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Analysis of Reactions between Crown Ethers and Alkali or Alkaline Earth Metal Cations in Aqueous Solutions by Capillary Zone Electrophoresis

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Complex formation constants of six crown ethers, benzo-12-crown-4, benzo-15-crown-5, benzo-18-crown-6, dibenzo-18-crown-6, dibenzo-21-crown-7, and dibenzo-24-crown-8 (B12C4, B15C5, B18C6, DB18C6, DB21C7, and DB24C8, respectively) with alkali and alkaline earth metal cations have been measured in aqueous solutions by capillary zone electrophoresis. The procedure involved the measurement of change in the electrophoretic mobility of the ligands upon increasing the metal ion concentration in the carrier electrolyte solution. A substantial increase in apparent electrophoretic mobility was observed for the crown ethers with increasing concentrations of the metal ions. The variations in increased electrophoretic mobility were attributed to the different stability of the complexes formed between the cations and the crown ether. The complex formation constants obtained with alkali metal cations were in the orders of: $K^+ > Na^+ > Rb^+ > Cs^+$ (B18C6), $K^+ > Na^+ > Rb^+ > Cs^+$ (DB18C6), $Rb^+ > Cs^+ > K^+$ (DB21C7), and $Rb^+ > Cs^+$ (DB24C8); while with alkaline earth metal cations it was: $Ba^{2+} > Sr^{2+} > Ca^{2+}$ (B18C6) and $Ba^{2+} > Sr^{2+}$ (DB18C6). All the ligands examined showed no change in their apparent electrophoretic mobility upon changing Li^+ and Mg^{2+} concentrations, indicating less reactivity with the cations. From the results obtained in this study, the electrophoretic method was proved to be preferable for analyzing the reactivity of the crown ethers and the selectivity toward metal cations.

The formation of complexes of macrocyclic polyethers with various cations has been extensively investigated in recent years and comprehensive reviews of the subject are available.[1—5] Nevertheless, the study of a large number of these ligands has presented a challenge in interpreting the cation binding behaviour in terms of the observed selectivities and solvation characteristics of the ligands under various experimental conditions. In such complexes, cations are held principally by electrostatic forces, i.e, ion–dipole interactions, and the equilibrium constants of complex formation are strongly affected by the solvent medium, and the relative sizes of the cation and the crown ether cavity. The complex formation constants of the crown ether with various metal ions in various solutions have been measured by various methods including calorimetric titrations or potentiometry by using ion-selective electrodes and by spectrophotometry.[2,6,7] However, due to severe limitations imposed by the very low solubility in water of these crown ethers, especially those having aromatic rings adjoining the macrocyclic polyether rings, data on the aqueous stability constants are very few.[1,3]

Capillary zone electrophoresis (CZE) has been shown to be a very effective analytical technique for a wide range of reactions and therefore has received considerable attention in efforts to separate and analyze various compounds. The migration time or the electrophoretic mobility varies mainly according to the charge-to-mass ratio of the species of interest and hence the method has promise for studying various reactions in different media solutions. For instance, Takayanagi et al.[1] analyzed the ion association and complex formation among 2,3-11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctade-2,11-cene (dibenzo-18-crown-6 or DB18C6), alkali metal ions, and picrate in an aqueous solution by CZE. In the proposed method, the change in apparent electrophoretic mobility of DB18C6 was used to analyze the complex formation reaction from a non-charged ligand to a positively charged complex. The change in number of charges and/or the change in apparent molecular mass affect the electrophoretic mobility. Valenzuela et al. have reported preliminary data concerning the analysis of sulfonium compounds using CZE, and concluded the technique to be rapid and highly effective.[8] Although the complex formation constants in water of 2,3-benzo-1,4,7,10,12-pentaoxacyclodode-2-cene (benzo-15-crown-5 or B15C5), 2,3-benzo-1,4,7,10,12,16-hexaoxacyclooctadode-2-cene (benzo-18-crown-6 or B18C6), DB18C6 and 2,3,14,15-dibenzo-1,4,7,10,13,16,19,22-octaoxacyclotetraeicosane-2,14-cene (dibenzo-24-crown-8 or DB24C8)–metal ions have been reported,[1,9,10] no data on the stabilities of 2,3-benzo-1,4,7,10-tetraoxacyclodode-2-cene (benzo-12-crown-4 or B12C4) and 2,3-11,12-dibenzo-1,4,7,10,13,16,19-heptaoxacyclooctade-2,11-cene (dibenzo-21-crown-7 or DB21C7)–metal ion complexes in water have been reported.

In this study, the equilibrium constants of the complex formation of the six crown ether compounds, B12C4, B15C5, B18C6, DB18C6, DB21C7, and DB24C8 with the alkali and alkaline earth metal cations in an aqueous solution have been measured by the CZE method. The analysis procedure was based on the measurement of change in electrophoretic mobility of the crown ethers upon changing metal cation concentrations. Some of the complex formation constants in aqueous solution obtained in this study agreed well with the reported values, and the ones between B12C4 and DB21C7 with alkali and alkaline earth metal ions were measured for the first time. In addition to the complex formation constants, the selectivity of crown ethers towards alkali metal cations was estimated and compared with the reports in the literature.

Experimental

Apparatus. An Applied Biosystems Model 270A Capillary electrophoresis system with a UV detector was used. Fused silica capillary of 50 μm i.d. was purchased from GL Sciences, and was cut to a required length and used; the size was a total length of 72 cm with 50 cm length to the detector window. The electropherograms were recorded by a Hitachi D-2000 Chromato Integrator.

Reagents. Phosphate migrating buffer solutions composed of H_3PO_4–Li_3PO_4, NaH_2PO_4–Na_2HPO_4, KH_2PO_4–K_2HPO_4, H_3PO_4–RbOH, and H_3PO_4–CsOH (pH 7.0) were used for the experiments in alkali metal ions. For alkaline earth metal ions, acetate buffer solutions containing $Mg(OH)_2$–CH_3COOH, $Ca(OH)_2$–CH_3COOH, $Sr(OH)_2$–CH_3COOH, and $Ba(OH)_2$–CH_3COOH (pH 5.5) were used. In each buffer, the accurate metal ion concentrations were measured as follows: all the metal hydroxides were standardized by titration with potassium hydrogen phthalate (Wako) before mixing them with the acids. Potassium hydroxide, NaOH, LiOH, $Mg(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$ were purchased from Wako, while RbOH, CsOH, and $Ca(OH)_2$ were from Kanto. Each of all alkali and alkaline earth metal chlorides purchased from Wako was dissolved in water and used without further treatment. Dibenzo-18-crown-6 and benzo-18-crown-6 were synthesized as described in the literature[5] and recrystallized from benzene and hexane, respectively. Dibenzo-21-crown-7 was purchased from Wako, and dibenzo-24-crown-8, benzo-15-crown-5, and benzo-12-crown-4 were purchased from Tokyo Kasei Kogyo. Stock solutions of all the crown ether compounds were prepared by dissolving them in ethanol to give the final concentrations: 4×10^{-4} M for dibenzo-18-crown-6 and 1×10^{-3} M for the rest of crown ethers (1 M = 1 $\mathrm{mol\,dm^{-3}}$). Distilled and de-ionized water was used throughout the experiment.

Procedure for the CZE Measurement. Two different migrating buffer solutions were used. Phosphate buffer (pH 7.0) for alkali metal ions and acetate buffer (pH 5.5) for alkaline earth metal ions with both phosphate and acetate total concentration being 5.0×10^{-3} $\mathrm{mol\,dm^{-3}}$. Corresponding metal chlorides (MCl or MCl_2) with concentrations ranging up to 4.0×10^{-2} $\mathrm{mol\,dm^{-3}}$ were contained in the migrating buffer solutions. They were used to fill the cathodic and anodic reservoirs and then the capillary by a vacuum system. Sample solutions were prepared by diluting the stock solutions of crown ethers with water to give 5×10^{-6} $\mathrm{mol\,dm^{-3}}$ solutions. The sample solutions also contained 3% (v/v) ethanol for monitoring the velocity of electroosmotic flow (EOF) and a concentration of alkali metal ion (M^+) or alkaline earth metal ion (M^{2+}) equal to that of the migrating solution. Sample solutions containing the crown ethers as analytes were injected hydrodynamically by a vacuum system for 3 s (injection volume: about 9 nl) from the anodic end of the capillary. A voltage of 10 kV was applied and the analytes, crown ethers, were photometrically detected at 200 nm at the cathodic end of the capillary. The capillary was kept in a compartment thermostated at 35 °C throughout the experiment. By measuring the migration times of crown ethers and ethanol as an EOF marker, the apparent electrophoretic mobility of crown ethers and the velocity of EOF were calculated. For every experiment, three measurements were done and averaged to obtain a value as accurate as possible.

Results and Discussion

Migration Behavior of Crown Ethers with Increasing Concentrations of Alkali Metal Ion. Changes in the migration times of crown ethers from that of the EOF were observed when excess alkali metal ions except for lithium ion were added to the solutions. Crown ethers as neutral ligands would show no change in migration, i.e., their migration time would be equal to that of a neutral marker (EOF). In this study, it was observed that all the crown ethers migrated faster than the EOF, indicating the formation of cationic species in the solution, because the analytes, crown ethers, were injected at the anodic end of the capillary. It is worthwhile to note that a positive charge has been created in the electrophoretic buffer, which can be attributed to the interaction between the crown ethers as ligands and the alkali metal cations resulting in complexes.

The changes in the migration time differed from one crown ether to another depending largely on how strongly they interacted with the cations. An electropherogram shown in Fig. 1 shows the change in the migration time of three crown ethers (B18C6, DB18C6, and DB21C7) in the presence of K^+ ion. The difference in migration time from the EOF increased in the order: DB21C7 < DB18C6 < B18C6. The electropherograms with other monovalent cations were also recorded. Sodium ion affected the migration of only DB18C6 and B18C6 in the order: B18C6 < DB18C6, while Rb^+ and Cs^+ tended to change the migration time of four crown ethers: DB24C8 < DB18C6 < B18C6 < DB21C7.

Complexation Analysis of Crown Ether–Alkali Metal Ion. Only four crown ether compounds, B18C6, DB18C6, DB21C7, and DB24C8 had detectable differences in the migration time from that of EOF upon interacting with alkali metal cations. Figure 2(a) shows the change in apparent electrophoretic mobility, $\mu'_{\mathrm{ep(L)}}$, of the three crown ethers that interacted with K^+ ion. The mobility of all three crown ethers increased but to a different extent with increasing metal ion concentrations. The increases in the mobility with increasing concentrations of alkali metal ions indicate that the equilibrium reaction, complex formation reaction in this case, proceeds and positively charged complex is largely produced at higher alkali metal concentrations. Similar results were observed when $\mu'_{\mathrm{ep(L)}}$ vs. M^+ concentration dependences were plotted for the other ligands as shown in Figs. 2(b) and 2(c) for Rb^+ and Cs^+ ions, respectively. B18C6 and DB18C6 also showed similar pattern of mobility increase upon increasing Na^+ concentrations up to 4.0×10^{-2} $\mathrm{mol\,dm^{-3}}$. Such increases in the mobility of crown ethers upon increasing metal ion concentrations indicate a difference in complex-forming reactivity of the crown ethers with alkali metal ions.

The complex formation between alkali metal ions and crown ethers as ligands takes place according to the follow-

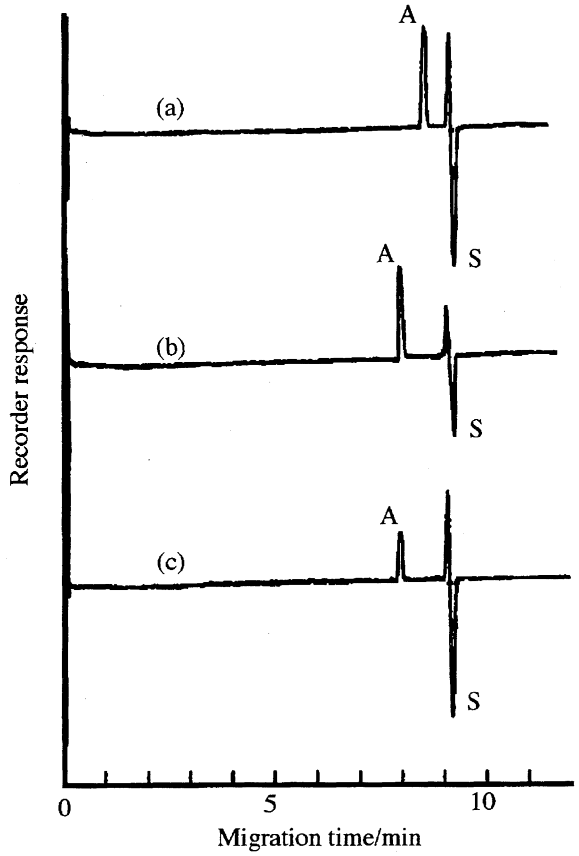

Fig. 1. Typical electropherograms of (a) DB21C7, (b) DB18C6, and (c) B18C6 in the presence of K^+ ion. CE conditions are cited in the text. Migrating solutions: 5.0×10^{-3} mol dm^{-3} phosphate buffer $+3.0\times10^{-2}$ mol dm^{-3} KCl. Sample solutions: 5.0×10^{-6} mol dm^{-3} crown ether $+5.0\times10^{-3}$ mol dm^{-3} phosphate buffer $+3.0\times10^{-2}$ mol dm^{-3} KCl + 3.0% (v/v) ethanol. A, analytes (crown ether); S, neutral marker (ethanol).

ing reaction (1), where K_{ML} is a complex formation constant given by Eq. 2, as was written in our preceding study.[1]

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

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

The apparent electrophoretic mobility of the crown ether, $\mu'_{\mathrm{ep(L)}}$, is contributed from the mobility of free crown ether, L, and the complexed one, $\mathrm{ML^+}$; which can be written as :

$$\mu'_{\mathrm{ep(L)}} = \frac{[\mathrm{L}]}{[\mathrm{L}]+[\mathrm{ML^+}]}\mu_{\mathrm{ep(L)}} + \frac{[\mathrm{ML^+}]}{[\mathrm{L}]+[\mathrm{ML^+}]}\mu_{\mathrm{ep(ML^+)}}, \tag{3}$$

where $\mu_{\mathrm{ep(L)}}$ and $\mu_{\mathrm{ep(ML^+)}}$ are the electrophoretic mobility of L and $\mathrm{ML^+}$ respectively. Equation 3 can be transformed to Eq. 4 by taking into account the mass balance of the ligand and the complex formation constant as expressed in Eq. 2.

$$\mu'_{\mathrm{ep(L)}} = \frac{1}{1+K_{\mathrm{ML}}[\mathrm{M^+}]}\mu_{\mathrm{ep(L)}} + \frac{K_{\mathrm{ML}}[M^+]}{1+K_{\mathrm{ML}}[M^+]}\mu_{\mathrm{ep(ML^+)}}. \tag{4}$$

A non-linear least-squares method[1] was used to obtain the values of K_{ML}, $\mu_{\mathrm{ep(L)}}$, and $\mu_{\mathrm{ep(ML^+)}}$ in Eq. 4. In this method, a series of pairs of known concentrations of $\mathrm{M^+}$ and experimentally obtained $\mu'_{\mathrm{ep(L)}}$ values were put into Eq. 4, and the values of K_{ML}, $\mu_{\mathrm{ep(L)}}$, and $\mu_{\mathrm{ep(ML^+)}}$ were optimized by the errors between the calculated and the experimental values of $\mu'_{\mathrm{ep(L)}}$ being the smallest. In Figs. 2a, b, and c, the solid lines correspond to the simulation of the mobility change using Eq. 4 and the optimized values; each line agreed well with the experimentally obtained $\mu'_{\mathrm{ep(L)}}$ values. Table 1 summarizes the complex formation constants and the values of electrophoretic mobility obtained in this work as well as the log K_{ML} values previously reported by others for the systems studied. It can be seen that agreement in K_{ML} between the values reported and those measured in this study is satisfactory, although there are differences in experimental methods and procedures involved.

Dibenzo-21-crown-7 is a larger ligand with a cavity diameter of about 3.4—4.3 Å. It has been observed that as the polyether ring increases in size beyond 18 atoms including the six oxygen atoms, the complexing ability for the smaller ions disappears, and even the complexation power for the larger ions diminishes.[5] In this study, DB21C7 is complexed well by larger alkali metal cations that results in stable complexes in the order: $\mathrm{Rb^+}$ complex > $\mathrm{Cs^+}$ complex > $\mathrm{K^+}$ complex. Though $\mathrm{Cs^+}$, the biggest monovalent ion among them, is supposed to interact most strongly with the larger rings, $\mathrm{Rb^+}$ seemed to complex more even with DB24C8 as shown in Table 1. The $\mathrm{Rb^+}$ ion, with an ionic radius of 1.47 Å, can fit nicely into the hole of DB21C7 compared to $\mathrm{Cs^+}$ (1.67 Å) despite of the ligand flexibility. Smaller cations, $\mathrm{Li^+}$ and $\mathrm{Na^+}$, showed no detectable complexation with DB21C7; this can be explained by their higher solvation energy which works against their coordination. Although it was not easy to compare the reactivity of all the ligands due to flexibility of the larger ones, it was found that B18C6 was more reactive than DB18C6 in all the systems examined.

Migration of Crown Ethers with Increasing Concentrations of Alkaline Earth Metal Ion. The change in the migration time of crown ethers upon interaction with alkaline earth metal ions was examined in a similar manner as in the case of alkali metals. Figure 3 shows a typical electropherogram of six crown ethers explored in this study upon interacting with $\mathrm{Ba^{2+}}$. The difference in migration time between crown ethers from the EOF was greater for B18C6, while B15C5 and B12C4 migrated very close to the EOF marker. The peaks for B15C5 and B12C4 were overlapping throughout the experiment indicating that these two crown ethers interacted in an almost similar degree with $\mathrm{Ba^{2+}}$ ion. Other electropherograms demonstrated that $\mathrm{Sr^{2+}}$ interacts with B18C6 and DB18C6, and $\mathrm{Ca^{2+}}$ only with B18C6. Such difference in migration time of the analytes from that of EOF means that positively charged complexes have been formed as is discussed with alkali metal ions.

Complexation Analysis of Crown Ether–Alkaline Earth Metal Ion. The complex formation analysis between crown ethers and alkaline earth metal ions was carried out as described above for alkali metals. The observed apparent

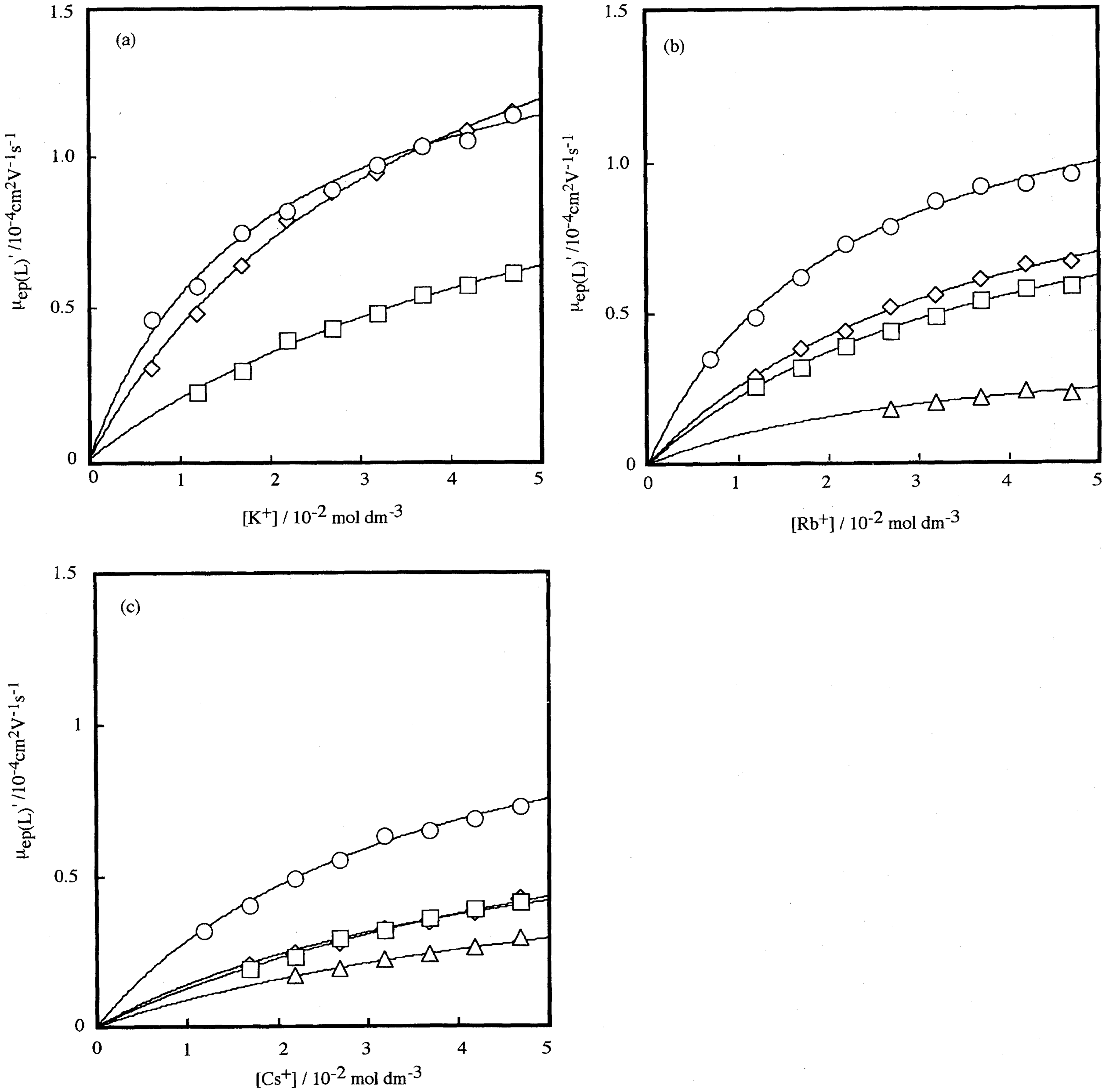

Fig. 2. Change in electrophoretic mobility of (◇) B18C6, (○) DB18C6, (□) DB21C7, and (△) DB24C8 with increasing alkali metal ion concentration. Metal ion: (a), K^+; (b), Rb^+;(c), Cs^+.

electrophoretic mobilities, $\mu'_{\mathrm{ep(L)}}$, were plotted against increasing M^{2+} ion concentrations up to 4.0×10^{-2} mol dm^{-3}. Figure 4 shows the increase in $\mu'_{\mathrm{ep(L)}}$, of the six crown ethers with increasing Ba^{2+} ion concentration. Such an increase in the apparent electrophoretic mobility was also demonstrated by B18C6 and DB18C6 among the alkaline earth metal ions in the presence of Sr^{2+} and by B18C6 upon increasing Ca^{2+} ion. For Ba^{2+} ion, the increase in electrophoretic mobility of the complexes was in the order: B18C6 > DB24C8 > DB18C6 > DB21C7 > B15C5 > B12C4, but for Sr^{2+} it was: B18C6 > DB18C6. Again such a large increase in mobility indicates that the reactivity of crown ethers is high. The logarithmic values of the complex formation constants, $\log K_{\mathrm{ML}}$, and the electrophoretic mobility values of the complexes between crown ethers and the alkaline earth metal cations are summarized in Table 2. For Ba^{2+} ion, the stability of complexes increased in the order: B12C4 < B15C5 < DB24C8 < DB18C6 < DB21C7 < B18C6, while for Sr^{2+} ion the stability was in the order: DB18C6 < B18C6. Agreement between reported values of the complex formation constant and those measured in this study was rather good except for the data of the $\log K_{\mathrm{ML}}$ value for the Sr^{2+}–B18C6 complex. Since this electrophoretic method is reliable as is seen in the other complexes, the constant for Sr^{2+}–B18C6 measured in this study would be a more reliable value.

The complex formation constants of B12C4 and DB21C7 with the alkali or alkaline earth metal ions in aqueous solution were measured for the first time. Also no data are available

Table 1. Complex Formation Constants and Electrophoretic Mobility Values

Crown ether	Value or Constant	Alkali metal ion				
		Cs^+	Rb^+	K^+	Na^+	Li^+
DB18C6	$\mu_{ep(ML^+)}$[a]	1.01±0.58	1.39±0.05	1.56±0.12	1.17±0.07	—[f]
	$\log K_{ML}$	0.83±0.68	1.13±0.04	1.66±0.08	1.18±0.05	—
	$\log K_{ML}$[b]	0.83	1.08	1.67	1.16	
B18C6	$\mu_{ep(ML^+)}$[a]	1.09±0.04	1.42±0.05	2.07±0.10	0.92±0.10	—
	$\log K_{ML}$	1.11±0.02	1.23±0.03	1.73±0.04	1.42±0.09	—
	$\log K_{ML}$[c]	0.88	1.15	1.74	1.38	
DB21C7	$\mu_{ep(ML^+)}$[a]	1.29±0.05	1.43±0.06	1.42±0.09		—
	$\log K_{ML}$	1.45±0.03	1.67±0.05	1.21±0.05	—	—
	$\log K_{ML}$[d]	4.20	—	4.30	2.40	
DB24C8	$\mu_{ep(ML^+)}$[a]	0.70±0.30	0.41±0.03	—	—	—
	$\log K_{ML}$	1.15±0.03	1.49±0.07	—	—	—
	$\log K_{ML}$[e]	1.25	1.52			

a) Dimension: 10^{-4} $cm^2\,V^{-1}\,s^{-1}$. (Obtained by the calculations using Eq. 4; Error: 3σ). b) Reported values from Ref. 10 (spectrophotometry). c) Reported values from Ref. 3 (conductometry). d) Reported values in methanol medium (Ref. 7). e) Reported values from Ref. 6. f) Migration of crown ether overlapped to that of EOF at any metal ion concentrations examined, and therefore, the mobility and the stability constants could not be determined.

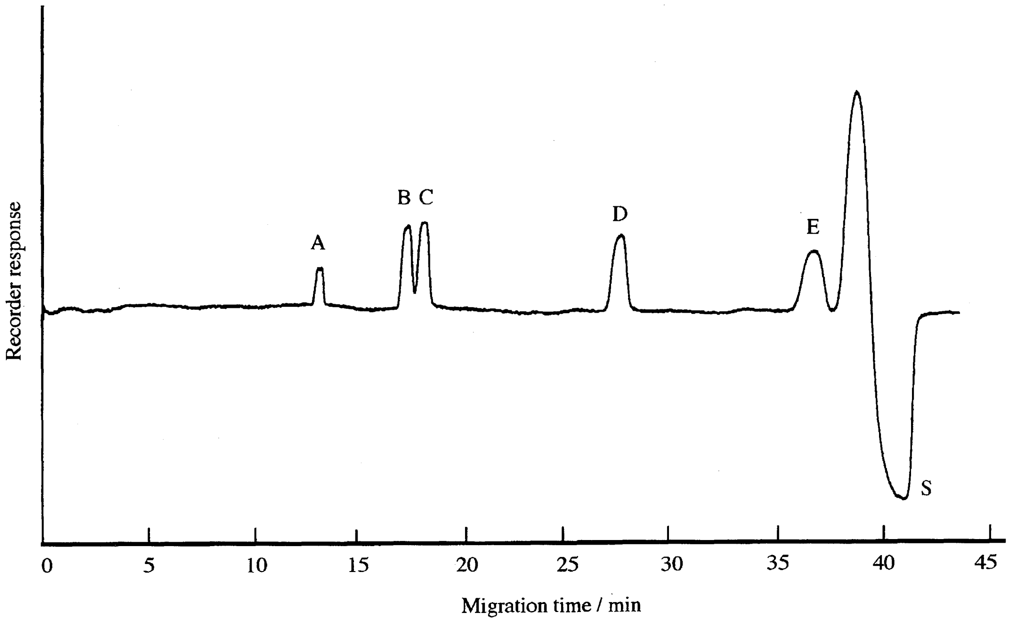

Fig. 3. Typical electropherogram of six crown ethers in the presence of Ba^{2+} ion. Sample solutions: 5.0×10^{-6} mol dm^{-3} crown ether +5.0×10^{-3} mol dm^{-3} acetate buffer +1.5×10^{-2} mol dm^{-3} $BaCl_2$+3.0% (v/v) ethanol. Migrating solutions: 5.0×10^{-3} mol dm^{-3} acetate buffer +1.5×10^{-2} mol dm^{-3} $BaCl_2$. A, B18C6; B, DB21C7; C, DB18C6; D, DB24C8; and E, B12C4 and B15C5 (overlapping). (S) is neutral marker (ethanol).

for the complex formation constants between alkaline earth metal cations and B15C5. Pedersen observed that the greater the number of potential coordination sites in the ring, provided the sites are coplanar and symmetrically distributed, the more stable is the complex.[5] The two ligands B12C4 and DB21C7 do not fit well into this category and as a result may have weak complexation potential to be measured by other methods.

Among the advantages of CZE is the possibility of evaluation of such weak complexation processes as those observed between the biggest divalent ion, Ba^{2+} and small crown ethers such as B12C4 and B15C5. The stable complexation between Ba^{2+} ion and DB21C7 can easily be interpreted from the size-fit concept. Even K^+ ion of nearly the same ionic radius (1.34 Å for Ba^{2+} and 1.33 Å for K^+) formed a stable complex with DB21C7, though of less stability than that of Ba^{2+} ion. A complex formation constant between B15C5 and Ba^{2+} was also measured in spite of the weak coordination potential of this crown ether caused by the smaller number of oxygen donor atoms. Previous studies have shown that B15C5 was not able to react with the alkaline earth metal ions, Ca^{2+}, Sr^{2+}, and Ba^{2+} in 70 wt% CH_3OH, a medium of higher entropy change than water.[2] Calcium ion, though strongly solvated to have an impact on DB18C6, formed a stable complex with B18C6. Magnesium ion showed no detectable complexation with all the crown ethers examined

Table 2. Complex Formation Constants and Electrophoretic Mobility Values

Crown ether	Value or Constant	Alkaline earth metal ion			
		Ba^{2+}	Sr^{2+}	Ca^{2+}	Mg^{2+}
DB18C6	$\mu_{\mathrm{ep(ML^{2+})}}$ [a]	3.11±0.15	2.40±0.19	—	— [d]
	$\log K_{\mathrm{ML}}$	1.96±0.06	1.22±0.05	—	—
	$\log K_{\mathrm{ML}}$ [b]	1.98	1.00		
B18C6	$\mu_{\mathrm{ep(ML^{2+})}}$ [a]	3.50±0.02	3.36±0.12	0.43±0.01	—
	$\log K_{\mathrm{ML}}$	2.88±0.21	1.96±0.05	1.64±0.03	—
	$\log K_{\mathrm{ML}}$ [c]	2.90	2.41		
B12C4	$\mu_{\mathrm{ep(ML^{2+})}}$ [a]	0.53±0.03	—	—	—
	$\log K_{\mathrm{ML}}$	1.44±0.05	—	—	—
DB24C8	$\mu_{\mathrm{ep(ML^{2+})}}$ [a]	3.18±0.49	—	—	—
	$\log K_{\mathrm{ML}}$	1.20±0.11	—	—	—
DB21C7	$\mu_{\mathrm{ep(ML^{2+})}}$ [a]	3.02±0.31	—	—	—
	$\log K_{\mathrm{ML}}$	2.07±0.14	—	—	—
B15C5	$\mu_{\mathrm{ep(ML^{2+})}}$ [a]	1.26±0.08	—	—	—
	$\log K_{\mathrm{ML}}$	0.96±0.04	—	—	—

a) Dimension: 10^{-4} cm^2 V^{-1} s^{-1}. (Obtained by calculations using Eq. 4; Error: 3σ). b) Reported values from Ref. 10 (spectrophotometry). c) Reported values from Ref. 3 (conductometry). d) Migration of crown ether overlapped to that of EOF at any metal ion concentrations examined, and therefore, the mobility and the stability constants could not be determined.

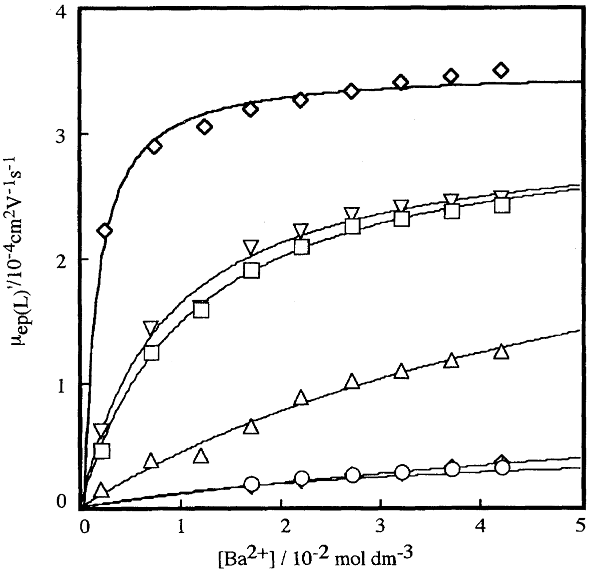

Fig. 4. Change in electrophoretic mobility of (○) B12C4, (▲) B15C5, (◇) B18C6, (□) DB18C6, (▽) DB21C7, and (△) DB24C8 with increasing Ba^{2+} ion concentration.

and as the case for lithium, its low complexing power is attributed to its tendency to be strongly solvated.

Comparison of the $\log K_{\mathrm{ML}}$ values given in Tables 1 and 2 allows us to conclude that cation selectivity regarding crown ligands is much more pronounced in the case of the divalent cations where the $\log K_{\mathrm{ML}}$ values for formation of the Ba^{2+}–ligand complexes are much larger than those for formation of the corresponding K^+–complexes. Also taking into account the higher basicity of an aliphatic ether oxygen atom than an aromatic ether oxygen atom, it can be expected that the stabilities of the complexes of a given metal ion with the three crown ethers in water decrease in the order: 18C6 > B18C6 > DB18C6. The data in Tables 1 and 2 are consistent with this expectation, that is for all cases examined the B18C6 complex is more stable than the DB18C6 complex.

Conclusion

Capillary zone electrophoresis has been shown to be an efficient and reliable method for reaction analysis in more detail in aqueous solutions. Its applicability will be further examined for similar complexation systems involving nonmetallic cations.

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