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# Ion Association of Primary Ammonium Ions with Aromatic Anions by Capillary Zone Electrophoresis

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Ion associability of some alkylammonium-type ion association reagents with the positional isomers of aromatic anions has been examined in an aqueous solution through electrophoretic mobility changes of the corresponding anions in capillary zone electrophoresis. Ion associability of the alkylammonium ions was investigated for monovalent and divalent cationic groups, considering the hydrophilicity and hydrophobicity of cationic groups and the hydration of the ionic sites. When such monovalent cationic reagents as hexylmethylammonium, hexyltrimethylammonium, and hexyltriethylammonium ions were used, the ion associability increased with an increase in the number and bulkiness of alkyl groups of the cations. On the other hand, hexylammonium ion, a primary ammonium ion, showed different behavior: Higher ion associability was obtained with aromatic anions possessing two carboxylate groups at adjacent positions. Also ion associability of the primary diammonium ions with phthalate and naphthalene-2,3-dicarboxylate ions was the highest among their positional isomers, which was the reverse behavior from that obtained with quaternary diammonium ions. Such characteristic ion associability in the primary ammonium ions could be explained from the hydrophilicity of the ionic groups of the pairing ions: A primary ammonium group is more ion associable with hydrophilic anionic groups.

Ion association reaction has been widely used for the separation, concentration and detection of ions in analytical and separation chemistry.[1,2] In the separation of positional isomers of aromatic anions by capillary zone electrophoresis (CZE), ion association reaction in an aqueous solution has been proved to be highly promising for the improvement of resolution for ionic species.[3—5] In addition to the excellent resolution of ionic substances, the CZE method was found to be a very useful tool for the analysis of ion associability in an aqueous solution, which was based on the electrophoretic mobility measurement,[6,7] where ion associability is one of the reagent properties of both the cation and the anion contributing to the ion association constant. Recently, some factors contributing to ion associability have been demonstrated by the authors. Such factors are the hydrophobicity, the number of methylene groups, of cationic and anionic pairing ions,[7,8] multipoint interaction,[9] association probability,[10] hydration,[10,11] and stacking of aromatic moieties.[12] In the previous works,[7—12] the ion associability of aromatic anions examined as model pairing ions was found to be higher in such isomers as to be less hydrophilic around ionic groups as in the following order: naphthalene-2,6-dicarboxylate > naphthalene-2,3-dicarboxylate and isophthalate, terephthalate > phthalate.

In this study, the authors aimed at clarifying another type of ion associability, and some hydrophilic ion association reagents, monovalent and divalent primary ammonium ions, were investigated. Relatively large ion associability was obtained in naphthalene-2,3-dicarboxylate and phthalate ions with the primary diammonium ions such as propane-1,3-diammonium, pentane-1,5-diammonium, and heptane-1,7-diammonium ions; the pairing cations were found to be most ion-associable with the *ortho*-dicarboxylate ions among their positional isomers. In order to explain the ion associability of the primary diammonium ions, factors contributing to the ion associability were deduced from the ion association constants of some ion associates.

## Experimental

**Apparatus.** The capillary electrophoresis system and the recorder used were the same as in our previous work.[9] Capillaries attached to the system were a fused silica capillary (GL Sciences) and a CElect-N polymer-coated capillary (SUPELCO). The size of the capillaries was commonly: 72 cm total length, 50 cm effective length from the sample injection point to the UV detector and 50 μm inner diameter.

**Reagents.** Aromatic anions examined as analytes (detected species) were the isomers of two naphthalene-*n*-carboxylates (*n*-NC, *n*- = 1- and 2-), two naphthalene-*n*-sulfonates (*n*-NS, *n*- = 1- and 2-), four naphthalene-*m*,*n*-disulfonates (*m*,*n*-NDS, *m*,*n*- = 1,5-; 1,6-; 2,6-; 2,7-), three naphthalene-*m*,*n*-dicarboxylates (*m*,*n*-NDC, *m*,*n*- = 1,4-; 2,3-; 2,6-), and three phthalates (phthalate, PH; isophthalate, *i*-PH; terephthalate, *t*-PH). These reagents were purchased from Tokyo Kasei Kogyo. The sulfonate compounds were received as sodium salts and used after dissolving them in water. The carboxylic compounds were received as their acid forms and were dissolved in water with equivalent amounts of sodium hydroxide.

Hexylamine, hexylmethylamine, hexyltrimethylammonium bromide ($HxTMA^+ \cdot Br^-$), propane-1,3-diammonium dichloride ($PrDA^{2+} \cdot 2Cl^-$), pentane-1,5-diammonium dichloride ($PeDA^{2+} \cdot 2Cl^-$), and 1,7-diaminoheptane were purchased from Tokyo Kasei Kogyo. Hexyltriethylammonium bromide ($HxTEA^+ \cdot Br^-$) was purchased from Aldrich. They were used as pairing cations as received. These reagents were dissolved in water or dilute hydrochloric acid solution and examined as pairing cations. Hexylamine, hexylmethylamine, 1,7-diaminoheptane were dissolved in water with equivalent amounts of hydrochloric acid to give their salt solutions; they are abbreviated as $HxA^{+}{\cdot}Cl^{-}$, $HxMMA^{+}{\cdot}Cl^{-}$, $HpDA^{2+}{\cdot}2Cl^{-}$, respectively.

The monovalent and divalent analyte anions, and the monovalent and divalent pairing cations are abbreviated as $A^{-}$, $A^{2-}$, $C^{+}$, and $C^{2+}$, respectively. Migrating buffer solutions were prepared from $KH_2PO_4$ and $Na_2HPO_4$ (Wako). Water used was deionized and distilled.

**Procedure for CZE Measurement.** Electrophoretic solutions were prepared with the buffer components at the total phosphate concentration of $1\times10^{-2}$ mol dm$^{-3}$; the pHs of the electrophoretic solutions were adjusted to 7.0 by mixing the two kinds of phosphate solutions. Known amounts of an ion association reagent were added to the electrophoretic solutions. The electrophoretic solutions thus prepared were transferred to both a cathodic and an anodic reservoir, and then filled in a capillary by a vacuum system. A sample solution containing $1\times10^{-5}$ mol dm$^{-3}$ of analyte anions was introduced into the capillary by the vacuum system for 3 s; the injection volume was about 9 nl. In the case of monovalent pairing cations, their adsorption on the inner wall of the capillary was very slight; therefore, a silica capillary would be used. When the divalent pairing cations were used, a CElect-N capillary was adopted, because such divalent cations were easy to adsorb on the inner wall of the silica capillary, which reduced the electroosmotic flow (EOF) and made the detection of analyte anions difficult. The polarity of the injection end of the capillary was anodic in the silica capillary and cathodic in the CElect-N capillary. A voltage of 25 kV was then applied and electrophoresis was started. Analyte anions were detected photometrically at 230 nm at the opposite side of the injection end. The electroosmotic flow was monitored with 3 % (v/v) ethanol added in the sample solution, as in the previous works.[7—9] Throughout the experiments, the capillary was held in a thermostated compartment kept at 35 °C. Electric currents produced were less than 25 μA during the electrophoresis; therefore, the effect of Joule's heat on the electrophoretic mobility seemed to be depressed. The apparent electrophoretic mobility of anions, $-\mu'_{\mathrm{ep}}$, was calculated in the usual manner.

## Results and Discussion

**Resolution Improvement of Aromatic Anions with Monovalent Pairing Cations.** Electropherograms of nine kinds of aromatic anions with monovalent pairing cations are shown in Fig. 1. In the absence of monovalent pairing cation, an ion association reagent, the positional isomers were not resolved (Fig. 1a), whereas some of the isomers could be resolved in the presence of monovalent pairing cations, as shown in Figs. 1b and 1c. The resolution improvement of carboxylate isomers was prominent when the hydrophobic pairing ion, $HxTEA^{+}$, was used (Fig. 1c). Such resolution improvement of the positional isomers with $HxTEA^{+}$ was similar to our previous study using some quaternary ammonium ions as ion association reagent.[7]

**Mobility Change of Aromatic Anions with the Monovalent Pairing Cations and the Determination of Ion Association Constants.** The apparent electrophoretic mobility of the aromatic anions, $-\mu'_{\mathrm{ep}}$, was plotted against the concentrations of monovalent pairing cations ($C^{+}$); some examples are shown in Fig. 2. Most of the $-\mu'_{\mathrm{ep}}$ values decreased with increasing concentrations of $C^{+}$. Such decreases can be attributed to the formation of the ion associates with their pairing cations, which results both in an apparent increase in molecular mass and in an apparent decrease in charge.

Ion association constants were determined by analyzing

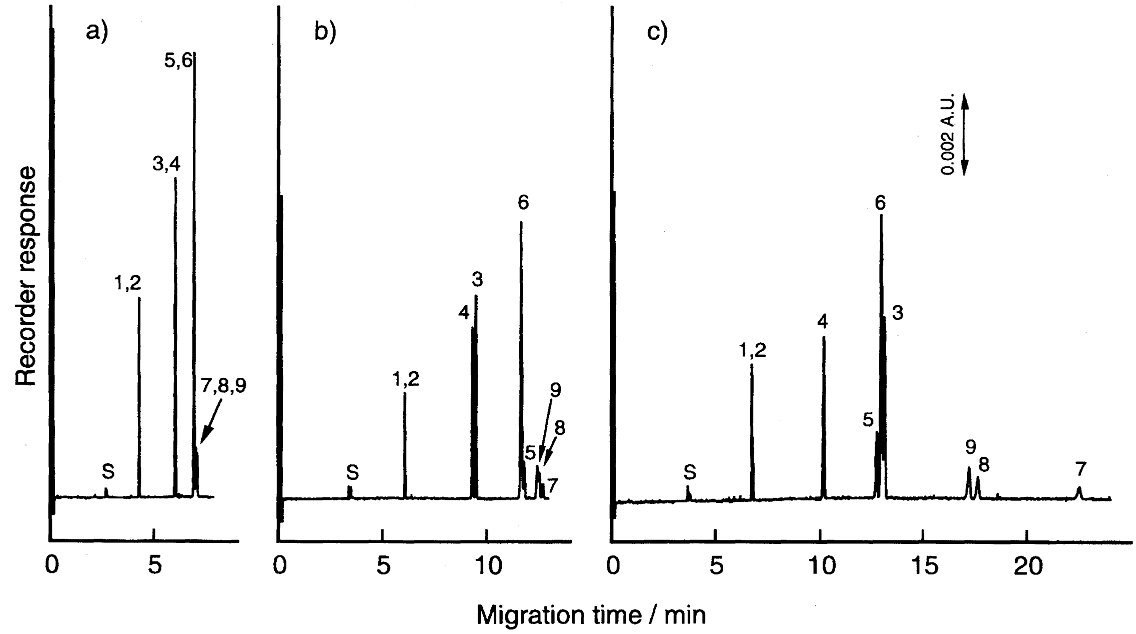

Fig. 1. Electropherograms of aromatic anions in the absence and in the presence of monovalent ion association reagent. Electrophoretic solution: $1\times10^{-2}$ mol dm$^{-3}$ phosphate buffer (pH 7.0)+$1.5\times10^{-2}$ mol dm$^{-3}$ $C^{+}{\cdot}Cl^{-}$. Pairing ion: a), none; b), $HxA^{+}$; c) $HxTEA^{+}$. Sample: 9 kinds of $1\times10^{-5}$ mol dm$^{-3}$ anions. CE conditions: applied voltage, 25 kV; detection wavelength, 230 nm; capillary room temperature, 35 °C; injection period, 3 s. Capillary: 50+22 cm fused silica capillary. Signal identifications: 1, 1-NS; 2, 2-NS; 3, 2,3-NDC; 4, 2,6-NDC; 5, 1,5-NDS; 6, 2,6-NDS; 7, PH; 8, *i*-PH; 9, *t*-PH. S: ethanol (EOF marker).

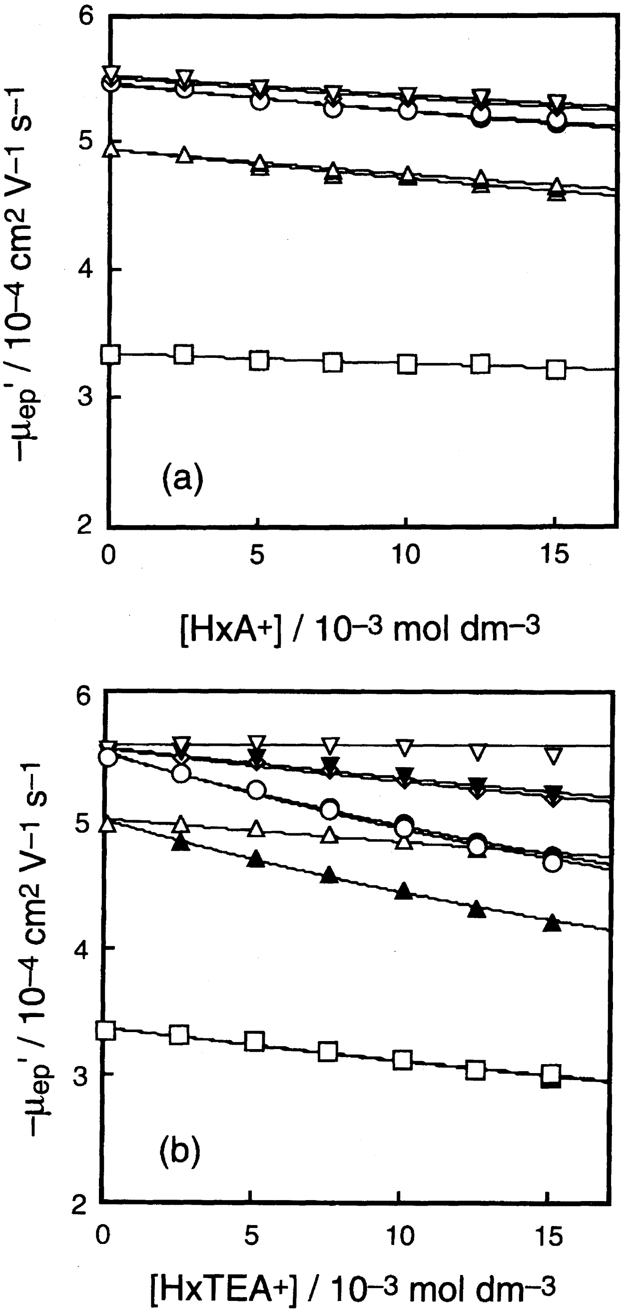

Fig. 2. Changes in apparent electrophoretic mobility of aromatic anions with increasing concentrations of monovalent ion association reagent. Conditions, except for the concentrations of pairing ion, as in Fig. 1. Pairing ion: (a), $HxA^+$; (b), $HxTEA^+$. □, 1-NS; ■, 2-NS; ○, 1,5-NDS; ●, 2,6-NDS; △, 2,3-NDC; ▲, 2,6-NDC; ▽, PH; ▼, *i*-PH; ◇, *t*-PH.

the change in the electrophoretic mobility. A 1:1 ion associate was assumed to be formed between a pairing cation, $C^+$, and an analyte anion, $A^{n-}$, as is shown in the reaction (1), with an equilibrium constant given by Eq. 2.

$$C^+ + A^{n-} \rightleftarrows C^+ \cdot A^{n-} \qquad (1)$$

$$K_{ass} = \frac{[C^+ \cdot A^{n-}]}{[C^+][A^{n-}]}. \qquad (2)$$

An ion association constant, $K_{ass}$, can be related to the apparent electrophoretic mobility; the relationship between $K_{ass}$ and $-\mu'_{ep}$ is represented in Eq. 3:

$$-\mu'_{ep} = \frac{1}{1+K_{ass}[C^+]}(-\mu_{ep}) + \frac{K_{ass}[C^+]}{1+K_{ass}[C^+]}(-\mu_{epIA}), \qquad (3)$$

where $-\mu_{ep}$ and $-\mu_{epIA}$ are the electrophoretic mobility of a certain analyte anion and its ion associate, respectively. Ion association constants were determined by a non-linear least-squares method (NLLS method), where a series of $C^+$ concentrations and corresponding $-\mu'_{ep}$ values were input in Eq. 3 in the same manner as in the previous studies.[7—10] When the ion associate is $(C^+ \cdot A^-)$ type, it should be electrically neutral; therefore, the value of $-\mu_{epIA}$ can be assumed to be zero. The assumption was proved to be valid for ion associates with various kinds of pairing cations.[10] In the case when the ion associate was $(C^+ \cdot A^{2-})$ type, the value of $-\mu_{epIA}$ was also optimized by the NLLS method, as well as the values of $-\mu_{ep}$ and $K_{ass}$. Values of $-\mu_{epIA}$ obtained by the NLLS method were in the ranges from 1.8 to 2.5 ($\times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$) for the ion associates of $C^+ \cdot A^{2-}$; the values were appropriate from the viewpoint of the apparent charge and mass.

Ion association constants of the aromatic anions obtained with the monovalent pairing cations are summarized in Table 1. Solid curves in Fig. 2 are the simulated results calculated by using the optimized values, $-\mu_{ep}$, $-\mu_{epIA}$, and $K_{ass}$. The experimental values and the simulated lines are in good agreement with each other, which suggests that the proposed method is valid for the analysis of the ion association equilibrium in an aqueous solution.

**Ion Associability of Aromatic Anions with Divalent Pairing Cations.** Electropherograms in the absence of and in the presence of divalent pairing cations as an ion association reagent are shown in Fig. 3. In the absence of the pairing cation, the migration order of analyte anions was in the inverse to that obtained with the silica capillary. This is because the capillary used was a polymer-coated one and the applied polarity was the inverse to that with a silica capillary. Though the positional isomers could not be resolved in the absence of the ion association reagent, as shown in Fig. 3a, the resolution was improved in the presence of $PrDA^{2+}$ as shown in Fig. 3b. For comparison, an electropherogram using propane-1,3-bis(triethylammonium) $\{PrB(TEA)^{2+}\}$ is also shown in Fig. 3c. The migration order of each isomer was different between Figs. 3b and 3c. A typical difference is as follows: A longer migration time was required in 2,3-NDC than 2,6-NDC with $PrDA^{2+}$, whereas 2,3-NDC migrates faster than 2,6-NDC with $PrB(TEA)^{2+}$. This result indicates that the ion associability of 2,3-NDC and 2,6-NDC can be reversed depending on the kind of cationic groups of the pairing ions.

The resolution of the positional isomers with the primary diammonium ions was compared with each other. Electropherograms obtained with $PrDA^{2+}$, $PeDA^{2+}$, and $HpDA^{2+}$ are shown in Fig. 4. The resolution of the isomers was getting worse as the number of methylene groups binding two ammonium groups of the pairing cations increased. The

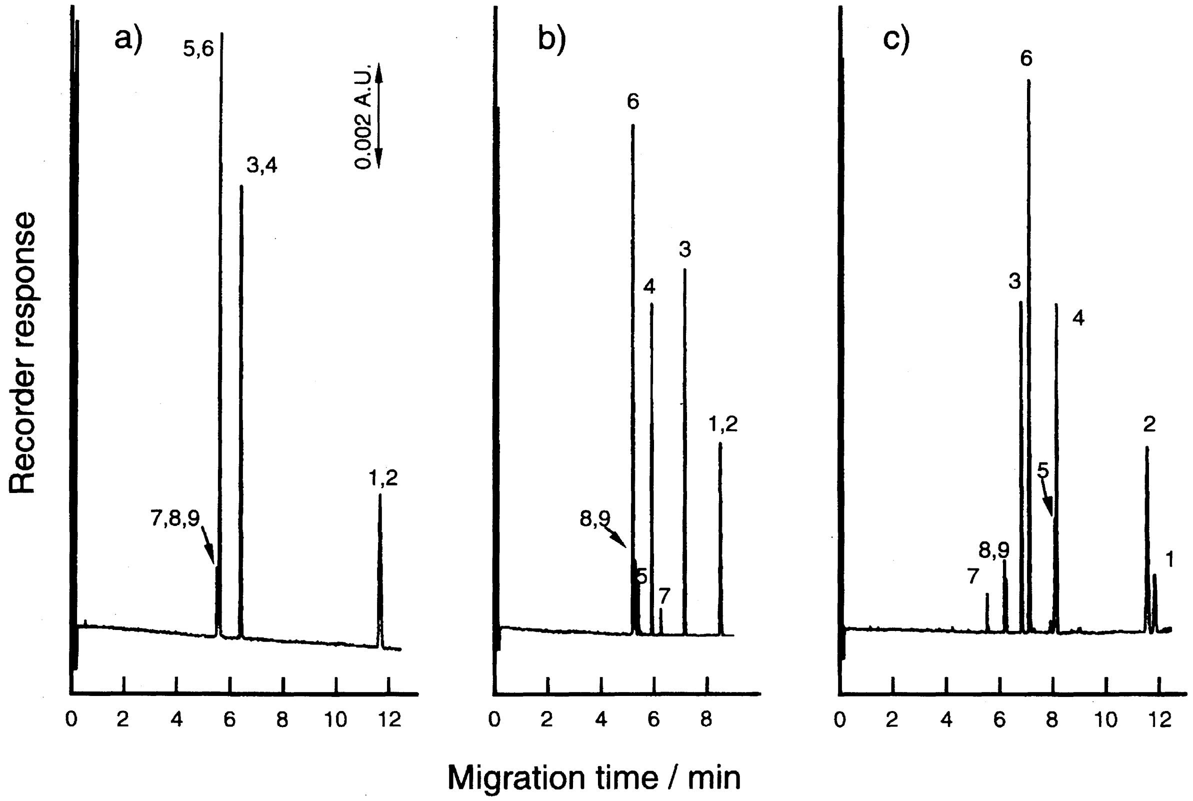

Fig. 3. Electropherograms of aromatic anions in the absence and in the presence of divalent ion association reagent. Electrophoretic solution: $1\times10^{-2}$ mol dm$^{-3}$ phosphate buffer (pH 7.0)+$5\times10^{-3}$ mol dm$^{-3}$ $C^{2+}\cdot 2Cl^{-}$. Pairing ion: a), none; b), PrDA$^{2+}$; c), PrB(TEA)$^{2+}$. Sample solution and CE conditions are the same as in Fig. 1. Capillary: 50+22 cm, CElect-N capillary. Signal identifications: 1, 1-NS; 2, 2-NS; 3, 2,3-NDC; 4, 2,6-NDC; 5, 1,5-NDS; 6, 2,6-NDS; 7, PH; 8, *i*-PH; 9, *t*-PH.

apparent electrophoretic mobility of aromatic anions, $-\mu'_{\mathrm{ep}}$, was plotted against the concentrations of the primary diammonium ions; the examples are shown in Fig. 5. From Fig. 5b, one may notice that the positional isomers were hardly separated with HpDA$^{2+}$, but $-\mu'_{\mathrm{ep}}$ values decreased with increasing concentrations of HpDA$^{2+}$; that is, the ion associability of the positional isomers is almost the same.

Ion association constants of the analyte anions with the primary diammonium ions were also determined using the change in the electrophoretic mobility. A 1:1 ion associate was assumed to be formed between a pairing cation, $C^{2+}$, and an analyte anion, $A^{n-}$, as is shown in reaction (4), with an equilibrium constant given by Eq. 5.

$$C^{2+} + A^{n-} \rightleftarrows C^{2+}\cdot A^{n-} \tag{4}$$

$$K_{\mathrm{ass}} = \frac{[C^{2+}\cdot A^{n-}]}{[C^{2+}][A^{n-}]}. \tag{5}$$

An ion association constant, $K_{\mathrm{ass}}$, can also be related to the apparent electrophoretic mobility as in Eq. 6:

$$-\mu'_{\mathrm{ep}} = \frac{1}{1+K_{\mathrm{ass}}[C^{2+}]}(-\mu_{\mathrm{ep}}) + \frac{K_{\mathrm{ass}}[C^{2+}]}{1+K_{\mathrm{ass}}[C^{2+}]}(-\mu_{\mathrm{epIA}}). \tag{6}$$

The ion association constants were also determined using the NLLS method in the same manner in the previous section. When the ion associate is ($C^{2+}\cdot A^{2-}$) type, the value of $-\mu_{\mathrm{epIA}}$ can be assumed to be zero from the viewpoint of the apparent charge. The ion association constants of the aromatic anions obtained with the primary diammonium ions are summarized in Table 1. The $K_{\mathrm{ass}}$ values with divalent quaternary ammonium ions are also shown in Table 1 for comparison. The values of $-\mu_{\mathrm{epIA}}$ for the ion associates of PeDA$^{2+}\cdot$1-NS and HpDA$^{2+}\cdot$1-NS obtained are $-2.72$ and $-2.39$ ($\times10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$), respectively. These values indicate that the ion associates which formed are positively charged and that the analysis method is quite valid. The solid curves, which show the results of a simulation, and the experimental results agreed well with each other, as shown in Fig. 5.

**Factors Contributing to Ion Associability.** Ion association reaction in solutions has been discussed on the basis of electrostatic interactions proposed by Bjerrum,[13] and later by Fuoss[14] and other workers.[15—17] Ionic distance and charge density have been considered to have a main role in the reaction. In some cases of the ion associates examined in this study, the ion associability can also be explained by the electrostatic interaction. In many cases, however, some other factors seem to contribute to the ion associability. Ion associability of the ammonium ions with analyte anions was considered by comparing the ion association constants obtained in this study.

The previous paper showed that the hydrophobicity of each pairing ion, the number of methylene groups, played an important role on the improvement of ion associability in aqueous medium.[7,8] In the monovalent pairing cations ex-

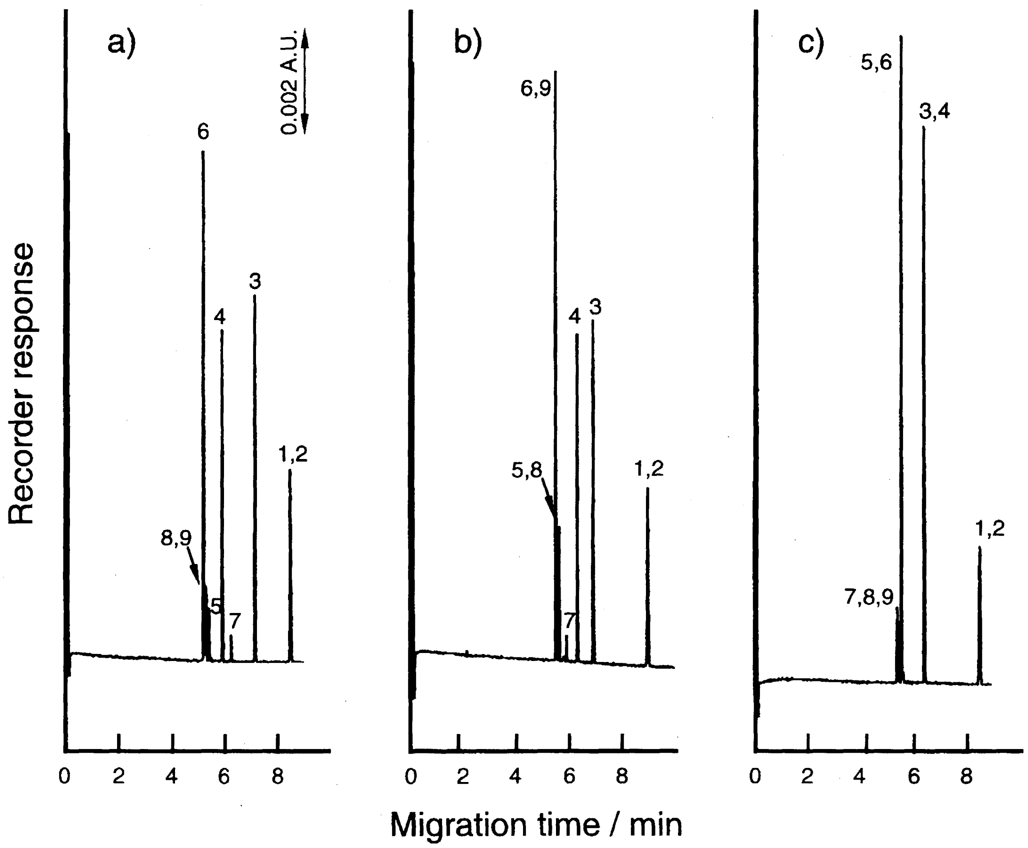

Fig. 4. Electropherograms of aromatic anions with alkanediammonium ion. Electrophoretic solution: $1\times10^{-2}$ mol dm$^{-3}$ phosphate buffer (pH 7.0)+$5\times10^{-3}$ mol dm$^{-3}$ $C^{2+}\cdot 2Cl^-$. Pairing ion: a), PrDA$^{2+}$; b), PeDA$^{2+}$; c) HpDA$^{2+}$. Sample solution, CE conditions, Capillary and Signal identifications are the same as in Fig. 3.

amined in this study, except for HxA$^+$ a primary one, the $K_{ass}$ values increased with an increase in the number of methylene groups of the cations; the order of ion associability is HxMMA$^+$<HxTMA$^+$<HxTEA$^+$. Such increase in the ion associability can be also explained by the hydrophobicity concept. However, ion associability of HxA$^+$ seems different from those of the secondary and quaternary ammonium ions. In HxA$^+$, the electrostatic interaction through each hydrophilic group, $-NH_3^+$ and ($-CO_2^-$ or $-SO_3^-$), will contribute mainly to ion associability; ion associability of HxA$^+$ with the aromatic anions examined is larger than that of HxMMA$^+$ by the comparison of $K_{ass}$ values. One may also notice that 2,3-NDC and PH showed the largest ion associability with HxA$^+$ among the monovalent cations. These two anions possess anionic groups on the adjacent positions, and the charge density around the anionic site should be high, which will greatly promote the electrostatic interaction with HxA$^+$. Introduction of a methyl group to the primary ammonium ion will reduce the hydrophilicity of the cation, as well as electrostatic interaction with the analyte anions, which results in weak ion associability, as is shown in HxMMA$^+$. As a result of the compromise of two effects, hydrophilicity and hydrophobicity, the general order of the ion associability is HxA$^+$>HxMMA$^+$<HxTMA$^+$<HxTEA$^+$.

The ion associability was also examined with the primary diammonium ions. Their ion associability with the divalent anions, except for 2,3-NDC and PH, increased with an increase in the methylene number of the pairing cations; ion associability is in the order of PrDA$^{2+}$<PeDA$^{2+}$<HpDA$^{2+}$. Such an order should be due to the positive contribution of the hydrophobicity as well as by the multipoint interaction.[9] The contribution of the hydrophobicity is also noted by the comparison of the type of the pairing cations. Ion associability of the primary diammonium ions with divalent aromatic anions, except for 2,3-NDC and PH, is smaller than those of the quaternary diammonium ions; the order is PrDA$^{2+}$< PrB(TEA)$^{2+}$, PeDA$^{2+}$<PeB(TEA)$^{2+}$, and HpDA$^{2+}$<HpB-(TEA)$^{2+}$.

In the case of 2,3-NDC and PH, however, $K_{ass}$ values are larger with the primary diammonium ions than with the quaternary diammonium ions, which will be also explained from the hydrophilicity related to the high charge density around the anionic sites, similarly to what was discussed in the monovalent cations. Also, the ion associability values of 2,3-NDC and PH with the primary diammonium ions are in the order of PrDA$^{2+}$>PeDA$^{2+}$>HpDA$^{2+}$, which is also explained by the multipoint interaction.[9]

The difference in log $K_{ass}$ values between monovalent and divalent anions is about 0.6 in average. Such a difference, 0.6 in logarithmic units, should be due to the association probability and the electrostatic interaction. The association probability is deduced to be 0.3 in logarithmic units ( = log 2); that is, the probability of the divalent anions becomes twice as large as that of monovalent anions, and the rest of 0.3 can

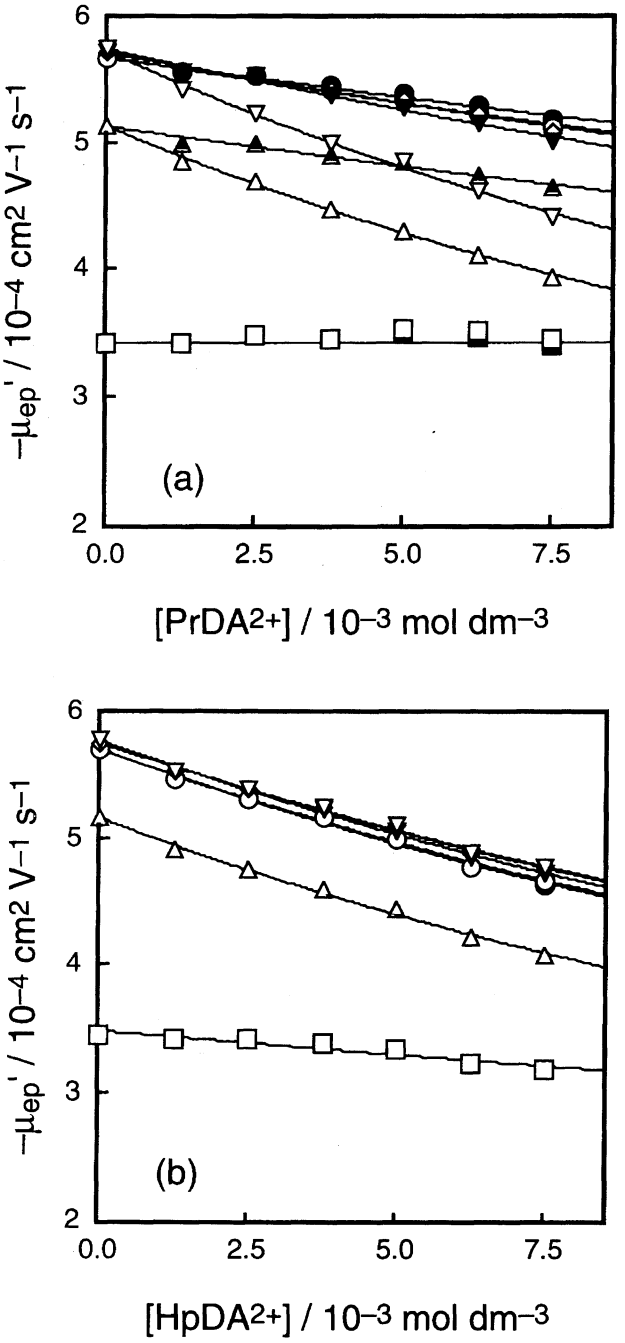

Fig. 5. Change in apparent electrophoretic mobility of anions with increasing concentrations of alkanediammonium ion. Conditions, except for the concentrations of pairing ion, as in Fig. 4. Pairing ion: (a), $PrDA^{2+}$; (b), $HpDA^{2+}$. □, 1-NS; ■, 2-NS; ○,1,5-NDS; ●, 2,6-NDS; △, 2,3-NDC; ▲, 2,6-NDC; ▽, PH; ▼, *i*-PH; ◇, *t*-PH.

be assigned to electrostatic interaction related to the number of charges.

**Conclusion.** The degree of the ion associability among positional isomers can be changed by the type of ion association reagents. Such anions as naphthalene-2,3-dicarboxylate and phthalate are found to be more associable among their isomers with the primary diammonium ions than with the quaternary diammonium ions. Factors contributing to the

Table 1. Ion Association Constants for Aromatic Anions

| Cationic reagents[a)] | $\log K_{ass}^{b)}$ | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1-NC | 2-NC | 1-NS | 2-NS | PH | *i*-PH | *t*-PH | 1.5-NDS | 1.6-NDS | 2.6-NDS | 2.7-NDS | 1.4-NDC | 2.3-NDC | 2.6-NDC |
| $HxA^+$ | 0.06±0.36 | 0.39±0.10 | 0.39±0.20 | 0.39±0.20 | 0.70±0.18 | 0.70±0.18 | 0.70±0.17 | 0.90±0.13 | 0.91±0.09 | 0.91±0.09 | 0.91±0.09 | 0.78±0.12 | 0.85±0.09 | 0.90±0.10 |
| $HxMMA^+$ | —[c)] | 0.11±0.36 | — | — | — | 0.18±0.20 | 0.08±0.20 | 0.54±0.03 | 0.58±0.04 | 0.58±0.04 | 0.60±0.03 | — | 0.48±0.06 | 0.74±0.05 |
| $HxTMA^+$ | — | 0.48±0.20 | 0.53±0.10 | 0.53±0.10 | — | 0.40±0.20 | 0.40±0.20 | 1.00±0.06 | 1.00±0.03 | 0.97±0.04 | 1.00±0.04 | — | — | 1.00±0.04 |
| $HxTEA^+$ | 0.64±0.18 | 0.96±0.06 | 0.90±0.10 | 0.91±0.10 | — | 0.83±0.22 | 0.86±0.13 | 1.28±0.07 | 1.28±0.07 | 1.26±0.06 | 1.26±0.06 | 0.80±0.17 | 0.73±0.19 | 1.30±0.05 |
| $PrDA^{2+}$ | — | — | — | — | 1.58±0.06 | 1.26±0.11 | 1.18±0.13 | 1.14±0.11 | 1.14±0.09 | 1.07±0.13 | 1.10±0.16 | 1.20±0.15 | 1.59±0.04 | 1.12±0.14 |
| $PrB(TEA)^{2+}$ [d)] | — | — | 1.15±0.08 | 1.10±0.09 | 1.18±0.09 | 1.49±0.04 | 1.46±0.06 | 1.81±0.04 | 1.78±0.04 | 1.67±0.05 | 1.70±0.05 | 1.45±0.06 | 1.39±0.06 | 1.69±0.04 |
| $PeDA^{2+}$ | — | — | 0.57±0.30 | 0.57±0.30 | 1.50±0.06 | 1.40±0.08 | 1.32±0.09 | 1.36±0.07 | 1.36±0.08 | 1.29±0.07 | 1.32±0.05 | 1.36±0.06 | 1.56±0.06 | 1.36±0.07 |
| $PeB(TEA)^{2+}$ [d)] | — | — | 1.29±0.05 | 1.27±0.05 | 1.16±0.14 | 1.57±0.10 | 1.56±0.09 | 1.96±0.07 | 1.93±0.07 | 1.86±0.07 | 1.88±0.07 | 1.53±0.09 | 1.45±0.09 | 1.91±0.08 |
| $HpDA^{2+}$ | — | — | 0.81±0.29 | 0.81±0.29 | 1.44±0.07 | 1.47±0.05 | 1.43±0.07 | 1.47±0.06 | 1.48±0.07 | 1.48±0.07 | 1.48±0.07 | 1.42±0.07 | 1.54±0.05 | 1.54±0.05 |
| $HpB(TEA)^{2+}$ [d)] | — | — | 1.32±0.04 | 1.33±0.04 | 1.10±0.11 | 1.56±0.06 | 1.57±0.06 | 1.97±0.05 | 1.96±0.05 | 1.91±0.05 | 1.93±0.05 | 1.52±0.04 | 1.43±0.06 | 1.95±0.06 |

a) Abbreviated reagents: $PrB(TEA)^{2+}$, propane-1,3-bis(triethylammonium); $PeB(TEA)^{2+}$, pentane-1,5-bis(triethylammonium); $HpB(TEA)^{2+}$, heptane-1,7-bis(triethylammonium). b) Error: $3\sigma$. c) The constants could not be determined because of their weak ion associability. d) Values are cited from Ref. 9, except for 1-NS and 2-NS.

ion associability were deduced to the hydrophilicity related to charge density, number of charge and electrostatic interaction, and also to the hydrophobicity related to the number of methylene group. In addition to the contributions of multipoint interaction, hydration and stacking of aromatic moieties previously clarified, this study demonstrated that the hydrophilicity can contribute to the improvement of ion associability of organic ions, in the same manner as classically established in inorganic ion associates. By considering the contribution of several such effects to ion associability and by utilizing the ion association reaction in an aqueous solution, the resolution of analyte ions by CZE will be achieved more easily.

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