Thermodynamic Study of Ion-Association Reactions between Aromatic Anions and Tetrabutylammonium Ion in an Aqueous Solution

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A temperature effect on ion-association reactions in an aqueous solution has been studied between nine kinds of aromatic anions and tetrabutylammonium ion (TBA^+). The ion-association constants (K_{ass}) were determined by analyzing the change in the electrophoretic mobility of anions, which was obtained by capillary zone electrophoresis, by a non-linear least-squares method. The mobility of the analyte anions decreased with increasing the amount of TBA^+ added in migrating solutions. The thermodynamic parameters in the reaction were obtained from the change in the K_{ass} values by the change in temperature. The values of the entropy change (ΔS°) were positive in the ion-association reactions of all of the anions examined, being in the ranges from 5.8 to 46.1 J K^{-1} mol^{-1}; the contribution of $T\Delta S^\circ$ in the examined ion associates to the Gibbs free-energy changes is larger than that of enthalpy changes ($-\Delta H^\circ$), except for phthalate ion. The results suggest that some hydrated water molecules were released in the formation of such hydrophobic ion associates, as well as in the cases of previously reported inorganic ion associates.

Keywords Ion association, thermodynamic parameters, capillary zone electrophoresis, aromatic anions, tetrabutylammonium ion

Capillary zone electrophoresis (CZE) is very useful for the separation and determination of various substances. Several separation modes have been proposed so far for improving the separation and detection of analytes.[1-3] The ion-association mode (IA mode), which involves ion-ion interactions in an aqueous solution, is one of such separation modes. The mode has been utilized for the separation of position isomers, such as naphthalenesulfonates[4,5] and chelate anions[6,7], by using a cationic polymer[4] and quaternary ammonium ions[5-7], respectively.

The CZE technique also offers many advantages in analytical and physical chemistry. The authors have aimed at utilizing the electrophoretic mobility of ions for analyzing the chemical equilibria of the ion-association reaction between a hydrophobic ion and its pairing ion under such experimental conditions that the ions of interest are present at low-concentration levels and their pairing ions at higher concentration levels. By using the change in mobility, the authors succeeded in analyzing the ion-association equilibria by a slope method[8] and a non-linear least-squares method.[9,10] In the ion association between organic anions and quaternary ammonium ions in aqueous solutions, the hydrophobicity of pairing ions has been found to play an important role in an increase of the ion associability; one methylene group can contribute to an increase in the log K_{ass} value by about 0.06 logarithmic unit[9], where K_{ass} is an ion-association constant.

One of the other advantages in the CZE technique is the utilization of a temperature-controlling apparatus, which enables thermodynamic studies. Concerned in thermodynamic studies of ion-association reactions in an aqueous solution, it has been carried out so far by using a conductometric method and calorimetric method.[11-13] By using the conductometric method, a number of ion-association reactions both in aqueous and organic solutions containing inorganic electrolytes have been analyzed since Bjerrum first reported a theoretical aspect of ion association.[14] However, organic ion associates are less soluble in water, and therefore the weak interaction between hydrophobic ions in aqueous solutions has never been analyzed by the conventional conductometric method.

In this study, thermodynamic parameters in ion-association reactions in an aqueous solution were determined on the basis of the ion-association constants obtained in the temperature ranges from 20 to 50° C, and were compared with those classically obtained for inorganic ion associates.

Experimental

Apparatus

A Beckman P/ACE System 5500B with a P/ACE

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Diode Array Detector was used as a capillary electrophoresis system (CE). A fused-silica capillary, attached to the CE, was purchased from GL Sciences and prepared in a similar manner as in a previous work.[9] The size of the capillary was 57 cm in total length, a 50 cm in effective length to the detector, and a 75 μm in inner diameter. The capillary was placed in a temperature-controlling apparatus with a circulating liquid coolant. The control of CE, treatment of electropherograms and analysis of the mobility were carried out with a program, System Gold ver. 8.10 (Beckman), on a work station (IBM PS/Value Point 466DX2/Si).

Reagents

The aqueous solutions of organic anions of interest (called analyte anions) were prepared by using their sodium salts or acids (Tokyo Kasei). The reagents were sodium naphthalene-1-sulfonate (1-NS), sodium naphthalene-2-sulfonate (2-NS), disodium naphthalene-1,5-disulfonate (1,5-NDS), disodium naphthalene-2,6-disulfonate (2,6-NDS), 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). They were used without further purification. Carboxylic compounds were dissolved in water with two equivalent amounts of sodium hydroxide. Hereinafter, the anions are represented as A^{n-}, where "$n-$" is a negative charge, -1 or -2.

A buffer component in migrating solutions, sodium tetraborate (borax), was purchased from Wako, tetrabutylammonium bromide ($TBA^+ \cdot Br^-$) being purchased from Tokyo Kasei. Water used was a deionized and distilled one.

Procedure for measuring the electrophoretic mobility of aromatic anions by capillary zone electrophoresis (CZE)

Migrating solutions consisted of 1.0×10^{-2} mol dm^{-3} borax (pH 9.2) and various amounts of TBA^+ ($0-2.0\times10^{-2}$ mol dm^{-3}) as an ion-pairing reagent. A sample solution containing nine kinds or less of 2×10^{-5} mol dm^{-3} analyte anions (organic anions) and 3%(v/v) ethanol as a marker of electroosmotic flow (EOF) was injected from the anodic end of the capillary for 3 s by using a pressure apparatus. A voltage of 15 kV was then applied and CZE separation of the analyte anions was started. The analyte anions were detected photometrically at 230 nm with a 6 nm bandpath. Throughout the experiments, the temperature of the capillary was kept at a certain value with the apparatus in the ranges from 20°C to 50°C within a deviation of ±0.1°C. More than three measurements were carried out to obtain the mean values of the electrophoretic mobility of the analyte anions. The deviation of the migration times was less than 0.1 min. The electrophoretic mobility of the analyte anions was calculated by using the migration times and the velocity of EOF according to an ordinary manner.

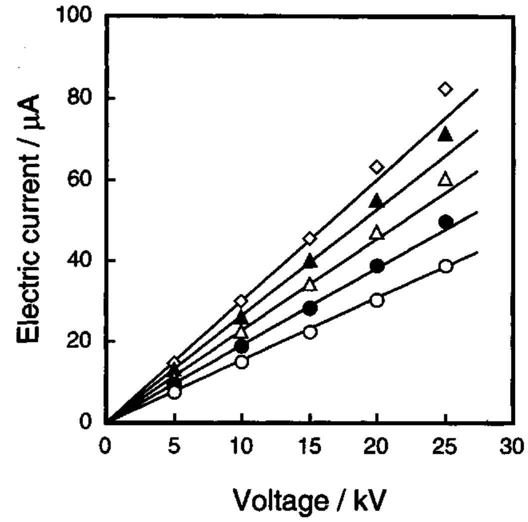

Fig. 1 Electric current in a capillary tube as a function of applied voltage. Migrating solution: 1×10^{-2} mol dm^{-3} borax $+(0-2.0)\times10^{-2}$ mol dm^{-3} $TBA^+ \cdot Br^-$. Capillary temperature was set at 35°C. $[TBA^+ \cdot Br^-]/10^{-2}$ mol dm^{-3}: ○, 0; ●, 0.5; △, 1.0; ▲, 1.5; ◇, 2.0.

Results and Discussion

Temperature control of the capillary

It is necessary for a discussion of thermodynamics to evaluate the cooling capacity of the apparatus and the accuracy of the temperature control. In this work, the authors used a CZE system equipped with a temperature-controlling apparatus with a circulating liquid coolant, instead of air, for the purpose of accurate temperature control. Relationships between the applied voltage and the electric current were examined; the obtained results are shown in Fig. 1. Though the electric-resistance, inverse of the slope, gradually decreased with increasing voltages and increasing TBA^+ concentrations, the linearity of the plots was good over the $TBA^+ \cdot Br^-$ concentrations examined, when the applied voltage was less than 15 kV. The deviations from the lines at higher voltages and higher concentration ranges of $TBA^+ \cdot Br^-$ seem to have been caused by an increase in the electrophoretic mobility of ions, which resulted from an increase in the temperature of the migrating solutions. In further experiments in this study, an applied voltage of 15 kV was adopted for depressing the heat generation in the migrating solutions and keeping the temperature at the set values of the cooling apparatus.

Electric currents were also examined at an applied voltage of 15 kV by varying $TBA^+ \cdot Br^-$ concentration in the migrating solution and the temperature. The electric current increased linearly with an increase in the concentration of $TBA^+ \cdot Br^-$ at all examined temperature ranges from 20 to 50°C. The effect of temperature on the electric current, introduced mainly by the migrating buffer components, was calculated to be (2.15±0.05)% increase per one degree (standard temperature: 25°C).

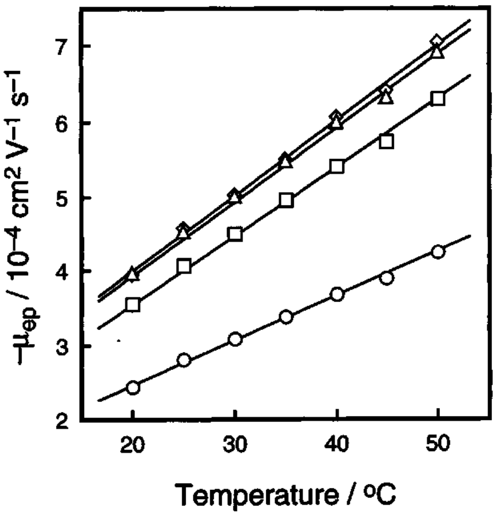

Fig. 2 Effect of set capillary temperature on electrophoretic mobility of analyte anions. Sample: 2×10^{-5} mol dm^{-3} of nine kinds of anions. Migrating solution: 1.0×10^{-2} mol dm^{-3} borax. CE conditions: applied voltage, 15 kV; detection wavelength, 230 nm; injection period, 3.0 s. ○, 1-NS and 2-NS; △, 1,5-NDS and 2,6-NDS; □, 2,3-NDC and 2,6-NDC; ◇, PH, i-PH and t-PH.

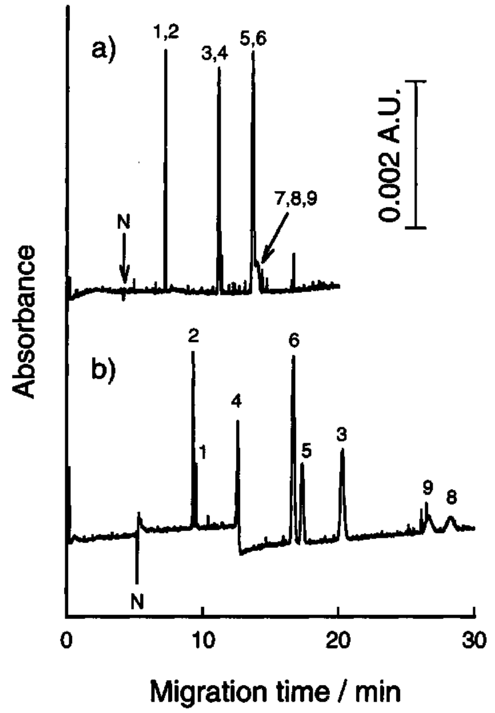

Fig. 3 Typical electropherograms of analyte anions. Sample solution and CE conditions are same as in Fig. 2. Capillary temperature was set at 35° C. Migrating solution: a), 1.0×10^{-2} mol dm^{-3} borax; b), 1.0×10^{-2} mol dm^{-3} borax+2.0×10^{-2} mol dm^{-3} $TBA^+\cdot Br^-$. Analyte anions: 1, 1-NS; 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. N: neutral substance (ethanol).

From the results, it is concluded that the generated Joule's heat is within the capacity of the cooling apparatus and the set temperature of the migrating solution is well maintained under the present experimental conditions.

Effect of temperature on the electrophoretic mobility of analyte anions

To investigate the stability of the capillary temperature, an approach concerning the electrophoretic mobility of analyte anions was also used; the results are shown in Table 1 and Fig. 2. The electrophoretic mobility of analyte anions ($-\mu_{ep}$) increased linearly along with an increase in the temperature by about $(2.15\pm0.05)\%$ per one degree (standard temperature: 25° C). Such an increase is almost identical with the increase in the electric currents, which also suggests that the temperature of the migrating solution can be kept at the set temperature.

Figure 2 also indicates that the position isomers can not be separated only by changing the temperature. In fact, the position isomers could not be separated by a borax buffer used as a migrating solution without $TBA^+\cdot Br^-$ over the set temperature ranges from 20 to 50° C.

Separation of position isomers based on an ion-association reaction in an aqueous solution

Electropherograms of nine kinds of analyte anions are shown in Fig. 3. In a simple migrating solution of the borax buffer, the isomers of aromatic sulfonate ions and aromatic carboxylate ions could not be separated, as shown in the electropherogram of Fig. 3(a). This is because each isomer possesses the same molecular mass and charge, and each isomer seems to be hydrated in a similar manner. The isomers, however, can be well separated by the addition of $TBA^+\cdot Br^-$ in the migrating solution, as shown in Fig. 3(b). The migration order of each analyte anion and the separation behavior agreed well with previous studies[8,9], examined by a different apparatus.

Mobility change of aromatic anions by the addition of $TBA^+\cdot Br^-$ in the migrating solution

Apparent electrophoretic mobility of anions under a certain condition ($-\mu_{ep}'$) decreased from its electrophoretic mobility ($-\mu_{ep}$) with increasing the concentration of TBA^+ in the migrating solution. As examples, the results obtained in 1,5-NDS and 2,3-NDC are shown in Fig. 4(a) and (b), respectively. The decreases in the $-\mu_{ep}'$ values can be attributed to the formation of ion associates between TBA^+ and the analyte anions, which causes a decrease in the apparent charge of the analyte anion and an increase in its apparent molecular mass. The extent of the decrease in $-\mu_{ep}'$ was larger in 1,5-NDS than in 2,3-NDC, which indicates that the order of the ion associability of the two analyte ions with TBA^+ is 1,5-NDS>2,3-NDC. The extent of the decrease in the $-\mu_{ep}'$ values of the analyte anions was enhanced in all of the analyte anions with increasing the temperature, as shown in Fig. 4. These results indicate that the higher

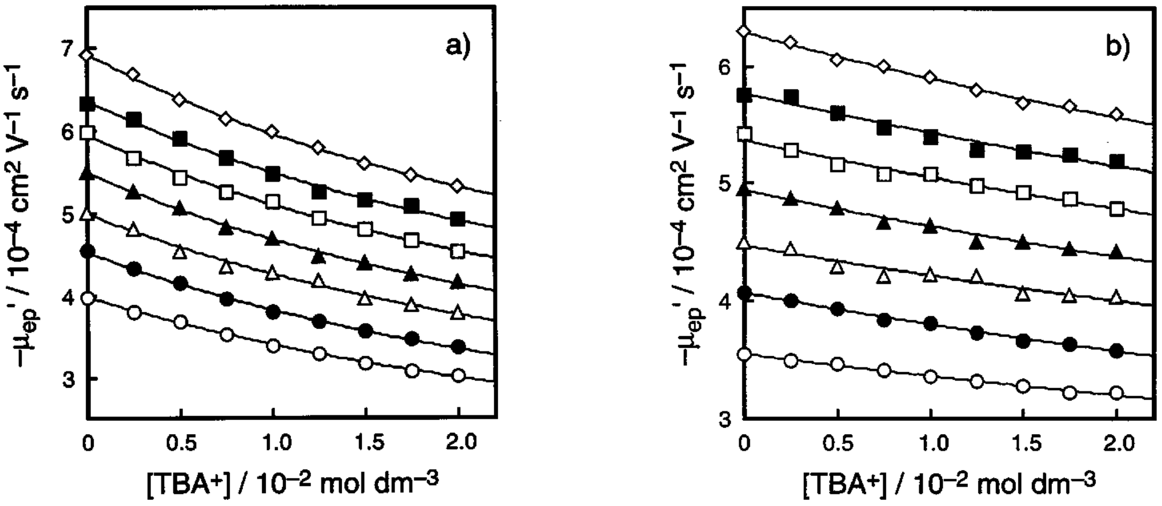

Fig. 4 Change in electrophoretic mobility of analyte anions as a function of [TBA$^+$]. Sample solution is the same as in Fig. 2. Migrating solution: 1.0×10^{-2} mol dm^{-3} borax (pH 9.2)+(0–2.0)$\times10^{-2}$ mol dm^{-3} TBA$^+\cdot$Br$^-$. CE conditions, except for temperature, are the same as in Fig. 2. Set capillary temperature: ○, 20°C; ●, 25°C; △, 30°C; ▲, 35°C; □, 40°C; ■, 45°C; ◇, 50°C. a) 1,5-NDS; b) 2,3-NDC.

the temperature is, the more the analyte anions can react with TBA$^+$.

Determination of ion association constants

The authors have already reported a reliable calculation method for analyzing ion association equilibria by using a non-linear least-squares (NLLS) method;[9] the NLLS method was also used in this study.

The 1 : 1 ion associates treated in this work are presented in the reaction

$$\mathrm{TBA^+ + A^{n-} \overset{K_{ass}}{\rightleftharpoons} TBA^+\cdot A^{n-}} \qquad (1)$$

The apparent electrophoretic mobility of analyte anions ($-\mu_{ep}'$) can be related to the TBA$^+$ concentration as

$$-\mu_{ep}' = \frac{1}{1+K_{ass}[\mathrm{TBA^+}]}(-\mu_{ep}) + \frac{K_{ass}[\mathrm{TBA^+}]}{1+K_{ass}[\mathrm{TBA^+}]}(-\mu_{epIA}), \qquad (2)$$

where K_{ass} is the ion-association constant and $-\mu_{epIA}$ is the electrophoretic mobility of a 1 : 1 ion associate, respectively. After a series of the set of experimentally obtained value of $-\mu_{ep}'$ and [TBA$^+$] were input to Eq. (2), the values of $-\mu_{ep}$, $-\mu_{epIA}$ and K_{ass} were optimized by a NLLS method. The values of $-\mu_{ep}$, $-\mu_{epIA}$ and K_{ass} obtained over the temperature ranges from 20°C to 50°C are summarized in Tables 1, 2 and 3, respectively. The optimized values of $-\mu_{ep}$ were almost identical with those of the experimental values, and those of $-\mu_{epIA}$ were very close to the theoretical values, 0 for monovalent anions and $-\mu_{ep}\times(Z+z)/(M+m)^{2/3}$ for divalent anions, where Z and z are the charges of TBA$^+$ and A^{2-}, and M and m are the molecular mass of TBA$^+$ and A^{2-}, respectively. The solid-line curves in Fig. 4, simulation of $-\mu_{ep}'$ using Eq. (2) and optimized $-\mu_{ep}$, $-\mu_{epIA}$, and K_{ass} values, agreed well with the experimental results, which suggests that the ion-association reaction considered in this study is valid and that the values of K_{ass} can be preferably used for discussing the thermodynamic parameters.

Thermodynamic parameters related to ion-association reactions

The ion-association constants obtained in this work were treated by using the usual thermodynamic functions,

$$-\ln K_{ass} = \Delta H^\circ/RT - \Delta S^\circ/R, \qquad (3)$$

where ΔH° and ΔS° are the enthalpy and entropy changes under the standard condition, respectively. Plots using Eq. (3) are shown in Fig. 5. The enthalpy and entropy changes were obtained from the slopes and the intercepts of the ordinate of the plots, respectively. The thermodynamic parameters obtained in this work are also summarized in Table 3. As can be seen in Table 3, the entropy changes obtained in this study are all positive, and are in the ranges from 5.8 to 46.1 J K^{-1} mol^{-1}. The relationships between $T\Delta S^\circ$ and ΔH° at 298 K are shown in Fig. 6. Previously reported thermodynamic parameters for inorganic ion associates[11,12,15] are also shown in Fig. 6 with filled symbols. The plots obtained in this study show a linear relationship, with a slope of 0.8 and a minus intercept of the ordinate. Figure 6 also indicates the area where the contribution of entropy change ($T\Delta S^\circ$) to the Gibbs free-energy change (ΔG°) is larger than that of enthalpy change (ΔH°); the

Table 1 Experimentally obtained and calculated values of electrophoretic mobility ($-\mu_{ep}$) of aromatic anions

Temperature/ °C	$-\mu_{ep}/10^{-4}$ cm^2 V^{-1} s^{-1}								
	1-NS	2-NS	1,5-NDS	2,6-NDS	2,3-NDC	2,6-NDC	PH	i-PH	t-PH
20	2.41±0.04	2.43±0.03	3.98±0.03	3.99±0.05	3.55±0.03	3.56±0.03	—	3.98±0.07	3.97±0.05
	(2.43)	(2.43)	(3.97)	(3.97)	(3.55)	(3.55)	(3.95)	(3.95)	(3.95)
25	2.79±0.07	2.81±0.04	4.52±0.05	4.54±0.03	4.07±0.05	4.08±0.04	4.56±0.08	4.57±0.04	4.54±0.06
	(2.81)	(2.81)	(4.53)	(4.53)	(4.07)	(4.07)	(4.57)	(4.57)	(4.57)
30	3.04±0.13	3.05±0.10	4.98±0.13	4.99±0.13	4.47±0.12	4.49±0.13	5.04±0.09	5.02±0.13	5.01±0.14
	(3.08)	(3.08)	(5.00)	(5.00)	(4.50)	(4.50)	(5.03)	(5.03)	(5.03)
35	3.34±0.09	3.36±0.05	5.48±0.08	5.48±0.09	4.94±0.10	4.96±0.07	5.52±0.08	5.52±0.11	5.51±0.13
	(3.38)	(3.38)	(5.48)	(5.58)	(4.96)	(4.96)	(5.50)	(5.50)	(5.50)
40	3.64±0.10	3.65±0.10	5.94±0.10	5.94±0.10	5.36±0.09	5.40±0.12	6.01±0.10	6.01±0.09	5.99±0.11
	(3.68)	(3.68)	(5.98)	(5.98)	(5.41)	(5.41)	(6.05)	(6.05)	(6.05)
45	3.89±0.08	3.90±0.08	6.35±0.12	6.35±0.11	5.76±0.12	5.78±0.17	6.42±0.13	6.43±0.17	6.41±0.15
	(3.89)	(3.89)	(6.32)	(6.32)	(5.74)	(5.74)	(6.41)	(6.41)	(6.41)
50	4.24±0.09	4.26±0.11	6.93±0.08	6.93±0.12	6.29±0.06	6.32±0.11	7.02±0.15	7.04±0.10	7.02±0.10
	(4.25)	(4.25)	(6.91)	(6.91)	(6.30)	(6.30)	(7.04)	(7.04)	(7.04)

Error: 3σ. Values in parentheses are experimentally obtained values. —: deviation was too large to calculate $-\mu_{ep}$ value.

Table 2 Calculated values of electrophoretic mobility of ion associates ($-\mu_{epIA}$)

Temperature/ °C	$-\mu_{epIA}/10^{-4}$ cm^2 V^{-1} s^{-1}								
	1-NS	2-NS	1,5-NDS	2,6-NDS	2,3-NDC	2,6-NDC	PH	i-PH	t-PH
20	0.05±0.29	0.01±0.16	0.80±0.14	0.83±0.21	0.67±0.41	0.65±0.07	—	0.97±0.64	0.97±0.38
25	0.04±0.41	0.08±0.20	0.90±0.22	0.94±0.12	0.73±0.48	0.72±0.12	0.95±1.33	0.99±0.27	1.01±0.42
30	0.05±0.91	0.04±0.61	1.14±0.50	1.23±0.45	1.01±1.40	1.09±0.38	1.30±1.95	1.29±1.06	1.33±0.97
35	0.02±0.64	0.20±0.29	1.37±0.31	1.42±0.32	1.29±0.91	1.21±0.19	1.54±1.59	1.51±0.85	1.50±0.92
40	0.03±0.69	0.01±0.60	1.72±0.38	1.81±0.33	1.64±0.82	1.61±0.32	1.96±1.82	1.99±0.69	1.98±0.76
45	0.01±0.53	0.01±0.44	1.99±0.47	2.03±0.38	1.90±1.16	1.89±0.47	2.32±2.60	2.36±1.19	2.31±1.06
50	0.01±0.64	0.02±0.67	2.28±0.28	2.27±0.38	2.05±0.55	2.03±0.33	2.51±3.04	2.50±0.67	2.55±0.64

Error: 3σ. —: deviation was too large to calculate $-\mu_{epIA}$ value.

Table 3 Ion association constants of aromatic anions with TBA$^+$ and thermodynamic parameters

Temperature/ °C	log K_{ass}								
	1-NS	2-NS	1,5-NDS	2,6-NDS	2,3-NDC	2,6-NDC	PH	i-PH	t-PH
20	1.10±0.07	1.14±0.03	1.35±0.02	1.38±0.04	0.85±0.08	1.49±0.02	—	0.99±0.12	1.04±0.07
25	1.17±0.08	1.23±0.04	1.38±0.03	1.42±0.02	0.94±0.07	1.51±0.03	0.74±0.21	1.10±0.05	1.12±0.07
30	1.11±0.11	1.22±0.05	1.37±0.08	1.42±0.08	0.90±0.24	1.52±0.07	0.65±0.33	1.05±0.17	1.09±0.16
35	1.10±0.11	1.18±0.05	1.39±0.05	1.43±0.05	0.96±0.14	1.52±0.03	0.70±0.24	1.06±0.12	1.12±0.14
40	1.11±0.10	1.17±0.10	1.40±0.05	1.45±0.05	0.96±0.12	1.55±0.06	0.72±0.28	1.10±0.10	1.12±0.10
45	1.13±0.07	1.19±0.06	1.40±0.07	1.45±0.06	0.98±0.17	1.55±0.08	0.67±0.43	1.09±0.18	1.11±0.15
50	1.11±0.08	1.18±0.09	1.43±0.04	1.47±0.05	1.02±0.06	1.54±0.05	0.69±0.53	1.11±0.08	1.16±0.08
ΔS°/J K^{-1} mol^{-1}	20.1±1.2	24.0±1.5	39.1±0.5	43.2±0.4	46.1±1.2	40.9±0.5	5.8 ±1.5	38.8±1.4	38.5±1.1
ΔH°/kJ mol^{-1}	−0.42±0.36	0.41±0.44	3.86±0.16	4.88±0.16	8.65±0.41	3.66±0.16	−2.32±0.47	5.65±0.44	5.32±0.33

Error: 3σ. —: deviation was too large to calculate K_{ass}.

area consists of two cases: one is that both values of $T\Delta S^\circ$ and ΔH° are positive and $T\Delta S^\circ > \Delta H^\circ$; the other is that $T\Delta S^\circ$ is positive and larger than $-\Delta H^\circ$. All of the reactions except for 1-NS and PH are classified into the former case. Therefore, such ion-association reactions are classified as entropy-driven reactions. Furthermore, 1-NS is classified into the latter case, and the reaction is also classified as an entropy-driven reaction. In the case of PH, on the other hand, $-\Delta H^\circ$ is larger than $T\Delta S^\circ$; thus, it can not be classified as a entropy-driven one.

The obtained thermodynamic parameters were compared with the previously reported ones. Though the data available now are scarce, it can be seen from the plots in Fig. 6 that the thermodynamic parameters of

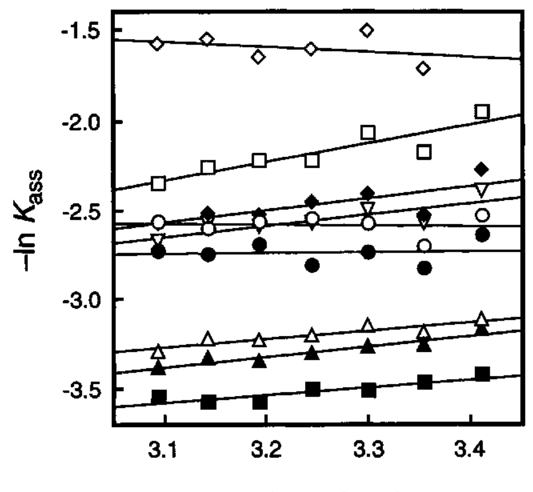

Fig. 5 Plots of $-\ln K_{ass}$ as a function of the inverse of absolute temperature. ○, 1-NS; ●, 2-NS; △, 1,5-NDS; ▲, 2,6-NDS; □, 2,3-NDC; ■, 2,6-NDC; ◇, PH; ◆, i-PH; ▽, t-PH.

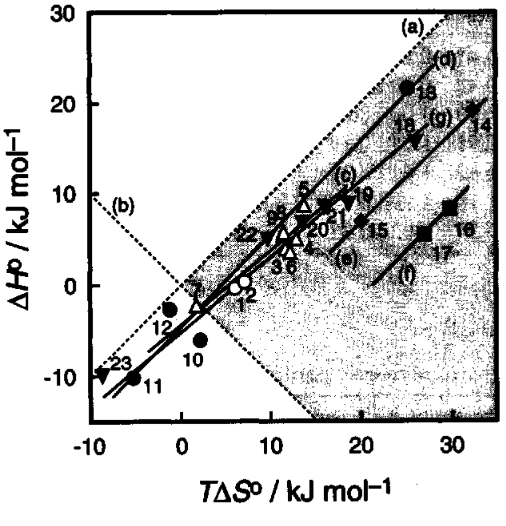

Fig. 6 Plots of ΔH° against $T\Delta S^\circ$ at 298 K. Open symbol: organic ion associate between aromatic anions and TBA$^+$. 1, 1-NS; 2, 2-NS; 3, 1,5-NDS; 4, 2,6-NDS; 5, 2,3-NDC; 6, 2,6-NDC; 7, PH; 8, i-PH; 9, t-PH. Closed symbol: inorganic ion associate. 10, $Tl^+{\cdot}Cl^-$; 11, $Tl^+{\cdot}Br^-$; 12, $Tl^+{\cdot}NO_3^-$; 13, $Ag^+{\cdot}IO_3^-$; 14, $Mg^{2+}{\cdot}SO_4^{2-}$; 15, $Ca^{2+}{\cdot}SO_4^{2-}$; 16, $La^{3+}{\cdot}[Fe(CN)_6]^{3-}$; 17, $La^{3+}{\cdot}[Co(CN)_6]^{3-}$; 18, $[Co(NH_3)_6]^{3+}{\cdot}Cl^-$; 19, $[Co(NH_3)_6]^{3+}{\cdot}Br^-$; 20, $[Co(NH_3)_6]^{3+}{\cdot}I^-$; 21, $[Co(en)_3]^{3+}{\cdot}Br^-$; 22, $[Co(en)_3]^{3+}{\cdot}I^-$; 23, $[Co(en)_3]^{3+}{\cdot}N_3^-$. Type of ion associate: ○ and ●, $C^+{\cdot}A^-$; △, $C^+{\cdot}A^{2-}$; ◆, $C^{2+}{\cdot}A^{2-}$; ■, $C^{3+}{\cdot}A^{3-}$; ▼, $C^{3+}{\cdot}A^-$. Lines were all obtained by a least square method: (a), slope=1.0, the intercept of the ordinate=0 ($\Delta H^\circ = T\Delta S^\circ$); (b), slope=$-1.0$, ($-\Delta H^\circ = T\Delta S^\circ$); (c), ion associates with TBA$^+$; (d), inorganic ion associates of $C^+{\cdot}A^-$; (e), inorganic ion associates of $C^{2+}{\cdot}A^{2-}$; (f), inorganic ion associates of $C^{3+}{\cdot}A^{3-}$; (g), inorganic ion associates of $C^{3+}{\cdot}A^-$. Gray area indicates that the reactions proceed with larger contribution of entropy than that of enthalpy.

inorganic ion associates can be classified into four groups: the first is a group of ($C^+{\cdot}A^-$) ion associates, the second a group of ($C^{2+}{\cdot}A^{2-}$) ion associates, the third a group of ($C^{3+}{\cdot}A^{3-}$) ion associates and the fourth a group of cobalt ammine (en) complexes ($C^{3+}{\cdot}A^-$). The plots of the thermodynamic data obtained in this study show a very similar line to the plots of the fourth group, and these ion associates are classified to be ones formed between bulky cations and bulky anions or less hydrated halide ions. The lines of the plots of the first, second and third groups show the slope of 1 and the intercept of the ordinate with a negative value. The order of the values of the intercept are ($C^+{\cdot}A^-$) ion associates <($C^{2+}{\cdot}A^{2-}$) ion associates <($C^{3+}{\cdot}A^{3-}$) ion associates. It should be attributed to the increased electrostatic interactions.

When an ion associate forms from two separate ions, an entropy change of the system can occur on account of a decrease in the number of solute particles and an increase in the number of water molecules released from the solvation shell. The positive entropy change observed in the present ion-association reaction indicates that a number of water molecules should be released during the reaction as a compromise of the two effects. The positive entropy change, release of a number of water molecules, is significant in the case of ($C^{3+}{\cdot}A^{3-}$) ion associates. Such inorganic ions are strongly hydrated in aqueous solution, as is considered on the basis of electrostatic interaction, and therefore the ion-association reaction accompanies significant entropy change. From the viewpoint of the electrostatic interactions, it is noted that the ion associability and entropy changes of the organic anions with TBA$^+$ examined in this study are unexpectedly large, though the ionic radius of TBA$^+$ is the largest (473 pm) of all the cations[16] tested and the pairing anions such as NS$^-$, NDS^{2-} and NDC^{2-} are relatively large ions compared with the inorganic anions.[16] Other additive encouraging factors may exist in such ion-association reactions, as well as the ion associates of cobalt ammine (en) complexes. One of these factors affecting the ion associability is considered to be the so-called "water-structure-enforced ion association", which was proposed by Diamond[17] and is now known as hydrophobic interactions. This type of ion association can occur in a highly structured solvent, such as water, between hydrophobic ions. The positive entropy changes in the formation of organic ion associates in an aqueous solution agree with the fact that water molecules in an "ice-berg" structure are released in hydrophobic ion association. Because of such a hydrophobic interaction, the entropy change in organic ion associates is larger than the enthalpy change; the change in enthalpy can be attributed to the positive change on account of the release of solvated water molecules and the negative one on account of the association of pairing ions.

The authors have already indicated the contribution of the ionic bulkiness to ion associability;[9,10] the ion associability of the quaternary ammonium ions increased by about $10^{0.06}$ in K_{ass} unit per increase in one methylene moiety. As shown in the preceding paragraph, almost all of the ion-association reactions studied in this work were entropy-driven reactions; this fact also indicates the importance of hydrophobic interactions. In general, hydrophobic ions can easily precipitate as their ion associates in the presence of bulky pairing ions, even at relatively low concentrations. Therefore, equilibrium and thermodynamic studies are difficult to carry out. As successfully performed in this study, the proposed method with CZE seems to be a more promising technique than that with conductometry.

In conclusion, the ion-association reaction has been favorably analyzed by using the electrophoretic mobility obtained by CZE, and the thermodynamic parameters were obtained. From a comparison of the data of the present study with those of other classical studies, the ion associate of aromatic anions with TBA^+, as well as those of cobalt ammine (en) complexes, was revealed to contain a hydrophobic character.

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