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ORIGINAL CONTRIBUTION

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Solubilized states of water and formation of reversed micelles in polyoxyethylated nonylphenyl ethers in cyclohexane media

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Abstract The limiting amounts of solubilization of water in the concentration range 0–200 mmol kg^{-1} polyoxyethylene (6 and 10) nonylphenyl ethers (NP-6 and NP-10)/cyclohexane solutions were measured by the Karl-Fischer method at 25 °C. Utilizing NMR, ESR, and near infrared spectroscopic techniques, the states of water in the solubilization region obtained were examined as a function of the molar ratio of water to surfactants at various surfactant concentrations. In NP-6 system, three solubilized states of water, i.e., water interacted directly with the oxyethylene moiety of surfactant, bound water next to the hydrated oxyethylene moiety, and bulk-like water were built up. However, in NP-10 system only directly interacted water was present. It was found that the directly interacted water is distributed between monomeric surfactants and reversed micelles, and others are distributed to swollen micelles and W/O microemulsions. In addition, the minimum amounts of water required to form reversed and swollen micelles were calculated.

Key words Reversed micelle – W/O microemulsion – Polyoxyethylene nonylphenyl ether

Introduction

The micellar size and microproperties of solubilized water in the interior of Aerosol OT (AOT) reversed micelles have been extensively studied by utilizing spectroscopic or calorimetric techniques [1–8]. However, even though identical AOT/solvent systems have been employed, these techniques have yielded different results concerning the types and states of solubilized water. Fairly recently, we applied several spectroscopic methods to investigate the states of water solubilized by AOT [9] or butyldodecyldimethylammonium bromide [10] reversed micelles, where three states of water were found to exist in their interior in varying proportions. These states are related to the formation of reversed and swollen micelles or W/O microemulsions. In nonionic surfactant/water/apolar solvent systems, spectroscopic and calorimetric measurements indicate that the states of water can be classified as follows: i) primary binding of water to the surfactant, ii) self-association of surfactant, and iii) the formation of reversed micelles in the solubilization process [11–15]. We also recently studied the solubilized states of water in homogeneous oxyethylene dodecyl ethers/cyclohexane systems [16], and found using NMR and fluorescence spectroscopy that two types of solubilized water exist in surfactant solutions: one is distributed between monomeric surfactants and reversed micelles, while the other is distributed to swollen reversed micelles.

In this study, the solubilized states of water in polyoxyethylated nonylphenyl ether/cyclohexane solutions were further examined spectroscopically as a function of the concentration of water and discussed in connection with the formation of reversed micelles.

Experiments

Polyoxyethylene nonylphenyl ethers containing an average oxyethylene unit of 6 or 10 (NP-6 or NP-10) moles were utilized (Lion Co., Ltd). Samples were purified by a distribution method in which a solvent system of water and butanol was employed to remove electrolytes, catalyst, and polyethylene glycol, then dried at 3 mm Hg at 80 °C previous described [17]. Cyclohexane of guaranteed reagent grade was used in all experiments (Nacalai Tesque, Inc).

The amount of water solubilized by each surfactant in cyclohexane was measured at 25 °C by Karl-Fischer titration [16]. The solubilization equilibrium in these systems required about 7 days which is similar to hexaethylene glycol dedecyl ether systems [16]. In the system without water, the water content in 200 mmol kg^{-1} surfactant solutions had 0.05 in molar ratio of water to surfactant (Rw).

The chemical shifts to solubilized water and carbon atoms in oxyethylene moiety of surfactant, δ_H and δ_c, were respectively measured at 25 °C by HITACHI R-24B and JEOL FX-100 spectrometers. TMS was used as an internal standard for δ_H.

The rotational correlation time (τ_c) of 2,2,6,6-tetramethyl-4-(phosphonooxy)piperidine (Aldrich) used as an ESR probe in solubilized water was measured by a JEOL-FEIX spectrometer. Since this probe is water soluble, it can monitor the states of water in a pool of reversed micelles. In all samples, each line of the ESR spectra was symmetric, indicating the probes are located in similar environments of water pool and hence the values of τ_c were calculated according to Yoshioka [18]. The concentration of the probe was 1×10^{-4} mol kg^{-1} and the microwave power was kept at 5 mW.

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

The intensities of scattered light and the refractive indices of solutions were measured by an Otsuka Electronics DLS 700 spectrometer and DRM-1020 double beam differential refractometer, respectively. All measurements were carried out at 90° because of no angular dependence. Average micellar weight was determined using the Debye plots from surfactant solutions of 175–225 mmol kg^{-1} [19, 20]. The apparent hydrodynamic diameter of the aggregates was measured at 200 mmol kg^{-1} surfactants and calculated from the Einstein–Stokes equation on the basis of the resultant translational diffusion coefficient that was determined using the correlation function [21].

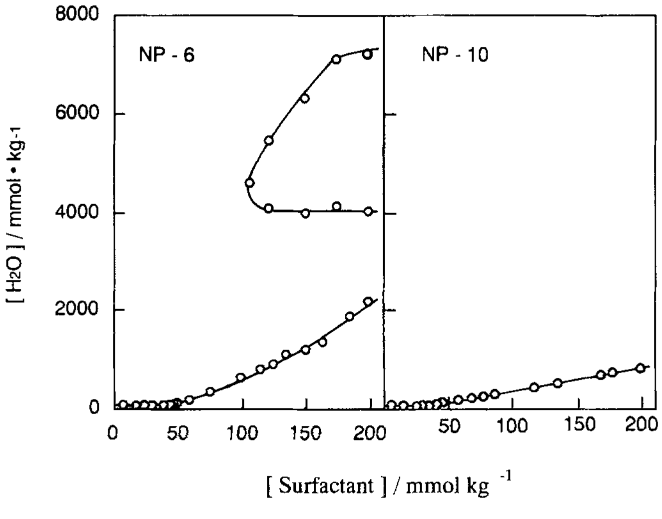
Results and discussion

Solubilization capacity of water

The limiting amount of solubilization of water by surfactant in cyclohexane was examined at 25 °C from 0 to 200 mmol kg^{-1}, Fig. 1 shows the results. In NP-6 system, the amount of solubilized water abruptly starts to increase at 42 mmol kg^{-1} and is followed by a curvature. At greater than about 100 mmol kg^{-1} a blue translucent region became apparent. In the NP-10 system, the start of increase occurs at 33 mmol kg^{-1}, and is followed by a slightly linear increase, although no blue translucent region was observed.

The concentration at which the limiting amounts abruptly increase is regarded as the critical micelle concentration (CMC), as in the case of hexaethylene glycol dodecyl ether/cyclohexane systems [16]. The existence of CMC could be verified from the change of micellar weight with Rw as mentioned later. NP-10's lower CMC may be due to its higher lipophobicity [14], and could possibly represent the aggregation number of reversed micelles, i.e., NP-10 has comparatively more aggregation number. This hypothesis can be confirmed using the resultant micellar weight (see later section). Based on the solubilization region above the CMC, NP-6 clearly shows a greater capacity for water solubilization at 25 °C.

Fig. 1 Limiting amounts of solubilized water versus concentration of surfactants (NP-6 and -10) in cyclohexane at 25 °C



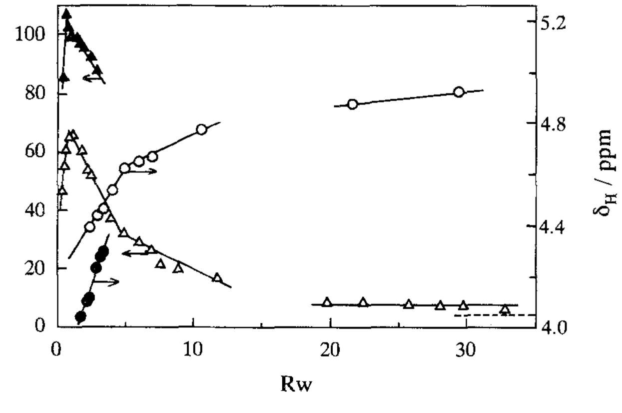
The appearance of the blue translucent region above 100 mmol kg^{-1} in NP-6 system is not surprising based on the phase diagrams of water solubilization as a function of temperature studied by Shinoda et al. [22], i.e., it should appear at less than 25 °C and greater than 100 mmol kg^{-1} because the temperature of maximum solubilization of water decreases with increasing concentration of surfactant.

Solubilized states of water

Utilizing ESR, ^{1}H- and ^{13}C-NMR, and near infrared spectroscopic techniques, we examined the solubilized states of water above the CMC (25 °C) as a function of Rw at various concentrations of surfactants. Figures 2 and 3 show typical results indicating the relationship of τ_c and δ_H for NP-6 and -10, and δ_c for NP-6 as a function of Rw, respectively. The values of τ_c, a measure of the microviscosity of water around the probe, showed the maximum around Rw = 0.7 – 0.9 for each surfactant, but clearly inflected at Rw = 5 and approached that in bulk water expressed with dashed line for NP-6. Such inflection behavior was also observed at the same Rw in the δ_H- or δ_c-Rw profiles for NP-6; the δ_H or δ_c values also indicate the different states in binding between surfactant and solubilized water. They do not approach those in bulk water. In Fig. 3, the peak assignments of the carbon atoms in the molecular formula of surfactant are determined using reports by Ribeiro et al. [23, 24]. Similar results were observed at other concentrations.

The peak in τ_c and the inflection points in δ_H and δ_c suggest that different types of water exist during interactions with the oxyethylene moieties of surfactants. This may be supported by examining water's near infrared spectra obtained in the region of OH overtone frequency ($2\nu_{OH}$) [9, 10, 16], with Fig. 4 showing the observed spectral changes in the $2\nu_{OH}$ region at various values of Rw at 200 mmol kg^{-1} surfactant solutions. It should be noted that the intensities at the 1420 nm band, assigned to the "free" OH (non hydrogen-bonded) species, gradually increase with Rw in both systems [9, 10, 16], whereas at the 1650 nm band for only the NP-6 system, being assigned to the hydrogen-bonded species, the intensities increase above Rw = 5 and show large peaks at Rw = 23.8. These spectral features suggest three states of water are present for NP-6 and one for NP-10 existing in proportions that vary as a function of Rw, i.e., (1) below Rw = 5 for NP-6 and Rw = 4 for NP-10, water binds directly to the oxyethylene moieties of surfactants, (2) in the range of Rw = 5-10 the succeeded water is held together next to the hydrated oxyethylene moieties due to a hydrogen bond, and (3) above Rw = 20 bulk-like water is build up. State (1) is also verified to occur the resultant shifts (Fig. 3). State (3) for NP-6 is supported by the fact that τ_c approaches the observed values of bulk water above Rw = 20 (Fig. 2).

Fig. 2 δ_H and τ_c versus Rw for NP-6 (open) and NP-10 (closed) at 200 mmol kg^{-1}. Dashed lines indicate the observed τ_c values in bulk water.



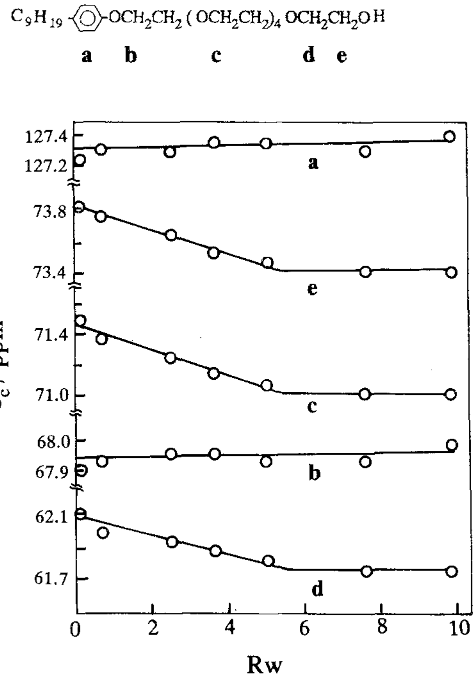


Fig. 3 δ_c versus Rw for NP-6 at 200 mmol kg^{-1}

Relationship between formation of reversed micelles and solubilized states of water

When the Rw values corresponding to these maximum or inflection points obtained at various concentrations of

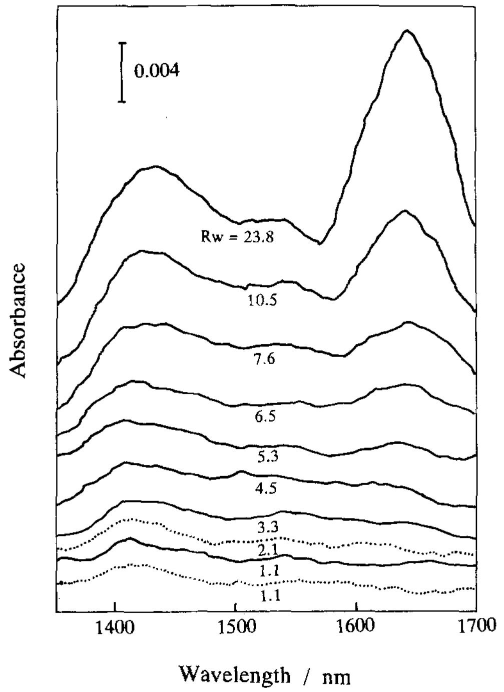


Fig. 4 Near infrared spectra versus Rw at 200 mmol kg^{-1} surfactant Solid line: NP-6, Dotted line: NP-10

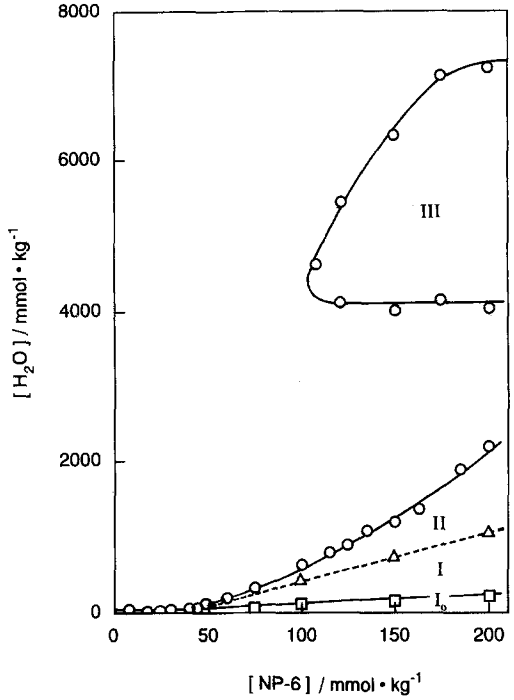


Fig. 5 Phase diagram of solubilized water in NP-6

surfactants shown in Figs. 2 and 3 were plotted in Fig. 1, the region in NP-6 system was divided into four realms, i.e., I_0, I and II by straight lines passing through CMC values and III, while in NP-10 system it consisted of two realms, I_0 and I as shown in Figs. 5 and 6, respectively. Then the micellar weight and sizes of those surfactant aggregates in each realm were measured to examine the relationship between the formation of reversed micelles and the solubilized states of water by utilizing light-scattering techniques. Figure 7 shows the change of the average aggregation number ($\bar{n}$) and the hydrodynamic diameters (d_h) of micelles with Rw.

As seen in Fig. 7, $\bar{n}$ values linearly increased from Rw = 0.9 and Rw = 0.7 extrapolated to $\bar{n} = 1$ for NP-6 and NP-10, respectively, but in the former they inflected at the same Rw = 5 as in the τ_c, δ_H, or δ_c profiles shown in Figs. 2 and 3, respectively. The values of $\bar{n}$ were larger in larger oxyethylene chains systems, as in the homogeneous oxyethylene dodecyl ethers/nonpolar solvent [14]. However, the d_h values linearly increased with Rw in both systems. In the blue translucent region observed in NP-6 systems the values of $\bar{n}$ and d_h at Rw = 35 were 6500 and 29 nm, respectively, although they are not given in Fig. 7.

From the results obtained above, the realm I_0 in both systems could be clearly taken as a monomeric surfactant solution. This could also be supported from the facts that

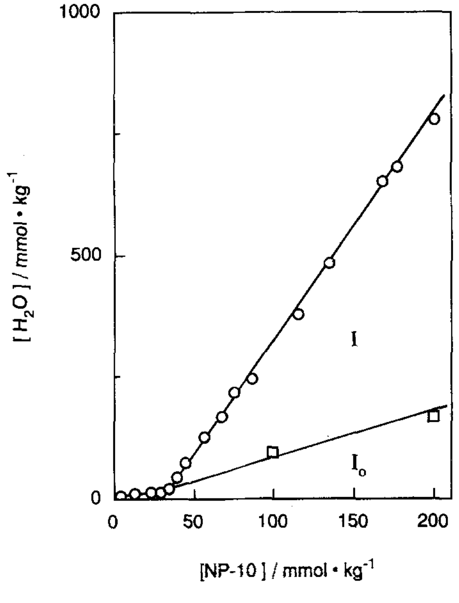


Fig. 6 Phase diagram of solubilized water in NP-10

the τ_c maximum, arising from the change from monomeric surfactants to reversed micelles, was observed at Rw = 0.9 for NP-6 and Rw = 0.7 for NP-10 as shown in Fig. 2. Therefore, realms I and II in Fig. 5 are micellar solutions. Then, the micelles formed in realms I and II can be regarded as reversed and swollen micelles, respectively, from

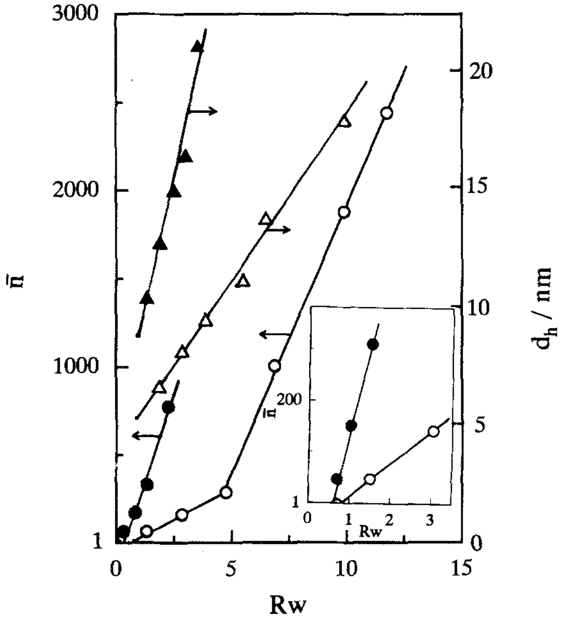


Fig. 7 $\bar{n}$ and d_h versus Rw in NP-6 (open) and NP-10 (closed) systems

Table 1 Parameters of formation of reversed micelles in cyclohexane

	CMC/mmol kg^{-1}	Rrm	Rsw
		Rw	Rw
NP-6	40	1.0	6.0
NP-10	33	0.85	–

the different solubilized states in the interior of micelles and from the different micellar sizes, as was defined in reversed micelles of Aerosol OT and butyldodecyldimethylammoium bromide systems [9, 10]. These considerations indicate that NP-10 forms only reversed micelle in cyclohexane. On the other hand, realm III was taken, of course, to be W/O microemulsions including bulk-like water in the interior of reversed micelles.

From these results, the dashed and solid lines drawn within the solubilization regions shown in Figs. 5 and 6 could be denoted as the minimum amounts of water required to form reversed and swollen micelles (abbreviated as Rrm and Rsw, respectively). These values were calculated from the slopes of these straight lines, taking the Rw at CMC into account. However, the minimum amounts of water required to form W/O microemulsions in NP-6 systems could not be estimated because those amounts depend on the concentration of surfactant. Table 1 presents Rrm and Rsw together with CMC. It was found that the Rrm values, being about unity for both surfactants, were consisted with that for hexaethylene glycol dodecyl ether in cyclohexane [16]. It is noteworthy that the Rsw value is just one water molecule per oxyethylene unit of surfactant. Similar results were obtained in penta- and hexaethyleneglycol dodecyl ether/ cyclohexane systems [15, 16].

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