

Stability Constants of Complexes of Crown Ether Surfactant with Several Kinds of Alkali Metal Cations

by

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(Received on Oct. 14, 2022; accepted on Dec. 9, 2022)

Abstract

In the previous study we showed that the critical micelle concentration (CMC) of dodecanoyloxymethyl-18-crown-6 (C11Φ6) in the presence of 0.22 mol kg⁻¹ alkali metal cation 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. To investigate the cause of these observations, we evaluated stability constants of C11Φ6/alkali metal cation complexes from electric conductivity data in this work. The stability constant of C11Φ6/alkali metal cation complex was found to be the largest for Rb⁺. Excluding the case of K⁺, in which the obtained stability constant was much smaller than the expected value although the reason is unknown, the stability constant decreased with the deviating of the cationic diameter from the hole size of the crown ether ring as previously reported for octanoyloxymethyl-18-crown-6 having the higher CMC. The larger stability constant and the lower cation selectivity than 18-crown-6 were observed, suggesting that the oxygen atom of carbonyl group in joint part between crown ring and alkyl chain of C11Φ6 participates in the complexation with alkali metal ion.

Keywords: Crown ether surfactant; Stability constant; Alkali metal ion complex

1 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 researchers have studied water-soluble crown ether surfactants [1–4]. Ozeki *et al.* investigated the concentration dependence of surface tension for aqueous solutions of dodecyloxymethyl-18-crown-6 in the absence and presence of KCl and observed that all surface tension vs. logarithm of surfactant concentration curves had several break points below the critical micelle concentra-

tion (CMC) [5, 6]. 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 [7], we synthesized dodecanoyloxymethyl-(C11Φ5) and octanoyloxymethyl-15-crown-5 (C7Φ5) and measured surface tensions of their aqueous solutions in the absence and presence of alkali and ammonium chlorides to investigate the effect of selective inclusion of added cation on their adsorbed films and aggregation behaviors. It was observed that all surface tension vs. logarithm of surfactant concentration curves had two break points. One break point at the higher concentration corresponded to the CMC and another break point was suggested to be 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 cation [8], two break points were also observed in all surface tension vs. logarithm of surfactant concentration plots and the CMC of C11Φ6 was found to be the highest for K^+ having an ionic diameter comparable to the hole size of 18-crown-6 ring.

Then, we used C7Φ6 exhibiting the higher CMC and measured electric conductivities of aqueous C7Φ6 solutions in the presence of alkali metal cations to evaluate stability constants of C7Φ6/alkali metal cation complexes [9]. 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. Additionally, C7Φ6 was found to exhibit 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.

In this study, we measured electric conductivities of aqueous solutions of the same surfactant C11Φ6 as the previous study [8] with alkali metal cations and evaluated stability constants of C11Φ6/alkali metal cation complexes to confirm that the dependence of CMC of crown ether surfactant on the ionic diameter of alkali metal ion, which observed in the previous work [8], is attributed to the selective cation inclusion of its crown ring.

2 Experimental

Dodecanoyloxymethyl-18-crown-6 (C11Φ6) were synthesized from dodecanoyl chlorides (99% purity) and 2-hydroxymethyl-18-crown-6 (93%) purchased from Tokyo Chemical Industry Co., Ltd. as described previously [8]. Sodium (99.5%), potassium (99.5%), rubidium (98%) and cesium (99.5%) chlorides purchased from Nacalai Tesque Inc. were dried at 120°C for 10h before use. Solvent was ultrapure water produced by the Milli-Q Labo.

The electric conductivities of $5.00 \times 10^{-4} \text{ mol dm}^{-3}$ alkali metal cation solutions with increasing C7Φ6 concentrations were measured at $25 \pm 0.1^\circ\text{C}$ 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 C11Φ6/alkali metal ion complexes were evaluated as follows [10]. Assum-

ing that the 1 : 1 complex is formed and ignoring the activity coefficients because of low salt concentration the stability constant is written as

$$K_S = \frac{[\text{ML}^+]}{[\text{M}^+][\text{L}]} \quad (1)$$

where $[\text{ML}^+]$, $[\text{M}^+]$ and $[\text{L}]$ are the molar concentrations of complex, free cation and free surfactant, respectively. Since total concentrations of surfactant and cation are represented by

$$C = [\text{L}] + [\text{ML}^+] \text{ and } C_S = [\text{M}^+] + [\text{ML}^+], \quad (2)$$

respectively, the concentration of complex is given by

$$[\text{ML}^+] = \frac{1}{2} \left\{ C + C_S + \frac{1}{K_S} - \sqrt{\left(C + C_S + \frac{1}{K_S} \right)^2 - 4C C_S} \right\} \quad (3)$$

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

$$\Lambda_{\text{obs}} = \frac{C_S - [\text{ML}^+]}{C_S} \Lambda_{\text{M}^+} + \frac{[\text{ML}^+]}{C_S} \Lambda_{\text{ML}^+} \quad (4)$$

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.

3 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 C11 Φ 6 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 C11 Φ 6 is $0.6 - 2 \times 10^{-4} \text{ mol dm}^{-3}$ [8]. 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, as observed for the complexation of C7 Φ 6 with alkali metal cation [9].

In all cases, the molar conductivity increased with the increasing C11 Φ 6 concentration. This means that the molar conductivity of C11 Φ 6/alkali metal cation complex is larger than that of free alkali metal cation, indicating that the size of the moving entity is smaller for the alkali metal cation complex than for the uncomplexed cation. The same phenomena were observed for the C7 Φ 6/alkali metal cation complexes [9] and the complexes of Li^+ and Na^+ with 15-crown-5 in propylene carbonate [10]. The cause of the increase in molar conductivity with increasing concentration of crown compound remains unsolved.

It was found that the stability constant of C11 Φ 6/alkali metal cation complex was the largest for Rb^+ against our expectation. The cause of this is that the stability constant of C11 Φ 6/ K^+ complex is much smaller than the expected value, although the origin of the small stability constant for K^+ is left unsolved. Excluding the case of K^+ , the dependence of the stability constant

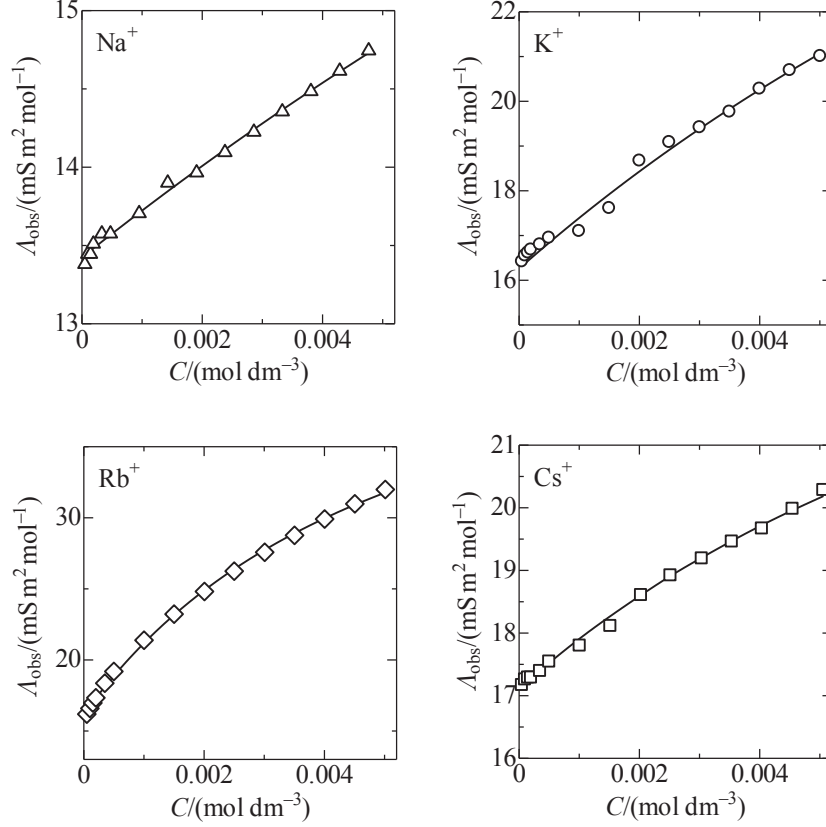


Fig. 1 Molar conductivity observed vs. C11Φ6 concentration curves for 5.00×10^{-4} mol dm $^{-3}$ alkali metal chloride solutions. $\triangle$: Na $^{+}$, $\circ$: K $^{+}$, $\diamond$: Rb $^{+}$, $\square$: Cs $^{+}$.

Table 1 $\Lambda_{M^{+}}$, $\Lambda_{ML^{+}}$ and K_S evaluated for C11Φ6/alkali metal ion systems by curve-fitting technique and the literature values of K_S for C7Φ6 [9] and 18-crown-6 [11] /alkali metal ion systems.

	C11Φ6			C7Φ6	18-crown-6
	$\Lambda_{M^{+}}$ /(mS m 2 mol $^{-1}$)	$\Lambda_{ML^{+}}$ /(mS m 2 mol $^{-1}$)	$\log(K_S)$ /mol $^{-1}$ dm 3)	$\log(K_S)$ /mol $^{-1}$ dm 3)	$\log(K_S)$ /mol $^{-1}$ dm 3)
Na $^{+}$	13.4	25.2	1.43	2.51	0.80
K $^{+}$	16.3	40.8	1.70	2.66	2.03
Rb $^{+}$	16.2	47.9	2.31	2.58	1.56
Cs $^{+}$	17.1	27.1	1.96	2.44	0.99

of C11Φ6/alkali metal cation complex on the ionic diameter of cation was almost the same as C7Φ6/cation complex: the stability constant decreased as an ionic diameter of cation departed from the hole size, although the difference in stability constant was small among four alkali metal ions, that is, the selectivity of cation inclusion of C11Φ6 was the lower than that of 18-crown-6. The larger stability constant and the lower cation selectivity of crown ether surfactant than 18-crown-6 would suggest that the oxygen atom of carbonyl group in joint part between crown ring and alkyl chain of crown ether surfactant participates in the complexation with alkali metal cation.

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