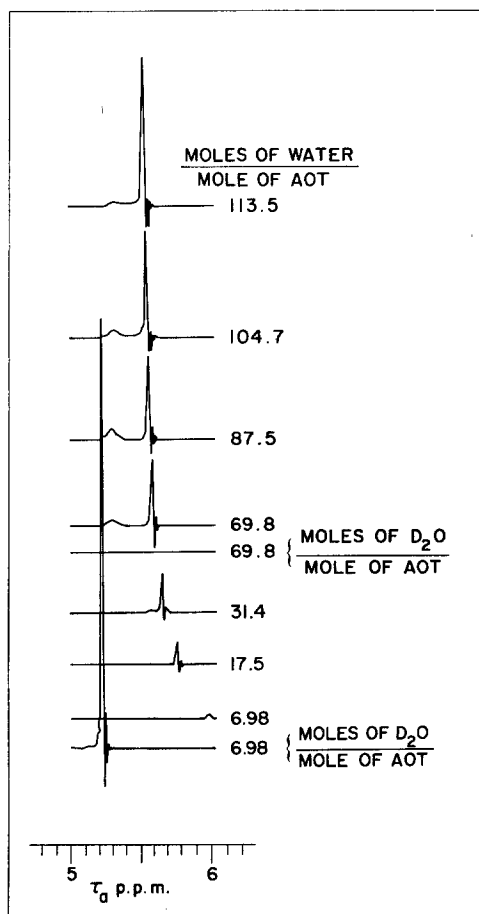


FIG. 2. Proton magnetic resonance spectra for the colorless and first turbid regions of water-Aerosol OT-*n*-octane systems at 25°C.

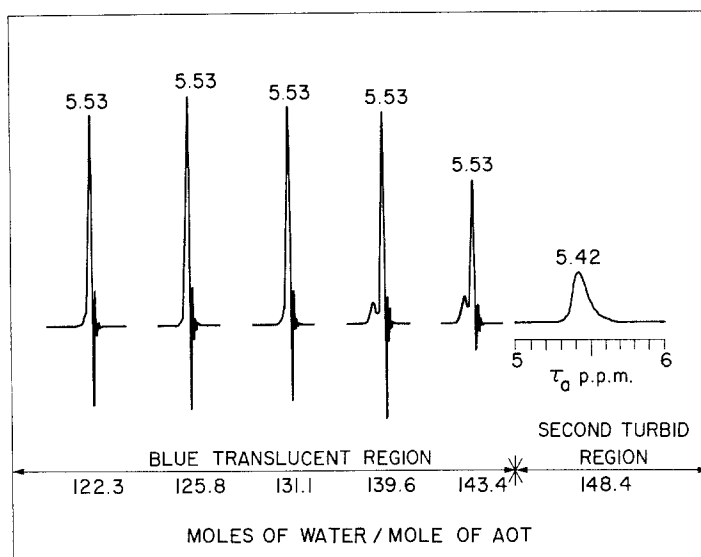


FIG. 3. Proton magnetic resonance spectra for the blue translucent and second turbid regions of water-Aerosol OT-*n*-octane systems at 25°C.

indicating some influence of the micellar environment on water structure. It is interesting to note also that separated water observed above 31.4 moles of water per mole of AOT, although considerably closer to "free" water in behavior, shows greater proton restriction as it first separates. One would expect some partitioning of AOT and octane into this separated water which could be responsible for these observations. Indeed, independent analysis of the separated phase indicates an AOT concentration greater than its critical micelle concentration in water (8).

As seen in Fig. 3 and Table I, if the water content is increased to 122.3 moles per mole of AOT and beyond, the peak due to separated water no longer exists but that due to solubilized water continues to increase in area. Since the peak corresponding to water solubilized in this blue-translucent one-phase region exhibits no significant shift from that seen just before the transition, it is apparent that the process of clearing begins well before the transition point and merely represents the point where return of separated water is complete. Reorganization and growth apparently continue to occur above 122.3 moles of water per mole of AOT since the pmr peak area (Table I) continues to increase and a blue color develops.

A final comment may be made concerning the events leading up to the second turbid region and the interpretation of pmr observations. Although peak areas for solubilized water in the blue-translucent region increase with increasing water content the region prior to turbidity exhibits broadening at the base of the peak and the appearance of a secondary peak. Since this is a one-phase system which is approaching a phase transition point it is possible that these observations represent some preliminary aggregation of micelles. This view is strengthened by independent analysis of the separated phases beyond a molar ratio of 145, which shows that virtually all the water and AOT plus some *n*-octane are in the lower layer, whereas the upper layer is essentially pure *n*-octane (8). Thus, aggregation of the large water-swollen AOT micelles may be responsible for the final phase transition and pmr measurements are picking this up even before it becomes significantly apparent visually.

The equilibria associated with these phenomena are obviously too complex to allow interpretation based upon the pmr technique alone. However, these measurements, made directly on clear and turbid systems, were most helpful in first observing these transitions and the apparent location of water in each situation. On the basis of

these observations we are now in a position to carry out more direct analyses of this system and others closely related to it (8).

In general, it would appear that proton magnetic resonance measurements offer those interested in the complex equilibria associated with micellar solubilization of water an excellent tool for study, particularly if higher degrees of resolution and peak detection can be utilized.

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