© 2005 The Chemical Society of Japan Bull. Chem. Soc. Jpn., **78**, 1457–1462 (2005)

Ion-Association Analysis between Inorganic Anions and Symmetrical Tetraalkylammonium Ions in Aqueous-Acetonitrile Media by Capillary Zone Electrophoresis

Julius Mbuna, Toshio Takayanagi, Mitsuko Oshima, and Shoji Motomizu*

Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushimanaka, Okayama 700-8530

Received November 19, 2004; E-mail: motomizu@cc.okayama-u.ac.jp

Weak ion-association equilibrium was analyzed in a water-acetonitrile solution at 25 °C by capillary zone electrophoresis using an ordinary silica capillary. The ion associates examined were formed between some inorganic anions and symmetrical tetraalkylammonium ions, where a series of acetonitrile compositions up to 62.2% (m/m) were investigated. Ion-association constants, K_{ass}, were determined by analyzing the changes in the electrophoretic mobility; the K_{ass} values for most of the anions increased up to about 47% (m/m) acetonitrile, beyond which they remained constant, or decreased slightly. The ion-association equilibrium between tetramethylammonium and bromide ions in aqueous-acetonitrile and in aqueous-ethanol media were compared through the Gibbs free energy of transfer, which revealed that the extent of the equilibrium in aqueous-acetonitrile media is dependent mainly on the increasing instability of Br^-. On the other hand, those in aqueous-ethanol media depend on the instabilities of both tetramethylammonium and bromide ions.

Methanol and acetonitrile are widely used in capillary electrophoresis either as neat reagents[1–6] or binary/ternary mixtures.[7–9] Apart from the use of solvents in non-aqueous capillary electrophoresis,[10,11] acetonitrile has an advantage on reducing the analysis time, owing to its low viscosity.[12,13] Thus, the separation of phenols can be realized in neat acetonitrile in the presence of common inorganic anions.[14,15] Separations have also been carried out in aqueous-acetonitrile media, in which acetonitrile is added to either the migrating buffer[8] or a background electrolyte.[16] Sarmini and Kenndler investigated the effect of acetonitrile on the acid-dissociation constants (pK_a) and the electrophoretic mobility of substituted aromatic carboxylic acids.[16] Varying the composition of acetonitrile in the electrolyte solution led to an increase in the pK_a values and the mobility of the carboxylate ions. To clarify the mechanism contributing to solvent-induced selectivity changes, Kimberly and Lucy analyzed the electrophoretic mobility of aromatic carboxylate and sulphonate ions by varying the composition of acetonitrile in the migrating buffer.[8] They measured the electrophoretic mobility of the anions at different acetonitrile compositions to attribute the observed selectivity changes partly to dielectric friction. Thus, the changes in the electrophoretic mobility due to the addition of an organic solvent to the migrating buffer can be used to investigate some observed phenomena (e.g. changes in selectivity) in capillary zone electrophoresis.

The ion-association reaction has been expansively used to change the electrophoretic mobility of analytes. In addition to mobility development, ion-association equilibria have been analyzed, in which the ion-association constants (K_{ass}) are determined by measuring the mobility of bulky organic species.[17–23] However, studies dealing with the reactions of small inorganic anions, often accompanying weak ion-association, are comparatively few. Little work has been reported on weak ion-association in organic-water binary mixtures; we have reported on weak ion-association reactions in aqueous-ethanol[24] and aqueous-dioxane media.[25] The present paper describes an investigation of a weak ion-association reaction in aqueous-acetonitrile media. In this study, the ion-association system between inorganic anions and symmetrical tetraalkylammonium ions was examined by measuring the mobility of inorganic anions in a buffer containing a variable composition of acetonitrile. Since similar ion-association reactions have been investigated in amphiprotic ethanol[24] as well as aprotic, low permittivity, and non-polar dioxane[25] as a binary solvent, it was of interest to investigate the association reactions with aprotic, protophobic, and polar acetonitrile. A comparison of the ion-association constants in different classes of solvents can be used in modeling.[26] In addition, the equilibrium can be treated by the Gibbs free energy of transfer[27,28] to explain the ion-association constants determined in an aqueous-organic mixed solvent.

Experimental

Apparatus. The electrophoretic mobility of anions was measured by a Hewlett Packard ^{3D}CE system (Waldbronn, Germany). A fused-silica capillary (Agilent Technologies, Germany) with 50 µm i.d., 375 µm o.d., 40 cm effective length, and 48.5 cm total length was held in a capillary cassette and attached on the system. The temperature of the capillary cassette was controlled at 25.0 ± 0.1 °C by an air-blowing system, while that of the vials compartment was kept at 25.0 ± 0.2 °C by circulating temperature-controlled water. System control and data acquisition were made by a Chemstation software (Hewlett Packard).

Reagents. All solutions employed were prepared using Milli-Q Labo water (18.0 MΩ cm, Millipore Japan, Tokyo, Japan), and were filtered through 0.45 µm syringe filters (Advantec, Tokyo, Japan) before use. Sodium salts of Br^-, SCN^-, NO_3^-, $S_2O_3^{2-}$,

Published on the web August 4, 2005; DOI 10.1246/bcsj.78.1457

$S_4O_6{}^{2-}$, and $[Co(NO_2)_6]^{3-}$, as well as potassium salts of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$, were of reagent grade (Wako Pure Chemicals, Osaka, Japan), and were used after being dissolved separately in water. 4-Methyl-3-penten-2-one (Tokyo Kasei Kogyo, Tokyo, Japan) was added to the sample solution at 0.02% (v/v) and used as a neutral marker. Buffer components of acetic acid and sodium acetate were from Wako. Acetonitrile used was of HPLC grade (Wako). Migrating buffers containing 0, 15.6, 31.1, 46.7, and 62.2% (m/m) acetonitrile (mass/mass percentage) were prepared by mixing them with aqueous acetate buffer (10 mM, pH 4.0; $M = mol\,dm^{-3}$). Quaternary ammonium chlorides of tetramethylammonium, Me_4N^+; tetraethylammonium, Et_4N^+; tetrapropylammonium, Pr_4N^+; tetrabutylammonium, Bu_4N^+; and tetrapentylammonium, Am_4N^+, were from Tokyo Kasei Kogyo, and were dissolved in water to make individual 0.2 M stock solutions. Two series of migrating solutions were prepared, depending on the ionic strength (I), controlled or not. Since the electrophoretic mobilities of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ are more readily affected by changes in the ionic strength,[29] their associations with the tetraalkylammonium ions were performed under constant ionic strength ($I = 31$ mM) with NaCl, where the maximum concentration of tetraalkylammonium ions was 21 mM. The other set of migrating solutions consisted of a series of solutions containing a maximum of 35 mM tetraalkylammonium ion, and was used to examine the ion-association reactions for other anions (Br^-, $NO_3{}^-$, SCN^-, $S_2O_3{}^{2-}$, $S_4O_6{}^{2-}$, and $[Co(NO_2)_6]^{3-}$).

Measurements of Electrophoretic Mobility. After the capillary was filled with the migrating solution by applying a pressure to an inlet buffer vial, a sample solution containing analyte anions was hydrodynamically introduced into the capillary (50 mbar for 3 s). A potential of −10 kV was applied, and the analyte anions were detected by a diode array detector at a 220 nm channel. The capillary was flushed with the corresponding migrating solutions for 3 min between successive runs. Three replicate measurements were made with a migrating solution to obtain an effective electrophoretic mobility of anions, μ_{eff}. A series of concentrations of quaternary ammonium salt were examined to investigate the mobility change along with the ion-association equilibrium, while keeping the concentration of the acetate buffer constant.

Since ordinary fused-silica capillary was used for the mobility measurements, the simultaneous detection of the electroosmotic flow and the analyte anions was quite difficult; therefore, the William and Vigh method[30] was adopted. The electrophoretic mobilities of the inorganic anions were measured by both single separation (double injection) and the improved double-separation (triple injection) modes of the William–Vigh method.[24,30] The double-separation mode was used exclusively for the mobility measurement of hexacyanoferrate(II) and hexacyanoferrate(III) ions, while both modes were used for other anions. Since the application of a voltage for longer time intervals leads to an improved reproducibility of the results, this approach facilitated reliable measurements of the electrophoretic mobility of such anions as possessing large mobility without a long capillary.

Results and Discussion

Effect of the Acetonitrile Composition on the Effective Electrophoretic Mobility of Anions and the Ion-Association Constants. When one measures the electrophoretic mobility and chemical equilibrium, the composition of the migrating solution sometimes affects the equilibrium of interest. In the present study, different concentrations of acetate buffer (5 mM and 10 mM) slightly affected the electrophoretic mobility of the anions, or changes in the electrophoretic mobility. Similarly, NaCl added to control the ionic strength slightly affected it.

Figure 1 shows the changes in the electrophoretic mobility of the anions with increasing concentrations of Bu_4N^+ at different acetonitrile compositions. Except for hexacyanoferrate(II), hexacyanoferrate(III), nitrate, and hexanitrocobaltate(III) ions, the migration order of the anions was unchanged. Along with an increasing amount of acetonitrile, the migration order of hexacyanoferrate(II) and hexacyanoferrate(III) ions was reversed, which indicated that the association property of hexacyanoferrate(II) and hexacyanoferrate(III) ions with Bu_4N^+ was reversed. A reversal of the migration order is also noted concerning the closely migrating hexanitrocobaltate(III) and nitrate ions. It can be pointed out that the use of the acetonitrile as a buffer additive uniformly alters the electrophoretic mobility of most anions, which is known.

A 1:1 ion associate is supposed to be formed between a cation, C^{n+}, and an anion, A^{m-}. $C^{n+} + A^{m-} \rightleftharpoons CA^{(n-m)+}$, with its equilibrium, $K_{ass} = [CA^{(n-m)+}]/[C^{n+}][A^{m-}]$, where K_{ass} is an ion-association constant.

The effective electrophoretic mobility of an anion, μ_{eff}, at equilibrium is given by

$$\mu_{eff} = \mu_A/(1 + K_{ass}[C^{n+}]) + K_{ass}[C^{n+}]\mu_{CA}/(1 + K_{ass}[C^{n+}]), \tag{1}$$

where μ_A is the electrophoretic mobility of an anion, A^{m-}, and μ_{CA} is that of the ion-associate, $CA^{(n-m)+}$.

When the ion associate is formed between equally charged cationic and anionic species, Eq. 1 is simplified as

$$\mu_{eff} = \mu_A/(1 + K_{ass}[C^{n+}]). \tag{2}$$

Eqs. 1 and 2 were applied to the experimentally obtained effective electrophoretic mobility under different concentrations of tetraalkylammonium ions by a non-linear least-squares analysis, and the K_{ass} values, as well as the μ_A values, were determined (Table 1). The solid curves in Fig. 1 are simulated curves using the K_{ass} and μ_A values. The simulated results agreed well with the experimental data; therefore, side reactions, such as ion association between tetraalkylammonium and chloride ions, are considered to be negligible. Increases in K_{ass} with increasing bulkiness of the pairing cation from Me_4N^+ to Am_4N^+ were also observed, consistent with earlier observations.[24,33] Similarly, hexacyanoferrate(III) ion showed the strongest interaction with most cations, while Br^- and $NO_3{}^-$ showed weak interactions. The hexanitrocobaltate(III) ion gave small K_{ass} values compared to the hexacyanoferrate(III) ion, although both ions are trivalent and their ionic diameter should be close. As can be noted concerning the μ_A values, $[Co(NO_2)_6]^{3-}$ is more solvated than $[Fe(CN)_6]^{3-}$, and the obtained K_{ass} value would be small.

Because the acetonitrile composition in a migrating solution is increased, there is a small change in the electrophoretic mobility of most anions, μ_A, as summarized in Table 2. The change in the electrophoretic mobility is evidently smaller than that in aqueous-ethanol media.[24] Acetonitrile has low viscosity compared to other solvents, such as water, ethanol, or dioxane,

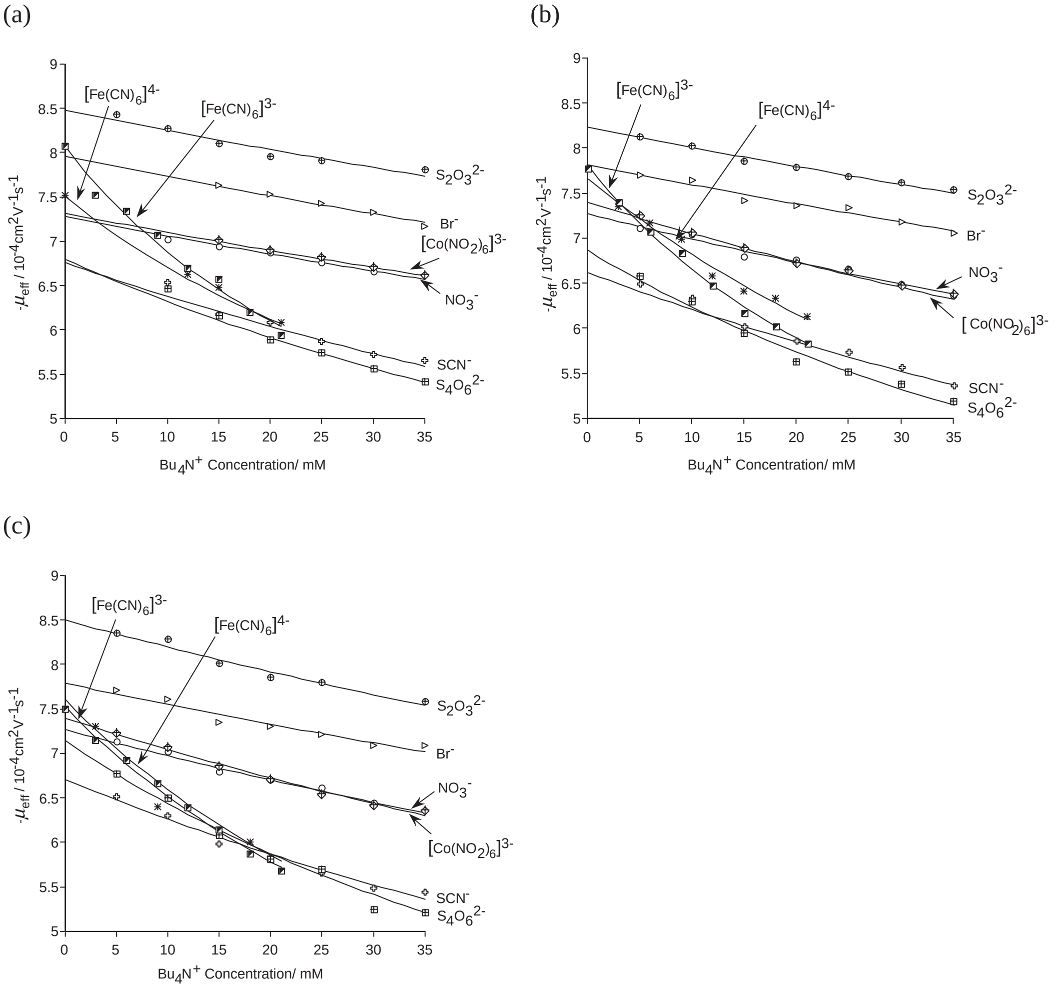

Fig. 1. Changes in electrophoretic mobility of anions along with ion association with tetrabutylammonium (Bu_4N^+) ion at different acetonitrile compositions in the migrating buffer. Acetonitrile composition: (a) 0%, (b) 31.1%, and (c) 62.2% (m/m).

and therefore its effect on the electrophoretic mobility may small. Nitrate and hexanitrocobaltate(III) ions showed a slightly higher mobility at a larger acetonitrile content. An increase in the electrophoretic mobility of anions with increasing acetonitrile composition was also observed by Sarmini and Kenndler.[16] The electrophoretic mobility of hexacyanoferrate(II) ion is less affected by a change in the acetonitrile composition than that of the hexacyanoferrate(III) ion. This behavior contradicts predictions made by the Hubbard–Onsager equation and empirical studies on dielectric friction,[31,32] which maintain that highly charged species are more affected by dielectric friction than those with lower charge. The K_{ass} values determined in this study (aqueous-acetonitrile) are comparable to aqueous-ethanol media,[24] with a few exceptions. However, the K_{ass} values in aqueous-acetonitrile are smaller than those obtained in aqueous-dioxane media.

Evaluation of K_{ass} through the Gibbs Free Energy of Transfer. Kalidas et al. reviewed the fundamentals of the Gibbs free energy of transfer (ΔG_t°) and its critical evaluation for single cations from water to various mixed organic-aqueous solutions.[27] Porras et al. used the concept of the Gibbs free energy of transfer to explain the decrease in the association constant between β-cyclodextrin and benzoate ion in aqueous-methanol and aqueous-acetonitrile mixed solvents.[28]

For equilibrium of the 1:1 association reaction, $C^{n+} + A^{m-} \rightleftharpoons CA^{(n-m)+}$, the reaction is dominated by the stability and instability of the reactants (cation and/or anion) and the product (ion associate). Positive values of the Gibbs free energy by a change in the solvent indicate that the product in water is more stable relative to a mixed solution, while the negative values of the product is more stable in a mixed organic-water solution than in water.

The Gibbs free energy of transfer was considered in this study on the tetraalkylammonium ions and Br^- in aqueous-acetonitrile and aqueous-ethanol mixed solutions from water as the solvent. The Gibbs free energy of transfer for tetraalkylammonium ions corresponding to the experimental acetonitrile and ethanol compositions was thus discussed under (m/m) solvent fractions by interpolation of the data contained in a review by Kalidas et al.[27] An interpolation of data published by Marcus for the Gibbs free energy of transfer gave energy values for Br^- in aqueous-acetonitrile[34] and aqueous-ethanol[35] media. The Gibbs free energy of transfer of given tetraalkylammonium and bromide ions was computed by

$$\ln {}_{m}\gamma_i = \Delta G_t^\circ/RT = ({}_{S1}G_i^\circ - {}_{S2}G_i^\circ)/RT, \tag{3}$$

Table 1. Logarithmic Values of K_{ass} between Tetraalkylammonium Ions and Inorganic Anions Determined at 25 °C and Different Acetonitrile Composition

Anion	Me_4N^+/% (m/m) acetonitrile					Et_4N^+/% (m/m) acetonitrile				
	0	15.5	31.1	46.7	62.2	0	15.5	31.1	46.7	62.2
$[Fe(CN)_6]^{4-}$	1.18 ± 0.05	1.30 ± 0.10	1.20 ± 0.10	1.29 ± 0.06	1.06 ± 0.06	1.04 ± 0.11	1.16 ± 0.11	0.99 ± 0.12	1.08 ± 0.10	1.33 ± 0.18
$[Fe(CN)_6]^{3-}$	1.25 ± 0.07	1.40 ± 0.13	1.20 ± 0.11	1.40 ± 0.09	1.11 ± 0.17	1.21 ± 0.13	1.13 ± 0.06	1.08 ± 0.13	1.04 ± 0.06	1.15 ± 0.14
$[Co(NO_2)_6]^{3-}$	0.26 ± 0.07	0.44 ± 0.10	0.48 ± 0.16	0.40 ± 0.10	0.41 ± 0.11	0.46 ± 0.03	0.30 ± 0.17	0.32 ± 0.12	0.54 ± 0.17	0.79 ± 0.12
$S_4O_6{}^{2-}$	0.61 ± 0.10	0.61 ± 0.04	0.91 ± 0.13	1.18 ± 0.10	0.91 ± 0.06	0.70 ± 0.04	0.61 ± 0.09	0.96 ± 0.06	0.87 ± 0.10	0.78 ± 0.06
$S_2O_3{}^{2-}$	0.41 ± 0.10	0.25 ± 0.03	0.56 ± 0.15	0.70 ± 0.12	0.70 ± 0.14	0.27 ± 0.07	0.35 ± 0.12	0.34 ± 0.08	0.47 ± 0.12	0.43 ± 0.08
Br^-	0.33 ± 0.12	0.24 ± 0.04	0.37 ± 0.13	0.25 ± 0.16	0.21 ± 0.13	0.20 ± 0.05	0.10 ± 0.17	0.20 ± 0.14	0.09 ± 0.11	0.29 ± 0.12
$NO_3{}^-$	0.34 ± 0.08	0.32 ± 0.11	0.37 ± 0.16	0.39 ± 0.14	0.31 ± 0.08	0.22 ± 0.10	0.29 ± 0.07	0.30 ± 0.11	0.29 ± 0.13	0.42 ± 0.08
SCN^-	0.56 ± 0.05	0.29 ± 0.14	0.48 ± 0.06	0.54 ± 0.13	0.43 ± 0.06	0.33 ± 0.02	0.43 ± 0.05	0.51 ± 0.04	0.39 ± 0.11	0.51 ± 0.13

Anion	Pr_4N^+ % (m/m) acetonitrile					Bu_4N^+ % (m/m) acetonitrile				
	0	15.5	31.1	46.7	62.2	0	15.5	31.1	46.7	62.2
$[Fe(CN)_6]^{4-}$	1.29 ± 0.11	1.11 ± 0.08	1.38 ± 0.08	1.46 ± 0.09	1.21 ± 0.07	1.29 ± 0.08	1.12 ± 0.01	1.13 ± 0.09	1.17 ± 0.07	1.26 ± 0.05
$[Fe(CN)_6]^{3-}$	1.42 ± 0.07	1.44 ± 0.13	1.25 ± 0.18	1.33 ± 0.05	1.40 ± 0.09	1.42 ± 0.10	1.28 ± 0.06	1.41 ± 0.06	1.31 ± 0.07	1.28 ± 0.06
$[Co(NO_2)_6]^{3-}$	0.60 ± 0.09	0.65 ± 0.09	0.63 ± 0.12	0.95 ± 0.16	0.73 ± 0.12	0.52 ± 0.18	0.65 ± 0.05	0.74 ± 0.10	0.80 ± 0.11	0.74 ± 0.06
$S_4O_6{}^{2-}$	0.95 ± 0.01	1.01 ± 0.05	1.00 ± 0.04	1.20 ± 0.17	1.08 ± 0.09	0.96 ± 0.04	0.98 ± 0.01	1.09 ± 0.07	1.16 ± 0.10	1.12 ± 0.06
$S_2O_3{}^{2-}$	0.52 ± 0.05	0.47 ± 0.25	0.41 ± 0.13	0.61 ± 0.18	0.57 ± 0.14	0.50 ± 0.12	0.32 ± 0.08	0.45 ± 0.08	0.62 ± 0.24	0.62 ± 0.11
Br^-	0.32 ± 0.08	0.30 ± 0.04	0.57 ± 0.09	0.41 ± 0.10	0.54 ± 0.17	0.47 ± 0.03	0.48 ± 0.07	0.47 ± 0.10	0.49 ± 0.10	0.47 ± 0.13
NO_{3-}	0.43 ± 0.05	0.37 ± 0.04	0.62 ± 0.10	0.49 ± 0.11	0.61 ± 0.17	0.49 ± 0.03	0.54 ± 0.08	0.60 ± 0.09	0.52 ± 0.24	0.64 ± 0.08
SCN^-	0.65 ± 0.04	0.71 ± 0.02	0.81 ± 0.08	0.74 ± 0.10	0.76 ± 0.13	0.77 ± 0.05	0.84 ± 0.03	0.82 ± 0.04	0.61 ± 0.06	0.85 ± 0.08

Anion	Am_4N^+ % (m/m) acetonitrile				
	0	15.5	31.1	46.7	62.2
$[Fe(CN)_6]^4$	1.28 ± 0.13	1.27 ± 0.10	1.29 ± 0.10	1.30 ± 0.10	1.31 ± 0.06
$[Fe(CN)_6]^{3-}$	1.31 ± 0.10	1.29 ± 0.08	1.23 ± 0.14	1.42 ± 0.10	1.20 ± 0.13
$[Co(NO_2)_6]^{3-}$	0.65 ± 0.05	0.67 ± 0.02	0.84 ± 0.11	0.74 ± 0.10	0.72 ± 0.09
$S_4O_6{}^{2-}$	1.06 ± 0.03	1.14 ± 0.03	1.11 ± 0.05	1.27 ± 0.05	1.17 ± 0.05
$S_2O_3{}^{2-}$	0.40 ± 0.16	0.45 ± 0.09	0.58 ± 0.10	0.69 ± 0.12	0.49 ± 0.11
Br^-	0.36 ± 0.04	0.36 ± 0.05	0.63 ± 0.09	0.62 ± 0.12	0.54 ± 0.09
$NO_3{}^-$	0.42 ± 0.05	0.58 ± 0.05	0.72 ± 0.07	0.62 ± 0.11	0.65 ± 0.06
SCN^-	0.91 ± 0.04	0.90 ± 0.06	0.99 ± 0.04	1.00 ± 0.07	1.00 ± 0.04

K_{ass} determined by Eq. 1 or 2, error: 3σ

Me_4N^+ = Tetramethylammonium ion

Et_4N^+ = Tetraethylammonium ion

Pr_4N_+ = Tetrapropylammonium ion

Bu_4N^+ = Tetrabutylammonium ion

Am_4N^+ = Tetrapentylammonium ion

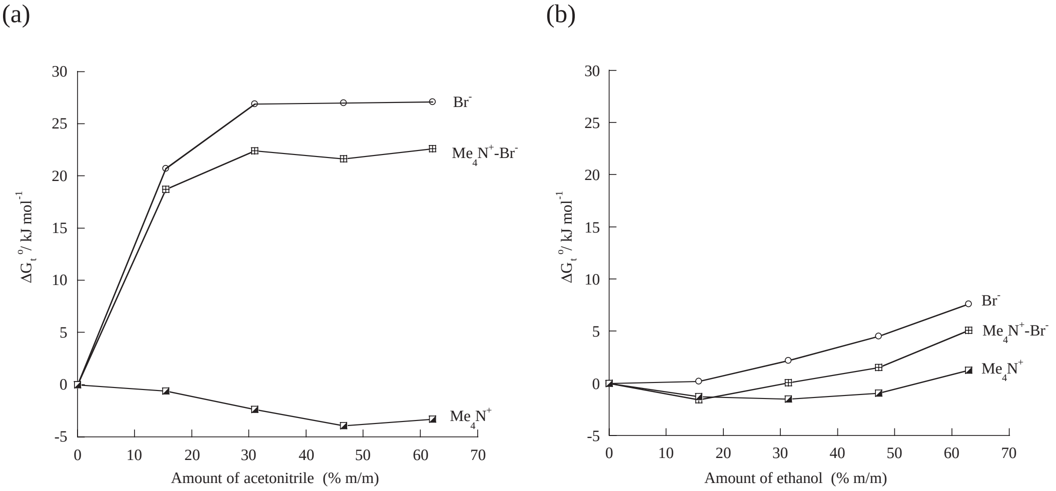

Fig. 2. Standard Gibbs free energy of transfer for Me_4N^+, Me_4N^+-Br^-, and Br^- as a function of aqueous-organic compositions (% m/m). Solvent: (a), aqueous-acetonitrile; (b) aqueous-ethanol.

Table 2. The Electrophoretic Mobility of Anions at Different Acetonitrile Composition

Anion	$-\mu_A/10^{-4}$ cm^2 V^{-1} s^{-1}				
	% (m/m) acetonitrile				
	0	15.5	31.1	46.7	62.2
$Fe(CN)_6{}^{4-}$	7.86	7.68	7.81	7.87	7.88
$Fe(CN)_6{}^{3-}$	8.10	7.84	7.81	7.64	7.52
$Co(NO_2)_6{}^{3-}$	7.35	7.29	7.49	7.50	7.53
$S_4O_6{}^{2-}$	6.86	6.80	6.94	7.07	6.92
$S_2O_3{}^{2-}$	8.42	8.19	8.26	8.33	8.27
Br^-	7.92	7.87	7.97	7.92	7.81
$NO_3{}^-$	7.25	7.28	7.35	7.34	7.26
SCN^-	6.75	6.76	6.92	6.98	6.73

where ΔG_t° is the standard Gibbs free energy of transfer, ${}_{S1}G_i^{\circ}$ is the Gibbs free energy in the standard state in solvent S1 (water), and ${}_{S2}G_i^{\circ}$ is the Gibbs free energy in the standard state in solvent S2 (mixed solution).

Plots of the Gibbs free energy of transfer for the species involved in ion association are shown in Fig. 2. Ion association between Me_4N^+ and Br^- is selected as a typical example. In aqueous-acetonitrile media (Fig. 2a), the addition of acetonitrile stabilizes the Me_4N^+ ion to a small extent. On the other hand, acetonitrile substantially affects the stabilities of Br^- and the ion associate, Me_4N^+-Br^-. Thus, the equilibrium would be dominated by ΔG_t° of Br^- and Me_4N^+-Br^-. As a result, a small increase in K_{ass} is observed for an increased acetonitrile composition, as is summarized in Table 1. While in aqueous-ethanol media (Fig. 2b), ΔG_t° of Br^- increases steadily along with an increase of the ethanol composition, those of Me_4N^+ and Me_4N^+-Br^- decrease to a minimum, followed by an increase. Up to the minimum ΔG_t° for Me_4N^+ and Me_4N^+-Br^-, the combined effect of an increase in the stability of Me_4N^+ and a decrease in the stability of Me_4N^+-Br^-, often outweigh an increase in the instability of Br^-, which results in a decrease in K_{ass}. Beyond the composition showing minimum ΔG_t°, the combined instability of the Me_4N^+ and Br^- outweigh the instability of the Me_4N^+-Br^-. Thus, the K_{ass} values increase in aqueous-ethanol media.

Conclusion

Acetonitrile as a buffer additive did not significantly alter the electrophoretic mobility of the inorganic anions, but slightly decreased. Ion-association constants were determined using the changes in the electrophoretic mobility, and the dielectric constant of the mixed solvents was supposed to have influenced the equilibrium. The K_{ass} values determined in aqueous-acetonitrile were comparable to those obtained in aqueous-ethanol media, but smaller than those in aqueous-dioxane media. According to the Gibbs free energy of transfer, the increasing instability of Br^- caused an increase in the ion-association constants in aqueous-acetonitrile media.

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

References

1 J. L. Miller, M. G. Khaledi, and D. Shea, *Anal. Chem.*, **69**, 1223 (1997).

2 Y. Esaka, K. Yoshimura, M. Goto, and K. Kano, *J. Chromatogr., A*, **822**, 107 (1995).

3 I. E. Valko, H. Sirèn, and M.-L. Riekkola, *J. Microcolumn Sep.*, **11**, 119 (1996).

4 S. P. Porras, M.-L. Riekkola, and E. Kenndler, *Chromatographia*, **53**, 290 (2001).

5 J. Muzikar, T. Van de Goor, B. Gaš, and E. Kenndler, *Electrophoresis*, **23**, 375 (2002).

6 M. Vaher, M. Koel, and M. Kaljurand, *Electrophoresis*, **23**, 426 (2002).

7 S. P. Porras, M.-L. Riekkola, and E. Kenndler, *J. Chromatogr., A*, **924**, 31 (2001).

8 I. R. Kimberly and C. A. Lucy, *Electrophoresis*, **23**, 383 (2002).

9 A. Jouyban, S. C. Grosse, M. W. Coleman, H. K. Chan, E. Kenndler, and B. J. Clark, *Analyst*, **127**, 277 (2002).

10 A. Karbaum and T. Jira, *Electrophoresis*, **20**, 3396 (1999).

11 S. P. Porras, R. Kuldvee, S. Palonen, and M.-L. Riekkola, *J. Chromatogr., A*, **990**, 35 (2003).

12 Y. Marcus, "Ion Properties," Marcel Dekker, New York (1997).

13 K. Izutsu, "Electrochemistry in Nonaqueous Solutions," Wiley-VCH, Weinheim (2002).

14 T. Okada, *Chem. Commun.*, **1996**, 1779.

15 T. Okada, *J. Chromatogr., A*, **771**, 275 (1997).

16 K. Sarmini and E. Kenndler, *J. Chromatogr., A*, **833**, 245 (1998).

17 T. Takayanagi and S. Motomizu, *Chem. Lett.*, **1995**, 593.

18 T. Takayanagi, E. Wada, and S. Motomizu, *Analyst*, **122**, 57 (1997).

19 T. Takayanagi, H. Tanaka, and S. Motomizu, *Anal. Sci.*, **13**, 11 (1997).

20 T. Takayanagi and S. Motomizu, *Anal. Sci.*, **13**, 783 (1997).

21 T. Takayanagi, Y. Ohba, H. Haruki, E. Wada, and S. Motomizu, *Anal. Sci.*, **14**, 311 (1998).

22 T. Takayanagi, N. Ban, H. Takao, N. Nakamura, M. Oshima, and S. Motomizu, *Anal. Sci.*, **15**, 593 (1999).

23 L. C. Manege, T. Takayanagi, M. Oshima, T. Iwachido, and S. Motomizu, *Bull. Chem. Soc. Jpn.*, **72**, 1301 (1999).

24 J. Mbuna, T. Takayanagi, M. Oshima, and S. Motomizu, *Bull. Chem. Soc. Jpn.*, **77**, 1465 (2004).

25 J. Mbuna, T. Takayanagi, M. Oshima, and S. Motomizu, 53rd Japan Society of Analytical Chemistry Annual Meeting, 1st–3th September 2004, p. 84.

26 H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolyte Solutions," Reinhold, New York (1964), p. 70.

27 C. Kalidas, G. Hefter, and Y. Marcus, *Chem. Rev.*, **100**, 819 (2000).

28 S. P. Porras, M.-L. Riekkola, and E. Kenndler, *Electrophoresis*, **23**, 367 (2002).

29 S. Motomizu and T. Takayanagi, *J. Chromatogr., A*, **853**, 63 (1999).

30 B. A. William and G. Vigh, *Anal. Chem.*, **68**, 1174 (1996).

31 I. R. Kimberly and C. A. Lucy, *J. Chromatogr., A*, **964**, 213 (2002).

32 D. Li and C. A. Lucy, *Anal. Chem.*, **73**, 1324 (2001).

33 J. Mbuna, T. Takayanagi, M. Oshima, and S. Motomizu, *J. Chromatogr., A*, **806**, 191 (2004).

34 Y. Marcus, *Pure Appl. Chem.*, **55**, 977 (1983).

35 Y. Marcus, *Pure Appl. Chem.*, **62**, 899 (1990).