

Packing of Polyethylene Oxide Chains in a Mixed Micelle

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ABSTRACT

The effects of an anionic surfactant, sodium dodecyl sulfate (SDS), on the micellar properties of a nonionic surfactant such as homogeneous heptaethylene glycol n-dodecyl ether (7ED) have been studied by the charge transfer solubilization of 7,7,8,8-tetracyanoquinodimethane, pNa, and electric conductivity measurements. Attention has been paid to changes in packing of polyethylene oxide chains in the mixed micelle and to binding of the counterions onto the micelle surface. All measurements were made on solutions ranging in 7ED concentration from 1×10^{-6} to 1×10^{-1} M, while the SDS concentration was maintained constant. It has been shown that the binding of Na^+ ions to the mixed micelle occurs in the 7ED concentration region where the packing of polyethylene oxide chains in the micelle is loose, while release of Na^+ ions is observed when the packing is compact. The results of electric conductivity correspond well with those mentioned above. However, in the region of high 7ED concentration, the decreasing mobility of the mixed micelles affects the electric conductivity more than the increasing degree of ionic dissociation of the micelle.

INTRODUCTION

In 1956, Yoda et al. (1) found a remarkable difference between the electric conductivities of an anionic surfactant in the presence and absence of a nonionic surfactant, and they suggested a possibility of mixed micelle formation between the surfactants. In the same year, Maclay (2) noticed that small amounts of an anionic surfactant raise the cloud point of a nonionic surfactant. He also attributed this phenomenon to the formation of mixed micelles. After these works a number of investigations regarding the mixed micelles were published (3-8). Among them, some authors have been interested in the electrical properties of the mixed micelles, such as the zeta potential (3), the ionic dissociation and the mobility of the micelles (5,6). Especially Schick and Manning (7) studied a micelle formation in a mixture of sodium dodecyl sulfate and polyoxyethylene n-dodecyl ethers, and they suggested that the mode of packing of the ethylene oxide chains would have certain influences on the degree of ionic repulsion of the ionic component in the mixed micelle.

Recently Deguchi et al. (9-12) studied the charge trans-

fer solubilization of 7,7,8,8-tetracyanoquinodimethane (TCNQ) by nonionic surfactants. According to their results, in a solubilized state of TCNQ, the absorption bands due to formation of a charge transfer complex between TCNQ and the surfactant micelle have been observed in the visible region (480 nm) and in the IR region (700-750 and 850 nm) (9). Further, using these bands, it has been suggested that the factors affecting the cloud point are related to the changes in the packing of the nonionic surfactant molecules in the micelle (12).

In light of these investigations, the packing of ethylene oxide chains in mixed micelles seems to play an important role in the micellar properties mentioned above. In the present work, we have studied the packing of ethylene oxide chains in mixed micelles of homogeneous heptaethylene glycol n-dodecyl ether (7ED) and sodium dodecyl sulfate (SDS) by the charge transfer solubilization of TCNQ, and the results are combined with those of electric conductivity and pNa measurements.

EXPERIMENTAL PROCEDURES

Materials

The nonionic surfactant used in this experiment was heptaethylene glycol n-dodecyl ether supplied from Nikko Chemicals Co. Ltd. (Tokyo, Japan). This sample was guaranteed to have homogeneous polyethylene glycol chain length as the result of thin layer chromatography, IR spectrum, gas-liquid chromatography, and cloud point.

SDS was synthesized by the method of Dreger et al. (13) and purified by five recrystallizations from ethanol followed by ethyl ether extraction.

Purities of these surface active agents were confirmed by surface tension measurements. The surface tension curves of each surfactant have no minimum at the critical micelle concentration (cmc).

TCNQ was synthesized according to the method of Acker (14) and purified by repeated recrystallization from acetonitrile. The melting point of this sample as determined by differential thermal analysis coincided well with the published result (14).

The water used in all the experiments was purified by passage through a mixed-bed ion exchange resin, and then by distillation from alkaline potassium permanganate solution in the presence of sodium hydroxide in a Pyrex glass vessel. This water had an electric conductivity ca. 1×10^{-6} mho/cm at 25°C.

TABLE I

Color Series of the Surfactant Solutions in Which TCNQ is Solubilized^a

Concentration of 7ED (m mol/liter)	Concentration of SDS (m mol/liter)	Color of the solutions
0.1	0.0	pink
1.0	0.0	blue
10.0	0.0	olive green
100.0	0.0	brown olive
0	10.0	pink
0.1	10.0	faint lavender
1.0	10.0	lavender
10.0	10.0	olive green
100.0	10.0	brown olive

^aTCNQ = 7,7,8,8-tetracyanoquinodimethane; 7ED = homogeneous heptaethylene glycol n-dodecyl ether; SDS = sodium dodecyl sulfate.

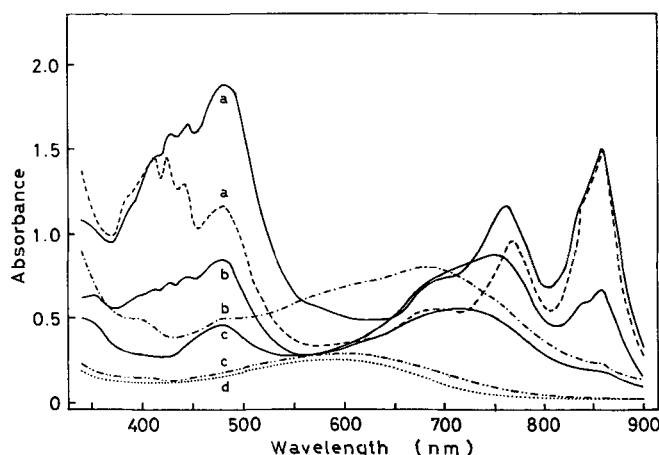


FIG. 1. The absorption spectra of 7,7,8-tetracyanoquinodimethane (TCNQ) solubilized in homogeneous heptaethylene glycol n-dodecyl ether (7ED) solutions with 10 mM of sodium dodecyl sulfate (SDS) (broken lines) and without SDS (solid lines). 7ED concentrations are (a) 100 mM, (b) 10 mM, (c) 1.0 mM, (d) 0 mM.

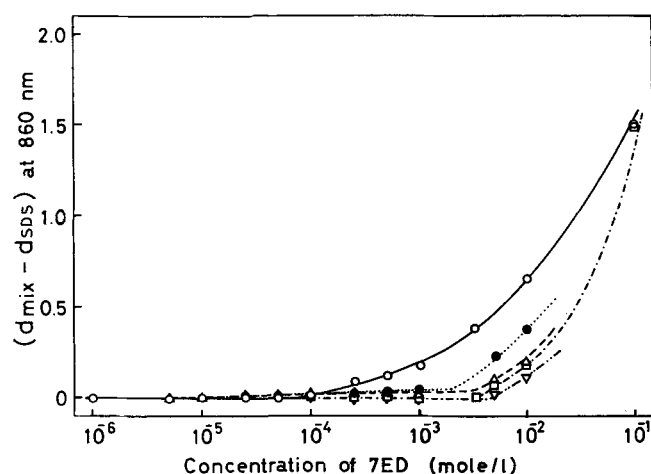


FIG. 2. Difference between two absorbance data in the presence and absence of sodium dodecyl sulfate (SDS) at 860 nm vs. homogeneous heptaethylene glycol n-dodecyl ether concentration. SDS concentrations (mM): (○) 0, (●) 4.0, (△) 6.3, (□) 10.0, (▽) 15.0.

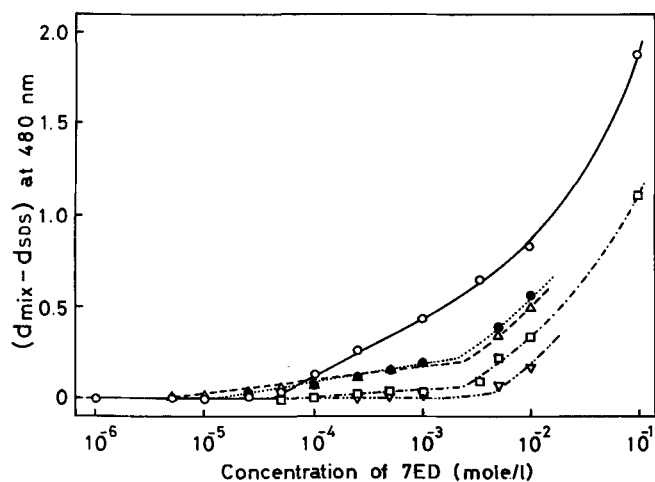


FIG. 3. Difference between two absorbance data in the presence and absence of sodium dodecyl sulfate (SDS) at 480 nm vs. homogeneous heptaethylene glycol n-dodecyl ether concentration. SDS concentrations (mM): (○) 0, (●) 4.0, (△) 6.3, (□) 10.0, (▽) 15.0.

Procedures

The procedures for solubilizing TCNQ were similar to those reported by Muto et al. (15), and the absorption spectra of TCNQ were measured in a quartz cell of 1 cm length using a spectrophotometer, Hitachi EPS-3T, at 25°C.

Electric conductivity measurements were carried out at $25 \pm 0.1^\circ\text{C}$ using the electric conductivity meter, Model 1DB, Tōa Denpa Kōgyō Co. Ltd. (Tokyo, Japan).

An ion meter, 1M-1B, Tōa Denpa Kōgyō Co. Ltd., was used for pNa measurements at $25 \pm 0.1^\circ\text{C}$. The cell used was the type

Na-glass electrode	sample solution	NH_4NO_3 (3.0 M)	KCl (saturated)	calomel electrode
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The calibration of the ion meter was performed by using standard 0.1 and 0.001 M solutions of sodium chloride.

RESULTS AND DISCUSSION

When TCNQ was solubilized in a mixed surfactant solution of 7ED and SDS, a remarkable color change was observed with increasing concentration of 7ED. A representative color change process is tabulated in Table I, and the absorption spectrum of this process is shown in Figure 1. The SDS solution of 10 mM had a broad absorption maximum around 600 nm which is regarded as a charge transfer absorption band between TCNQ and the SDS micelle (15,16). Addition of 7ED to this SDS solution made this absorption increase. When the additive 7ED concentration had reached 10 mM, new absorption bands at 480, 690, and 860 nm became appreciable. Further addition of 7ED produced very complicated absorption spectra, with maxima at 413, 425, 443, 480, 695, 765, and 860 nm. These absorption maxima were also observed for a corresponding 7ED solution. Among these absorption maxima, the three bands at 480, 715-765, and 860 nm with a shoulder at 840 nm seem predominantly to characterize the interactions of TCNQ with 7ED micelle. The so-called alpha band (480 nm) is not yet assigned unequivocally. The beta band (715-765 nm), which had a tendency to shift to longer wavelength with increasing concentration of 7ED, has been attributed to monomeric TCNQ anion radical TCNQ^- (9,17). The gamma band (860 nm) with the shoulder at 840 nm may also be due to TCNQ anion radicals (17-19).

As shown in Figure 1, the absorption spectra of TCNQ in 1.0 mM 7ED solution with and without SDS were quite different. In the absence of SDS, the three characteristic absorption bands (480, 715, and 860 nm) owing to charge transfer interactions between 7ED micelle and TCNQ were observed, while these absorption maxima were not found in the presence of SDS. These absorptions were not appreciable until 7ED concentration in the mixture reached ca. 5.0 mM. At a sufficiently high 7ED concentration such as 100 mM, all of the characteristic absorption bands to TCNQ-7ED micelle interactions appeared in the spectra both for the 7ED solution and for the mixture, although these spectra were not yet equal in the absorbances. These results suggest that the interactions between TCNQ and 7ED micelle are considerably inhibited by the presence of the SDS micelle. This effect of SDS is shown in Figures 2 and 3. In Figure 2, the absorbance at 860 nm is plotted against 7ED concentration. In the absence of SDS, a bend point is observed at 7.0×10^{-5} M, which corresponds to the cmc of 7ED (9,20). However, in the case of the mixed surfactant solutions, the absorbance observed is based on the overlap of the interactions of TCNQ with 7ED and those of TCNQ with SDS as suggested in the preceding paper (21), so that the absorbance at 860 nm was corrected by subtracting the absorbance for SDS solution at the same wavelength. The resultant absorbance was lowered by

TABLE II

7ED Concentrations at the Bend (m mol/liter)^a

Concentration of SDS (m mol/liter)	Wavelength	
	480 nm	860 nm
0.0	0.040	0.070
4.0	2.5	2.2
6.3	2.6	3.2
10.0	2.7	3.4
15.0	4.3	4.0

^a7ED = homogeneous heptaethylene glycol n-dodecyl ether; SDS = sodium dodecyl sulfate.

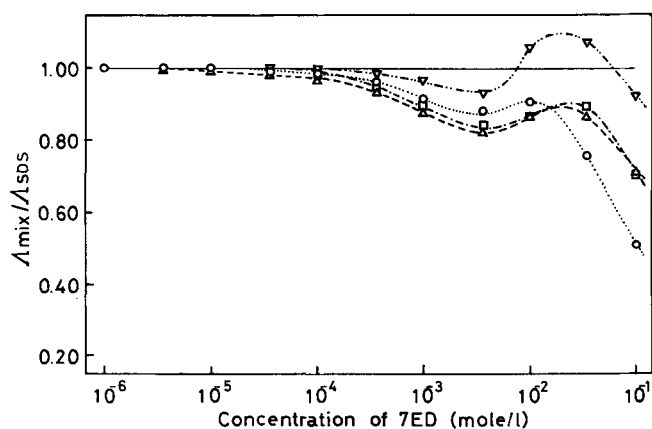


FIG. 4. The ratio of equivalent conductivities for sodium dodecyl sulfate (SDS) in the presence of homogeneous heptaethylene glycol n-dodecyl ether against those in SDS solutions. SDS concentrations (mM): (○) 4.0, (△) 6.3, (□) 10.0, (▽) 15.0.

increasing additions of SDS, and it was noticed that each curve had a bend, above which the absorbance increased steeply. Both the lowered absorbance and the bend are also found in Figure 3, where the absorbance at 480 nm is shown as a function of 7ED concentration. The 7ED concentrations at the bends are estimated and listed in Table II. In the present case, since the absorption bands used (480 and 860 nm) are characteristic to the interactions of TCNQ with 7ED micelle (9,15), evidently SDS ceases to suppress these interactions at the bends. As seen in Table II, larger amounts of added SDS result in higher 7ED concentration at the bend, so that this suppression may be due to consumption of 7ED by SDS. If the concentration of SDS is kept constant above the cmc, 7ED will at first distribute itself between the SDS micelle and the bulk solution, and if the SDS concentration is kept constant below the cmc, it seems likely that 7ED will form mixed micelles with SDS at a certain 7ED concentration below the cmc (6,22-24). This mixed micelle formation of 7ED and SDS is supported by the fact that the absorbance at 480 nm increased appreciably even when both concentrations of SDS and of 7ED were lower than each cmc (Fig. 3).

It has been reported that the intensity of charge transfer interactions between TCNQ and a surfactant micelle is influenced by the packing of surfactant molecules in the micelle (11,25). Deguchi and Meguro studied the effects of inorganic salts and urea on the micellar structure of a nonionic surfactant by the charge transfer solubilization of TCNQ, and they suggested that the additives which enhance the charge transfer interaction made the arrangement of 7ED molecules in the micelle more compact, and vice versa. According to their results, the increase of the compactness of 7ED micelle indicates a decrease of the water content of the outer polyoxyethylene shell of the micelle (12). In this case, the depressed charge transfer interactions between TCNQ and 7ED in the 7ED concentration region below the

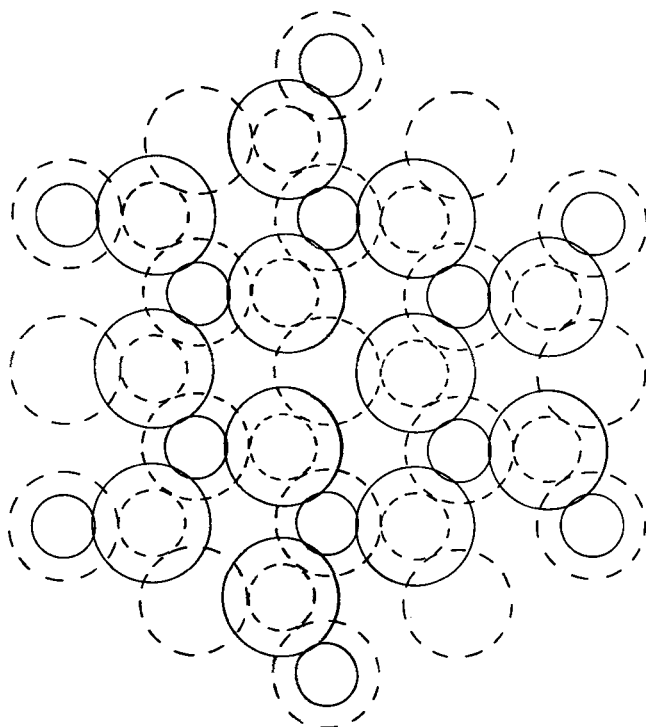


FIG. 5. A possible arrangement of DS^- ions and homogeneous heptaethylene glycol n-dodecyl ether (7ED) molecules in a big mixed micelle which contains equimolar surfactants. Large and small broken circles show the cross sections of the sulfate group and an alkyl chain of 7ED at an interface between the oily core and the outer polyoxyethylene shell, respectively. A large solid circle refers to the cross section of the polyoxyethylene chain at the surface of the mixed micelle, and small solid circle refers to the cross section of Na^+ counterions, which are located arbitrarily assuming a degree of the ionic dissociation 0.33. It seems likely that the binding of Na^+ ion onto the sulfate group can be prevented by steric hindrance of the polyoxyethylene chains. The degree of this steric hindrance will increase with decreasing mol ratio of sodium dodecyl sulfate to 7ED in the mixed micelle and with increasing radius of curvature of the micelle surface.

bend are attributable to the looser packing of 7ED molecules in the mixed micelle: polyoxyethylene chains of 7ED would be more hydrated in the mixed micelle than in 7ED micelle. However, the degree of hydration of the polyoxyethylene chains in the mixed micelle seems to decrease considerably in the 7ED concentration region above the bend. Maybe the structure and/or composition of the mixed micelle begins to change at the bend.

Electric conductivity measurements were also carried out for the mixed surfactant solutions of SDS and 7ED. The concentration of SDS was kept constant and only the 7ED concentration was varied in a series of measurements. If there had been no interaction between these two surfactants, the equivalent conductivity for SDS would have decreased monotonically with increasing viscosity of the mixtures according to the Walden's rule. The results are shown in Figure 4, where Λ_{mix} and Λ_{SDS} refer to the equivalent conductivities for SDS in a mixture (SDS x mM and 7ED y mM) and in the corresponding SDS solution (SDS x mM), respectively. When the SDS concentration was below the cmc, the ratio $\Lambda_{mix}/\Lambda_{SDS}$ began to decrease at a certain 7ED concentration considerably below cmc, whereas the decrement occurred above the cmc of 7ED in the presence of SDS above its cmc. From these facts, the cooperative mixed micelle formation between these two surfactants is confirmed (5). The equivalent conductivity ratio reached a minimum value at a 7ED concentration of some 3.3 mM, and then increased up to a maximum value observed in the 7ED concentration region between 10 mM

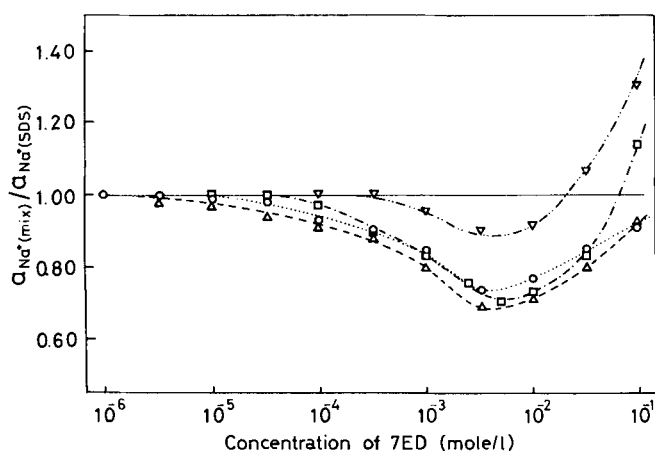


FIG. 6. The ratio of activities for Na^+ ion in the mixture against those in sodium dodecyl sulfate (SDS) solutions. SDS concentration (mM): (○) 4.0, (Δ) 6.3, (□) 10.0, (▽) 15.0.

and 30 mM. Upon further addition of 7ED, the ratio decreased steeply.

Electric conductivities of surfactant solutions above the cmc are considered to be governed by both the mobility of micelles and the degree of ionic dissociation of the micelles (5). Corkill et al. (6) studied a micellization in mixtures of sodium dodecyl sulphate and dodecyl hexaoxyethylene glycol monoether and suggested that the degree of dissociation of the mixed micelle species increased with increasing nonionic content, but the micelle mobilities proved the contrary. The appearance of the minimum electric conductivity ratio in the present case can be explained from these facts. However, it is in the 7ED concentration region corresponding to the bends (Figs. 2 and 3) that the minimum ratio was obtained. Therefore, the increment of the ratio, i.e., the increment of the degree of dissociation of the mixed micelle, may be related to the increase in compactness of the polyoxyethylene chains and consequently to the decrease in hydration of the chains in the mixed micelle. Since Na^+ ion has a relatively large ionic radius (2.3 Å) (26), the approach and binding of Na^+ ions onto ionic heads of DS^- ions in the mixed micelle may be blocked by the closely packed polyoxyethylene shell. This possibility is shown schematically in Figure 5 using the molecular areas of 53.4 Å² (27) and 64.8 Å² (28) for SDS and 7ED, respectively. Further, the cross section of an alkyl chain is assumed to be 20.5 Å², and the model of a truncated cone packing of the polyethylene oxide chains suggested by Schick et al. (7) is adopted.

Measurements of pNa were also carried out in parallel with the electric conductivity measurements. The results are shown in Figure 6 as an activity ratio, $a_{\text{mix}}/a_{\text{SDS}}$, where a_{mix} and a_{SDS} refer to the activities of Na^+ ion in mixed surfactant solutions and in the blank SDS solution, respectively. The ratio decreased gradually above a certain 7ED concentration and reached its minimum value in the concentration region of 5 mM. These results are consistent with those of electric conductivity. Above this 7ED concentration region, the ratio increased steeply. This means that Na^+ ions began to be released from the mixed micelle. In the high 7ED concentration region, free Na^+ ion still increases in number. However, the electric conductivity ratio decreased. This difference can be ascribed to the

viscosity. According to the results of viscosity measurements, the viscosity of the mixed surfactant solution increased steeply in the region where the concentration of 7ED exceeds 10 mM. Although Walden products were not constant, this increase in viscosity would decrease the mobility of the mixed micelle.

The decrement of the activity ratio of Na^+ ion in the low 7ED concentration region suggests that the ionic heads of DS^- ions in the mixed micelle are open to Na^+ ions in the bulk solution. This result is compatible with the loose polyoxyethylene chain packing of the mixed micelle mentioned before. Perhaps the degree of counterion binding on the surface of the mixed micelle will depend on the number of DS^- ions incorporated into the micelle. On the contrary, the increment of the activity ratio in the region of high 7ED concentration has a relation to the close packing of the polyoxyethylene chains in the mixed micelle. The hydrophilic group of the DS^- ion seems to be covered by the compact shell of polyoxyethylene chains.

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