

Momotani Juntanken, Ltd., Minatoku, Osaka (Japan)

Solubilization properties of nonionic surfactant-polymeric acid complexes

S. Saito

With 9 figures and 1 table

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Introduction

The interaction or complex formation between a polyoxyethylene type nonionic surfactant and a polymeric acid in aqueous solution has been confirmed by measurements of viscosity (1), pH (1), precipitation (2–4) and surface tension (5). Not only the nonionic surfactants in aqueous solution (3, 4) but also colloid dispersions stabilized by them (6) are flocculated by polymeric acids together with salts or acid. Thus, as a result of such complex formation any properties of both components in solution are affected.

In an aqueous mixture of an *ionic* surfactant and a *nonionic* polymer, the surfactant is abruptly bound to the polymer above a certain surfactant concentration, and above which the surfactant clusters around the polymer chain like micelle (7–12). Because of this binding the solubilization property of the *ionic* surfactant is changed at that concentration, and the relation between the polymer and solubilizate plays a dominant role in the solubilization ability of the complex (7, 13). This paper is concerned with the solubilization properties of the *nonionic* surfactants in the presence of polymeric acids, and it is of interest to see if a critical concentration above mentioned would exist also in the interaction between nonionic surfactant and polymeric acid.

Experimental

1. *Nonionic surfactants*: Three kinds of polyoxyethylene octyl phenyl ethers [(EO)_nOP; *n*: 10, 15, and

20 on average] were employed. (EO)₁₀OP was Triton X-100 of Röhm & Haas Co., U.S.A., and this is different from that used before (2, 3, 14). (EO)₁₅OP was a product of Kao Soap Co., Tokyo. (EO)₂₀OP, a product of the Laboratory of Nikko Chemicals Co., Tokyo, was the same as used previously (14). Their aqueous solutions were passed through columns of ionic exchangers to remove ionic impurities (2).

2. *Polymeric acids*: Three kinds of polyacrylic acid (PAA) with average degrees of polymerization (DP) 75, 2000, and 5000 were the same as before used (4). They were roughly fractionated as described (1). Unless otherwise noted, PAA with DP 2000 was employed. Polymethacrylic acid (PMA) with DP 1.71×10^4 was the same as before used (4). The concentrations of their aqueous solutions were determined by titration.

3. *Viscosity*: Viscosity of surfactant-polyacid solutions was measured with an Ostwald viscometer. Surfactant solutions of the same concentrations as the complex solutions were used as the reference solvents (1).

4. *Solubilization*: An oil-soluble dye Yellow OB and naphthalene were employed as solubilizates. Yellow OB was of reagent grade of Tokyo Kasei Co., Tokyo, and naphthalene of reagent grade was recrystallized twice from ethanol-water. The amount of Yellow OB solubilized was determined by absorption at 440 nm in ethanol solution with the relation of optical density $\times 7 \cdot 10^{-5} M$ (15). The concentration of naphthalene in (EO)_nOP solution was measured also spectroscopically in ethanol solution at 275 nm with the relation of optical density $\times 2.3 \cdot 10^{-4} M$ against the same alcoholic surfactant solution as solvent, since the surfactants used have absorption in the same wavelength range.

Results and discussion

1. *Viscosity change in the interaction of nonionic surfactant and polymeric acid*. Previously it was

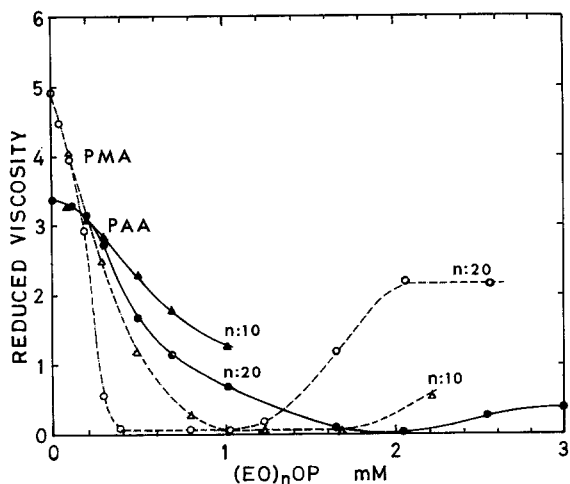


Fig. 1. Change in the reduced viscosity of 11.6 mN PAA (continuous lines) or PMA (broken lines) solutions by addition of $(EO)_nOP$ (n : 10 and 20) of various concentrations at 20 °C

found that the reduced viscosity of an aqueous PAA solution is lowered slightly by addition of the nonionic surfactant at very low concentrations (region 1) and then appreciably (region 2), and through a flat zone (region 3) it turns upwards and becomes flat again at higher concentrations (region 4) (fig. 1, and also fig. 1 of ref. 1). When the interaction is stronger, the transition of the regions 1 and 2 occurs at a lower surfactant concentration. The

surfactant interaction with PMA is the case, and the transition point is low and not clearly observed. Such viscosity changes reflect the states of binding of nonionic surfactant on the polyacid (1). It is believed that the binding takes place by the extensive hydrogen bonding between ether oxygens of the surfactant and carboxyls of the polyacid reinforced cooperatively by the hydrophobic bonding, and the degree of the hydrogen bonding is mainly related to the viscosity decline in the region 2 (1).

2. *Solubilization change at the transition between regions 1 and 2.* In the binding of an ionic surfactant to a nonionic polymer, the solubilization property of the surfactant is changed, and the change sets in at the surfactant concentration corresponding to a sudden increase in the binding. Therefore, at first, the change at the transition of the regions 1 and 2 is examined.

Figures 2–5 demonstrate solubilization of Yellow OB in $(EO)_nOP$ solutions (n : 10 in fig. 2; n : 15 in fig. 3; and n : 20 in figs. 4 and 5) in the presence of various concentrations of PAA or PMA at 20 °C. Without polyacid, the amount of the dye solubilized increases steadily above the CMC, and with PAA it begins to increase abruptly from a surfactant concentration below the CMC, and this point almost coincides with the starting concentra-

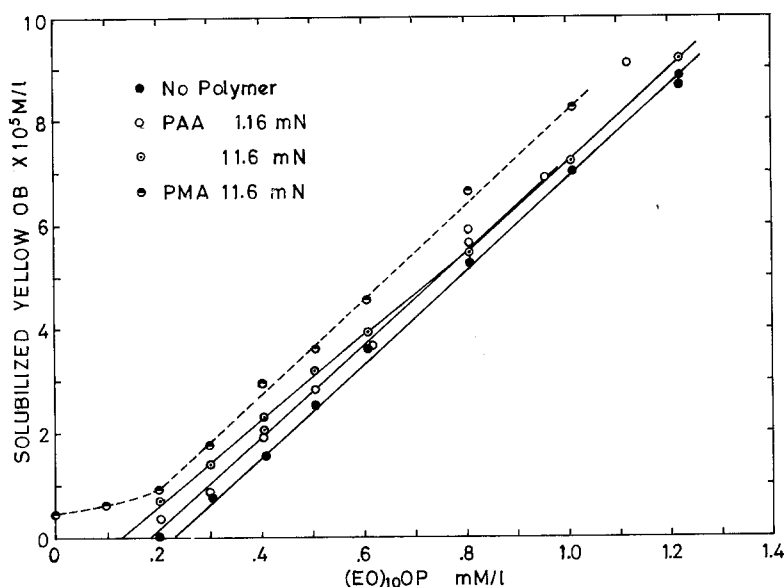


Fig. 2. Yellow OB solubilization in $(EO)_{10}OP$ solutions in the presence of PAA (continuous lines) or PMA (a broken line) at 20 °C

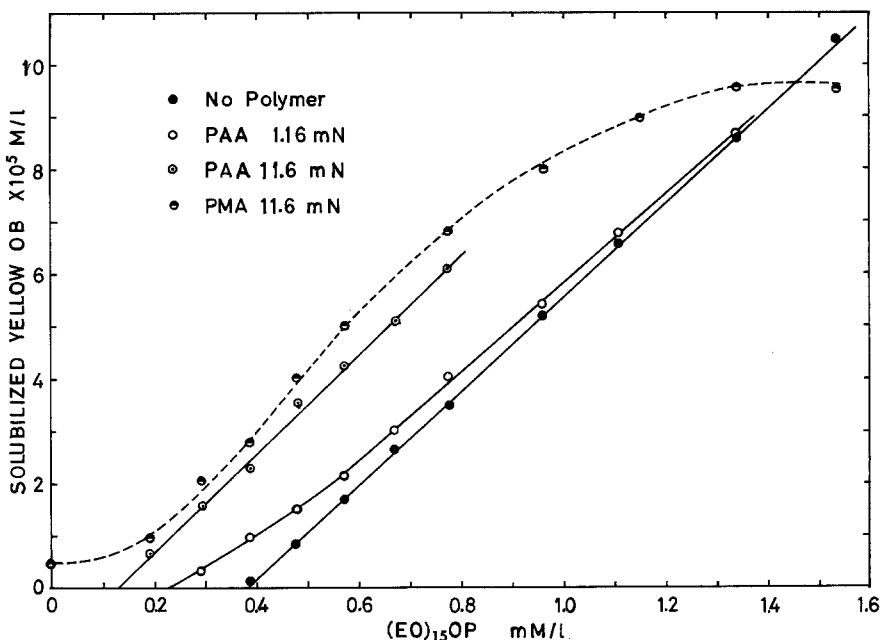


Fig. 3. Yellow OB solubilization in $(EO)_{15}OP$ solutions in the presence of PAA (continuous lines) or PMA (a broken line) at $20^\circ C$

tion of the conspicuous viscosity drop (the transition of the regions 1 and 2), as shown in figure 1. It is not certain whether this transition is induced by the initiation of the surfactant uptake or of a sort of aggregation of the surfactants bound on a polyacid chain, but clearly from this concentration up the binding

of the surfactant increases and concomitantly the dimension of the polyacid chain shrinks.

It might be questioned if the dye solubilization affects the shape of the complex. The viscosity of a $(EO)_{10}OP$ -PMA solution before and after saturated solubilization of the dye was almost unchanged, and the result implies

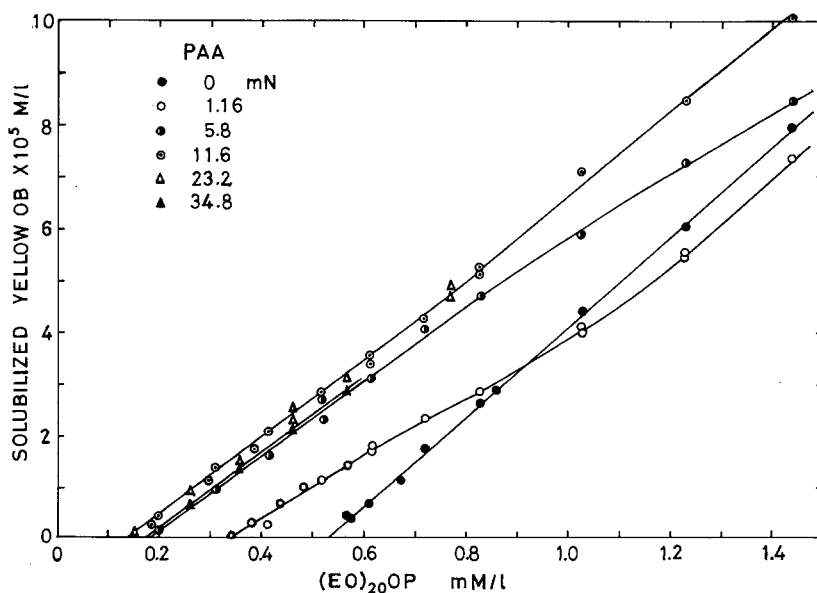


Fig. 4. Yellow OB solubilization in $(EO)_{20}OP$ solutions in the presence of PAA at $20^\circ C$

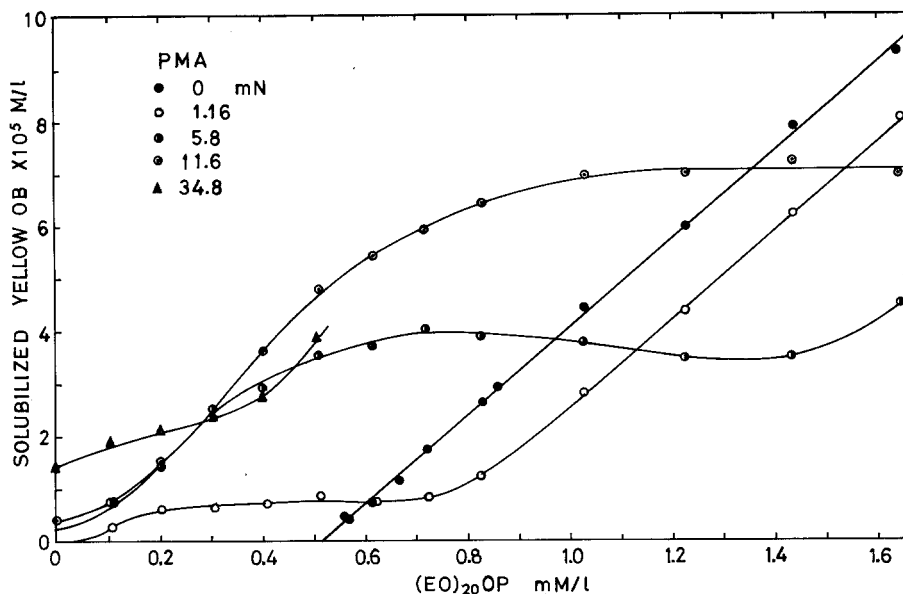


Fig. 5. Yellow OB solubilization in $(EO)_{20}OP$ solutions in the presence of PMA at 20 °C

that the macroscopic shape of the complex remains unchanged by the solubilization process.

It may be possible to consider that some form of surfactant micelles participates in this solubilization, but the ordinary micelles are not directly adsorbed on the polyacid chain because the above-mentioned critical point is below the CMC. Thus, this critical surfactant concentration in the presence of polyacid may be the concentration at the beginning of micelle-like accumulation of the surfactant on the polyacid chain, and it may be denoted as CMC_p .

As shown typically in those PAA systems in figure 4, CMC_p is dependent on the polyacid concentration in the dilute region. However, since the degree of dissociation of polyacid affects the surfactant binding (1), CMC_p is to be related to the pH of the solution. The pH of 1.16, 11.6 and 23.2 mN PAA (DP 2000) solutions are 4.40, 3.46, and 3.25, respectively, and by addition of 0.6 mN HCl they turn to 3.31, 3.20, and 3.05, respectively. By the same HCl addition, the CMC of $(EO)_{10}OP$ solution and CMC_p (0.14 mM) with 11.6 mN PAA are unchanged, but CMC_p with 1.16 mN PAA is lowered and coincides with those of 11.6 and 23.2 mN PAA without HCl addition (fig. 6). Around pH 3.4–3.2, the dissociation of PAA may be almost suppressed, and the CMC_p with

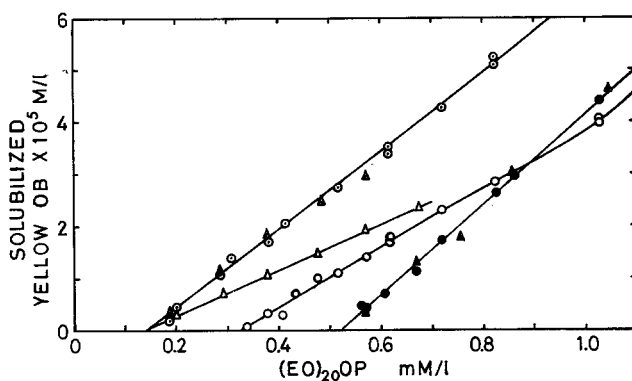


Fig. 6. Yellow OB solubilization in $(EO)_{20}OP$ solutions in the presence of 1.16 or 11.6 mN PAA without (circles) and with 0.6 mN HCl (triangles) at 20 °C. \circ , Δ : surfactant alone and with HCl; \circ , Δ : surfactant + 1.16 mN PAA without and with HCl; \odot , \triangle : surfactant + 11.6 mN PAA without and with HCl, respectively

Table 1. CMC and CMC_p in 11.6 mN PAA (DP 2000) solution at 20 °C

Surfactant	CMC	CMC_p
$(EO)_{10}OP$	0.22 mM	0.12 mM
$(EO)_{15}OP$	0.38 mM	0.125 mM
$(EO)_{20}OP$	0.52 mM	0.14 mM

undissociated PAA is independent of polyacid concentration. Accordingly, the CMC_p with

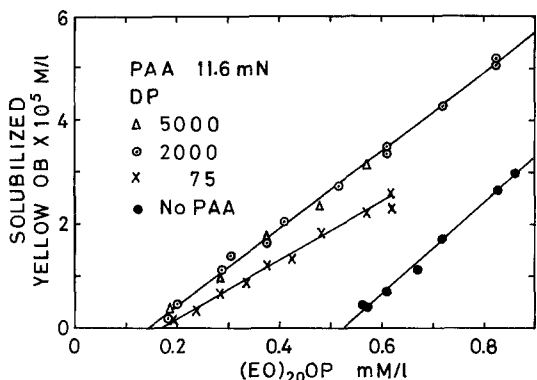


Fig. 7. Yellow OB solubilization in $(EO)_{20}OP$ solutions in the presence of 11.6 mN PAA of different degrees of polymerization (DP) at 20 °C

a dissociated polyacid (i.e., at low concentrations) is called an apparent CMC_p . Table 1 shows the CMC of $(EO)_nOP$ and CMC_p in the presence of 11.6 mN PAA. The ratio $(CMC - CMC_p)/CMC$ is greater with increasing n of $(EO)_nOP$ in spite of higher CMC, and this supports the previous conclusion that the hydrogen-bonding mechanism works in the interaction (1).

In very small surfactant/polyacid ratios, for example, at 34.8 mN PAA and at low surfactant concentration, the CMC_p rises slightly (fig. 4). This may be interpreted as that the micelle-wise binding on a polyacid chain is then suppressed to some extent, because there are too many sites available for the surfactant binding.

As shown in figure 7, CMC_p is slightly dependent on the degree of polymerization (DP) of PAA in its low DP range, in which the amount of the dye solubilization is lower than in the higher DP range presumably because of lesser surfactant binding (4).

CMC_p is dependent on the kind of polyacid. In $(EO)_nOP$ -PMA systems (figs. 2, 3 and 5), since an aqueous PMA solution itself can dissolve the dye to some extent, CMC_p is not pinpointed but apparently lower than those of the analogous PAA systems, and the reduced viscosity also declines correspondingly (in fig. 1, the region 1 is not seen in the PMA systems and the bottoms of the curves (region 3) are located in the region of lower surfactant concentration). As PMA is more hydrophobic than PAA, the degree of the hydrogen bonding of PMA with the surfactant enhances cooperatively, and therefore, the former is able to bind the surfactant more abundantly.

Because Yellow OB (1-o-tolyl-azo-2-naphthylamine) possesses an amino group which might react to polymeric acid, this could affect the solubilization. Figure 8 shows the solubilization results of naphthalene in $(EO)_nOP$ solutions with PAA or PMA, indicating that, though the pattern of the solubilization curves is different, the CMC_p 's determined with both solubilizates are almost the same within experimental error.

It has been observed that adsorption of nonionic surfactant on carbon black (16) and on a solid polymeric acid (14) increases with

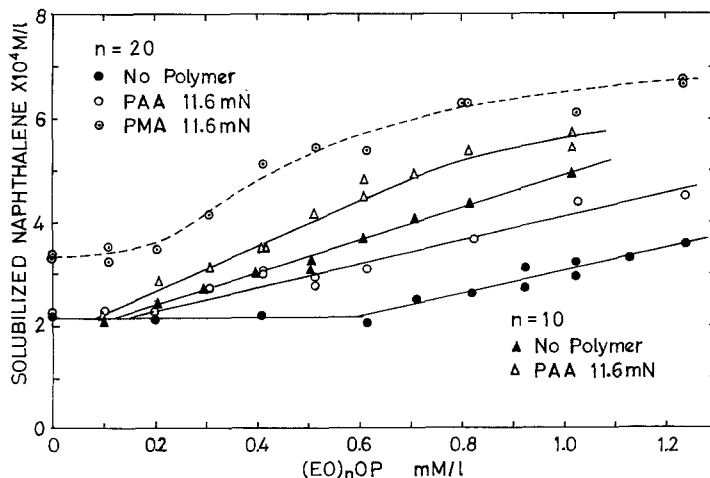


Fig. 8. Naphthalene solubilization in $(EO)_nOP$ (n : 10 and 20) solutions in the presence of PAA (continuous lines) or PMA (a broken line) at 20 °C

temperature elevation. Therefore, the binding of the surfactant on PAA also might increase at higher temperature. However, the CMC_p for $(EO)_{20}OP$ -PAA system is independent of temperature between 20°–40 °C (fig. 9). The logarithm of the CMC of $(EO)_{20}OP$ plotted against reciprocal absolute temperature gives a straight relation, resulting the conventional heat of micelle formation $\Delta H_m = 7.1 \text{ Kcal/mole}$. On the other hand, the micelle-like binding on PAA evolves no heat, for which the endothermic dehydration and the exothermic hydrogen bonding between ether oxygens and carboxyls may account.

3. *Mechanism of solubilization by the complex.* Comparison of the solubilization patterns (figs. 2, 4, 5 and 8) of the complex solutions for Yellow OB and naphthalene and also of the reduced viscosity curves (fig. 1) suggests that variation of the gross shape of the complex as a function of surfactant concentration has little correlation with the change in the amount of solubilization, except at the transition point of the regions 1 and 2, and therefore, a specific interaction between the polyacid and solubilizate enclosed in the complex is to be ascribed to the difference.

Generally, the solubilization in a surfactant-polymer solution is governed by the amount of the surfactant bound to the polymer and by the solubilizing ability of the complexes thus formed and of free micelles, if present (13).

In small surfactant/polyacid ratios, the solubilization is entirely due to the complex, and in the larger ratios, in which the solubilization curve of the complex system is in parallel with the micellar solubilization line (surfactant alone), the free micelles also contribute to the solubilization. This is shown markedly in the PMA systems (fig. 5).

It is known that PAA and PMA in water can dissolve nonpolar aromatic substances (17, 18) and Yellow OB (this work) to some extent, and PMA does more strongly. According to Barone et al. (17), this dissolution occurs in local hydrophobic cores of the polyacid chain. When a polyacid binds nonionic surfactants, the hydrations at ether oxygens and at carboxyls are partially released. It may be possible to consider that the barrier to access of a hydrophobic solubilizate to a hydrophobic part of the polyacid chain is lowered by this binding, and the surfactant bound helps the solubilizate accommodate in the new environment of the complex. In the complex the polyacid affects solubilizate. For example, the maximum of absorption spectrum of Yellow OB dissolved in an aqueous $(EO)_nOP$ solution is located at 455 nm, and it shifts to 452 and 447 nm in the presence of PAA and PMA, respectively. The effect is specific and confined to the range of close contact in the complex, and this may determine the pattern of solubilization curve of the complex system.

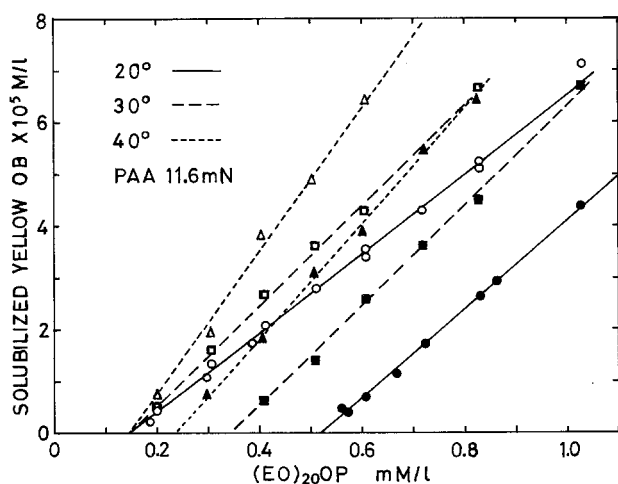


Fig. 9. Yellow OB solubilization in $(EO)_{20}OP$ solutions in the presence of 11.6 mN PAA at 20°, 30°, and 40 °C. The open and filled marks indicate the solubilization with and without PAA, respectively

Summary

The complex of a polyoxyethylene-type nonionic surfactant and a polymeric acid (polyacrylic and polymethacrylic acids) in aqueous solution has a different solubilization power from that of the micelles of the surfactant solution alone. From solubilization experiments it was found that the binding of the surfactant to a polyacid becomes abruptly conspicuous above a certain surfactant concentration, which is lower than the CMC of the surfactant. This critical concentration is considered as the concentration at the beginning of the micelle-like binding of the surfactant on the polyacid and is denoted as CMC_p . CMC_p is dependent upon the concentration of the polyacid when it is dissociated or at low concentrations, but is constant when undissociated and the ratio surfactant/polyacid is not too small. CMC_p is also dependent on the kind of polyacid, and on the degree of polymerization only in the low range. CMC_p is independent of temperature. In a series of nonionic surfactants of the same lipophilic moieties, the effect of polyacid addition on the CMC_p is the larger the longer the polyoxyethylene chain. The interaction between polyacid and solubilizate plays a key role in the solubilization by the complex.

Zusammenfassung

Der Komplex aus nichtionogenem Tensid vom Polyoxyäthylentyp und einer Polymersäure (Polyacryl- oder Polymethacrylsäure) in wässriger Lösung unterscheidet sich im Solubilisationsvermögen von dem der Tensidmizellen. Aus Solubilisationsversuchen wurde gefunden, daß die Bindung des Tensids an die Polymersäure bei einer bestimmten Tensidkonzentration plötzlich stark anwächst; diese liegt unter der eigentlichen CMC des Tensids. Diese kritische Tensidkonzentration ist als die anfängliche Konzentration zu verstehen, bei welcher die Tenside mit der Polymersäure mizell-ähnlich assoziieren; demnach wird sie als CMC_p bezeichnet. Die CMC_p ist von der Konzentration der Polymersäure abhängig, falls diese dissoziiert oder in niedriger Konzentration vorliegt. Sie ist davon unabhängig, wenn die Polymersäure undissoziiert oder das Verhältnis Tensid/Polymersäure nicht zu klein ist. Die CMC_p ist auch von der Art der Polymersäuren abhängig. Der Polymerisationsgrad der Polymersäure beeinflusst die CMC_p nur im Bereich geringerer Polymerisationsgrade. Die CMC_p ist von der Temperatur unabhängig. In einer homologen Reihe der Tenside mit den gleichen lipophilen Teilen vergrößert sich der Effekt der Polymersäure auf die CMC_p mit der Länge der Polyoxyäthylenkette des Tensids. Die Wechselwirkung zwischen Polymersäure und Solubilisat im Komplex spielt eine Hauptrolle für die Solubilisierung.

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Author's address:

Dr. Shuji Saito
 Momotani Juntanken, Ltd., Minatoku,
 Osaka 552 (Japan)