Highly Efficient Adsolubilization of 2-Naphthol on Alumina by Anionic and Nonionic Surfactant Mixtures

Kunio Esumi*, Naoko Okamoto* and Tomokazu Yoshimura*

Abstract

The adsolubilization of 2-naphthol by mixtures of an anionic surfactant, sodium dodecyl sulfate (SDS), and nonionic surfactants, hexaoxyethylenedecyl ether (C10E6), and hexaoxyethylenedodecyl ether (C12E6) on alumina was investigated. Adsorption and adsolubilization were performed using a feed concentration of SDS under various fixed concentrations of the nonionic surfactants. The adsolubilization of 2-naphthol increased with an increase of the fixed nonionic surfactant concentration, showed a maximum and then decreased with a further increase of nonionic surfactant concentration for both SDS/C10E6 and SDS/C12E6 systems. The adsolubilization of 2-naphthol was greater for SDS/C10E6 and SDS/C12E6 systems than that for SDS single system. Furthermore, the adsolubilization efficiency defined by ratio of 2-naphthol adsolubilized to total surfactant adsorbed amount was higher for SDS/C12E6 system than that for SDS/C10E6 system at the maximum adsolubilization. This difference in the efficiency between SDS/C10E6 and SDS/C12E6 systems is attributed to the properties of the mixed-surfactant adsorbed layer which are affected by the hydrocarbon chain lengths of nonionic surfactants.

Key-words: Adsolubilization of 2-naphthol, Surfactant mixtures, Alumina

1. Introduction

Surfactants adsorb as layers or micellar-type aggregates onto the surface of solids in water. Some hydrophobic compounds which do not adsorb on these solids can be incorporated in these layers in the presence of surfactants. This phenomenon is called adsolubilization. Until now, many studies of adsolubilization have been reported using single surfactant systems. Since mixtures of ionic and nonionic surfactants show often synergistic effects, the adsorption of one surfactant is sometimes enhanced by addition of the other surfactant. Surfactant mixtures provide several advantages over single surfactant, because the adsorption of surfactants on particles can be controlled using appropriate surfactants and solution properties.

We studied adsolubilization of yellow OB and azobenzene using mixed surfactant layers formed by sequential addition of anionic surfactant and nonionic surfactants with various oxyethylene chain lengths on positively charged alumina particles. The adsolubilization of yellow OB increased when the oxyethylene chain length of nonionic surfactant became shorter. However, an opposite result was obtained for the adsolubilization of azobenzene. Thus, it was found that adsolubilization of water-insoluble compounds is considerably affected by properties of mixed surfactant layers. Recently, it has been reported that adsolubilization of 2-naphthol on alumina can be enhanced by adsorption of a mixture of anionic surfactant, sodium dodecyl sulfate (SDS) and nonionic surfactant, hexaoxyethylenedecyl ether (C10E6) where the total surfactant concentrations were varied at constant molar ratios of SDS and C10E6. Since SDS has greater adsolubilization power than that of C10E6, further experiments involving adsorption from mixtures containing various SDS concentrations at fixed C10E6 concentrations may be interesting to demonstrate a highly efficient adsolubilization by surfactant mixtures. In addition, since mixed surfactant layers formed on particles operate as an adsolubilization reservoir, the effects of
hydrocarbon chain length of CnE6 on the adsolubilization are also important.

In this study, adsolubilization of 2-naphthol on alumina by surfactant mixtures of SDS and CnE6 (n = 10, 12) was investigated by varying SDS concentration with fixed CnE6 concentrations.

2. Experimental

2.1 Materials

SDS was obtained commercially and used after several recrystallizations with ethanol. C10E6 and C12E6 were supplied by Nikko Chemicals Co., and used as received. α-Alumina was kindly supplied by Showa Denkou Co.; its surface area and average particle size were 30.2 m2 g⁻¹ and 0.3 μm, respectively. Water used was purified with the use of a Mill-Q Plus System (Millipore). The other chemicals used were of analytical grade.

2.2 Methods and Measurements

Adsolubilization of 2-naphthol was carried out as follows. A series of solutions were prepared containing fixed concentrations of 2-naphthol (0.4 mmol dm⁻³), NaCl (10 mmol dm⁻³), and CnE6 in SDS aqueous solutions. The solutions were then added to alumina (0.1 g/10 ml) in glass vials with caps. All suspensions were adjusted to about pH 3.5 with HCl, and the glass vials were equilibrated at 25°C for 24 h in a shaker-water bath. After equilibration, the solids were separated by centrifugation and the supernatant was analyzed for 2-naphthol (at 328 nm, using a UV detector) and for surfactants (using an RI detector of a high-performance liquid chromatograph, HPLC) at 40°C and a Capcell Pak C18 UG column. A mixture of methanol and water was used as the mobile phase for the HPLC assays. The eluent flow rate was 100 ml min⁻¹, and the surfactant retention times were about 7 min for SDS, and 1 min for CnE6.

The surface tensions of SDS/CnE6 (n=10, 12) aqueous mixtures in the presence of 10 mmol dm⁻³ NaCl were measured at 25°C using a Krüss K 12 tensiometer. The Wilhelmy plate technique was used in the measurements. The critical micelle concentrations (cncms) of C10E6, C12E6, and SDS in the presence of 10 mmol dm⁻³ NaCl were 0.7, 0.1, and 4.0 mmol dm⁻³, respectively.

3. Results and Discussion

The adsorption of SDS/CnE6 mixtures was studied at the alumina–water interface from mixtures at several fixed concentrations of CnE6. Figure 1 shows the total adsorbed amount of surfactants as a function of feed concentration of SDS. A previous study indicates that the adsorption of C10E6 alone on alumina is very low because C10E6 does not have sufficient power to displace enough water molecules from the strongly hydrated alumina surface to enable adsorption. On the other hand, SDS alone adsorbs appreciably on alumina. Since the alumina surface is positively charged at pH 3.5 (the isoelectric point of alumina is 9.0), the electrostatic attraction with the anionic SDS will be dominant. At low SDS concentrations, SDS adsorbs onto alumina, orienting its hydrocarbon chain to the aqueous phase, while at high SDS concentrations SDS bilayers are probably formed on the alumina surface. In this study, at below equilibrium concentration of 4 mmol dm⁻³ SDS, an SDS monolayer on alumina will be formed judging from the calculated occupied area of SDS and the result of dispersion stability of alumina particles. One can see from Fig.1 that the adsorbed amount of surfactants increases with increasing fixed concentration of C10E6 from 0.1 to 0.75 mmol dm⁻³, and then decreases when the fixed concentration of C10E6 is 1.0 mmol dm⁻³. Since the adsorption of SDS on alumina from SDS/C10E6 mixtures with various fixed C10E6 concentrations increases compared to that of single SDS system (data not shown), the increase in the total adsorbed amount of surfactants is mainly due to the adsorption of both SDS and C10E6. It is suggested that the initial electrostatic adsorption of SDS provides a number of hydrophobic sites that is sufficient to enable hydrophobic adsorption of C10E6. However, when the fixed concentration of C10E6 is 1.0 mmol dm⁻³, the adsorption is decreased compared to that at 0.75 mmol dm⁻³ C10E6, probably due to the formation of
mixed micelles in the bulk solution in which desorption of surfactants and incorporation of surfactants into mixed micelles may occur.

In order to characterize the adsorption layer of SDS/C_{10}E_{6} onto alumina, the ratio (\(\alpha\)) of C_{10}E_{6} adsorbed to the total surfactant adsorbed amount was calculated and plotted in Figure 2. All the plots show that \(\alpha\) decreases with increasing feed concentration of SDS, since the ratio of concentration of C_{10}E_{6} in the total feed concentration decreases with increasing SDS feed concentration. In the case of the fixed C_{10}E_{6} concentration (0.1 mmol dm\(^{-3}\)), the adsorption layer is dominated by SDS molecules. When the fixed C_{10}E_{6} concentration increases, \(\alpha\) increases. It is interesting to note that at the higher fixed concentrations of C_{10}E_{6} (0.5, 0.75 and 1.0 mmol dm\(^{-3}\)), \(\alpha\) is in all cases almost 0.33 at the feed SDS concentration of 2 mmol dm\(^{-3}\). This may indicate that the mixed surfactant layer consists of 1:2 molar ratio of C_{10}E_{6} and SDS, with the hydrocarbon chain of C_{10}E_{6} oriented into the hydrocarbon chains of SDS adsorbing on alumina.

Figure 3 shows the adsolubilization of 2-naphthol on alumina by SDS/C_{10}E_{6} mixtures. The adsolubilized amount of 2-naphthol increased with increasing feed concentration of SDS and then decreased gradually with a further increase of feed SDS concentration for all the SDS/C_{10}E_{6} mixtures. In particular, a pronounced decrease of adsolubilization after 2 mmol dm\(^{-3}\) SDS for the fixed C_{10}E_{6} concentration of 1.0 mmol dm\(^{-3}\) is probably due to the formation of mixed micelles in the bulk solution. That is, 2-naphthol is partitioned between the mixed surfactant adsorbed layer and mixed micelles when mixed micelles are present in the bulk solution. Furthermore, it should be noted that at the feed concentration of 2 mmol dm\(^{-3}\) SDS the adsolubilized amount of 2-naphthol increases with an increase of the fixed C_{10}E_{6} concentration, shows a maximum at 0.75 mmol C_{10}E_{6} and then decreases with a further increase of C_{10}E_{6}.

Adsorption and adsolubilization experiments were also carried out using SDS/C_{12}E_{6} mixtures. Figure 4 shows the total adsorbed amount of surfactants on alumina as a function of feed concentration of SDS at various fixed C_{12}E_{6} concentrations.
here that adsorption of C₁₂E₆ on alumina is also very low, similar to that of C₁₀E₆. It is seen that the total adsorbed amounts of surfactants for all the various fixed C₁₂E₆ concentrations are not considerably different. To understand the behavior of mixed adsorption of SDS/C₁₂E₆, we plotted the ratio of C₁₂E₆ adsorbed to the total adsorbed amount of surfactants in Figure 5. Since the fixed concentrations of C₁₂E₆ except 0.1 mmol dm⁻³ are higher than the cmc of single C₁₂E₆, it is expected that the adsorption of SDS is decreased compared to that of single SDS adsorption due to incorporation of SDS adsorbed into free mixed micelles in the bulk. Therefore, the total adsorbed amounts of surfactants for the fixed concentrations of C₁₂E₆ (0.25-0.75 mmol dm⁻³) result in similar values. On the other hand, the feature of adsolubilization of 2-naphthol is quite different from that of adsorption of surfactants (Figure 6): the adsolubilized amount of 2-naphthol becomes larger with an increase of the fixed C₁₂E₆ concentration, shows a maximum at 0.5 mmol dm⁻³ C₁₂E₆, and then considerably decreases.

It is interesting to discuss the effect of hydrocarbon chain length of CₙE₆ on the adsolubilization of 2-naphthol using SDS/CₙE₆ (n=10, 12) mixtures. The CₙE₆ investigated in this study show very low adsorption on alumina, but the adsorption of these surfactants was significant in the presence of SDS in the system. It is thought that the electrostatic adsorption of SDS provides a sufficient number of hydrophobic sites for the adsorption of CₙE₆. When the hydrocarbon chain of CₙE₆ (i.e., C₁₂E₆) is equal to that of SDS, the hydrocarbon chains of SDS are equally shielded from hydrophilic environment by the hydrocarbon chains of the co-adsorbing C₁₂E₆. On the other hand, when the hydrocarbon chain of CₙE₆ (i.e., C₁₀E₆) is shorter than that of SDS, part of the SDS hydrocarbon chain would be exposed to the aqueous solution or the hydrophilic oxyethylene chains of C₁₀E₆. Therefore, it is understood that the volume of the hydrophobic environment created by the adsorption of SDS and CₙE₆ surfactants onto alumina is greater for SDS/C₁₂E₆ system than that for SDS/C₁₀E₆ system at the same adsorption density. A similar effect of surfactant structure on the adsorption of SDS and nonionic surfactant mixtures has been reported. From Figs. 2 and 5, although the values of α in the two systems are not different at the fixed concentrations of 0.75 mmol dm⁻³ C₁₀E₆ and 0.50 mmol dm⁻³ C₁₂E₆, the volume of the hydrophobic environment of SDS-CₙE₆ (n=10, 12) mixed layers onto alumina would be greater for SDS/C₁₂E₆ system than that for SDS/C₁₀E₆ system. These properties of mixed adsorbed layers show that the maximum adsolubilization of 2-naphthol is enhanced by using SDS/C₁₂E₆ system rather than SDS/C₁₀E₆ system. In particular, the efficiency of adsolubilization, which can be defined as the ratio of adsolubilization amount of 2-naphthol to total adsorbed amount of surfactants, is plotted as function of total adsorbed amount of surfactants in Figure 7. Here, the data used are for fixed CₙE₆ concentrations of 0.75 mmol dm⁻³ C₁₀E₆ and 0.5 mmol dm⁻³ C₁₂E₆ which are SDS/CₙE₆ (n=10, 12) systems that show the largest adsolubilization among the other fixed CₙE₆ concentrations. These two plots of SDS/CₙE₆ (n=10,12) systems clearly indicate that the efficiency of adsolubilization of 2-naphthol is higher for SDS/C₁₂E₆ system than that for SDS/C₁₀E₆ system and further that these two systems

Fig. 5 Plots of α against feed concentration of SDS at various fixed C₁₂E₆ concentrations : (O) 0.1 ; (■) 2.5 ; (□) 0.5 ; (▲) 0.75 mmol dm⁻³ C₁₂E₆.

Fig. 6 Adsolubilization of 2-naphthol against feed concentration of SDS at various fixed C₁₂E₆ concentrations : (O) 0 ; (Ο) 0.1 ; (■) 0.25 ; (□) 0.5 ; (▲) 0.75 mmol dm⁻³ C₁₂E₆.
Highly Efficient Adsolubilization of 2-Naphthol on Alumina by Anionic and Nonionic Surfactant Mixtures

enhance the adsolubilization considerably compared to that of single SDS system.

To understand the role of mixed surfactant adsorbed layer on the adsolubilization in detail, structural studies of these mixed layers using several spectroscopic techniques will be needed in the future.

4. Conclusions

Adsolubilization of 2-naphthol on alumina by adsorption of surfactant mixtures such as SDS/C₁₀E₆ and SDS/C₁₂E₆ as a function of feed concentration of SDS at fixed C₆E₆ concentration shows that the adsolubilization amount of 2-naphthol is enhanced for two mixed systems compared to that of single SDS system. Furthermore, it is found that SDS/C₁₀E₆ system provides greater adsolubilization efficiency of 2-naphthol than that by SDS/C₁₂E₆ system. This difference for SDS/C₆E₆ (n=10, 12) systems is derived from the different environment properties of SDS/C₆E₆. Thus, adsorption of surfactant mixtures of anionic and nonionic ones at proper mixed ratios is a great advantage to enhance the adsolubilization of 2-naphthol on positively charged alumina.

References

陰イオン性と非イオン性界面活性剤混合系を用いたアルミナ粒子上の2-ナフトールの高効率な吸着可溶化

江角邦男*・岡本直子*・古村倫一*

*東京理科大学理学部応用化学科・界面科学研究所  東京都新宿区神楽坂1－3 (〒162-8601)

要　目

界面活性剤混合系（陰イオン性、ドデシル硫酸ナトリウム、SDS：非イオン性、ヘキサオキシエチレンデシルエーテル、C₆₈
E₄₈；ヘキサオキシエチレングリコールデシルエーテル、C₆₈E₄₈）を用いてアルミナ粒子への2-ナフトールの吸着可溶化をしました。界面
活性剤の吸着ならびに吸着可溶化は非イオン性界面活性剤の濃度を固定し、SDS 濃度を変化させて行った。SDS/C₆₈E₄₈ と SDS/
C₆₈E₄₈ の関係において 2-ナフトールの吸着可溶化量は非イオン性界面活性剤の固定濃度の増加とともに増加し、最大を示した後、
減少した。2-ナフトールの吸着可溶化量は SDS/C₆₈E₄₈ および SDS/C₆₈E₄₈ 系は SDS 単独系にくらべて大きくなくなった。さらに、
吸着した界面活性剤分子あたりの2-ナフトール分子の割合を吸着可溶化効率として最大吸着可溶化量でくらべると SDS/C₆₈E₄₈
系は SDS/C₆₈E₄₈ 系より高い吸着可溶化効率となった。この効率の違いは非イオン性界面活性剤の炭化水素鎖長に影響される混
合吸着層の性質に寄与することが考えられる。