Bull. Chem. Soc. Jpn. Vol. 80, No. 1, 183–188 (2007)

Ion-Association Extraction of Nitrobenzoate Ions with Tetrabutylammonium Ion into Nonionic Surfactant Micelles as Studied by Capillary Zone Electrophoresis

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Ion-associates formed between tetrabutylammonium ion (TBA^+) and substituted nitrobenzoate ions have been extracted into nonionic surfactant micelles in an aqueous solution. The micelle extraction property of the ion-associates was investigated through the changes in electrophoretic mobility in capillary zone electrophoresis, in which a nonionic surfactant, Brij 35 or Brij 58, was used as a micelle substrate. Prior to the extraction analysis, ion-association constants (K_{ass}) between TBA^+ and the benzoate ions as well as binding constants of the anions to the nonionic surfactant micelle (K_B) were determined through the mobility change. Binding of the ion-associates from aqueous to the micelle phases was observed, when both TBA^+ and the nonionic surfactant were present in the migrating solution. Micelle extraction constants for the ion-associates ($K_{ex,m}$), were also determined by using the mobility change, and the values were compared with the ion-association solvent extraction constants between water and chloroform.

Ion-association solvent extraction is widely used in analytical and separation sciences.[1,2] Hydrophobic ion-associates can be extracted into water-immiscible organic solvents, and the contribution of hydrophobicity to the extraction constants (K_{ex}) has been determined as well as the contribution of the extraction solvent. Anionic surfactants can be extracted into organic phases as ion-associate with cationic dyes, and the concentration of the surfactants has been determined at $\mu g\,L^{-1}$ levels.[3,4] However, many organic solvents have been recognized to be hazardous and toxic, and these solvents are highly restricted in regards to waste and water contamination. In Japan, dichloromethane, carbon tetrachloride, 1,2-dichloroethane, 1,1-dichloroethylene, *cis*-1,2-dichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,3-dichloropropene, and benzene have been added to the water pollution control act.[5] Although some of the halogenated solvents are useful in ion-association solvent extraction, the extraction matrix should be replaced with less toxic substances. Solid-phase extraction (SPE) and solid-phase micro-extraction (SPME) are promising alternatives to solvent extraction.[6–8] Cationic surfactants in river water have been extracted with anionic surfactants,[9] and an ion pair of methylene blue–dodecylbenzene sulfonate has been extracted onto a poly(vinyl chloride) membrane and photometrically determined.[10] Lead ions have been extracted into a polypropylene microtube[11] and octadecylsilanized SiO_2[12] after being derivatized with a cryptand by using tetrabromofluorescein as an ion-association reagent.

Nonionic surfactant micelles can be used as an extraction media to replace organic solvents; the micelles are a neutral matrix and would work as hydrophobic stationary phases without ion–ion interactions. However, chromatographic separation must be employed, because the micelle solution is pseudo-homogeneous and phase separation does not occur during micelle extraction. Some nonionic surfactants have been used as a modifier for the migrating solution in capillary zone electrophoresis (CZE), in addition to anionic surfactants.[13] Nonionic surfactant micelles are a pseudo-homogeneous hydrophobic media, and ionic substances themselves can bind to the micelle. Dansylamino acids were resolved with nonionic Tween 20 micelle by CZE[14] and aromatic anions with Brij 35 and Brij 58 micelles.[15] The hydrophobicity of the analyte anions were found to be a main characteristic of the binding reaction.[15] While anionic surfactant micelle is useful for the separation of nonionic substances, nonionic surfactants can be used to improve the separation of ionic analytes. Nonionic surfactant micelles can also work as extraction media for hydrophobic ion-associates. We have proposed ion association-nonionic micellar electrokinetic chromatography.[16,17] In the presence of both an ion association reagent and nonionic surfactant micelle, an analyte anion forms an ion-associate with the pairing cation, and the ion-associate that is formed is distributed/bound to the micelle. Figure 1 illustrates ion association-micelle extraction with the equilibrium constants; the micelle extraction reaction can be defined by two reactions which are the ion-association process (K_{ass}) and the binding process of the ion-associate to the micelle ($K_{B,IA}$). Electrophoretic mobility of the analyte ion, in this case, anionic A^-, is also shown with their species.

In this study, our goal was to determine the micelle-extraction constants of the ion-associates, $K_{ex,m}$, formed between tetrabutylammonium ion and substituted nitrobenzoate ions, because reliable ion-association solvent extraction constants ($K_{ex,S}$) are available.[1] The $K_{ex,m}$ values determined were compared with each other based on the number and position of the nitro group on the benzoate ions as well as the type of the nonionic surfactant micelle used. Further, the $K_{ex,m}$ values were compared with $K_{ex,S}$ values.

Published on the web January 12, 2007; doi:10.1246/bcsj.80.183

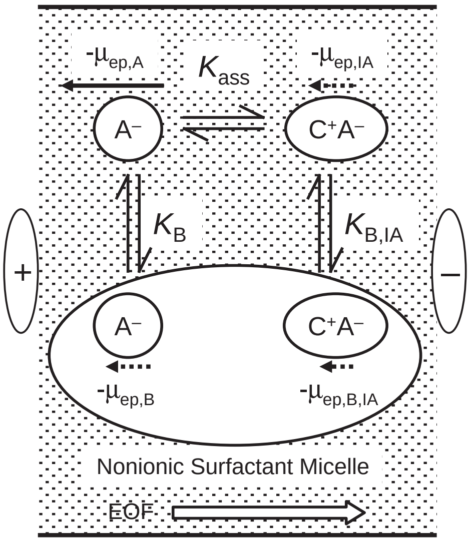

Fig. 1. Schematic illustration for micelle extraction of ion-associates in relation to the electrophoretic mobility.

Experimental

Apparatus. A Hewlett-Packard ^{3D}CE system with a photodiode array detector (Waldbronn, Germany) was used as a capillary electrophoresis system and for the measurement of the electrophoretic mobility. A fused silica capillary (Agilent Technologies, Waldbronn, Germany) with a total length of 64.5 cm, an effective length to the detector of 56 cm and an inner diameter of 50 µm was held in a capillary cassette and attached to the system. The temperature of the capillary cassette was controlled by an air-blowing system, while that of the vials by circulating temperature-controlled water. The migrating solution and the sample solutions were put in 1 mL vials and set in the system tray. A Hewlett-Packard ChemStation (ver. 5.01) was used for the control of the system, data acquisition, and the analysis of the electropherograms.

A Mettler-Toledo MP220 pH meter with a combined glass electrode was used for the pH adjustment after daily calibration with the standard pH solutions.

Reagents. Sodium tetraborate (borax, Wako Pure Chemical Industries, Osaka, Japan) was used to adjust the pH of the 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 ($1\,\mathrm{M} = 1\,\mathrm{mol\,dm^{-3}}$). Polyoxyethylene (23) lauryl ether (Brij 35, Wako) and polyoxyethylene (20) cetyl ether (Brij 58, Wako) were used as nonionic surfactants to form micelles; the surfactant was added to the migrating solution in the concentration ranges from 0 to 3.0%(w/v). The quaternary ammonium salt, tetrabutylammonium chloride (TBA^+Cl^-), was purchased from Tokyo Kasei Kogyo (Tokyo, Japan) and was used as the ion-association reagent. Seven benzoate ions were used as model analytes: benzoic acid (BC), 2-nitrobenzoic acid ($2NO_2BC$), 3-nitrobenzoic acid ($3NO_2BC$), 4-nitrobenzoic acid ($4NO_2BC$), 2,4-dinitrobenzoic acid ($24NO_2BC$), 2,6-dinitrobenzoic acid ($26NO_2BC$), and 2,4,6-trinitrobenzoic acid ($246NO_2BC$). The acids were obtained from Tokyo Kasei Kogyo and were used after being neutralized with an equivalent amount of sodium hydroxide. Water was purified by ion-exchange and distillation.

Procedure for the CZE Measurement. A migrating solution was prepared from 10 mM borax, a known amount of a nonionic surfactant, and/or a known amount of an ion-association reagent. The ionic strength of the migrating solution was controlled at 0.04 M with NaCl. The migrating solution thus prepared was poured into both cathodic and anodic reservoir vials as well as into a capillary by applying a pressure. A sample solution containing all 7 benzoate ions with a concentration of 2×10^{-5} M each was injected into the capillary from the anodic end for 5 s hydrodynamically by applying a pressure (50 mbar). A voltage of 20 kV was then applied and electrophoresis was started. The analyte anions were photometrically detected at 220 nm. Throughout the experiments, the capillary was held in a thermostatic compartment controlled at 25 ± 0.1 °C, and the vials at 25 ± 0.2 °C. Ethanol at the concentration of 1–3%(v/v) was added to the sample solution to monitor the velocity of the electroosmotic flow (EOF). The electrophoretic mobility of the analyte anions, $\mu_{\mathrm{ep,A'}}$, was calculated in an ordinary manner using Eq. 1:

$$\mu_{\mathrm{ep,A'}} = \frac{L_{\mathrm{T}} \times L}{V \times t} - \frac{L_{\mathrm{T}} \times L}{V \times t_{\mathrm{EOF}}}, \tag{1}$$

where L_{T}, L, V, t, and t_{EOF} are the total capillary length, the effective capillary length from the injection point to the detection point, the applied DC voltage, the migration time of the analyte anion, and the migration time of the electroosmotic flow, respectively. Three or more measurements were carried out to obtain the mean electrophoretic mobility. Equilibrium constants were determined through curve fitting with a series of the mobility data.

Results and Discussion

Ion-Association Reaction of the Benzoate Ions with Tetrabutylammonium Ion. Prior to the investigation of the micelle-extraction reaction of ion-associates, the ion-association reaction in an aqueous solution must be clarified in detail. We have proposed an accurate and reliable method to determine ion-association constants in an aqueous solution (K_{ass}) by using the changes in the electrophoretic mobility in capillary zone electrophoresis.[18–20] Only TBA^+Cl^- as an interacting reagent was contained in the migrating solution, and ion-association property of some nitrobenzoate ions were analyzed. The pK_{a} values of the benzoate ions used are smaller than 4.2,[21] and all of the benzoate ions are anions at the pH conditions of 9.2. Therefore, the analyte anions migrate slower than the electroosmotic flow in an ordinary fused-silica capillary. A typical electropherogram is shown in Fig. 2a. When tetrabutylammonium ion was added to the migrating solution, the migration order of the benzoate ions changed, Fig. 2b. $\mu_{\mathrm{ep,A'}}$ was measured for a series of TBA^+Cl^- concentrations. Changes in $\mu_{\mathrm{ep,A'}}$ of the benzoate ions with increasing concentrations of TBA^+Cl^- are shown in Fig. 3; the decrease in $\mu_{\mathrm{ep,A'}}$ is attributed to the formation of ion-associates with TBA^+, resulting in the increase in the apparent molecular mass and the decrease in the apparent charge of the ion-associates.

A 1:1 ion-association reaction (2) was proposed along with its equilibrium constant (3):

$$C^+ + A^- \rightleftharpoons C^+A^-, \tag{2}$$

$$K_{\mathrm{ass}} = \frac{[C^+A^-]}{[C^+][A^-]}, \tag{3}$$

where C^+, A^-, and C^+A^- are a pairing cation (TBA^+), an analyte anion, and its ion-associate, respectively. $\mu_{\mathrm{ep,A'}}$ is expressed as in Eq. 4, considering the net charge of the C^+A^-:[18]

$$\mu_{\mathrm{ep,A'}} = \frac{\mu_{\mathrm{ep,A}}}{1 + K_{\mathrm{ass}}[\mathrm{C}^+]}, \tag{4}$$

where $\mu_{\mathrm{ep,A}}$ is the electrophoretic mobility of the free benzoate ion. A series of TBA^+ concentration and $\mu_{\mathrm{ep,A'}}$ values were used, and the values of $\mu_{\mathrm{ep,A}}$ and K_{ass} were optimized by using a curve-fitting analysis.[18] Ion-association constants thus determined are summarized in Table 1. The ion-association constants are not so different among the nitrobenzoate ions. The results are attributed to two competitive effects: an increase in the hydrophobicity by the dispersion of the anionic charge[1,2] and a decrease in the net negative charge on the carboxylate group. The former effect should promote the hydrophobic ion association reaction, while the latter one should reduce the electrostatic interaction.

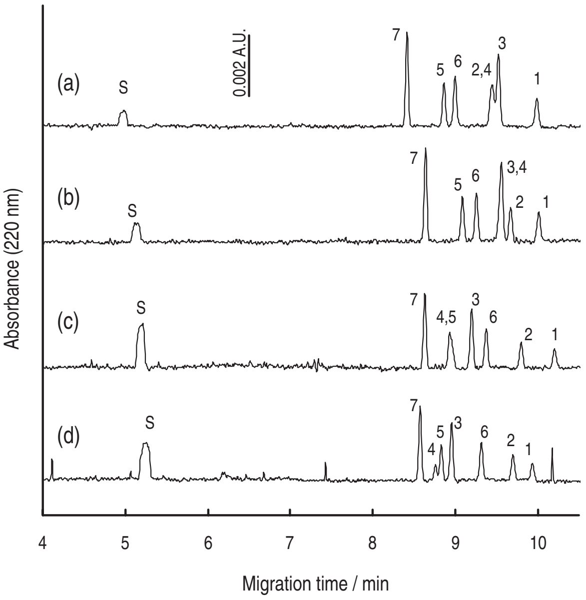

Fig. 2. Typical electropherograms for the benzoate ions in the absence and presence of TBA^+ and/or Brij 58. Migrating solution: (a), 10 mM borax + 20 mM NaCl; (b), 10 mM borax + 15 mM TBA^+Cl^- + 5 mM NaCl; (c), 10 mM borax + 20 mM NaCl + 2.0%(w/v) Brij 58; (d), 10 mM borax + 15 mM TBA^+Cl^- + 5 mM NaCl + 1.0%(w/v) Brij 58. Sample solution contains seven kinds of 2×10^{-5} M benzoate ions. Signals: 1, BC; 2, $2NO_2BC$; 3, $3NO_2BC$; 4, $4NO_2BC$; 5, $24NO_2BC$; 6, $26NO_2BC$; 7, $246NO_2BC$. S: ethanol (EOF marker). CZE conditions: applied voltage, 20 kV; detection wavelength, 220 nm; capillary temperature, 25.0 °C; injection period; 50 mbar × 5 s.

Binding Reaction of the Benzoate Ions to Nonionic Surfactant Micelle. The benzoate ions possess hydrophobic character, and they can bind to a nonionic surfactant micelle in an anionic form. We have previously developed an analytical method to study the binding reaction through capillary zone electrophoresis by using the changes in the electrophoret-

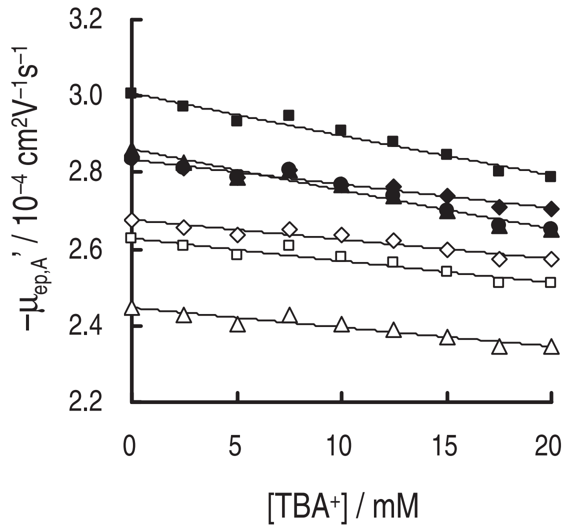

Fig. 3. Changes in electrophoretic mobility of the benzoate ions with increasing concentrations of TBA^+. Migrating solution, sample solution, and the CZE conditions are the same as in Fig. 2b except for the TBA^+ concentrations. ■, BC; ◆, $2NO_2BC$; ▲, $3NO_2BC$; ●, $4NO_2BC$; □, $24NO_2BC$; ◇, $26NO_2BC$; △, $246NO_2BC$.

Table 1. Ion-Association Constants, Binding Constants, and Binding Constants of Ion-Associate for Benzoate Ions

			Anions						
Constants	Pairing cation	Surfactant	BC	$2NO_2BC$	$3NO_2BC$	$4NO_2BC$	$24NO_2BC$	$26NO_2BC$	$246NO_2BC$
$\log K_{\mathrm{ass}}$[a)]	TBA^+		0.58 ± 0.16 (0.69)	0.37 ± 0.23	0.59 ± 0.16	0.55 ± 0.24 (0.55)	0.36 ± 0.29	0.30 ± 0.28	0.33 ± 0.31
$\log K_{\mathrm{B}}$[b)]		Brij 35	2.17 ± 0.11 (0.57 ± 0.12)	1.99 ± 0.38 (0.39 ± 0.36)	2.40 ± 0.06 (0.80 ± 0.06)	2.45 ± 0.04 (0.85 ± 0.04)	2.25 ± 0.16 (0.65 ± 0.16)	1.97 ± 0.14 (0.37 ± 0.13)	2.12 ± 0.10 (0.52 ± 0.10)
$\log K_{\mathrm{B}}$[b)]		Brij 58	2.37 ± 0.03 (0.52 ± 0.03)	2.22 ± 0.04 (0.37 ± 0.04)	2.73 ± 0.02 (0.88 ± 0.02)	2.81 ± 0.04 (0.97 ± 0.04)	2.53 ± 0.02 (0.68 ± 0.02)	2.18 ± 0.03 (0.33 ± 0.03)	2.38 ± 0.04 (0.53 ± 0.04)
$\log K_{\mathrm{B,IA}}$[b)]	TBA^+	Brij 35	3.48 ± 0.12 (1.87 ± 0.13)	3.50 ± 0.17 (1.90 ± 0.17)	3.58 ± 0.10 (1.97 ± 0.10)	3.61 ± 0.13 (2.00 ± 0.13)	3.60 ± 0.15 (2.00 ± 0.15)	3.53 ± 0.20 (1.93 ± 0.20)	3.57 ± 0.18 (1.96 ± 0.18)
$\log K_{\mathrm{B,IA}}$[b)]	TBA^+	Brij 58	3.55 ± 0.11 (1.71 ± 0.11)	3.45 ± 0.27 (1.61 ± 0.28)	3.69 ± 0.09 (1.85 ± 0.09)	3.72 ± 0.13 (1.88 ± 0.13)	3.63 ± 0.17 (1.79 ± 0.17)	3.43 ± 0.38 (1.59 ± 0.38)	3.55 ± 0.27 (1.70 ± 0.27)
$\log K_{\mathrm{ex,m}}$	TBA^+	Brij 35	4.06	3.87	4.17	4.16	3.96	3.83	3.90
$\log K_{\mathrm{ex,m}}$	TBA^+	Brij 58	4.13	3.82	4.28	4.27	3.99	3.73	3.88
$\log K_{\mathrm{ex,S}}$[c)]	TBA^+	—	0.68	1.33	1.72	1.67	—	1.69	2.60

a) Error: 3σ. Values in parentheses are previously reported values: Ref. 23. b) Error: 3σ. Values in parentheses are the ones divided with the aggregation number of the surfactant (n). c) Cited from Ref. 1. Solvent: chloroform. $K_{\mathrm{ex,S}} = [\mathrm{C^+A^-}]_{\mathrm{o}}/[\mathrm{C^+}][\mathrm{A^-}]$, where subscript "o" denotes the species in the organic phase.

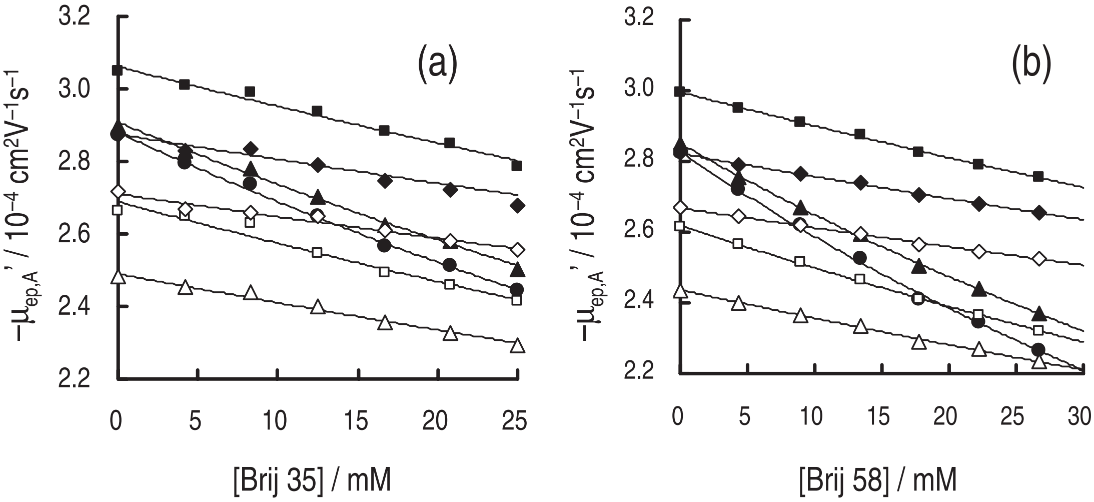

Fig. 4. Changes in electrophoretic mobility of the benzoate ions with increasing concentrations of nonionic surfactant. Nonionic surfactant: (a), Brij 35; (b), Brij 58. Migrating solution, sample solution, and the CZE conditions are the same as in Fig. 2c except for the concentrations of nonionic surfactant. ■, BC; ◆, $2NO_2BC$; ▲, $3NO_2BC$; ●, $4NO_2BC$; □, $24NO_2BC$; ◇, $26NO_2BC$; △, $246NO_2BC$.

ic mobility.[15] Only a nonionic surfactant, as an interacting reagent, was contained in the migrating solution, and the binding property of some nitrobenzoate ions were analyzed. A typical electropherogram of the benzoate ions in the presence of Brij 58, as a nonionic surfactant micelle, is shown Fig. 2c. The migration order of the analyte anions was different from the one obtained in the absence of Brij 58 (Fig. 2a). $\mu_{ep,A'}$ was measured at a series of concentrations of a nonionic surfactant micelle. Changes in the electrophoretic mobility of the benzoate ions with increasing concentrations of the nonionic surfactant are shown in Fig. 4; the decrease in $\mu_{ep,A'}$ is attributed to a large increase in the apparent molecular mass of the analyte anions when bound to the micelle. The binding reaction and its equilibrium constant, K_B, are expressed as Eqs. 5 and 6, respectively:

$$A^- + (NIS)_m \rightleftharpoons A^-\text{–}(NIS)_m \tag{5}$$

$$K_B = \frac{[A^-\text{–}(NIS)_m]}{[A^-][(NIS)_m]}, \tag{6}$$

where $(NIS)_m$ is the nonionic surfactant micelle and K_B is a binding constant of anion to the micelle. The concentration of the nonionic surfactant micelle, $[(NIS)_m]$, was calculated from the concentration of the nonionic surfactant, its critical micelle concentration, and its aggregation number.[22] The properties of the surfactants are summarized in Table 2. From the hydrophile–lipophile balance, Brij 35 is more hydrophilic than Brij 58, as can be expected from the structure. The nonionic surfactant micelles are much larger than the small molecule, such as the benzoate ions, and the electrically neutral micelles may not migrate so swiftly. Therefore, the electrophoretic mobility of the benzoate ion bound to the micelle ($\mu_{ep,B}$ in Fig. 1) become quite small and almost negligible compared to $\mu_{ep,A}$. $\mu_{ep,A'}$ is expressed as Eq. 7.

$$\mu_{ep,A'} = \frac{\mu_{ep,A}}{1 + K_B[(NIS)_m]}. \tag{7}$$

A series of $(NIS)_m$ concentrations and $\mu_{ep,A'}$ values were input and values of $\mu_{ep,A}$ and K_B were optimized by using a curve-fitting analysis.[15] K_B values thus determined are also summarized in Table 1. To compare the K_B values, the equilibrium constant based on the concentration of the surfactant molecule was also calculated by dividing K_B with the aggregation number (n): K_B/n, and they are also summarized in Table 1. From Table 1, the K_B/n values obtained are almost comparable to the K_{ass} values, although the binding reaction does not include ion–ion interactions. Because the micelles act as a hydrophobic media, hydrophobic interactions should contribute to the relatively large K_B values. However, the K_B/n values are not so different among the benzoate ions examined.

Table 2. Properties of the Nonionic Surfactants Cited from Ref. 22

Surfactants	Critical micelle concentration	Aggregation number of the surfactant molecule	H.L.B[a)]
Brij 35	9.0×10^{-5} M	40	17.2
Brij 58	3.9×10^{-6} M	70	16.0

a) Hydrophile–lipophile balance, $20 \times M_H/(M_H + M_L)$, where M_H and M_L are partial molecular mass of the hydrophilic group and that of lipophilic group of the surfactant molecule.

The K_B/n values were also compared with each other in relation to Brij 35 and Brij 58. The results are shown in Fig. 5a. From Fig. 5a, it is clear that the anions are likely to bind to a Brij 35 micelle as they are to a Brij 58 micelle. In other words, the nonionic surfactants behave similarly as hydrophobic media.

Binding Reaction of Ion-Associates to Nonionic Surfactant Micelle. In the presence of both nonionic surfactant micelle and an ion-association reagent, four species of a certain analyte anion must be considered, as is shown in Fig. 1: free anion (A^-), the anion bound to the micelle (A^-–$(NIS)_m$), ion-associate with C^+ (C^+A^-), and formed ion-associate bound to the micelle (C^+A^-–$(NIS)_m$). It was found in our previous study that TBA^+ does not easily bind to the micelle.[17] The electrophoretic mobility of A^-–$(NIS)_m$, C^+A^-, and C^+A^-–$(NIS)_m$ species are considered to be zero or negligible,

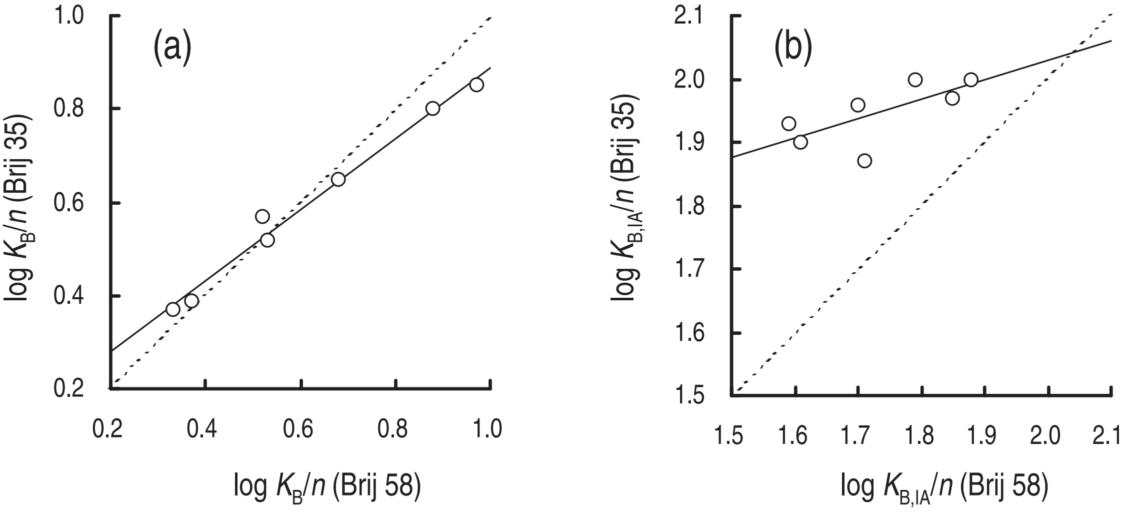

Fig. 5. Comparisons of K_B/n values and $K_{B,IA}/n$ for the benzoate ions obtained with Brij 58 and Brij 35 as micelle matrix. (a), comparison of K_B/n values; (b), comparison of $K_{B,IA}/n$ values.

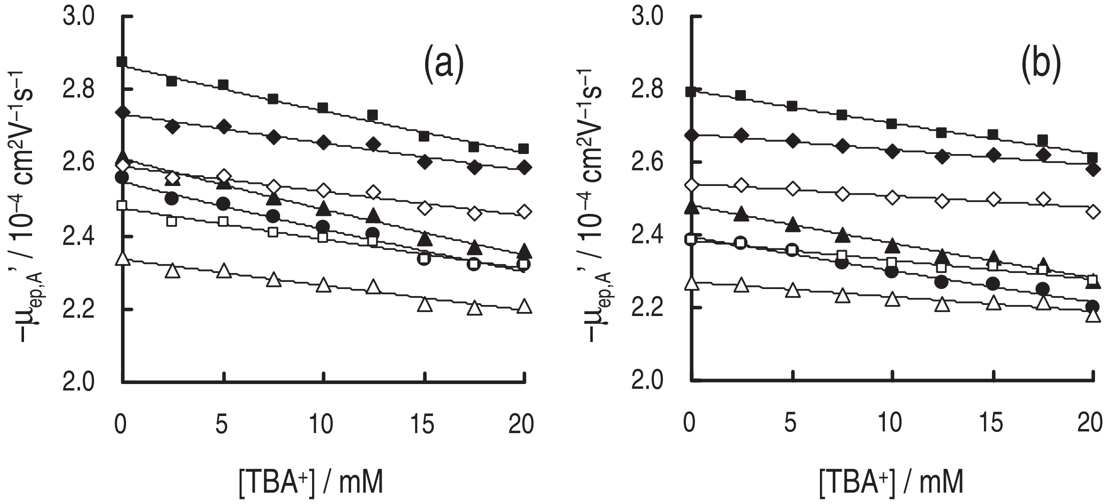

Fig. 6. Changes in electrophoretic mobility of the benzoate ions with increasing concentrations of TBA^+ in the presence of 1%(w/v) nonionic surfactant. Nonionic surfactant: (a), Brij 35; (b), Brij 58. Migrating solution, sample solution, and the CZE conditions are the same as in Fig. 2d except for the concentrations of TBA^+ and nonionic surfactant. ■, BC; ◆, $2NO_2BC$; ▲, $3NO_2BC$; ●, $4NO_2BC$; □, $24NO_2BC$; ◇, $26NO_2BC$; △, $246NO_2BC$.

and therefore, $\mu_{ep,A'}$ is written as:

$$\mu_{ep,A'} = \frac{\mu_{ep,A}[A^-]}{[A^-] + [A^-\text{–}(NIS)_m] + [C^+A^-] + [C^+A^-\text{–}(NIS)_m]} . \tag{8}$$

The binding reaction of the ion-associate, C^+A^-, to nonionic surfactant micelle is written as in Eq. 9, and its equilibrium in written in Eq. 10:

$$C^+A^- + (NIS)_m \rightleftharpoons C^+A^-\text{–}(NIS)_m \tag{9}$$

$$K_{B,IA} = \frac{[C^+A^-\text{–}(NIS)_m]}{[C^+A^-][(NIS)_m]}, \tag{10}$$

where $K_{B,IA}$ is a binding constant of ion-associate to the nonionic surfactant micelle. Independent analysis of $K_{B,IA}$ was difficult using the mobility change, because many unknown values appeared when the analysis was directly applied to Eq. 8. Therefore, we proposed an analysis method that uses the micelle extraction reaction involving the ion-associate.[17] The details were reported in our previous study.[17] The micelle extraction constant for the ion-associate, $K_{ex,m} = K_{ass} \times K_{B,IA}$, and therefore, Eq. 8 simplifies to Eq. 11:

$$\mu_{ep,A'} = \frac{\mu_{ep,A}}{1 + K_B[(NIS)_m] + K_{ex,m}[C^+][(NIS)_m]} . \tag{11}$$

$\mu_{ep,A'}$ for each anions was measured at a constant $[(NIS)_m]$ by varying the concentration of TBA^+. Typical electropherogram is shown in Fig. 2d, and the changes in the electrophoretic mobility of the benzoate ions are shown in Fig. 6. $K_{ex,m}$ values as well as $\mu_{ep,A}$ values in Eq. 11 were determined by varying the TBA^+ concentration and $\mu_{ep,A'}$ value that were obtained as experimental variables and K_B and holding the $[(NIS)_m]$ constant through the curve-fitting analysis. From $K_{ex,m}$, the $K_{B,IA}$ value was calculated by dividing $K_{ex,m}$ with K_{ass}. $K_{B,IA}$ values are also summarized in Table 1. For comparison, the equilibrium constant based on the concentration of the surfactant molecule was also calculated by dividing $K_{\mathrm{B,IA}}$ with the aggregation number (n): $K_{\mathrm{B,IA}}/n$, and they are also summarized in Table 1. Clearly, $K_{\mathrm{B,IA}}$ is larger than K_{B} value for each anion. The results can easily be understood based on the binding/distribution phenomena, i.e., electrically neutral or less charged species are more likely bind to hydrophobic media than more charged ones.[1,2] The $K_{\mathrm{B,IA}}/n$ values were also compared with each other based on the two surfactants Brij 35 and Brij 58. The result is shown in Fig. 5b. Although larger $K_{\mathrm{B,IA}}/n$ values were obtained with Brij 35 than Brij 58, the relationship was not clear, and the range with Brij 58 was narrow. Thus, we cannot discuss these results in detail at this stage.

Our aim in this study is to compare $K_{\mathrm{ex,m}}$ of the benzoate ions with $K_{\mathrm{ex,S}}$, because both the nonionic surfactant micelles and the organic solvents act as hydrophobic media to which ion-associates can distribute. $K_{\mathrm{ex,S}}$, summarized in Table 1 defined as in Eq. 12:

$$K_{\mathrm{ex,S}} = \frac{[\mathrm{C}^+\mathrm{A}^-]_{\mathrm{o}}}{[\mathrm{C}^+][\mathrm{A}^-]}, \tag{12}$$

where the subscript o denotes the species in the organic phase. The range of the $K_{\mathrm{ex,m}}$ values in relation to the position and the number of the nitro groups is narrow which means that the nitro groups have little effect especially compared to the $K_{\mathrm{ex,S}}$ values. The reason for the narrow range of $K_{\mathrm{ex,m}}$ values is not clear at this stage.

Conclusion

Equilibrium reactions of nitrobenzoate ions, including ion-association reaction with tetrabutylammonium ion, binding reaction to nonionic surfactant micelle, and binding of the ion-associate with tetrabutylammonium ion to the nonionic surfactant micelle have been investigated in this study by means of capillary zone electrophoresis. The difference in the equilibrium constants, K_{ass}, K_{B}, and $K_{\mathrm{B,IA}}$, were narrow among the nitrobenzoate ions. The range of the $K_{\mathrm{ex,m}}$ values was narrower than that of $K_{\mathrm{ex,S}}$ values.

This study was partly supported by a Grant-in-Aid for Scientific Research (No. 16350044) from the Japan Society for Promotion of Science (JSPS).

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