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Analysis of Reactions of Aromatic Anions with Quaternary Ammonium Ions in Ion Association–Nonionic Micellar Electrokinetic Chromatography

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Reactions in ion association–nonionic micellar electrokinetic chromatography have been analyzed using mobility change in capillary electrophoresis. Several quaternary ammonium ions and aromatic anions were used as pairing cations and anions, respectively, and three kinds of nonionic surfactant were used to form micelles in an aqueous solution. The apparent electrophoretic mobility of the analyte anions decreased with increasing concentrations of nonionic surfactant and/or pairing cation. The equilibrium reactions participating in this electrophoresis system are binding of anions to nonionic surfactant micelle (K_B), ion association of anions with pairing cation (K_ass), and distribution of the formed ion associates to the nonionic surfactant micelle ($K_\mathrm{B,IA}$). The equilibrium constants were determined by non-linear least-squares analyses by applying the analyses to the mobility decreases. Equilibrium constants of K_B and $K_\mathrm{B,IA}$ for monovalent anions were found to be larger than those for divalent anions, and $K_\mathrm{B,IA}$ values for each anions were larger than their K_B values. The results obtained can be explained from distribution phenomena of analytes between aqueous and organic phases.

Development of separation mode in capillary electrophoresis (CE) is one of attractive research fields in analytical and separation sciences. Thus far, capillary zone electrophoresis (CZE), capillary isotachophoresis (CITP), capillary isoelectric focusing (CIEF), capillary gel electrophoresis (CGE), and micellar electrokinetic chromatography (MEKC) have been developed for the analysis and resolution improvement of various types of analytes.[1—4] Among these modes of capillary electrophoresis, CZE and MEKC can utilize many kinds of interacting reagents; these reagents have thus been intensively developed and the corresponding separation modes have been established; the analytes of interest are resolved through the difference in their reactivity with the interacting reagents. Ion association–capillary zone electrophoresis (IA–CZE) is one of the separation modes in capillary electrophoresis, and such interacting reagents as ion-pairing ones have been reviewed in the literature.[5] The authors have also developed many ion association reagents for the resolution improvements of anionic positional isomers; they are monovalent[6] and divalent[7] quaternary ammonium ions, viologen cations,[8] alkylamines,[9] and polycyclic aromatic cations.[10] Various surfactants have also been investigated for MEKC separations.[11]

Considering the migration phenomena in CZE and MEKC, the electrophoretic mobility of analytes reflects their chemical species or dissolved state in the solutions. The mobility also changes according to the amounts of the interacting reagent added in the migrating solution and/or the degree of the interaction, and thus the resolution is improved. By using the mobility change induced by the interactions, chemical equilibria in aqueous solution can be analyzed quantitatively. The authors have investigated ion association reactions between organic cations and anions in an aqueous solution, and have clarified the factors contributing to ion associability by determining their ion association constants.[6—10] Interactions between aromatic anions and nonionic surfactant micelles, which are binding reactions of the anions to the nonionic surfactant micelle based on hydrophobicity, have also been somewhat clarified by a quantitative analysis.[12]

Simultaneous use of nonionic surfactant and ion association reagent can also provide an attractive separation mode for anionic species; the mode can be classified as ion association–nonionic micellar electrokinetic chromatography (IA/NI–MEKC). However, not much attention has been paid to such combinations yet.[13,14] In the separation mode, distribution reaction of ion associates from aqueous to nonionic surfactant micelle phases must be considered in addition to ion association reaction and the binding reaction. The reactions involved in IA/NI–MEKC are schematically illustrated in Fig. 1. In this study, the authors aimed at analyzing the distribution reaction of ion associates through the change in electrophoretic mobility. Binding reaction of anions and ion association reaction, as well as the side reactions suspected, were evaluated for the precise analysis of distribution reaction of ion associates. The equilibrium constants obtained were considered from the viewpoint of distribution phenomena between aqueous and organic phases.

Experimental

Apparatus. An Applied Biosystems 270A-HT Capillary Elec-

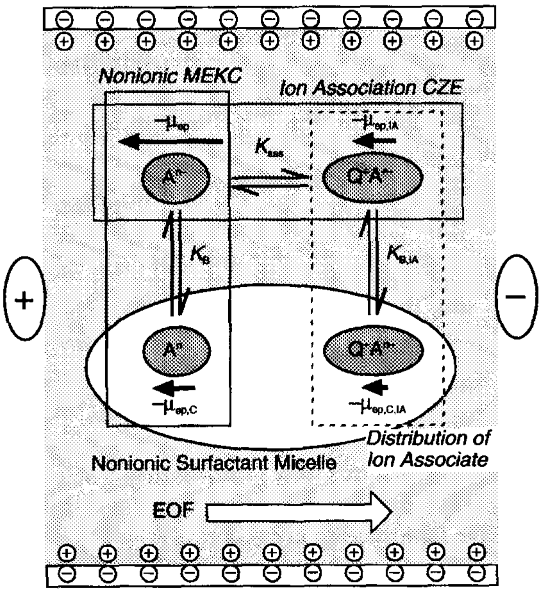

Fig. 1. Schematic illustration for ion association–nonionic micellar electrokinetic chromatography.

trophoresis System equipped with a UV detector was used. A fused silica capillary purchased from GL Sciences (Tokyo) was attached to the system after being cut; the capillary was 72 cm in total length, 50 cm in effective length from the sample injection point to the UV detector, and had a 50 μm inner diameter. A Hitachi D-2500 Chromato-Integrator was used for recording electropherograms.

Reagents. Sodium tetraborate (borax, Wako) was selected as a pH-adjusting component in migrating solution because of its lower ion associability and lower reactivity with the micelle; the pH of the migrating solution was controlled at 9.2 with its concentration at 10 mM (1 M = 1 mol dm^{-3}). Nonionic surfactants of polyoxyethylene (23) lauryl ether (Brij 35, Wako), polyoxyethylene (20) cetyl ether (Brij 58, Wako), and polyoxyethylene (20) stearyl ether (Brij 78, Aldrich) were used to form micelles which provided a hydrophobic medium; the surfactant was added in the migrating solution in the concentration ranges from 0 to 3.5%(w/v). Quaternary ammonium salts of tetraethylammonium bromide (TEA$^+$Br$^-$), tetrapropylammonium bromide (TPA$^+$Br$^-$), and tetrabutylammonium bromide (TBA$^+$Br$^-$) were purchased from Tokyo Kasei Kogyo and were used as ion association reagents. Aromatic anions including positional isomers adopted as analytes were sodium salts of naphthalene-1-sulfonate (1-NS), naphthalene-2-sulfonate (2-NS), naphthalene-1,5-disulfonate (1,5-NDS), and naphthalene-2,6-disulfonate (2,6-NDS), as well as 1-naphthoic acid (1-NC), 2-naphthoic acid (2-NC), naphthalene-2,3-dicarboxylic acid (2,3-NDC), naphthalene-2,6-dicarboxylic acid (2,6-NDC), phthalic acid (PH), isophthalic acid (i-PH), and terephthalic acid (t-PH). The acids were used after being neutralized with an equivalent amount of sodium hydroxide. The water used was de-ionized and distilled.

Procedure for the CE Measurement. A migrating solution was prepared from 10 mM borax, known amounts of a nonionic surfactant, and/or known amounts of an ion association reagent. The migrating solution thus prepared was poured into both a cathodic and an anodic reservoir, as well as into a capillary by the vacuum system. A sample solution containing 11 kinds of analyte anions at the concentration of 1×10^{-5} M was injected into the capillary from anodic end for 3 s hydrodynamically by the vacuum system (injection volume: about 9 nL). Then a voltage of 20 kV was applied and electrophoresis was started. The analyte anions were photometrically detected at 230 nm. Throughout the experiments, the capillary was held in a thermostated compartment controlled at 35 °C. To evaluate the velocity of electroosmotic flow, 3%(v/v) ethanol was added in the sample solution to detect it. The electrophoretic mobility of the analyte anions was calculated in an ordinary manner.

Results and Discussion

Electrophoretic Separation of Positional Isomers of Aromatic Anions by Ion Association–Nonionic Micellar Electrokinetic Chromatography. Positional isomers of aromatic anions are difficult to be resolved by capillary zone electrophoresis with only pH-adjusting components, because such anionic isomers possess the same charge, the same molecular weight, and similar molecular volumes. An example of electropherogram of the analyte anions including positional isomers is shown in Fig. 2a; the isomers are not resolved from each other. Interacting reagents are used to develop the resolution among the isomers. One approach for the resolution improvement is the use of nonionic surfactant, and the separation mode is classified as nonionic micellar electrokinetic chromatography (NI–MEKC). By adding Brij 58 as a nonionic surfactant in the migrating solution, one can improve resolutions among the isomers as shown in Fig. 2b. The development of the resolution is attributed to the difference in the reactivity among the anionic isomers with nonionic surfactant micelle.

The resolution was not still sufficient for isomeric phthalate ions with the nonionic surfactant, and therefore tetrabutylammonium bromide was additionally used; the electropherogram is shown in Fig. 2c. Resolution among three phthalate isomers, as well as among other isomers, was well developed. In this separation mode of ion association–nonionic micellar electrokinetic chromatography (IA/NI–MEKC), reactions suspected to be participating are ion association reaction between pairing cation and analyte anion in an aqueous solution and distribution of the ion associate formed to the surfactant micelle, in addition to the binding of analyte anions to the surfactant micelle.

An electropherogram separating the aromatic anions using TBA$^+$Br$^-$ is also shown in Fig. 3; the separation mode can be classified as ion association–capillary zone electrophoresis (IA–CZE). In IA–CZE, resolution among monovalent anions are less sufficient, and migration times for the anions are longer than those obtained by NI–MEKC or IA/NI–MEKC. Longer migration time in IA–CZE can be attributed to the adsorption of quaternary ammonium ions to the inner wall of the capillary, which reduces the velocity of the electroosmotic flow.

Changes in Electrophoretic Mobility of Aromatic Anions in the Presence of Both Nonionic Surfactant and Quaternary Ammonium Ion. In NI–MEKC, the electrophoretic mobility of analyte anions had decreased with increasing concentrations of nonionic surfactant.[12] It can be attributed to the increased molecular volume of the anions, as a result of binding reaction of the anions to the nonionic

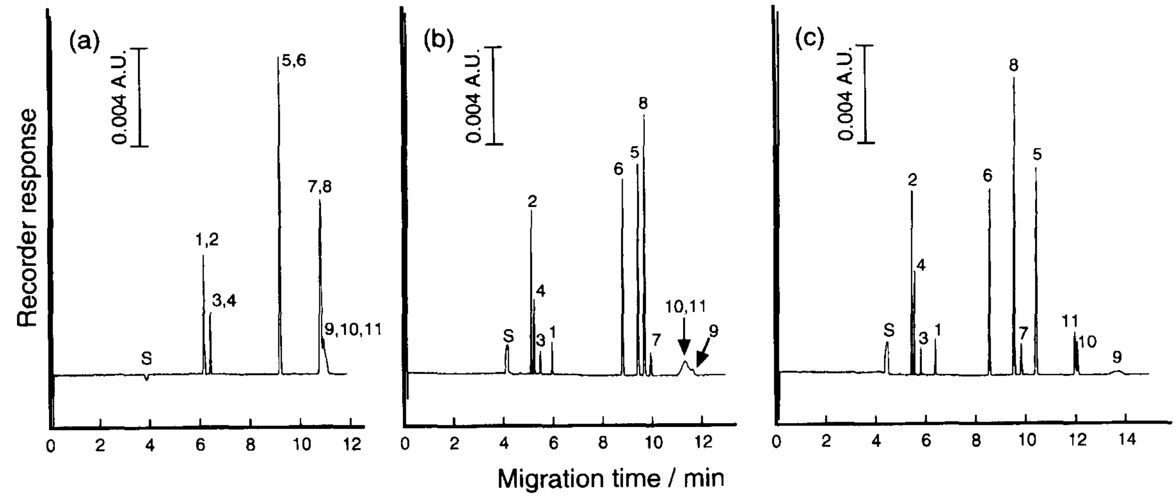

Fig. 2. Typical electropherograms for 11 kinds of aromatic anions in the absence and presence of nonionic surfactant and/or ion association reagent. CE conditions: applied voltage, 20 kV; detection wavelength, 230 nm; capillary temperature, 35 °C; injection period, 3 s. Migrating solution: (a), 10 mM borax; (b), 10 mM borax + 3.5%(w/v) Brij 58; (c), 10 mM borax + 3.5%(w/v) Brij 58 + 20 mM TBA^+Br^-. Sample solution: 1×10^{-5} M 11 kinds of aromatic anions + 3%(v/v) ethanol. Signal identifications: 1, 1-NC; 2, 2-NC; 3, 1-NS; 4, 2-NS; 5, 2,3-NDC; 6, 2,6-NDC; 7, 1,5-NDS; 8, 2,6-NDS; 9, PH; 10, i-PH; 11, t-PH.

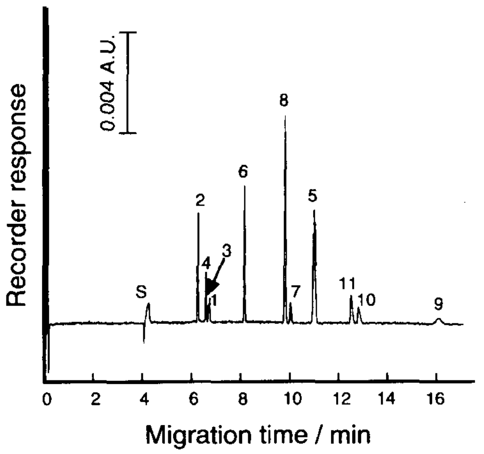

Fig. 3. Typical electropherogram for 11 kinds of aromatic anions in the presence of ion association reagent. CE conditions, sample solution, and signal identifications are the same as in Fig. 2. Migrating solution: 10 mM borax + 20 mM TBA^+Br^-.

surfactant micelle. Apparent electrophoretic mobility of the analyte anions also decreased in IA–CZE by ion association reaction between pairing cation in the migrating solution and analyte anions; this results in increase in apparent molecular volume of anion and decrease in apparent charge of anion.

In the case of IA/NI–MEKC, the mobility change of anions was also investigated by increasing the concentration of quaternary ammonium ion at a constant nonionic surfactant concentration, or by increasing the concentration of nonionic surfactant at a constant concentration of quaternary ammonium ion. Examples of the mobility change by increasing the concentrations of quaternary ammonium salt are shown in Fig. 4. With three kinds of nonionic surfactant, apparent electrophoretic mobility of the analyte anions, $-\mu'_{\mathrm{ep}}$, decreased with increasing concentrations of tetrabutylammonium ion. The apparent electrophoretic mobility also decreased with increasing concentrations of the nonionic surfactant at a constant concentration of tetrabutylammonium bromide.

Treatment of the Side Reactions. Before one analyses the reactions involved in the resolution improvement in IA/NI–MEKC, suspected side reactions must be identified; those reactions include those between borax components and the surfactant micelle and those binding quaternary ammonium ions to the surfactant micelle. The reaction between pH-adjusting components and the surfactant micelle was examined using another electrolyte, NaOH. Decreases in the mobility of the analyte anions by the increasing concentrations of the surfactant are almost identical, when borax or NaOH was used as pH-adjusting components. The decreases were also identical under different borax concentrations, 10 mM and 20 mM. Such results suggest that the borax components are less reactive and would not affect the reactions involved in the resolution improvement in IA/NI–MEKC.

The reaction between the surfactant and ion association reagent was studied in the following two experiments. Firstly, Sudan III was used as electrically neutral analyte and 3.5%(w/v) Brij 58 and 20 mM TBA^+Br^- were present in the migrating solution. If ion association reagent reacts with the surfactant micelle, Sudan III would migrate faster than EOF, because the micelle would possess apparently positive charge and Sudan III is strongly incorporated in the hydrophobic micelle. However, Sudan III migrated with the EOF, which suggested that no cationic micelle was formed. Sudan III also migrated with the EOF even when octyltrimethylammonium bromide or decyltrimethylammonium bromide was used instead of TBA^+Br^-. Secondly, benzyltrimethylammonium chloride was used as an analyte; its mobility change with increasing concentrations of Brij 58 was investigated to examine the binding reaction of cations directly. However, the mobility change obtained was slight. From the experimental results cited above, any reaction between the cationic reagent and the surfactant micelle is considered to

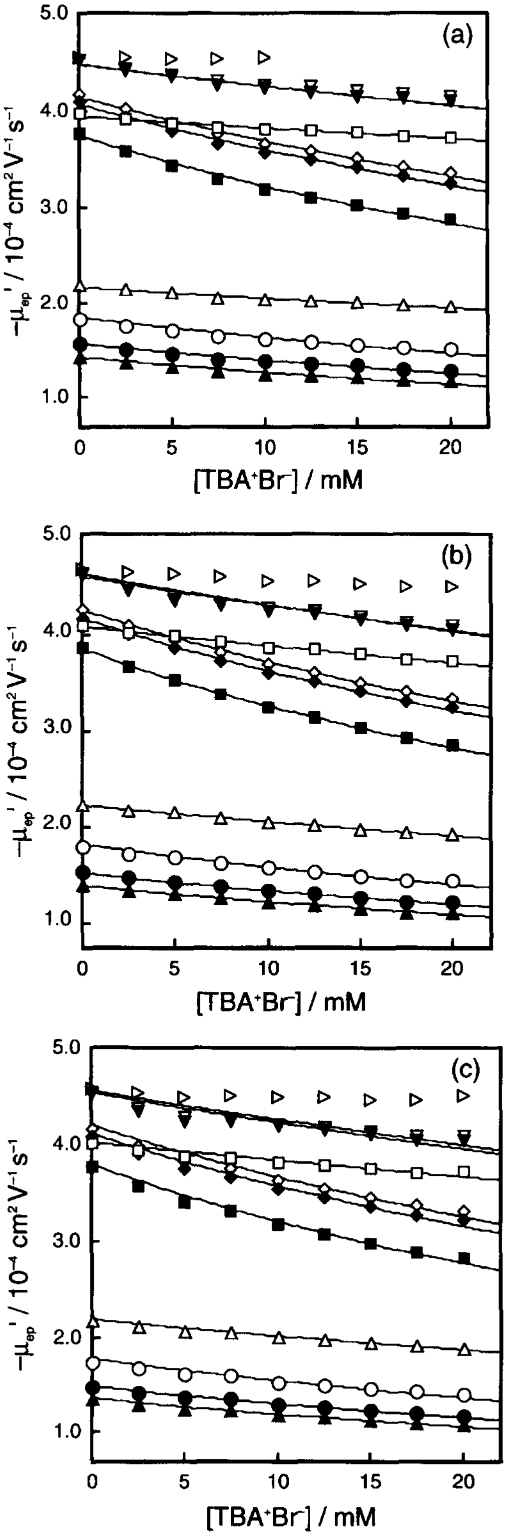

Fig. 4. Mobility change of aromatic anions with increasing concentrations of TBA^+Br^- in the migrating solution in the presence of 3.5%(w/v) nonionic surfactant. Nonionic surfactant: (a), Brij 35; (b), Brij 58; (c), Brij 78. CE conditions, sample solution, and migrating solution, expect for the concentration of TBA^+Br^-, are the same as in Fig. 2. Symbols: △, 1-NC; ▲, 2-NC; ○, 1-NS; ●, 2-NS; □, 2,3-NDC; ■, 2,6-NDC; ◇, 1,5-NDS; ◆, 2,6-NDS; ▷, PH; ▽, i-PH; ▼ t-PH.

be negligible.

The side reactions suspected would not participate in these electrophoretic migrations, therefore, we can treat the three reactions of interest without any corrections.

Binding Constants and Ion Association Constants. The aim of this study is to clarify the reactions in IA/NI–MEKC quantitatively. It is necessary to know the binding reaction of the anions to nonionic surfactant micelles and the ion association reaction before analyzing the distribution reaction of ion associates formed.

The analyte anions are bound to nonionic surfactant micelle as anionic form, and the binding reaction and its equilibrium constant, K_B, are expressed as in Eqs. 1 and 2, respectively.

$$A^{n-} + (NIS)_m \rightleftarrows A^{n-} - (NIS)_m \tag{1}$$

$$K_B = \frac{[A^{n-} - (NIS)_m]}{[A^{n-}][(NIS)_m]}, \tag{2}$$

where K_B is binding constant of anion and $[(NIS)_m]$ is the concentration of nonionic surfactant micelle calculated from the concentration of the nonionic surfactant, its critical micellization concentration, and its aggregation number.[15] Electrophoretic mobility of the analyte anions decreased by the binding reaction because of the apparently increased molecular volume. The present authors have determined the binding constants of the aromatic anions by analyzing the mobility change using non-linear least-squares analysis;[12] the values are summarized in Table 1.

When any ion association reagent, Q^+, is present in the migrating solution instead of nonionic surfactant, the analyte anions react with Q^+ and change its electrophoretic mobility. The ion association reaction and its equilibrium constant are written as in Eqs. 3 and 4, respectively.

$$Q^+ + A^{n-} \rightleftarrows Q^+A^{n-} \tag{3}$$

$$K_{ass} = \frac{[Q^+A^{n-}]}{[Q^+][A^{n-}]}, \tag{4}$$

where K_{ass} is ion association constant. The present authors had also determined the K_{ass} values between quaternary ammonium ions and the analyte anions using the electrophoretic method;[6] the K_{ass} values are also summarized in Table 1. The values of both K_B and K_{ass} were used in the analysis of distribution reaction of ion associates to the surfactant micelle.

Determination of Binding Constants of Ion Associates to the Nonionic Surfactant Micelle. In the presence of both nonionic surfactant micelle and ion association reagent, four species of a certain analyte anion must be considered, as is shown in Fig. 1; they are free anion (A^{n-}), the anion bound to the micelle ($A^{n-} - (NIS)_m$), ion associate with Q^+ (Q^+A^{n-}), and formed ion associate bound to the micelle ($Q^+A^{n-} - (NIS)_m$). In such conditions, the apparent electrophoretic mobility of an anion, $-\mu_{ep}'$, is contributed to from the four species, as is written in Eq. 5:

Table 1. Equilibrium Constants Determined by Using the Changes in Electrophoretic Mobility in Capillary Electrophoresis

Equilibrium constant	Nonionic surfactant	Ion association reagent	1-NC	2-NC	1-NS	2-NS	PH	i-PH	t-PH	1,5-NDS	2,6-NDS	2,3-NDC	2,6-NDC
			Analyte anions										
$\log K_B^{a)}$	Brij 35	—	2.70 (1.09)	3.22 (1.61)	3.06 (1.45)	3.20 (1.60)	2.19 (0.59)	2.24 (0.63)	2.27 (0.67)	2.50 (0.90)	2.56 (0.96)	2.31 (0.71)	2.51 (0.90)
$\log K_B^{a)}$	Brij 58	—	2.79 (0.94)	3.73 (1.53)	3.20 (1.35)	3.35 (1.50)	2.22 (0.37)	2.26 (0.41)	2.28 (0.43)	2.54 (0.70)	2.61 (0.76)	2.33 (0.49)	2.54 (0.69)
$\log K_B^{a)}$	Brij 78	—	(0.91)	(1.50)	(1.34)	(1.50)	(0.32)	(0.35)	(0.40)	(0.69)	(0.76)	(0.42)	(0.69)
$\log K_{ass}^{b)}$	—	TEA^+Br^-	—	—	—	—	—	—	—	0.91	0.85	—	0.92
$\log K_{ass}^{b)}$	—	TPA^+Br^-	—	—	0.77	0.81	—	0.70	0.70	1.17	1.17	—	1.25
$\log K_{ass}^{b)}$	—	TBA^+Br^-	0.87	1.17	0.98	1.06	—	0.87	0.90	1.39	1.44	0.70	1.48
$\log K_{B,IA}^{c)}$	Brij 58	TEA^+Br^-	—	—	—	—	—	—	—	3.66± 0.23	3.70±0.14	—	3.64±0.12
$\log K_{B,IA}^{c)}$	Brij 58	TPA^+Br^-	—	—	3.56±0.41	3.54±0.46	—	3.58±0.41	3.60±0.38	3.32±0.12	3.32±0.12	—	3.34±0.12
$\log K_{B,IA}^{c)}$	Brij 58	TBA^+Br^-	3.52±0.06 (1.68)	3.64±0.07 (1.79)	3.64±0.13 (1.80)	3.64±0.06 (1.80)	—	3.40±0.25 (1.55)	3.38±0.74 (1.53)	3.20±0.04 (1.35)	3.18±0.04 (1.33)	3.40±0.05 (1.56)	3.22±0.03 (1.37)
$\log K_{B,IA}^{c)}$	Brij 35	TBA^+Br^-	3.13±0.15 (1.53)	3.32±0.16 (1.72)	3.33±0.18 (1.73)	3.33±0.18 (1.74)	—	3.04±0.16 (1.44)	3.00±0.16 (1.40)	2.92±0.06 (1.32)	2.90±0.07 (1.30)	2.99±0.18 (1.39)	2.94±0.07 (1.34)
$\log K_{B,IA}^{c)}$	Brij 78	TBA^+Br^-	(1.69)	(1.79)	(1.81)	(1.81)	(—)	(1.55)	(1.54)	(1.37)	(1.34)	(1.56)	(1.38)

a) Cited values from Ref. 12. Values in parentheses are binding constant of analyte anions to nonionic surfactant (molecular unit). b) Cited values from Ref. 6. c) Error: 3 s. Values in parentheses are binding constant of ion associates to nonionic surfactant (molecular unit).

$$-\mu'_{ep} = \frac{(-\mu_{ep})[A^{n-}]+(-\mu_{ep,C})[A^{n-}-(NIS)_m]+(-\mu_{ep,IA})[Q^+A^{n-}]+(-\mu_{ep,C,IA})[Q^+A^{n-}-(NIS)_m]}{[A^{n-}]+[A^{n-}-(NIS)_m]+[Q^+A^{n-}]+[Q^+A^{n-}-(NIS)_m]}, \tag{5}$$

where $-\mu_{ep}$, $\mu_{ep,C}$, $-\mu_{ep,IA}$, and $-\mu_{ep,C,IA}$ are the electrophoretic mobility of A^{n-}, $A^{n-}-(NIS)_m$, Q^+A^{n-}, and $Q^+A^{n-}-(NIS)_m$, respectively. Distribution reaction or binding reaction of ion associate, Q^+A^{n-}, to nonionic surfactant micelle is written as in Eq. 6, and its equilibrium in Eq. 7:

$$Q^+A^{n-} + (NIS)_m \rightleftarrows Q^+A^{n-} - (NIS)_m \tag{6}$$

$$K_{B,IA} = \frac{[Q^+A^{n-} - (NIS)_m]}{[Q^+A^{n-}][(NIS)_m]}, \tag{7}$$

where $K_{B,IA}$ is binding constant of ion associate. Independent analysis of $K_{B,IA}$ was difficult in applying the mobility change,[14] because there appear many unknown values when the analysis was directly applied to Eq. 5. Therefore, the following extraction reaction of ion associate was utilized. The extraction equilibrium is written in Eq. 8, and is related to K_{ass} and $K_{B,IA}$:

$$K_{ex} = K_{ass} \times K_{B,IA} = \frac{[Q^+A^{n-} - (NIS)_m]}{[Q^+][A^{n-}][(NIS)_m]}, \tag{8}$$

where K_{ex} is extraction constant. In the present study, K_{ex} was used to analyze the reactions instead of K_{ass} and $K_{B,IA}$. Equation 5 can be reduced to Eq. 9 using K_B and K_{ex}, as well as Eqs. 2 and 8.

$$-\mu'_{ep} = \frac{(-\mu_{ep}) + K_B[(NIS)_m](-\mu_{ep,C}) + K_{ex}[Q^+][(NIS)_m](-\mu_{ep,C,IA})}{1 + K_B[(NIS)_m] + K_{ex}[Q^+][(NIS)_m]}. \tag{9}$$

When an analyte anion or the ion associate formed is bound to the micelle, the apparent molecular mass and/or the apparent molecular volume increases significantly. Therefore, the values of $-\mu_{ep,C}$ and $-\mu_{ep,C,IA}$ can be considered to be almost zero. A non-linear least-squares analysis also gave sufficiently small values for $-\mu_{ep,C}$ and $-\mu_{ep,C,IA}$ less than 10^{-6} cm^2 V^{-1} s^{-1}, and the assumption was proved to be quite valid. Therefore, Eq. 9 can be simplified to Eq. 10:

$$-\mu'_{ep} = \frac{(-\mu_{ep})}{1 + K_B[(NIS)_m] + K_{ex}[Q^+][(NIS)_m]}. \tag{10}$$

In Eq. 10, equilibrium constant of K_{ex} is included, and therefore the presence of nonionic surfactant micelle is required when using this equation, because chemical species of Q^+A^{n-} is not formed in the absence of nonionic surfactant micelle. The extraction constant, K_{ex}, can be determined using the concentrations of Q^+ and $(NIS)_m$, known equilibrium constant of K_B, and apparent electrophoretic mobility, $-\mu'_{ep}$, by applying a non-linear least-squares analysis. Once the value of K_{ex} is determined, $K_{B,IA}$ value can be calculated using Eq. 8 and the K_{ass} value provided. The binding constants of ion associates, $K_{B,IA}$, are also summarized in Table 1.

Comparison of Equilibrium Constants with the Kinds of Nonionic Surfactant. In the comparisons of K_B and $K_{B,IA}$ with the kinds of nonionic surfactant, the equilibrium constants were reduced to values based on the surfactant molecule, $K_{\mathrm{B(mon)}}$ and $K_{\mathrm{B,IA(mon)}}$, because the aggregation number of Brij 78 was not cited in the literature.[15] In the determination of $K_{\mathrm{B(mon)}}$ and $K_{\mathrm{B,IA(mon)}}$ values, concentration of the nonionic surfactant molecule was used instead of $[(\mathrm{NIS})_m]$. The reactions have been investigated using Brij 35, Brij 58, and Brij 78, where tetrabutylammonium bromide was used as an ion association reagent. Among the surfactants examined, Brij 35 is most hydrophilic and Brij 78 most hydrophobic on the basis of the calculation of hydrophile–lipophile balance (HLB);[15] HLB values for Brij 35, Brij 58, and Brij 78 are 17.2, 16.0, and 15.6, respectively. It has been noticed that the $K_{\mathrm{B(mon)}}$ values are almost identical in the comparison of the surfactant. In the comparison of $K_{\mathrm{B,IA(mon)}}$ values, no significant differences among three surfactants were observed. Therefore, the nonionic surfactant micelles examined possess similar binding property for the ion associates, as well as for the analyte anions.

Comparison of Equilibrium Constants with the Kinds of Pairing Cation. The reactions have been investigated using tetraethylammonium, tetrapropylammonium, and tetrabutylammonium ions, where Brij 58 was used as a nonionic surfactant. Obtained equilibrium constants are summarized in Table 1. It has been noticed that the ion association reaction proceeds through hydrophobic interaction and that the contribution of methylene group to ion association constant is about 0.06 ($\Delta\log K_{\mathrm{ass}}$).[6,16] In the comparison of $K_{\mathrm{B,IA}}$ values, however, there seem to be no significant differences among the cations examined. From the results, the nonionic surfactant micelle would not affect the binding reactions.

Comparison of Equilibrium Constants Among the Analyte Anions. Equilibrium constants of the reactions have been compared among the analyte anions from the viewpoint of their charge. It has been noticed that divalent anions are more associable with pairing cations than monovalent anions as is summarized in the K_{ass} values in Table 1. This can be explained by electrostatic interaction or probability factor.[6] Binding constants of the aromatic anions have also shown that monovalent anions are more likely bound to micelle on account of the distribution phenomena of ionic species to hydrophobic media,[12] as is summarized in the K_{B} values in Table 1.

The binding constants of the ion associates, $K_{\mathrm{B,IA}}$, are summarized in Table 1; the $K_{\mathrm{B,IA}}$ values for such ion associates as are formed from monovalent anions and pairing cations are larger than those formed from divalent anions and pairing cations. The results also agree with the distribution phenomena that electrically neutral or less charged species are more likely bound to hydrophobic media than more charged ones.[17,18] The results also suggest that the equilibrium constants obtained are quite valid.

Comparison of Three Equilibrium Constants. Since three equilibrium constants are such similar reactions that one spicies is formed from two species, and the dimension of the equilibrium reactions possesses the same dimension, $\mathrm{dm}^3\ \mathrm{mol}^{-1}$, we can compare the values directly.

Table 1 shows that ion association constant is smallest among three constants for each aromatic anion. The results can be understood from the fact that the contribution of ion association reaction is smaller than that of distribution reaction on extraction equilibrium of ion associates, that is, the contribution of methylene group to the equilibrium constants are 0.06 for $\log K_{\mathrm{ass}}$[6,16] and 0.6 for $\log K_{\mathrm{ex}}$.[17]

When K_{B} values and $K_{\mathrm{B,IA}}$ values are compared, it is also noticed that $K_{\mathrm{B,IA}}$ values are larger than K_{B} values for each aromatic anion. The results can be explained from distribution phenomena between aqueous and organic phases. Generally, less charged species are more likely distributed to hydrophobic media, and the results obtained in this study, comparison of K_{B} and $K_{\mathrm{B,IA}}$ values, well agree with the facts.

Conclusion

Binding or distribution phenomenon of ion associates to nonionic surfactant micelle was clarified by analyzing the mobility change in capillary electrophoresis. Treatment of ion association constant and binding reaction of ion associates as extraction constants of ion associates helped simple analysis of the reactions. Obtained equilibrium constants were reasonably explained from the viewpoints of distribution of ions or ion associates between aqueous and organic media. The proposed method would serve as a powerful technique for reaction analysis in aqueous solutions, resolution developments by the use of the interacting reagents, and designing and characterizing functional surfactants.

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