Formation of Reversed Micelles and W/O Microemulsions of Butyldodecyldimethylammonium Bromide in Chlorobenzene

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The limiting amounts of water solubilized by butyldodecyldimethylammonium bromide (BDDAB) in chlorobenzene increased rapidly at 0.01 mol kg^{-1} surfactant concentration at 30 °C. Using ^{1}H NMR, fluorescence, and near infrared spectroscopic techniques, the solubilized states of water in the region obtained above 0.01 mol kg^{-1} were examined as a function of R_w (=[H$_2$O]/[BDDAB]) at various concentrations of surfactant. It was found from these spectral features that three types of water exist in varying proportions in the interior of reversed micelles, i.e., below $R_w=4$ water is bound directly to the ionic head groups of the surfactant, in the range of $R_w=4$—10 the succeeded water is held together with the hydrated ionic groups by hydrogen bonds, and above $R_w=10$ bulk-like water is built up. These types of water could be discussed in connection with the formation of reversed and swollen micelles or W/O microemulsions. Further, the minimum R_w required for the formation of swollen micelles and W/O microemulsion and the critical swollen micelles or W/O microemulsion concentration could be estimated.

Solubilized water in reversed micelles has been used for the preparation of fine monodispersed colloidal particles.[1—4] For such applications of reversed micelles it is important to examine the solubilized states of water as well as its microscopic properties.[5—15] In contrast to Aerosol OT as anionic surfactants, information on the solubilized states of water by cationic surfactants is still scarce, probably because of the limited solubility of water. However, butyldodecyldimethylammonium bromide (BDDAB) and similar surfactant/chlorinated aromatic hydrocarbon systems can solubilize large amounts of water equivalent to Aerosol OT/apolar solvent ones.[16] In earlier works, Kon-No et al.[17] studied the properties of BDDAB reversed micelles in chlorobenzene and showed that their diameter increase linearly with increasing concentration of water and fairly monodisperse micelles are formed. Zana et al.[18,19] have studied surfactants similar to BDDAB on the effects of natures of alkyl chain or counter ions of surfactants and solvents on the uptake of water. However, they have still not studied the solubilized states of water in these systems in detail.

In this study, the concentration dependence of the limiting amounts of water solubilized by BDDAB in chlorobenzene were measured by Karl–Fischer titration at 30 °C. Using ^{1}H NMR, fluorescence, or near infrared techniques, the solubilized states of water were obtained in the solubilization region, examined as a function of the molar ratio of water to surfactant, R_w, at various surfactant concentrations. These states were discussed in connection with the formation of reversed micelles that can solubilize large amounts of water, or W/O microemulsions that consist of droplets with a bulk-like water core and a monomolecular surfactant film.[8]

Experimental

Butyldodecyldimethylammonium bromide (BDDAB) was synthesized by quaternizing of *N*,*N*-dimethyldodecylamine and butyl bromide, and was recrystallized from ethylacetate six times. The melting points of the products were 39.7—40.2 °C. Chlorobenzene of guaranteed reagent grade was used as a solvent.

The limiting amounts of water solubilized by BDDAB were measured at 30 °C as in a previous paper,[5] i.e., water was added to the surfactant solutions until very small amounts of water or precipitates separated from the solubilization systems, the water content dissolved in the transparent solutions obtained was measured by the Karl–Fischer method. The solubilization equilibrium checked by the titration required a week as in the case of AOT systems.[5] In the no-water system, the water content in 0.10 mol kg^{-1} solution was 0.02 molar ratio of water to surfactant.

The chemical shifts of solubilized water (δ_H) were measured at 30 °C by a JEOL FX-90Q spectrometer. TMS was used as an internal standard.

The internal relaxation time (ρ) of 1,6-diaminopyrene dihydrobromide used as a fluorescence probe in solubilized water was measured at 30 °C by a Horiba NAES-1100 time resolved fluorescence spectrometer. Excited light from a hydrogen lamp and fluorescence emitted from the sample were filtered with UV-330 bandpass filter and L-42 sharp cut filter, respectively. The sample solutions were degassed under vacuum by repeating three times the melt-freeze-pump method.

The near infrared spectra in the region of OH overtone frequency ($2\nu_{OH}$) of mixtures (90% D$_2$O+10% H$_2$O) solutilized by surfactant were measured by a Hitachi Model 330 spectrophotometer. Here, D$_2$O was used to obviate the coupling of OH stretches within one water molecule. D$_2$O solubilizing solution was used as a reference.

The average micellar weight and the apparent hydrodynamic diameter of the micelles were measured by a Malvern 4700 Submicron particle analyzer equipped with an argon ion laser at 30 °C. The former and the latter were measured from Debye plots of 0.070—0.10 mol kg^{-1} BDDAB concentrations and the Einstein–Stokes equation on the basis of the translational diffusion coefficient of 0.10 mol kg^{-1}

BDDAB samples evaluated from the correlation function, respectively.[20—22] All the measurements were done at 90° since there was no angular dependence. The refractive indices of solutions were measured by a Union Giken RM-102 double beam differential refractometer.

Results and Discussion

Solubilized Capacity of Water. To investigate the extent of the solubilized capacity of water, the limiting amounts of water solubilized by BDDAB in chlorobenzene were examined as a function of the concentration of surfactant. The results obtained are shown in Fig. 1. The limiting amounts of solubilized water were rapidly increased up to 0.01 mol kg^{-1}, followed by a linear increase. Then the solubilized capacity of water by surfactant could be estimated as 2.6 and 30.3 as R_w from the slopes of straight lines obtained below and above 0.01 mol kg^{-1}. Here the value obtained in the lower concentration region may indicate the uptake by small aggregates such as trimer or tetramer.[5]

Solubilized States of Water. Using ^{1}H NMR, fluorescence, and near infrared spectroscopic techniques, the solubilized states of water in the region above 0.01 mol kg^{-1} were examined as a function of R_w at various concentrations of surfactant. The change of ρ and δ_H at 0.10 mol kg^{-1} are shown in Fig. 2 as a representative example. The values of ρ, indicating a measure of the microviscosity of water around the probe, decreased with increasing R_w, but at $R_\mathrm{w}=3.3$ and 9.7 clearly inflected, followed by that in bulk water. Such two inflections were also observed at the same R_w values in the δ_H–R_w profile; δ_H is a weighted average of the shifts for water solubilizing in various environments and indicates a measure of the different binding states between surfactant and solubilized water. However, they did not approach that in bulk water. Similar results were also obtained at other concentrations.

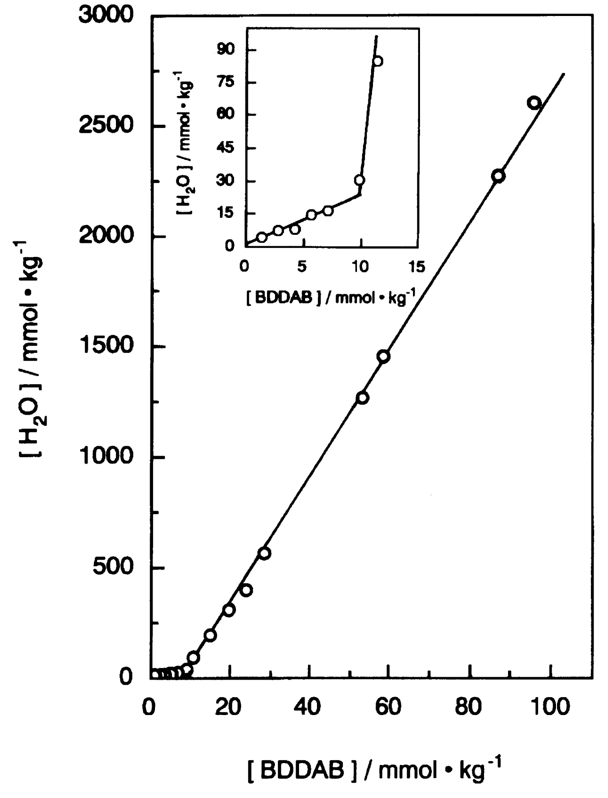

Fig. 1. Change of the limiting amounts of solubilized water with [BDDAB] in chlorobenzene.

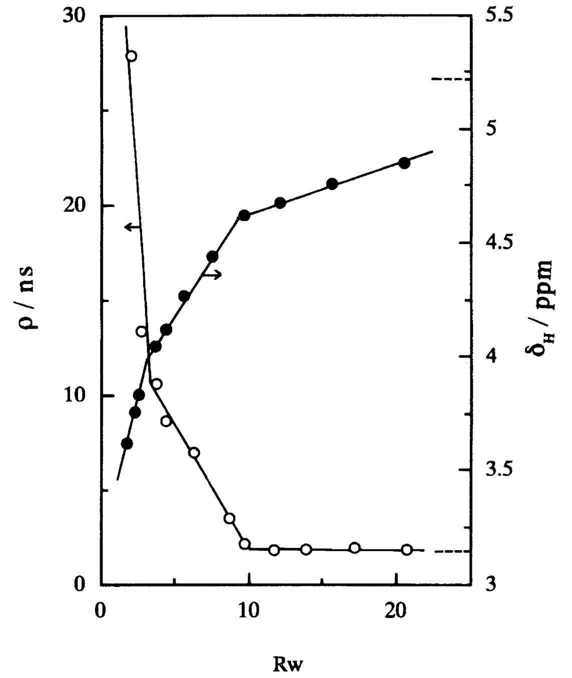

Fig. 2. Change of internal relaxation time ρ (open circles) and chemical shifts of solubilized water δ_H (closed circles) versus R_w. Dashed lines indicate the observed values in bulk water.

Such appearance of inflection points suggests that three types of water exist in varying proportions in the interior of reversed micelles. This suggestion might be clarified from the near infrared spectra of $2\nu_{\mathrm{OH}}$ of solubilized water.[23] Figure 3 shows the spectra obtained at various R_w. The intensities at the 1390 nm band assigned to the "free" OH (non hydrogen-bonded) increased with increasing R_w, but those of the 1650 nm band, resulting from hydrogen-bonded species, increased above $R_\mathrm{w}=4$ and a further great increase was observed above $R_\mathrm{w}=12$.[5,23] From these spectral features, it was found that three states of water exist in varying proportions as a function of R_w in the interior of BDDAB reversed micelles; in the region below $R_\mathrm{w}=4$, water is directly bounded to the ionic head groups of surfactant, $>\mathrm{N}^+(\mathrm{CH}_3)_2\mathrm{Br}^-$ and in the range of $R_\mathrm{w}=4$—10, the succeeded water is held together with the hydrated ionic groups by hydrogen bond. On the other hand, a great increase of the band at 1650 nm is due to build-up of bulk-like water in the interior of reversed micelles. This was verified because the observed

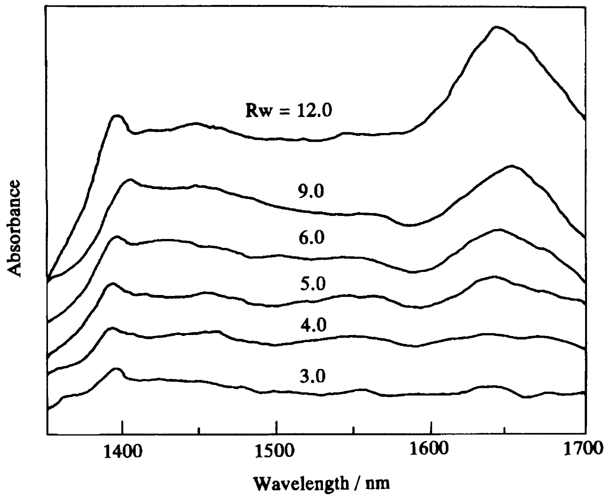

Fig. 3. Change of the near-infrared spectra in the OH overtone stretching region with R_w at 0.10 mol kg^{-1} BDDAB.

values of ρ approached that in bulk water above $R_w=10$ shown in Fig. 2. Therefore the solubilization region obtained above $R_w=10$ could be taken as the region of W/O microemulsions, which form bulk-like water in the interior of reversed micelles.[5,6]

Relationship between States of Solubilized Water and Micelle Formation. When R_w values corresponding to the inflection points of δ_H and ρ obtained at various concentrations of surfactant were plotted within the solubilization region shown in Fig. 1, the region could be divided into three realms (I, II, and III) by two straight lines (dashed and solid-drawn) passing through the inflection at 0.01 mol kg^{-1} BDDAB as shown in Fig. 4. Such different solubilized states of water might reflect the size of reversed micelles. The average aggregation number ($\overline{n}$) and the hydrodynamic diameters (d_h) of micelles were then measured as a function of R_w. As shown in Fig. 5, $\overline{n}$ and d_h were 24 and 3.1 nm at $R_w=3.0$ and increased with increasing R_w, but the latter inflected only at $R_w=10$ and the former inflected at both $R_w=3.5$ and 10. From a comparison of these results with Fig. 2, it is found that the R_w showing these inflection points agree clearly with those of the inflection points of observed values of δ_H and ρ. The agreement among these observed values indicates that each realm is applied to two kinds of reversed micelles and W/O microemulsions, i.e., realm I is fallen into the reversed micelles in which the water is joined to ionic head groups of surfactants and realm II corresponds to the swollen micelles in which the water is held together by the hydrated head groups.[5] Here, the reason why we call the reversed micelles formed in realms II swollen micelles is the existence of water joined together with the hydrated ionic groups of surfactants and a greater increase of $\overline{n}$ of reversed micelles. The realm III was taken, of course, as W/O microemulsions.

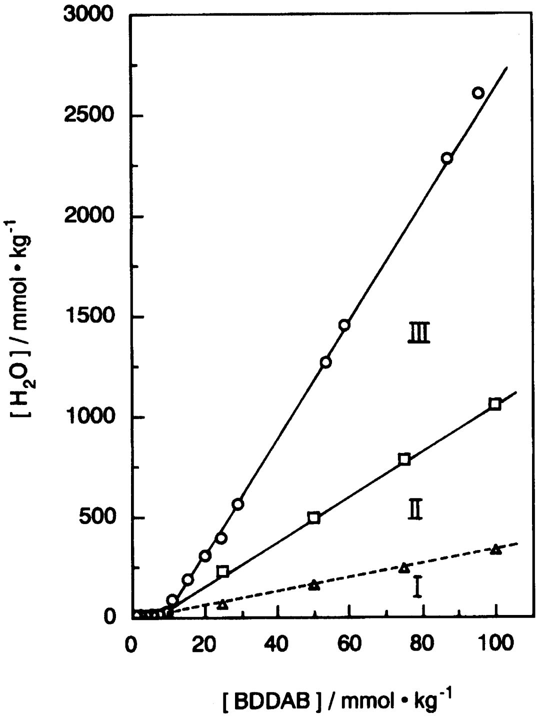

Fig. 4. Phase diagram of solubilized water of reversed micelles in BDDAB/chlorobenzene systems. ○: limiting amounts of solubilized water; □, △: inflection points of ρ or δ_H.

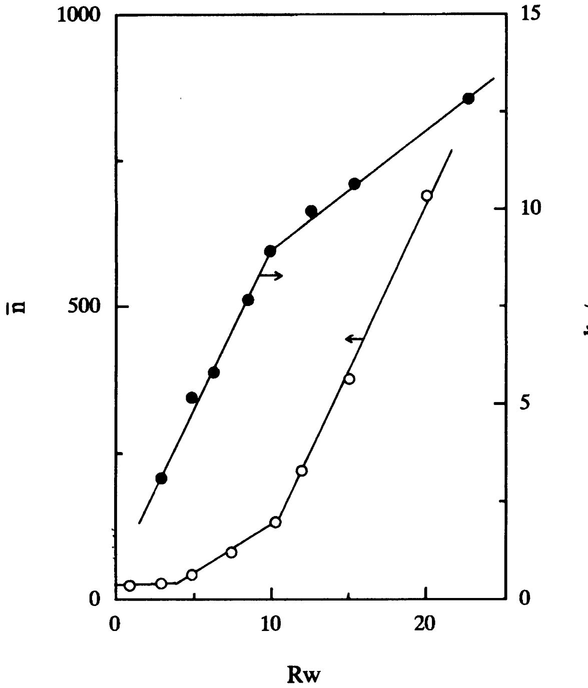

Fig. 5. Plots of average aggregation number $\overline{n}$ (open circles) and hydrodynamic diameter d_h (closed circles) versus R_w.

From these results, the dashed and solid lines drawn within the solubilization region shown in Fig. 4 could be denoted as the minimum amounts of water required for the formation of swollen micelles and W/O microemulsions, respectively. These amounts for the former and the latter could be estimated as R_w=3.7 and 11.0 from the slopes of these straight lines. Accordingly, the surfactant concentration corresponding to the inflection point in the limiting amounts of solubilization, i.e., 0.01 mol kg^{-1} should be regarded as "critical concentration of formation of swollen micelles or W/O microemulsions."

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