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Formation of AOT Reversed Micelles and W/O Microemulsions

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The dependence of limiting amounts of solubilized water upon the concentration of sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethanesulfonate (AOT) in apolar solvents was measured by the Karl-Fischer method at 30 °C. In the solubilization regions, two or three states of water, i.e., water bound directly to ionic head groups of AOT and water bound to the hydrated ionic groups or bulk-like water, were found to exist from NMR, ESR, fluorescence, and near infrared spectroscopic measurements. These types of water were related to the formation of reversed and swollen micelles or W/O microemulsions.

Many studies concerning the solubilization states of water in reversed micelles and W/O microemulsions of sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethanesulfonate (AOT) have been carried out[1)] using NMR,[2,3)] ESR,[2,4–7)] FT-IR,[8,9)] and Raman[10)] spectroscopic techniques. In these studies, however, the types of solubilization states or the number of water molecules bound directly to AOT were widely different among these techniques in spite of identical AOT/solvent systems.[2,4,8,11,12)] This may be due to the impurity contained in AOT using different purification methods, or a difference in the time required for solubilization equilibrium. These studies were also carried out at a given concentration of AOT.

In this paper the time required for solubilization equilibrium of water in nonaqueous solutions of carefully purified AOT was checked by Karl-Fischer titration. The solubilization states of water in the concentration range of 0—100 mmol kg^{-1} AOT in various apolar solvents were systematically studied by NMR, ESR, fluorescence, near infrared spectroscopic, and light-scattering techniques. The obtained states were discussed in connection with the formation of reversed micelles or W/O microemulsions.

Experimental

Sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethanesulfonate (AOT, Nakarai Chemicals Co., Ltd.) was purified according to a previous method.[13–15)] Cyclohexane, heptane, isooctane-(2,2,4-trimethylpentane), dodecane, and toluene of guaranteed reagent grade were used as solvents.

The limiting amounts of water solubilized by AOT in various solvents were measured at 30 °C by Karl-Fischer titration according to a previous paper,[16)] i.e., water was added into the surfactant solutions until very small amounts of water or precipitates separated from the solubilization systems. The solubilization equilibrium checked by the titration required one week just in the case of nonionic surfactant systems.[16)] The water content dissolved in the obtained transparent solutions was determined by the Karl-Fischer method. In the no-water system, the water content in a 100 mmol kg^{-1} AOT solution was 0.02 molar ratio of water to the surfactant. Here, the molar ratio of water to surfactant is abbreviated as R_w.

The chemical shifts of solubilized water (δ_H) were measured using a JEOL FX-90Q spectrometer. TMS was used as an internal standard.

The rotational correlation time (τ_c) and hyperfine splitting constant (a_N) of 2,2,6,6-tetramethyl-4-(phosphonooxy)piperidine used as an ESR probe in solubilized water was measured using a JEOL-FEIX spectrometer. The concentration of the probe was 1×10^{-4} mol kg^{-1}. The microwave power was kept at 5 mW throughout the measurements.

The internal relaxation time (ρ) of sodium 3,4,9,10-perylenetetracarboxylate used as a fluorescence probe in solubilized water was measured using a Horiba NAES-1100 time-resolved fluorescence spectrometer. Excited light from a hydrogen lamp and fluorescence emitted from the sample were filtered with UV-340 and L-42 colored optical filters, respectively. The sample solutions were degassed under vacuum by repeating three times the melt-freeze-pump method.

The near-infrared spectra of mixtures (90% D_2O+10% H_2O) solubilized by a surfactant were measured using a Hitachi Model 330 spectrophotometer. D_2O was used to obviate the coupling of OH stretches within one water molecule. A D_2O solubilizing solution was used as a reference.

The intensities of scattered light and refractive indices of solutions were measured using a Malvern 4700 Submicron particle analyzer equipped with an argon ion-laser and a Union Giken RM-102 double-beam differential refractometer, respectively. All of the measurements were carried out at 90° since there was no angular dependence. The average micellar weight was determined from Debye plots.[17,18)] The apparent hydrodynamic diameter of the micelles was measured at 100 mmol kg^{-1} AOT and calculated from the Einstein–Stokes equation on the basis of the translational diffusion coefficient of samples evaluated from the correlation function.[19)]

Results and Discussion

Solubilization Capacity of Water. In order to examine the solubilization capacity of water by AOT, the limiting amounts of solubilized water by AOT in various solvents were measured as a function of the concentration of the surfactant at 30 °C. The results obtained in cyclohexane are shown in Fig. 1 as a representative example. The limiting amounts increased abruptly at 8 mmol kg^{-1}, followed by a linear increase. Similar

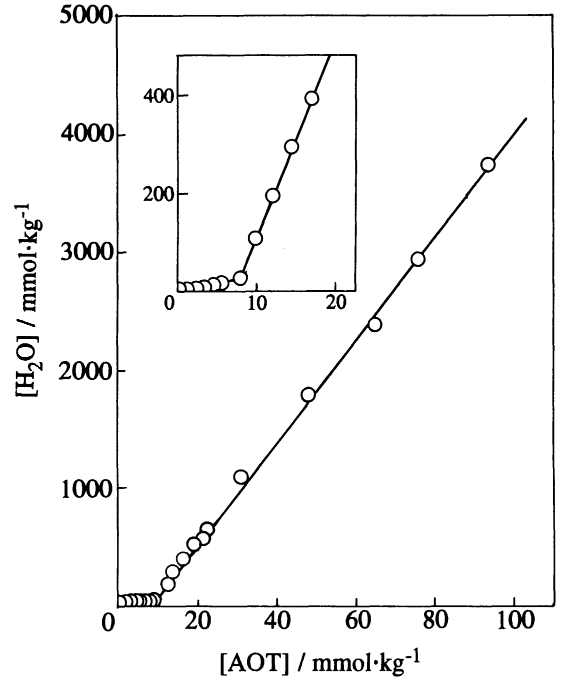

Fig. 1. Change in the limiting amounts of solubilized water with [AOT] in cyclohexane.

Table 1. Parameters of Solubilization Power in Various Solvents

Solvent	SP$_a$	SP$_m$
	R_w	R_w
Cyclohexane	3.6	42.2
Heptane	3.3	57.4
Isooctane[a]	3.6	23.8
Dodecane	3.5	15.9
Toluene	3.5	6.9

a) 2,2,4-Trimethylpentane.

curves were also obtained regarding other solvents.

Such an abrupt increase in the limiting amounts may be due to the fact that the reversed micelles having a constant micellar weight form at a concentration above about 8 mmol kg^{-1} AOT in apolar solvents.[20] Therefore, the slopes of the straight lines obtained below and above 8 mmol kg^{-1} indicate the solubilization powers (abbreviated as SP$_a$ and SP$_m$) of small aggregates, such as trimer or tetramer and reversed micelles having a sharp size distribution, respectively.

The values of SP$_a$ and SP$_m$ calculated from each slope are presented in Table 1. It was found that the magnitude of the solubilization capacity of water estimated from the SP$_m$ values is in the order heptane>cyclohexane>isooctane>dodecane>toluene. The maximum value was observed in heptane when the SP$_m$ values were plotted against the molar volume of solvent in Fig. 2, as was done by Hou and Shah.[21]

Solubilization States of Water. As can be seen in Fig. 1, the solubilization regions of water broadened at concentrations greater than about 8 mmol kg^{-1} AOT in any solvent. Using ^{1}H NMR, ESR, fluorescence, and near-infrared spectroscopic techniques, the states of water were examined as a function of the molar ratio of water to the surfactant at various concentrations of

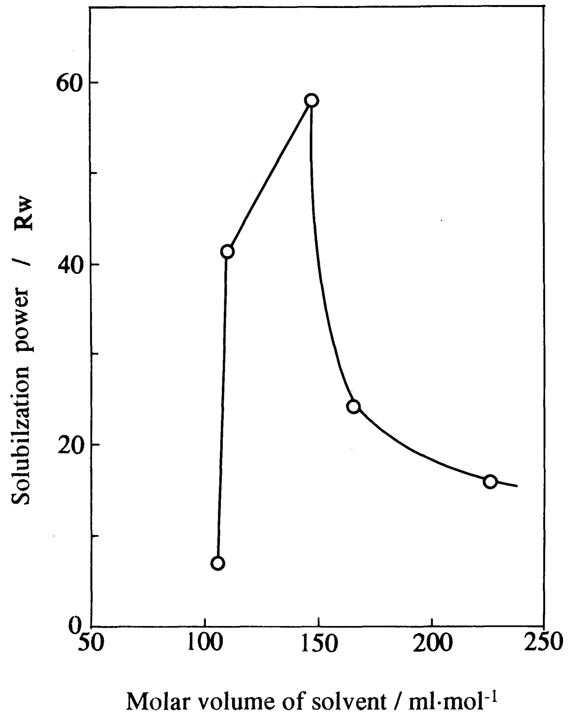

Fig. 2. Plots of SP$_m$ versus the molecular volume of solvents.

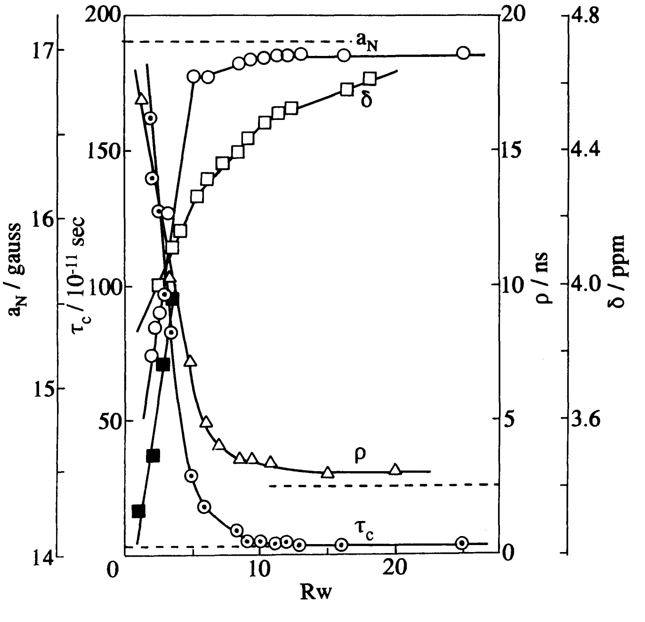

Fig. 3. Change of a_N, τ_c, ρ, and δ_H versus R_w in cyclohexane.
○: a_N, ⊙: τ_c, △: ρ, □: δ_H at 50 mmol kg^{-1} ■ at 6 mmol kg^{-1}. Dashed lines indicate the observed values in bulk water.

AOT. As a representative example, the changes of the a_N, τ_c, ρ, and δ_H values with R_w in cyclohexane are shown in Fig. 3. The a_N value, indicating a measure of the micropolarity of water around the probe,[5–7] increased with increasing R_w; at R_w=5, however, it clearly inflected and closely approached that in bulk water in the region above R_w=11. Such an inflection at R_w=5 was also observed in the δ_H–R_w profile obtained at 50 mmol kg^{-1} AOT; in that at 6 mmol kg^{-1} AOT, however, the δ_H values shifted linearly to a lower field up to the limiting amounts of water without any inflections. On the other hand, both the values of τ_c and ρ, which indicate a measure of the microviscosity of water around the probes,[4] decreased monotonously up to R_w=11, and followed by the values in bulk water. Similar profiles were also observed at other concentrations.

Such an appearance of inflection points suggests that three types of water exist in varying proportions in the interior of AOT reversed micelles. This suggestion might be clarified from the near-infrared spectra obtained in the region of the water OH overtone frequency ($2\nu_{OH}$), where "free" OH and hydrogen-bonded stretching bands.[22] Figure 4 shows the spectral changes in the $2\nu_{OH}$ region with R_w at 100 mmol kg^{-1} AOT in cyclohexane. The band at 1420 nm as assigned to the "free" OH (hydrogen-bonded), while those at 1450 and 1650 nm were due to energetically unfavored hydrogen-bonded and hydrogen-bonded species, respectively.[16,22,23] The growth of the 1420 nm band increased with increasing R_w, whereas those of the 1450 and 1650 nm bands were seen above R_w=5.7. However, the absorbance of the 1450 nm shoulder band was clearly faint, compared with those of the 1420 and 1650 nm bands. These spectral features clearly reveal the three states of water that exist in varying proportions as a function of R_w in the interior of AOT reversed micelles. The first is apparent only below R_w=5 and probably water solvating ionic head groups, $-SO_3^-Na^+$ of AOT, since neither the bands of 1450 nor 1650 nm appear. The second is present in the range of R_w=5—11 and corresponds to the water interacting with the ester and the hydrated ionic groups of AOT. This fact is clear from the appearance of 1450 and 1650 nm bands. However, the water existing in this region is not bulk-like water, since a_N, τ_c, and ρ did not approach those in bulk water, as can be seen in Fig. 3. In the region above R_w=11, a remarkable increase in the band at 1650 nm reflects the build-up of bulk-like water, so-called W/O microemulsions. This formation of W/O microemulsions could also be recognized from the approach of the observed values of a_N, τ_c, and ρ to those in bulk water, as can be seen in Fig. 3.

Relationship between the States of Solubilized Water and Micelle Formation in Cyclohexane. When the R_w values corresponding to the inflection points of the a_N or δ_H values at various concentrations of AOT in cyclohexane were plotted within the solubilization region shown in Fig. 1, the region was divided into three realms (I, II, and III) by two straight lines (dashed and solid-drawn) passing through the inflection at 8 mmol kg^{-1} AOT, as can be seen in Fig. 5. The micellar weight and hydrodynamic diameters (d_h) of the micelles were then measured using light scattering to examine the relationship between the solubilization states of water and micelle formation. Figure 6 shows the changes of d_h and aggregation number ($\overline{n}$) with R_w in cyclohexane and isooctane systems. An inflection in the d_h–R_w profile was found only at R_w=11 in isooctane systems, whereas in the $\overline{n}$ profiles two inflections were found at R_w=5 and

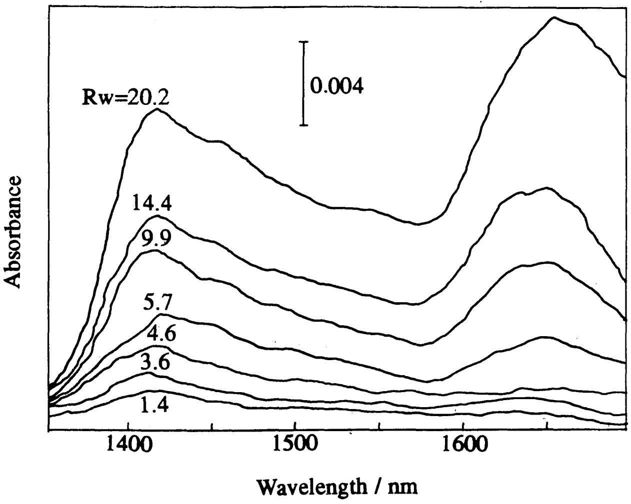

Fig. 4. Change in the near-infrared spectra in the OH overtone stretching region with R_w at 100 mmol kg^{-1} AOT.

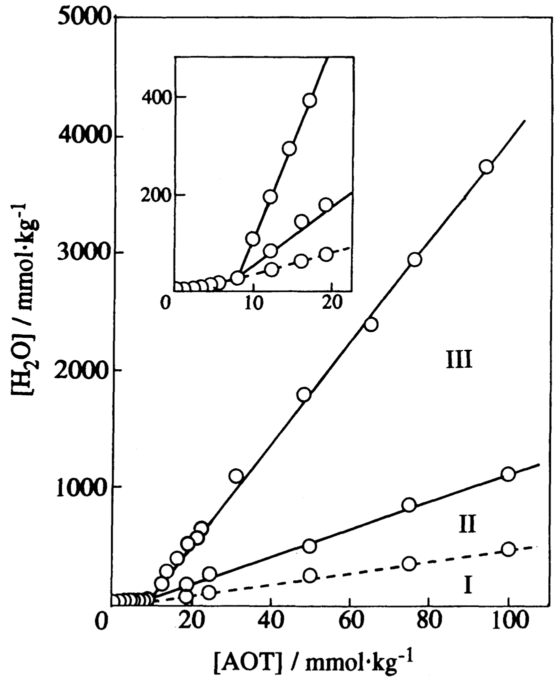

Fig. 5. Phase diagram of solubilized water in cyclohexane systems.

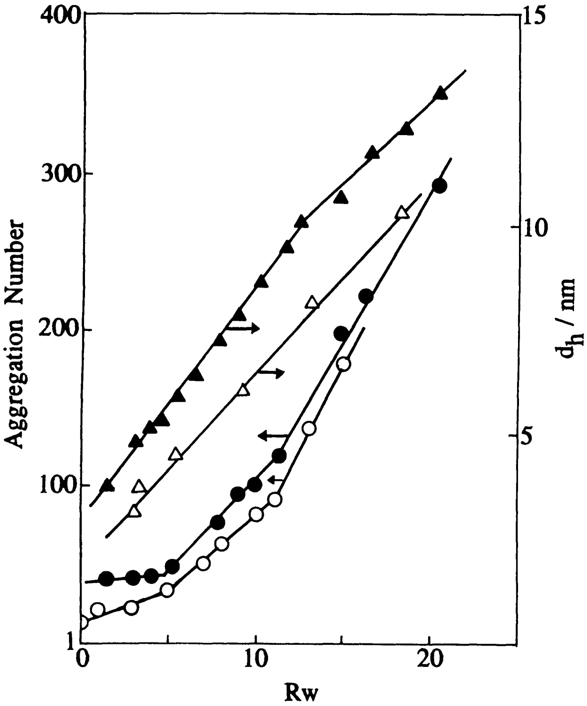

Fig. 6. Plots of $\bar{n}$ and d_h versus R_w in cyclohexane (open) and isooctane (closed) systems.

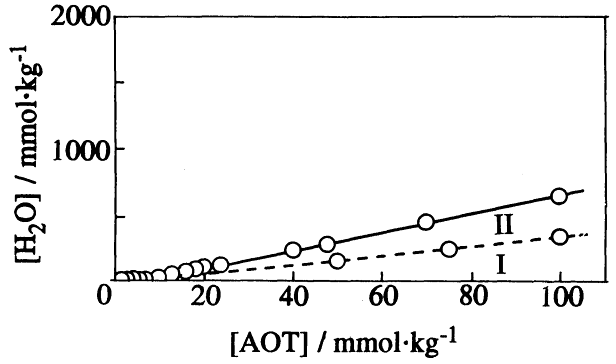

Fig. 7. Phase diagram of solubilized water in toluene systems.

Table 2. Parameters of Reversed Micelles and W/O Microemulsions in Various Solvents

Solvent	C_{swc}/mmol kg^{-1}	R_{sw}/R_w	$R_{w/o}/R_w$
Cyclohexane	8.0	4.9	12.0
Heptane	7.8	4.7	11.9
Isooctane	7.6	4.8	12.1
Dodecane	7.6	4.7	11.8
Toluene	8.5	3.5	—

11 in both solvents. In cyclohexane systems, the R_w values corresponding to two inflections were found to agree with those of the inflections in the a_N and δ_H values. This fact indicates that each realm can be applied into two reversed micelles and W/O microemulsions, i.e., each realm I and II below and above the dashed line corresponds to the reversed micelles formed by the water bound to the ionic head groups of AOT and by the water interacting with the hydrated head groups. Realm III was taken, of course, as W/O microemulsions. Here, we call the reversed micelles formed in realm II as being swollen micelles, since the solubilized water is still bound to AOT molecules.

These suggestions allow us to assign the dashed and solid lines to the minimum amounts of water required for the formation of swollen micelles and W/O microemulsions (each abbreviated as R_{sw} and $R_{w/o}$). Therefore, the concentration of AOT corresponding to the inflection point in the limiting amounts of solubilization is regarded as being "the critical concentration for the formation of swollen micelles or W/O microemulsions" (abbreviated as C_{swc}).

Relationship between the States of Solubilized Water and Micelle Formation in Other Solvents. Among the techniques utilized in this study, ^{1}H NMR was found to be a convenient tool to distinguish the type of solubilized water. The δ_H of solubilized water were additionally measured in other solvent systems as in cyclohexane systems. Although three realms were found in solubilization regions in heptane, isooctane and dodecane systems, in the toluene system realm III was not observed, as can be seen in Fig 7.

Table 2 presents the C_{swc}, R_{sw}, and $R_{w/o}$ values evaluated for various solvent systems. It is noteworthy that all of the values are independent of the type of solvent. These results imply that the solubilization processes of water by AOT are exactly the same, irrespective of the kind of solvents.

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