Novel Approach to the Reaction Analysis of Non-UV-Absorbing Crown Ether with Alkali Metal Ions in Aqueous Solution by Capillary Zone Electrophoresis Using Indirect Photometric Detection

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A novel analysis method for complex formation reactions of such a non-UV-absorbing crown ether as 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6 ether, 18C6) with alkali metal ions was established through the mobility change in capillary zone electrophoresis. Alkali metal ions at their concentrations of 1×10^{-4} mol dm^{-3} were photometrically detected by using 1-ethylquinolinium ion as an indirect photometric reagent. The apparent electrophoretic mobility of alkali metal ions decreased along with the increase in the concentrations of 18C6 in migrating solutions. The complex formation constants analyzed and determined by using the mobility change agreed well with the reported values.

Capillary zone electrophoresis (CZE) can offer a useful separation technique for ionic molecules, as well as a simple and accurate method for measuring electrophoretic mobility. By utilizing a migration principle in CZE, any reactions in migrating solutions can be analyzed by detecting analytes which can interact with some reagents in the migrating solutions and by investigating their apparent mobility, if one of reactants and a product can be detected by any method such as spectrophotometry. The complexation reactions of crown ethers with alkali metal ions[1-3] and alkaline earth metal ions[3] were investigated on the basis of photometric detection of crown ethers and of the change in their apparent electrophoretic mobility caused by the formation of positively charged complexes. The method, however, was limited to such compounds as light-absorbing ligands.

Crown ethers have been used as a buffer modifier for the separation and determination of alkali metal ions by indirect photometric methods.[4,5] However, no attentions were paid for the aim of the reaction analysis. In the present study, the authors aim at developing the analysis method using a CZE measurement, which can be applicable to less light-absorbing compounds by coupling it with an indirect photometric detection.. A precise analysis of complexation reactions between alkali metal ions and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6 ether, 18C6, L) is demonstrated as an example by detecting alkali metal ions at low concentrations. The CZE measurement is carried out by using migrating solutions containing excess amounts of 18C6 and a UV-absorbing cationic reagent and by injecting alkali metal ions as analytes. In the indirect photometric method shown here, the detection of alkali metal ions at concentration level of 0.1 mM (M = mol dm^{-3}) can be attained, and therefore the method is useful for the resolution improvement and sensitive determination of alkali metal ions.

A Hewlett Packard ^{3D}CE capillary electrophoresis system with a UV detector was used. A fused silica capillary (56+8.5 cm, 50 μm; Hewlett Packard) was attached to the system.

Migrating buffer solutions were prepared from boric acid (Wako) and tetraethylammonium hydroxide ($TEA^+\bullet OH^-$, Tokyo Kasei Kogyo). 1-Ethylquinolinium iodide ($EtQ^+\bullet I^-$, Tokyo Kasei Kogyo) used as an indirect photometric reagent and a certain amount of 18C6 (Tokyo Kasei Kogyo) up to 40 mM were added to the migrating solutions. Sample solutions were prepared from each alkali metal chloride ($M^+\bullet Cl^-$, Wako) and the H_3BO_3–$TEA^+\bullet OH^-$ buffer. The sample solution was injected from anodic end by applying pressure (150 mbar•s). A voltage of 10 kV was applied for the electrophoresis, and the analytes, M^+, were photometrically detected at 240 nm indirectly. Throughout the experiment, the capillary, the reservoir and the sample vials were kept at 25.0±0.1 °C. The electric current produced during the electrophoresis was about 1 μA under the experimental conditions, and therefore the temperature increase by the Joule's heat produced during the electrophoresis is considered to be well suppressed. The apparent electrophoretic mobility of M^+, as well as the velocity of an electroosmotic flow (EOF), was calculated in an ordinary manner using the migration time of the analyte signals and that of dip peak of the injected solution.

In the present method, any cations, except for analyte ions, in migrating solution must be less reactive with 18C6, because the effective concentration of 18C6 will be reduced through the reaction, and therefore an H_3BO_3–$TEA^+\bullet OH^-$ buffer and an indirect photometric reagent of $EtQ^+\bullet I^-$ were selected. Typical electropherograms detecting alkali metal ions are shown in Figure 1. Alkali metal ions, as well as EtQ^+, are positively charged, and therefore can migrate faster than the EOF. As can be seen from Figure 1, the resolution of K^+ and Cs^+ was poor in the absence of 18C6. However, the resolution was improved by adding 10

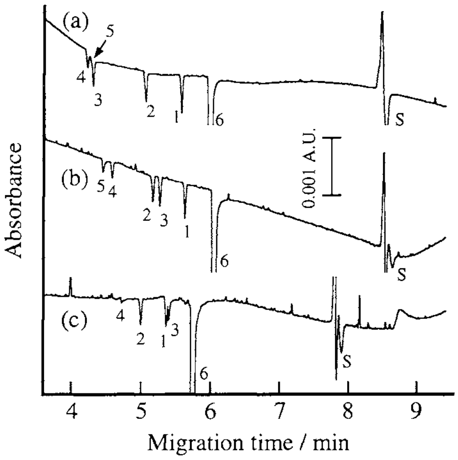

Figure 1. Typical electropherograms for alkali metal ions in the absence and presence of 18C6 in the migrating solution. Migrating solution: 10 mM H_3BO_3–$TEA^+\bullet OH^-$ buffer (pH 9.0) + 1.0 mM $EtQ^+\bullet I^-$ + (0–20) mM 18C6. [18C6]: a), none; b), 10 mM; c), 20 mM. Sample solution: 0.1 mM alkali metal ions + 10 mM H_3BO_3–$TEA^+\bullet OH^-$ buffer (pH 9.0). CZE conditions are shown in the text. Signal identifications: 1, Li^+; 2, Na^+; 3, K^+; 4, Rb^+; 5, Cs^+; 6, EtQ^+. S, EOF.

mM 18C6 in the migrating solution. The migration order of the alkali metal ions also changed by the addition of 18C6, which suggests that reaction between the analytes and 18C6 is involved.

Changes in the apparent electrophoretic mobility of alkali metal ions, $\mu_{ep,M}$', were plotted against the concentrations of 18C6 (Figure 2). The apparent electrophoretic mobility of EtQ^+ is also plotted. The mobility decreased with increasing concentrations of 18C6 in the migrating solutions, though the decreases for Li^+ and EtQ^+ are slight. The slight mobility changes for Li^+ and EtQ^+ indicate that such cations are less reactive with 18C6, which indicates that the selection of EtQ^+ as an indirect photometric reagent is successful for the aim of this study.

The authors previously proposed the analysis method for complexation reaction of crown ethers possessing UV-absorbing benzene rings,[2,3] where crown ethers were used as analytes and detected spectrophotometrically at 200 nm. The previous method could not be applied to any crown ether possessing no light-absorbing moiety. Therefore in this study, alkali metal ions were used as analytes and detected indirectly. A 1:1 complex is expected to be formed between M^+ and 18C6, as shown in the equilibrium (1), with an equilibrium constant given by Eq. (2).

$$M^+ + L \overset{K_{ML}}{\rightleftarrows} ML^+ \tag{1}$$

$$K_{ML} = \frac{[ML^+]}{[M^+][L]} \tag{2}$$

The apparent electrophoretic mobility of a certain M^+, $\mu_{ep,M}$', can be written as Eq. (3) by using the mass balance for M^+ and Eq. (2),

$$\mu_{ep,M}' = \frac{1}{1+K_{ML}[L]}\mu_{ep,M} + \frac{K_{ML}[L]}{1+K_{ML}[L]}\mu_{ep,ML} \tag{3}$$

where $\mu_{ep,M}$ and $\mu_{ep,ML}$ are the mobility of M^+ and its 1:1 complex with 18C6, respectively. A non-linear least-squares method[2,3] was also applied to the determination of K_{ML} in the present study. Solid curves in Figure 2 show the simulation of the mobility change using Eq. (3) and the optimized values; those are in good agreement with the experimentally obtained values. The values obtained in the present study are summarized in Table 1; the equilibrium constants agreed well with the reported values.[6,7] From good agreements between the experimental and the simulated results shown in Figure 1 and the obtained constants with the reported values, the proposed method is proved to be reliable. As the electrophoretic method was applied to the reaction analyses of acid dissociation and complex formation in gel matrices,[8] the proposed CZE method can also offer such stability constants.

Concerned with the values of $\mu_{ep,M}$, the magnitude is in the order of $Li^+ \ll Na^+ \ll K^+ \approx Cs^+ < Rb^+$, which agrees well with that of the reported one,[8] indicating the contribution of the hydration of the cations. On the other hand, the values of $\mu_{ep,ML}$ are almost identical among the complexes, which suggests that the crown ether complexes are in the similar ionic radii. The difference in the mobility between metal ions and their complexes is relatively large for K^+, Rb^+, and Cs^+, which involves the significant change in ionic radii, and therefore the reaction analysis is easy and accurate. In Na^+ and its complex, the difference is small, which should be attributted to a large hydration of Na^+ ion.

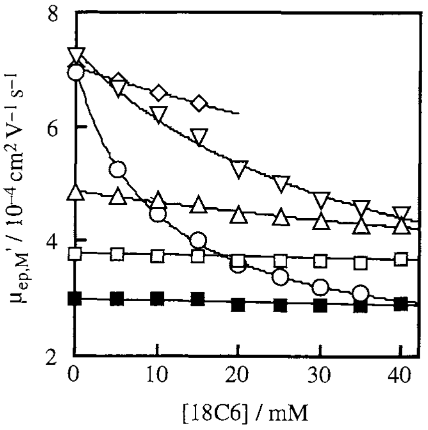

Figure 2. Mobility change of alkali metal ions in the presence of 18C6 in the migrating solution. Migrating solutions, sample solutions and CZE conditions, except for the concentration of 18C6, are the same as in Figure 1. □, Li^+; △, Na^+; ○, K^+; ▽, Rb^+; ◇, Cs^+; ■, EtQ^+.

Table 1. Electrophoretic mobility and complex formation constants obtained in this study

Value or	M^+				
constant	Li^+	Na^+	K^+	Rb^+	Cs^+
$\mu_{ep,M}$ [a]	3.75[e]	4.87±0.09	6.94±0.14	7.31±0.33	7.03±0.02
$\mu_{ep,ML}$ [a]	– [f]	2.33±0.52	1.98±0.11	1.90±0.62	1.91±0.27
log K_{ML} [b]	– [f]	0.90±0.12	2.00±0.03	1.46±0.09	0.97±0.03
log K_{ML} [c]	–	0.80±0.10	2.03±0.10	1.56±0.02	0.99±0.07
log K_{ML} [d]	–	<0.3	2.06	–	0.8

[a] Error: 3σ; dimension: 10^{-4} cm^2 V^{-1} s^{-1}. [b] Error: 3σ. [c] Reported values cited from reference 6 obtained by calorimetric titration. [d] Reported values cited from reference 7 obtained by potentiometry with ion selective electrodes. [e] Measured value. [f] Change in the mobility was too small to determine the value and the constant.

Alkali metal ions were found to be sensitively detected by using EtQ^+ in the present study, and the CZE determination method for alkali metal ions is now developing by using the indirect photometric reagent which was used in ion chromatography.[9]

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