Stability Constants of Complexes of Alkali Metal Cation with Crown Ether Surfactant Having 18-Crown-6

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Abstract: Our previous work showed that the critical micelle concentration (CMC) of dodecanoyloxymethyl-18-crown-6 (C11Φ6) in the presence of 0.22 mol kg^{-1} alkali metal ion was the highest for K^+ having an ionic diameter comparable to the hole size of 18-crown-6 ring and decreased as an ionic diameter of added cation departed from the hole size. In this study, we used octanoyloxymethyl-18-crown-6 (C7Φ6) having the higher CMC than C11Φ6, measured electric conductivities of aqueous C7Φ6 solutions in the presence of alkali metal ions and evaluated stability constants of C7Φ6/alkali metal ion complexes to confirm that the dependence of CMC of crown ether surfactant on the ionic diameter of alkali metal ion is attributed to the selective cation inclusion of its crown ring. As a result, it was found that the stability constant of C7Φ6/alkali metal ion complex was the largest for K^+ and decreased as a diameter of cation departed from the hole size as expected. C7Φ6 exhibited the larger stability constant and the lower cation selectivity than 18-crown-6, suggesting that the oxygen atom of carbonyl group in joint part between crown ring and alkyl chain of C7Φ6 participates in the complexation with alkali metal ion.

Keywords: Crown ether surfactant, stability constant, alkali metal ion complex

Introduction

Crown compounds having a hydrocarbon tail are multifunctional surfactants with the ability to include cation selectively and are called crown ether surfactants or amphipathic crown compounds. Many studies on water-soluble crown ether surfactants have been reported (Kuwamura and Kawachi, 1979; Moroi et al., 1979; Le Moigne and Simon, 1980; Okahara et al., 1980). Ozeki et al. studied the concentration dependence of surface tension for aqueous solutions of dodecyloxymethyl-18-crown-6 in the absence and presence of KCl (Ozeki et al., 1988; 1989). It was observed that all surface tension vs. logarithm of surfactant concentration curves had several break points below the critical micelle con-

centration (CMC). They suggested that these break points were attributed to the formation of premicellar aggregates with aggregation number from 2 to less than 5.

In the previous work (Miyazawa et al., 2015), we synthesized dodecanoyloxymethyl- (C11Φ5) and octanoyloxymethyl-15-crown-5 (C7Φ5) and measured surface tensions of their aqueous solutions in the absence and presence of ammonium and alkali chlorides to investigate the effect of selective inclusion of added cation on their adsorbed films and aggregation behaviors. All surface tension vs. logarithm of surfactant concentration curves were observed to have two break points. One break point at the higher concentration corresponded to the CMC and another break point was suggested to be

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attributed to the formation of premicelle with aggregation number of 2–4. In addition, it was found that the CMC of C11Φ5 in the presence of 0.22 mol kg⁻¹ salts was the highest for Na⁺ having an ionic diameter comparable to the hole size of 15-crown-5 ring and decreased as an ionic diameter of added cation departed from the hole size.

In the cases of dodecanoyloxymethyl-(C11Φ6) and octanoyloxymethyl-18-crown-6 (C7Φ6) without and with 0.22 mol kg⁻¹ alkali metal ion (Suzuki and Fujio, 2015), two break points were also observed in all surface tension vs. logarithm of surfactant concentration plots and it was found that the CMC of C11Φ6 was the highest for K⁺ having an ionic diameter comparable to the hole size of 18-crown-6 ring.

In this study, we used C7Φ6 exhibiting the higher CMC and measured electric conductivities of aqueous C7Φ6 solutions in the presence of alkali metal ions and evaluated stability constants of C7Φ6/alkali metal ion complexes to confirm that the dependence of CMC of crown ether surfactant on the ionic diameter of alkali metal ion is attributed to the selective cation inclusion of its crown ring.

Materials and Methods

Octanoyloxymethyl-18-crown-6 (C7Φ6) were synthesized from octanoyl chlorides (99% purity) and 2-hydroxymethyl-18-crown-6 (93%) purchased from Tokyo Chemical Industry Co., Ltd. as described previously (Suzuki and Fujio, 2015). Lithium (99%), sodium (99.5%), potassium (99.5%), rubidium (98%) and cesium (99.5%) chlorides purchased from Nacalai Tesque Inc. were dried at 120°C for 10 h before use. Solvent was ultrapure water produced by the Milli-Q Labo.

The electric conductivities of 5.00×10⁻⁴ mol dm⁻³ alkali metal ion solutions with increasing C7Φ6 concentrations were measured at 25±0.1°C under nitrogen gas flow. The DKK-TOA conductivity meter CM-30R was used with the conductivity cell CT-57101B having the cell constant of 106.3 m⁻¹.

Stability constants of C7Φ6/alkali metal ion complexes were evaluated as follows (Takeda et al., 1980). Assuming that the 1 : 1 complex is formed and ignoring the activity coefficients because of low

salt concentration the stability constant is written as

$$K_s = \frac{[ML^+]}{[M^+][L]}$$

where [ML⁺], [M⁺] and [L] are the concentrations of complex, free cation and free surfactant, respectively. Since total concentrations of surfactant and cation are represented by

$$C=[L]+[ML^+] \text{ and } C_s=[M^+]+[ML^+],$$

respectively, the concentration of complex is given by

$$[ML^+] = \frac{1}{2} \left\{ C + C_s + \frac{1}{K_s} - \sqrt{\left(C + C_s + \frac{1}{K_s} \right)^2 - 4C C_s} \right\}$$

Assuming that cations take one of two states, i.e., a free state and a complex state, and that the molar conductivities of free cation and complex, Λ_M^+ and Λ_{ML^+} , are different and do not depend on the surfactant concentration, the molar conductivity observed Λ_{obs} is represented by

$$\Lambda_{obs} = \frac{C_s - [ML^+]}{C_s} \Lambda_M^+ + \frac{[ML^+]}{C_s} \Lambda_{ML^+}$$

Therefore, the stability constant K_s and the molar conductivities, Λ_M^+ and Λ_{ML^+} , were obtained by fitting the above equations to the molar conductivity data measured with the increasing surfactant concentration and the constant cation concentration.

Figure 1. Molar conductivity observed vs. C7Φ6 concentration curves for 5.00 × 10⁻⁴ mol dm⁻³ alkali metal chloride solutions. ▽: Li⁺, △: Na⁺, ○: K⁺, ◇: Rb⁺, □: Cs⁺.

Table 1. Λ_{M^+} , Λ_{ML^+} and K_S evaluated for C7Φ6/alkali metal ion systems by curve-fitting technique and the literature values of K_S for 18-crown-6/alkali metal ion systems (Izzat et al., 1976).

	C7Φ6		18-crown-6	
	$\Lambda_{M^+}/(\text{mS m}^2 \text{mol}^{-1})$	$\Lambda_{ML^+}/(\text{mS m}^2 \text{mol}^{-1})$	$\log (K_S/\text{mol}^{-1} \text{dm}^3)$	$\log (K_S/\text{mol}^{-1} \text{dm}^3)$
Li ⁺	8.23±0.04	15.2±0.4	2.46±0.06	—
Na ⁺	12.93±0.12	19.3±0.9	2.51±0.14	0.80
K ⁺	14.92±0.02	18.0±0.1	2.66±0.05	2.03
Rb ⁺	18.68±0.06	24.0±0.4	2.58±0.07	1.56
Cs ⁺	15.82±0.03	22.5±0.3	2.44±0.04	0.99

Results and Discussion

Figure 1 shows the dependence of molar conductivity of $5.00 \times 10^{-4} \text{ mol dm}^{-3}$ alkali metal chloride solution on the C7Φ6 concentration. Solid lines in the figure represent the results of curve fitting mentioned above and the values of, Λ_{M^+} , Λ_{ML^+} and K_S evaluated are summarized in Table 1. Alkali metal cations can take one of three states, i.e., a free cation, a monomeric complex and a micellar complex, because the CMC of C7Φ6 is $3\text{--}4 \times 10^{-4} \text{ mol dm}^{-3}$ (Suzuki and Fujio, 2015). However, the curve fitting with two-state assumption works well as shown in Fig. 1, so it seems that the conductometry cannot distinguish between monomeric and micellar complexes.

In all cases, the molar conductivity increased as the C7Φ6 concentration increased. This means that the molar conductivity of C7Φ6/alkali metal ion complex is larger than that of free alkali metal ion, indicating that the size of the moving entity is smaller for the alkali metal ion complex than for the uncomplexed ion. The same phenomena were observed for the complexes of Li⁺ and Na⁺ with 15-crown-5 in propylene carbonate (Takeda et al., 1980). The cause of the increase in molar conductivity with increasing concentration of crown compound remains unsolved.

It was found that the stability constant of C7Φ6/alkali metal ion complex was the largest for K⁺ having an ionic diameter comparable to the hole size of 18-crown-6 ring and decreased as an ionic diameter of cation departed from the hole size as expected, although the difference in stability constant was very small among five alkali metal ions, that is, the selectivity of cation inclusion of C7Φ6 was the low-

er than that of 18-crown-6. The larger stability constant and the lower cation selectivity of C7Φ6 than 18-crown-6 would suggest that the oxygen atom of carbonyl group in joint part between crown ring and alkyl chain of C7Φ6 participates in the complexation with alkali metal ion.

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18-crown-6を有するクラウンエーテル界面活性剤とアルカリ金属イオンとの錯体の安定度定数

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要旨：以前の研究において、 0.22 mol kg^{-1} アルカリ金属イオン存在下でのdodecanoyloxymethyl-18-crown-6 (C11Φ6) の臨界ミセル濃度(CMC)が、18-crown-6環の孔径と同じイオン直径を持つ K^+ のとき最大であり、陽イオンの直径が孔径から離れるにつれて減少することを示した。本研究では、C11Φ6よりCMCが高いoctanoyloxymethyl-18-crown-6 (C7Φ6) を用い、クラウンエーテル界面活性剤のCMCのアルカリ金属イオン直径に対する依存性がクラウン環の陽イオンの選択包接に起因することを確認するために、アルカリ金属イオン存在下のC7Φ6溶液の電気伝導度を測定して、C7Φ6/アルカリ金属イオン錯体の安定度定数を求めた。その結果、C7Φ6/アルカリ金属イオン錯体の安定度定数は予想通り K^+ のとき最大で、陽イオン直径が孔径から離れるほど減少することが分かった。C7Φ6は18-crown-6より大きな安定度定数と低い陽イオン選択性を持っていた。このことから、C7Φ6のクラウン環とアルキル鎖を繋ぐ連結部分にあるカルボニル基の酸素原子もアルキル金属イオンとの錯形成に関与していることが示唆された。

キーワード：クラウンエーテル界面活性剤、安定度定数、アルカリ金属イオン錯体