Analysis of Ion Association Property of Aromatic Divalent Anions with Quaternary Ammonium Ions in Aqueous Solution through Mobility Change of Capillary Electrophoresis

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Formation of ion associate in an aqueous solution has been examined using some aromatic divalent anions and symmetric quaternary ammonium ions through the mobility change of capillary electrophoresis. The electrophoretic mobilities of the anions decreased with an increase in the concentrations of bulky quaternary ammonium ions. Ion association constants (K_{ass}) of 2,6-naphthalenedicarboxylate, 1,5-naphthalenedisulfonate, and 2,6-naphthalenedisulfonate with tetrabutylammonium ion as a pairing ion were determined to be $10^{1.4}$, $10^{1.4}$, and $10^{1.3}$, respectively, while mobility changes of 2,3-naphthalenedicarboxylate and phthalate ions were slight. Several quaternary ammonium ions were examined. The results suggest that the bulkiness of the pairing cations is related to the ion association in aqueous solutions.

Capillary electrophoresis (CE) came to be a powerful separation technique for ionic substances.[1] However, separation of similar compounds in same molecular weight and charge is still difficult. Recently, Iki et al. showed a usefulness of quaternary ammonium ions for unseparated anionic metal chelates.[2] Quaternary ammonium ions used are considered to work on ion-ion interactions; i.e., they act as pairing ions to neutralize the anionic charge of the metal chelates partially. Other role of quaternary ammonium ions is known to control the direction of electroosmotic flow and its rate.[3]

Concerned with ion association reaction, it has been used in various analytical methods coupled with two phase distribution, such as ion-pair solvent extraction, ion-pair micelle extraction, ion-pair chromatography, etc. Most of their analytical systems were based on hydrophobicity of the ion associate formed, and its distribution to the hydrophobic field.[4,5] Ion association in an aqueous solution is a homogeneous system, and favorable for the coming analytical method, because of its simple and clean systems without any organic solvents. In this paper, equilibrium analysis of 1:1 ion associate formed between aromatic divalent anions and quaternary ammonium ions in an aqueous solution is discussed through mobility change of capillary electrophoresis. As the mobility changes corresponding to the changes in charge, the mechanisms of protonation or complex formation have been elucidated.[6] This study aims the evaluation of the ion association reaction in homogeneous aqueous medium, independent from the distribution between two phases.

An Applied Biosystems 270A Capillary Electrophoresis System, equipped with a Hitachi D-2000 Chromato-Integrator, was used. A fused silica capillary attached was 50 µm i.d., 72 cm length, and 50 cm effective length to the UV detector. Reagents of sodium 1-naphthalenesulfonate (1-NS), sodium 2-naphthalenesulfonate (2-NS), disodium 1,5-naphthalenedisulfonate (1,5-NDS), disodium 2,6-naphthalenedisulfonate (2,6-NDS), 2,3-naphthalenedicarboxylic acid (2,3-NDC), 2,6-naphthalenedicarboxylic acid (2,6-NDC), phthalic acid (PH), isophthalic acid (i-PH), and terephthalic acid (t-PH) were examined as anionic substances. The acids were used after neutralization with twice equivalent amounts of sodium hydroxide. A borax buffer solution (pH 9.2 ; 1×10^{-2} mol dm^{-3}) was used as carrier solution. Three percents (v/v) of ethanol was added to the sample solutions for the marking. Sample solutions were injected on a vacuum for 3 seconds from anodic end (about 9 nl), and a voltage of 25 kV was applied for the electrophoresis. Solutes were detected at 230 nm, at which wavelength most of the anions possess molar absorptivities of about 5×10^4 dm^{3}mol^{-1}cm^{-1}. Electrophoretic mobilities of anions were obtained in an ordinary manner, as well as mobility of electroosmotic flow.[7]

A typical electropherogram of nine kinds of anions in an ordinary CE method is shown in Figure 1 A. In this system, anions with same molecular weight and charge, such as position isomer of naphthalenesulfonates and naphthalenedisulfonates, could not be separated. The electrophoretic mobilities of the anions ($-\mu_{ep}$) are in the order: PH^{2-} > NDS^{2-} > NDC^{2-} > NS^-. This order is reasonable in point of the molecular weight, hydration, and charge. The $-\mu_{ep}$ values of NDC are smaller than those of NDS, although the molecular weight of the former is smaller than that of the latter. This suggests that carboxylate groups are more solvated by water than sulfonate groups, hence, $-\mu_{ep}$ of NDS^{2-} becomes similar to that of PH^{2-}.

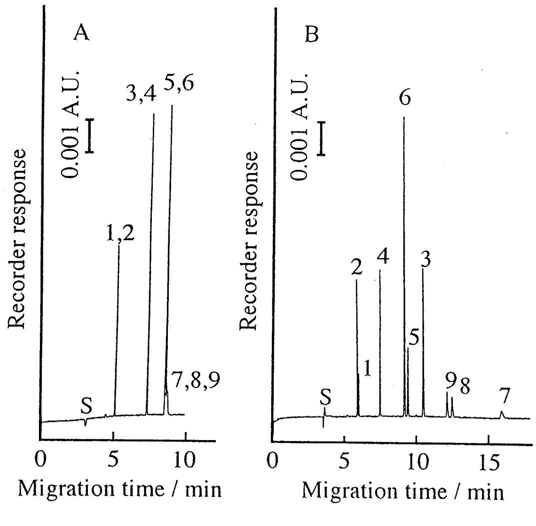

Figure 1. Typical electropherograms of aromatic anions.
1, 1-NS; 2, 2-NS; 3, 2,3-NDC; 4, 2,6-NDC; 5, 1,5-NDS; 6, 2,6-NDS; 7, PH; 8, i-PH; 9, t-PH . Concentrations of injected anions are 1×10^{-5} mol dm^{-3}. S, marker (ethanol).
A, carrier: 1×10^{-2} mol dm^{-3} borax.
B, carrier: 1×10^{-2} mol dm^{-3} borax + 2×10^{-2} mol dm^{-3} TBA^+Br^-.

The position isomers were well separated by the additional use of tetrabutylammonium bromide (TBA^+Br^-) as shown in Figure 1 B. Electropherogram of Figure 1 B shows longer migration time than that in Figure 1 A for each anion, which is attributed to the decrease of electroosmotic flow by an increase in ionic strength of the carrier solution. Electrophoretic mobilities of the anions were plotted as a function of TBA^+Br^- concentration (Figure 2). The mobilities decreased along with an increase in the concentration of TBA^+Br^-. Such decreases in electrophoretic mobilities are due to the ion association between the anions and a quaternary ammonium cation.

Ion association behaviors of some anions were analyzed on the basis of the mobility changes and on the assumption that only 1:1 ion associates can be formed in the solutions. Ion association equilibrium is written as:

$$Q^+ + A^{n-} \overset{K_{ass}}{\rightleftharpoons} Q^+ \cdot A^{n-} \qquad K_{ass} = \frac{[Q^+ \cdot A^{n-}]}{[Q^+][A^{n-}]} \qquad (1)$$

where Q^+, A^{n-}, and $Q^+ \bullet A^{n-}$ are a quaternary ammonium ion, an analyte anion, and a 1:1 ion associate, respectively. The equilibrium constant K_{ass} is an ion association constant. The ion association constant can be related to the electrophoretic mobilities as follows:

$$-\mu_{ep}' = \frac{(-\mu_{ep}[A^{n-}]) + (-\mu_{epIA}[Q^+ \cdot A^{n-}])}{[A^{n-}] + [Q^+ \cdot A^{n-}]} \qquad (2)$$

where $-\mu_{ep}'$, $-\mu_{ep}$, and $-\mu_{epIA}$ are electrophoretic mobilities of the anion in the presence of and in the absence of Q^+, and that of ion associate, $Q^+ \bullet A^{n-}$, respectively. From Eq . (1) and (2), Eq . (3) is given.

$$-\mu_{ep}' = -\mu_{epIA} - \frac{(-\mu_{ep}) - (-\mu_{ep}')}{[Q^+]} \cdot \frac{1}{K_{ass}} \qquad (3)$$

The slope and intercept of $-\mu_{ep}'$ vs. $-\{(-\mu_{ep}) - (-\mu_{ep}')\} / [Q^+]$ plots give the inverse value of ion association constant and the electrophoretic mobility of the ion associate, respectively.

The plots of Eq . (3) gave straight lines, as shown in Figure 3, and ion association constants of 2,6-NDC, 1,5-NDS, and 2,6-NDS with TBA^+ were obtained to be $10^{1.4\pm0.1}$, $10^{1.4\pm0.1}$ and $10^{1.3\pm0.1}$, respectively. The values of intercepts suggest that the charges of the ion associates are not completely neutralized. These values agree with the estimated values from weight - charge ratio of 1:1 ion associates. Mobility changes of other anions were too small to evaluate the ion association constants. From the results in Figure 2 , behavior of 2,3-NDC is quite different from 2,6-NDC and two NDS anions. This fact indicates that 2,3-NDC has less poor ability of forming ion associate than other divalent anions. In a similar manner, the mobility change of PH is quite smaller than those of other phthalate ions . The probable reasons for less ion associability of the divalent ions possessing adjacent corboxylates are: (1) the probability of the approach of Q^+ to 2,6-NDC, i-PH and t-PH are twice as much as in PH and 2,3-NDC, and (2) the adjacent two carboxylate groups are much more shielded by the hydration than the separated two groups.

Effect of the bulkiness of pairing cations was also examined. The mobility change or ion associability are in the following order: tetramethylammonium ion < tetraethylammonium ion < tetrapropylammonium ion < tetrabutylammonium ion. This order agrees with the extractability of ion associates examined by the ion-pair solvent extraction method.[4,5] This result indicates that this type of ion association does not follow only on simple electrostatic interactions but also on hydrophobic interactions, as well as in the result with 2,3-NDC.

Behavior of the ion association in an aqueous solution will be more clarified in the future study by the similar electrophoresis, including the effect of formula, fragments, and the application of ion association / capillary electrophoresis to new separation systems.

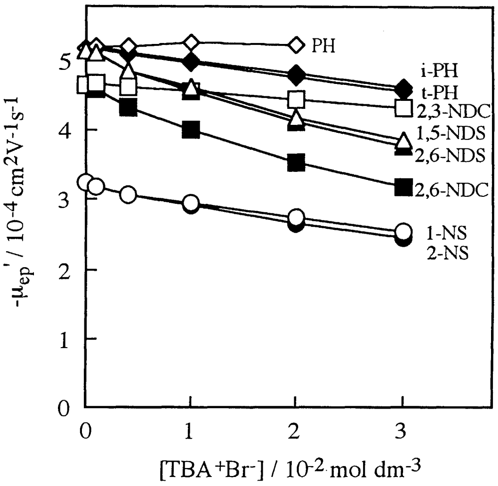

Figure 2. Mobility change of anions as a function of TBA^+Br^- concentration. CE conditions are cited in the text.

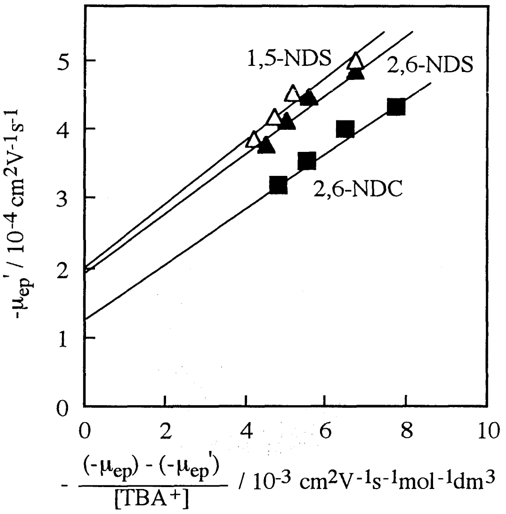

Figure 3. Plots of $-\mu_{ep}'$ vs. $-\{(-\mu_{ep}) - (-\mu_{ep}')\} / [TBA^+]$.

References

1 As recent review: C. A. Monnig and R. T. Kennedy, *Anal. Chem.*, **66**, 280R (1994).
2 N. Iki, H. Hoshino, and T. Yotsuyanagi, *J. Chromatogr.*, **652**, 539 (1993).
3 X. Huang, J. A. Luckey, M. J. Gordon, and R. N. Zare, *Anal. Chem.*, **61**, 766 (1989).
4 H. Matsunaga and T. Yotsuyanagi, *Nippon Kagaku Kaishi*, **1982**, 785.
5 S. Motomizu, *Bunseki Kagaku*, **38**, 147 (1989).
6 T. Hirokawa and Y. Kiso, *Anal. Sci.*, **8**, 737 (1992).
7 "Handbook of Capillary Electrophoresis," ed by J. P. Landes, et al., *CRC Press* (1993).