Effects of Crown Ethers on the Critical Micelle Concentration and the Micellar Catalysis of Sodium and Potassium Dodecyl Sulfates in Aqueous Solutions

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Synopsis. The catalytic micellar effects of potassium dodecyl sulfate on the hydrolysis of trimethyl orthobenzoate were found to be much retarded by 15-crown-5 or 18-crown-6.

It has been reported that complex-forming crown ethers lower the critical micelle concentration and increase the partial molal volumes and compressibilities of sodium decanoate in aqueous solutions.[1] The results have been interpreted in terms of the formation and association of Na^+–crown ether complexes with micelles, reducing the repulsion between the ionic groups at the micelle surface.

This article describes the effects of crown ethers on the critical micelle concentration (cmc) of sodium dodecyl sulfate (SDS) and potassium dodecyl sulfate (PDS) in aqueous solutions, and their effects on the rate of hydrolysis of methyl orthobenzoate in the PDS micellar systems.

When 15-crown-5 or 18-crown-6 was added to an aqueous SDS or PDS solution, an appreciable decrease in the specific conductivity of the solution was observed, and, as summarized in Table 1, the cmc, which was determined by the plot of conductivity against surfactant concentration, was found to decrease. The apparent enhancement of the micelle formation by the crown ethers is quite similar to that of sodium decanoate.[1] The magnitude of the decrease in cmc seems to have a correlation with the association constant of the crown ethers with alkali metal ions of the surfactants as shown in Table 1. 18-Crown-6 has higher association constants both with K^+ and Na^+ and gives lower cmc of PDS and SDS than 15-crown-5. The plot of cmc against the ratio of 18-crown-6 to PDS is shown in Fig. 1.

It is known that organic compounds often increase the cmc of surfactants, as is the case of urea in an aqueous SDS solution.[2] The effects of crown ethers described above may be the consequence of the formation of crown ether–metal ion complexes and their incorporation into the micelles, which leads to the decrease in the electrostatic repulsion between the anionic head groups of the micelles.

Table 1. Critical micelle concentration of SDS and PDS in the absence and presence of equimolar amounts of crown ethers

Surfactant	Crown ether	Cmc/mM 35 °C	Cmc/mM 23 °C	Association const (log K) of crown ether[a]
SDS	None	8.0	8.1	—
	15-Crown-5	6.7	7.2	0.70(Na^+)
	18-Crown-6	6.6	6.7	0.80(Na^+)
PDS	None	8.0		—
	15-Crown-5	6.5		0.74(K^+)
	18-Crown-6	4.1		2.03(K^+)

a) From Ref. 4 (at 25 °C).

A kinetic study was made to clarify the effects of crown ethers on the hydrolysis of methyl orthobenzoate in aqueous PDS solutions. The hydrolysis was followed by the change in absorbance of the product methyl benzoate at 228 nm at 35 °C and pH 3.41, which was adjusted by acetic acid. As shown in Fig. 2, the first order rate constant in PDS solution in the absence of crown ethers increases markedly above cmc. In the presence of a crown ether, however, the rate enhancement by the surfactant micelle is much decreased; 18-crown-6 has a larger inhibitory effect than 15-crown-5. Since the effects of crown ethers on the hydrolysis rate below cmc are small

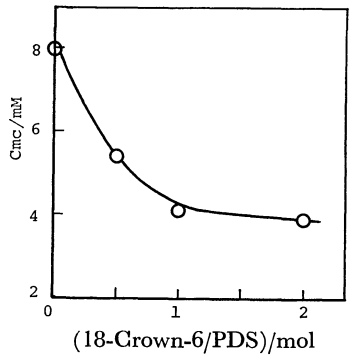


Fig. 1. The effect of 18-crown-6 on the cmc of PDS in aqueous solutions.

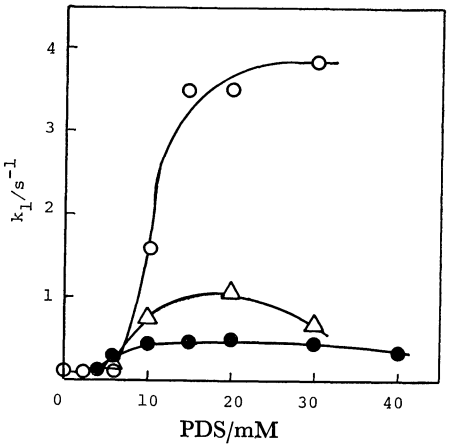
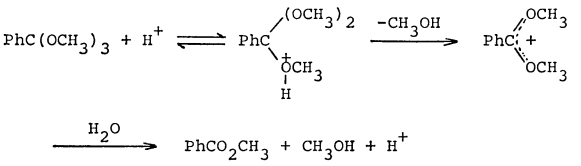


Fig. 2. First order rate constant for the hydrolysis of trimethyl orthobenzoate in the absence and presence of equimolar crown ethers (35 °C, pH 3.41). ○: PDS only, △: PDS-15-crown-5, ●: PDS-18-crown-6.

(first order rate constants are 0.052 and 0.054 s^{-1} for PDS concentrations of 2.0 and 4.0 mM, respectively, while those for PDS-18-crown-6 systems are 0.052 and 0.064 s^{-1} at the same concentrations, respectively), the rate retardation is obviously the consequence of the change of the nature of the micelles.

The reaction is considered to proceed by general acid catalysis, involving the proton transfer to the substrate followed by the formation of a carbenium ion by the elimination of methyl alcohol as shown in Scheme 1.[3] The catalytic effects of anionic micelles have been interpreted by the solubilization of the substrate in the Stern layer of the micelle where the proton concentration is higher than in the bulk water phase. The rate retardation by the crown ethers may be interpreted by the decrease in the charge density and hence the lower hydrogen ion concentrations on the surface of the micelles as implied by the decrease in the cmc by the addition of the crown ethers. A larger inhibitory effect of 18-crown-6 which has stronger complex-forming ability than 15-crown-5 seems to support the above consideration.



Scheme 1.

Since the complexation with crown ethers is considered to enhance the hydrophobic nature of potassium ion, the inclusion of the complexes into the micelle is likely to occur in the present systems, which would result in the decrease in the fraction of micelle charge.

It is interesting to note that, as shown in Fig. 2, in the presence of the crown ethers, the hydrolysis rate decreases at higher concentrations of the surfactant–crown ethers. Since no maximum rate is observed in the absence of the crown ethers, the interaction of the free crown ethers with hydroxonium ions may be responsible for the rate retardation.

The formation of crown ether–metal ion complexes and their interaction with micelles described above may serve as an experimental model system of biological ionophore-mediated metal ion-protein interactions.

References

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