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Ion Pair Formation of 1-Alkyl-3-methylimidazolium Salts in Water

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Ion pair formation in water of a series of 1-alkyl-3-methylimidazolium cations (1-butyl-, C_4mim^+; 1-hexyl-, C_6mim^+; 1-octyl-, C_8mim^+) with BF_4^-, PF_6^-, bis(trifluoromethylsulfonyl)imide (Tf_2N^-), and picrate (Pic^-) anions has been investigated by capillary electrophoresis at 25 °C. The formation constants at infinite dilution ($K_{IP}°$) of the 1:1 ion pairs have been determined. For all the anions, the $K_{IP}°$ value increases with increasing alkyl chain length of the cation (i.e., $C_4mim^+ < C_6mim^+ < C_8mim^+$). Except for Pic^-, the anion dependence of the $K_{IP}°$ value is always $BF_4^- < PF_6^- < Tf_2N^-$. The Pic^- anion has a larger $K_{IP}°$ value with C_8mim^+ than the other anions, whereas the $K_{IP}°$ value of Pic^- is smaller than or nearly equal to that of Tf_2N^- when the cation is C_4mim^+ or C_6mim^+; the $K_{IP}°$ value for Pic^- varies most sensitively with the alkyl chain length of the cation. The $K_{IP}°$ values of the picrate salts are compared with those of tetraalkylammonium picrates previously reported.

Introduction

Room temperature ionic liquids have attracted much interest as possible replacements for volatile organic solvents. Recently, increased attention has been directed toward the application of hydrophobic ionic liquids in various separation processes such as liquid−liquid extraction[1] and liquid chromatography.[2] In a system composed of a hydrophobic ionic liquid and an aqueous solution, a considerable amount of the component ions of the ionic liquid dissolve into the aqueous phase and may contribute to some aqueous reactions. Ion pair formation is one of the most fundamental reactions of ions, but the formation constants of hydrophobic ion pairs in water is generally difficult to measure by conventional techniques such as conductometry. No quantitative information is available for the aqueous ion pair formation of the component ions of ionic liquids. We previously investigated the ion pair formation of tetraalkylammonium ions with a picrate ion in water by using capillary electrophoresis and established the method of determination of the ion pair formation constants.[3] In this study, we have measured the aqueous ion pair formation constants of a series of 1-alkyl-3-methylimidazolium cations {i.e., 1-butyl-3-methylimidazolium (C_4mim^+), 1-hexyl-3-methylimidazolium (C_6mim^+), and 1-octyl-3-methylimidazolium (C_8mim^+), which are the most popular cationic components of ionic liquids at present}. The anions used are BF_4^-, PF_6^-, bis(trifluoromethylsulfonyl)imide (Tf_2N^-), and picrate (2,4,6-trinitrophenolate, Pic^-); the former three are commonly used as anionic components of ionic liquids, and the latest one is a typical ion pair extractant.

Experimental Section

Chemicals. C_4mimCl (TCI, > 98 %), C_6mimCl (Acros, > 98 %), C_8mimCl (Acros, 98 %), $NaBF_4$ (Aldrich, 98 %), and $NaPF_6$ (Aldrich, 98 %) were used as purchased without further purification. $LiTf_2N$ (Fluorochem) was dried in vacuum at 80 °C for 1 day prior to use. Water was distilled and further deionized with a Milli-Q Labo system (Millipore). Other reagents were of analytical grade and used as received. The concentration of picric acid in the aqueous solution was determined by neutralization titration.

Apparatus and Procedure. The instrument for capillary electrophoresis was assembled from a laboratory-built high-voltage power supply, a UV−vis detector (Jasco, CE-970), and a data integrator (Shimadzu, CR-6A). A coated capillary tube (MicroSolv Technology, CE100-SA, Zero Flow) of 50 μm i.d. and 365 μm o.d. was used; it was confirmed that in this capillary tube the electroosmotic flow was negligibly small below pH 5. The total length of the capillary was 620 mm, and the length from the injection end to the detection point was 500 mm. The instrument was placed in a compartment thermostated at (25 ± 0.1) °C, and forced-air cooling of the capillary was carried out with a fan.

In the measurements for the picrate system, the capillary tube and the cathodic and anodic reservoirs were filled with an aqueous solution containing the chloride salt of a 1-alkyl-3-methylimidazolium ion {for C_4mimCl: $(9.3 \times 10^{-3}$ to $4.7 \times 10^{-2})$ mol·dm^{-3}; for C_6mimCl: $(9.8 \times 10^{-3}$ to $4.9 \times 10^{-2})$ mol·dm^{-3}; for C_8mimCl: $(6.9 \times 10^{-3}$ to $2.8 \times 10^{-2})$ mol·dm^{-3}}; this solution was buffered at pH 3.2 to pH 3.3 with chloroacetic acid (3.0×10^{-3} mol·dm^{-3}) and tetramethylammonium hydroxide (1.5×10^{-3} mol·dm^{-3}). A sample solution was prepared by dissolving picric acid (1×10^{-4} mol·dm^{-3}) in the electrolyte solution that was identical with the running solution. A small amount of the sample solution (ca. 6×10^{-5} cm^3) was injected from the cathodic end of the capillary by siphoning, and the electrophoresis of the picrate ion was conducted by an applied voltage of 15.0 kV. The migration time of the picrate ion from the injection end to the detection point was measured by monitoring the light adsorption at wavelength of 356 nm.

The measurements for the BF_4^-, PF_6^-, and Tf_2N^- systems were conducted by using running solutions (pH 3.0 to pH 3.5), each of which contains the lithium or sodium salt of the anion {for $NaBF_4$: $(7.2 \times 10^{-3}$ to $2.0 \times 10^{-2})$ mol·dm^{-3}; for $NaPF_6$: $(7.0 \times 10^{-3}$ to $2.2 \times 10^{-2})$ mol·dm^{-3}; for $LiTf_2N$: $(6.9 \times 10^{-3}$ to $3.5 \times 10^{-2})$ mol·dm^{-3}}, chloroacetic acid (1.5×10^{-3} mol·dm^{-3}), and sodium hydroxide (7.4×10^{-4} mol·dm^{-3}). A sample solution containing the 1-alkyl-3-methylimidazolium chlorides (2×10^{-4} mol·dm^{-3} for each) was injected from the anodic end of the capillary. The 1-alkyl-3-methylimidazolium ions were electrophoresed at a voltage of 15.0 kV, and the

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Table 1. Molar Conductivities of Different Concentrations (*c*) of Potassium Tetrafluoroborate in Water at 25 °C[a]

I		II	
c	Λ	*c*	Λ
mmol·dm^{-3}	$\text{S·cm}^{2}\text{·mol}^{-1}$	mmol·dm^{-3}	$\text{S·cm}^{2}\text{·mol}^{-1}$
0.9574	157.07	0.9755	157.79
1.3972	156.48	1.4280	157.18
1.8351	155.95	1.7549	156.83
2.2467	155.54	2.0899	156.43
2.6414	155.35	2.4001	156.08
2.9961	155.00	2.7021	155.74
		3.0107	155.43

[a] The letters I and II denote two separate series of measurements.

migration time was measured by monitoring the light absorption at 210 nm.

Electronic conductivities of aqueous KBF_4 solutions were also measured to determine the limiting molar conductivity of KBF_4. The measurements were performed in a custom-made two-electrode cell (inner volume 300 cm^3; Pt-black electrodes; cell constant 0.10076 cm^{-1}) at (25 ± 0.005) °C under a nitrogen atmosphere with a linear-bridge conductometer system (Fuso, HECS-360 series). Initially, ca. 200 cm^3 of water was accurately weighed into the cell, and the conductivity was measured. Then a known amount of an aqueous solution of KBF_4 (prepared by weight) was added stepwise to the cell to give an appropriate concentration $\{(1.9 \times 10^{-4}$ to $3.0 \times 10^{-3})\ \text{mol·dm}^{-3}\}$, and the conductivity was measured after each addition. Two separate runs were made, and the results are listed in Table 1. The limiting molar conductivity of KBF_4 was calculated by using the Fuoss−Onsager−Skinner equation.[4]

Theory and Results

When a monovalent ion A and a counterion B form a neutral 1:1 ion pair (A·B), the apparent electrophoretic mobility of A ($\mu_{\text{app,A}}$) in the presence of B can be expressed as

$$\mu_{\text{app,A}} = \frac{[\text{A}]}{[\text{A}] + [\text{A·B}]}\mu_{\text{ep,A}} = \frac{\mu_{\text{ep,A}}}{1 + K_{\text{IP}}[\text{B}]} \tag{1}$$

where $\mu_{\text{ep,A}}$ and K_{IP} denote the electrophoretic mobility of the free A ion and the ion pair formation constant ($= [\text{A·B}][\text{A}]^{-1}[\text{B}]^{-1}$), respectively. The K_{IP} value in eq 1 can be substituted by the following equation:

$$K_{\text{IP}} = \gamma_{\text{A}}\gamma_{\text{B}}K_{\text{IP}}^{\circ} \tag{2}$$

where γ_{A}, γ_{B}, and K_{IP}° are the activity coefficient of A, that of B, and the ion pair formation constant at infinite dilution, respectively; the activity coefficient of the neutral ion pair is assumed to be unity. Therefore

$$\mu_{\text{app,A}} = \frac{\mu_{\text{ep,A}}}{1 + K_{\text{IP}}^{\circ}\gamma_{\text{A}}\gamma_{\text{B}}[\text{B}]} \tag{3}$$

Equation 3 is transformed into

$$\frac{1}{\mu_{\text{app,A}}} = \frac{K_{\text{IP}}^{\circ}}{\mu_{\text{ep,A}}}\gamma_{\text{A}}\gamma_{\text{B}}[\text{B}] + \frac{1}{\mu_{\text{ep,A}}} \tag{4}$$

If the $\mu_{\text{ep,A}}$ value is nearly independent of [B], the $1/\mu_{\text{app,A}}$ versus $\gamma_{\text{A}}\gamma_{\text{B}}[\text{B}]$ plot gives a linear relationship.

The $\mu_{\text{app,A}}$ value was calculated from its migration time (*t*) (i.e., $\mu_{\text{app,A}} = L_{\text{T}}\cdot L_{\text{D}}\cdot E^{-1}\cdot t^{-1}$), where L_{T}, L_{D}, and *E* are the total capillary length, the capillary length from the injection end to the detection point, and the applied voltage, respectively. The apparent mobilities are listed in Table 2. The concentration of the free B ion ([B]) was regarded as equal to its total concentration because the total concentration of A is much lower than that of B. The activity coefficients γ were calculated by the extended Debye−Hückel equation, $\log \gamma = -0.5091\{I/(\text{mol·dm}^{-3})\}^{1/2}/[1 + 0.3286 \times 10^{8}(\mathring{a}/\text{cm})\{I/(\text{mol·dm}^{-3})\}^{1/2}]$, where $\mathring{a}$ and *I* are the ion size parameter and the ionic strength, respectively. The $\mathring{a}$ value was evaluated from the limiting ionic molar conductivity (λ°) at 25 °C according to the empirical equation by Brüll, $\mathring{a}/(10^{-8}\ \text{cm}) = 216/\{\lambda^{\circ}/(\text{S·cm}^{2}\text{·mol}^{-1})\}$.[5] The literature values of λ° were used for Pic^{-}, PF_6^{-}, and Tf_2N^{-}; $\lambda^{\circ}/(\text{S·cm}^{2}\text{·mol}^{-1}) = 30.39$,[6] 59.28,[7] and 32.2,[8] respectively. The λ° value of BF_4^{-} was obtained to be 87.0 $\text{S·cm}^{2}\text{·mol}^{-1}$ from the limiting molar conductivity of KBF_4 (160.5 $\text{S·cm}^{2}\text{·mol}^{-1}$, determined in this study) and the λ° value of K^{+} (73.50 $\text{S·cm}^{2}\text{·mol}^{-1}$).[6] For the 1-alkyl-3-methylimidazolium ions, appropriate values of λ° were initially assumed. The $1/\mu_{\text{app},A}$ versus $\gamma_{\text{A}}\gamma_{\text{B}}[\text{B}]$ plot always gave a good linear relationship, and the K_{IP}° and $\mu_{\text{ep,A}}$ values were calculated from the slope and intercept. The λ° values of the 1-alkyl-3-methylimidazolium ions were estimated from the $\mu_{\text{ep,A}}$ values based on the relation $\lambda^{\circ} \approx \lambda = \mu_{\text{ep,A}}\cdot F$ (*F*, Faraday constant), and the final K_{IP}° and $\mu_{\text{ep,A}}$ values were obtained by a successive approximation method. Examples of the final $1/\mu_{\text{app,A}}$ versus $\gamma_{\text{A}}\gamma_{\text{B}}[\text{B}]$ plots are shown in Figure 1. The K_{IP}° values are summarized in Table 3. The λ values for $C_4\text{mim}^{+}$, $C_6\text{mim}^{+}$, and $C_8\text{mim}^{+}$ at $I = (7.8 \times 10^{-3}$ to $3.6 \times 10^{-2})\ \text{mol·dm}^{-3}$ were obtained to be (31.9 ± 0.2) $\text{S·cm}^{2}\text{·mol}^{-1}$, (28.3 ± 0.2) $\text{S·cm}^{2}\text{·mol}^{-1}$, and (25.6 ± 0.3) $\text{S·cm}^{2}\text{·mol}^{-1}$, respectively. The method's reliability was previously verified by the good agreement between the K_{IP}° values of sodium picrate from this capillary electrophoretic method and from the potentiometric one using a Na^{+}-selective electrode.[3]

It was recently reported that some 1-alkyl-3-methylimidazolium salts form micelles in aqueous solutions {e.g., the critical micelle concentrations for $C_4\text{mimBF}_4$ and $C_8\text{mimCl}$ are (0.8 and 0.1) mol·dm^{-3}, respectively}.[9] If significant amounts of micelles were present, eq 4 would not hold. The linear relationship between $1/\mu_{\text{app,A}}$ and $\gamma_{\text{A}}\gamma_{\text{B}}[\text{B}]$ shows that the micelle formation is negligible in the present experiments using low concentrations of the salts.

Discussion

For any of the anions, the K_{IP}° value increases with increasing alkyl chain length of the cation. Except for Pic^{-}, the K_{IP}° value for a given cation always varies in the anion order $BF_4^{-} < PF_6^{-} < Tf_2N^{-}$, which agrees with the increasing order of the anion size. The Pic^{-} anion has a larger K_{IP}° value with $C_8\text{mim}^{+}$ than the other anions, whereas the K_{IP}° value of Pic^{-} is smaller than or nearly equal to that of Tf_2N^{-} when the cation is $C_4\text{mim}^{+}$ or $C_6\text{mim}^{+}$; the K_{IP}° value for Pic^{-} varies most sensitively with the alkyl-chain length of the cation.

According to the Bjerrum theory,[10] the distances of closest approach of the cations to the anions calculated from the K_{IP}° values are (7 to 9) × 10^{-9} cm. These distance values are unreasonably small in view of the sizes and structures of the ions. This means that the ion pair formation constants in water are larger than that expected from the electrostatic interaction between the ions. Recently, the cation−anion interactions in vacuum have been evaluated using ab initio calculations;[11,12]

Table 2. Apparent Electrophoretic Mobilities of an Ion in the Presence of Different Concentrations (*c*) of a Salt at 25 °C[a]

c	μ_{app}	c	μ_{app}	c	μ_{app}
$mmol\cdot dm^{-3}$	$10^{-4}\ cm^2\cdot s^{-1}\cdot V^{-1}$	$mmol\cdot dm^{-3}$	$10^{-4}\ cm^2\cdot s^{-1}\cdot V^{-1}$	$mmol\cdot dm^{-3}$	$10^{-4}\ cm^2\cdot s^{-1}\cdot V^{-1}$
mobile ion = C_4mim^+, salt = $NaBF_4$		mobile ion = C_6mim^+, salt = $NaBF_4$		mobile ion = C_8mim^+, salt = $NaBF_4$	
7.17	3.209 ± 0.002	7.17	2.828 ± 0.004	7.17	2.546 ± 0.004
10.25	3.152 ± 0.004	10.25	2.776 ± 0.003	10.25	2.499 ± 0.003
14.34	3.120 ± 0.007	14.34	2.735 ± 0.005	14.34	2.458 ± 0.004
17.42	3.092 ± 0.003	17.42	2.712 ± 0.004	17.42	2.439 ± 0.003
20.49	3.055 ± 0.003	20.49	2.673 ± 0.005	20.49	2.400 ± 0.004
mobile ion = C_4mim^+, salt = $NaPF_6$		mobile ion = C_6mim^+, salt = $NaPF_6$		mobile ion = C_8mim^+, salt = $NaPF_6$	
7.02	3.174 ± 0.006	7.02	2.796 ± 0.005	7.02	2.516 ± 0.004
10.02	3.120 ± 0.005	10.02	2.740 ± 0.005	10.02	2.464 ± 0.005
14.03	3.058 ± 0.002	14.03	2.676 ± 0.002	14.03	2.403 ± 0.002
18.04	3.020 ± 0.005	18.04	2.639 ± 0.007	18.04	2.362 ± 0.005
22.05	2.984 ± 0.006	22.05	2.604 ± 0.006	22.05	2.328 ± 0.006
mobile ion = C_4mim^+, salt = $LiTf_2N$		mobile ion = C_6mim^+, salt = $LiTf_2N$		mobile ion = C_8mim^+, salt = $LiTf_2N$	
6.95	3.200 ± 0.005	6.95	2.819 ± 0.003	6.95	2.519 ± 0.003
13.89	3.050 ± 0.003	13.89	2.659 ± 0.003	13.89	2.339 ± 0.001
19.85	2.954 ± 0.005	19.85	2.560 ± 0.005	19.85	2.225 ± 0.006
27.79	2.854 ± 0.002	27.79	2.456 ± 0.002	27.79	2.108 ± 0.005
34.74	2.781 ± 0.004	34.74	2.382 ± 0.004	34.74	2.012 ± 0.004
mobile ion = Pic^-, salt = C_4mimCl		mobile ion = Pic^-, salt = C_6mimCl		mobile ion = Pic^-, salt = C_8mimCl	
7.70	3.024 ± 0.002	7.97	2.920 ± 0.007	6.93	2.744 ± 0.009
14.57	2.902 ± 0.001	14.95	2.754 ± 0.006	13.87	2.561 ± 0.017
21.03	2.803 ± 0.004	21.43	2.606 ± 0.006	20.80	2.375 ± 0.005
27.22	2.717 ± 0.006	27.57	2.492 ± 0.005	27.73	2.244 ± 0.016
30.67	2.659 ± 0.003	31.91	2.375 ± 0.006		

[a] Uncertainties represent standard deviations from three to five measurements.

the interaction calculated for 1-alkyl-3-methylimidazolium halides (alkyl = ethyl, propyl, and butyl) decreases with increasing alkyl chain length of the cation, and the interaction for 1-ethyl-3-methylimidazolium salts varies with the anion species in the order $BF_4^- > Tf_2N^- \approx PF_6^-$. These trends are quite different from those observed for the $K_{IP}°$ values in water. Therefore, the aqueous ion pairing of the 1-alkyl-3-methylimidazolium salts cannot be explained by the intrinsic interaction between the cations and anions. The term "hydrophobic interaction" may be used to explain such a tendency of the hydrophobic ions to associate in water. The hydrophobic interaction, however, is an apparent interaction caused by the hydration of the solutes. The aqueous ion pairing can be systematically discussed on the basis of the following thermochemical cycle:

$$\begin{tikzcd}
\text{Gas phase:} & C^+ \arrow[d, "\Delta G^\circ_h(C^+)"] & + & A^- \arrow[r, "\Delta G^\circ_{ip,g}"] \arrow[d, "\Delta G^\circ_h(A^-)"] & C^+\cdot A^- \arrow[d, "\Delta G^\circ_h(C^+\cdot A^-)"] \\
\text{Aq. phase:} & C^+ & + & A^- \arrow[r, "\Delta G^\circ_{ip,aq}"] & C^+\cdot A^-
\end{tikzcd}$$

$$\Delta G^\circ_{ip,aq} = \Delta G^\circ_{ip,g} + \Delta G^\circ_h(C^+\cdot A^-) - \Delta G^\circ_h(C^+) - \Delta G^\circ_h(A^-), \qquad (5)$$

where C^+, A^-, and $C^+\cdot A^-$ represent a cation, an anion, and their ion pair, respectively; $\Delta G^\circ_{ip,g}$ and $\Delta G^\circ_{ip,aq}$ denote the standard Gibbs energies of ion pairing in the gas and aqueous phases, respectively; ΔG°_h is the standard Gibbs energy of hydration. According to eq 5, the difference in $\Delta G^\circ_{ip,aq}$ between the cations for a given anion is equal to the sum of the differences in $\Delta G^\circ_{ip,g}$, $\Delta G^\circ_h(C^+\cdot A^-)$, and $-\Delta G^\circ_h(C^+)$. As the alkyl chain length of the cation increases, the $\Delta G^\circ_{ip,g}$ value increases (i.e., $C^+\cdot A^-$ becomes less stable in the gas phase) as described above; the $\Delta G^\circ_h(C^+)$ value is also expected to increase (i.e., C^+ becomes more hydrophobic and less strongly hydrated) and the same holds true for the $\Delta G^\circ_h(C^+\cdot A^-)$ value. From the above, the decrease of $\Delta G^\circ_{ip,aq}$ with increasing the alkyl chain length is caused by the increase of $\Delta G^\circ_h(C^+)$ (eq 5). Namely, the greater ion pairing ability in water of the 1-alkyl-3-methylimidazolium cation having a longer alkyl chain is attributed to the lower hydration of the cation. The dependence of the aqueous ion pair formation constant on the anion species (except for Pic^-), $BF_4^- < PF_6^- < Tf_2N^-$, can similarly be explained by the hydration of the anions, which is expected to decrease with increasing ionic size.

The $K_{IP}°$ values of the 1-alkyl-3-methylimidazolium picrates are compared with those of the tetraalkylammonium picrates previously studied.[3] In Figure 2, the log $K_{IP}°$ values are plotted against the number of methylene groups in the cation. The $K_{IP}°$ values for the 1-alkyl-3-methylimidazolium salts and those of the tetraalkylammonium ones are similar in magnitude and both increase with increasing number of methylene groups in the alkyl chain. However, the increment of log $K_{IP}°$ for an added methylene group is considerably larger for the former salts (0.10 to 0.11) than for the latter ones (0.03 to 0.07). The reason is not clear at this stage and further investigations on the cation–anion interaction and the hydration of the ions and ion pairs are needed.

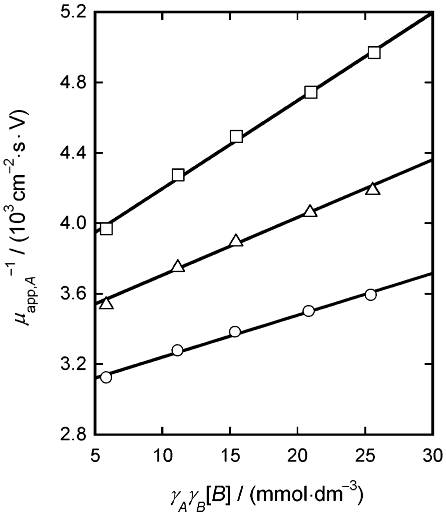

Figure 1. Plots of $1/\mu_{app,A}$ vs $\gamma_A\gamma_B[B]$. (A = 1-alkyl-3-methylimidazolium ion, B = Tf_2N^-) for ○, $C_4mim^+\cdot Tf_2N^-$; △, $C_6mim^+\cdot Tf_2N^-$; □, $C_8mim^+\cdot Tf_2N^-$ at 25 °C.

Table 3. Ion Pair Formation Constants of 1-Alkyl-3-methylimidazolium Salts in Water ($I \rightarrow 0$) at 25 °C[a]

anion	cation	$\frac{K_{IP}°}{dm^3 \cdot mol^{-1}}$	$\log\left(\frac{K_{IP}°}{dm^3 \cdot mol^{-1}}\right)$
BF_4^-	C_4mim^+	5.2 ± 0.4	0.71
	C_6mim^+	6.0 ± 0.4	0.78
	C_8mim^+	6.2 ± 0.4	0.80
PF_6^-	C_4mim^+	6.3 ± 0.3	0.80
	C_6mim^+	7.4 ± 0.4	0.87
	C_8mim^+	8.2 ± 0.4	0.91
Tf_2N^-	C_4mim^+	8.0 ± 0.4	0.90
	C_6mim^+	9.7 ± 0.5	0.99
	C_8mim^+	13.5 ± 0.4	1.13
Pic^-	C_4mim^+	6.2 ± 0.1	0.79
	C_6mim^+	10.2 ± 0.4	1.01
	C_8mim^+	16.4 ± 0.5	1.21

[a] Uncertainties represent standard errors from regression analysis.

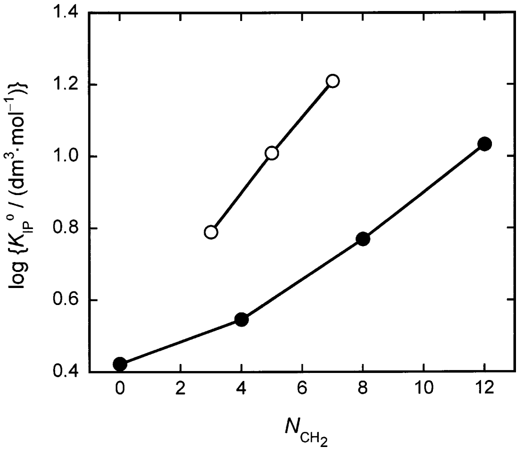

Figure 2. Dependence of the logarithmic ion pair formation constants in water on the number of methylene groups in the cation for ○, 1-alkyl-3-methylimidazolium picrates; ●, tetraalkylammonium picrates.

Conclusions

The capillary electrophoretic method allow us to determine the ion pair formation constants of hydrophobic 1-alkyl-3-methylimidazolium salts with BF_4^-, PF_6^-, Tf_2N^-, and Pic^- anions in water at 25 °C. This is the first report of the aqueous ion pair formation constants of the component ions of ionic liquids. For a given anion, the stability of the ion pair in water increases with increasing alkyl chain length of the 1-alkyl-3-methylimidazolium cation as a result of the decrease of hydration of the cation. When the anions are BF_4^-, PF_6^-, and Tf_2N^-, the cation associates more strongly with the larger anion. The Pic^- anion forms a more stable ion pair with C_8mim^+ than the other anions, but the ion pairing ability of Pic^- decreases rapidly as the alkyl chain length of the cation decreases. The effect of alkyl chain length on the ion pair formation with Pic^- is greater for the 1-alkyl-3-methylimidazolium ions than for tetraalkylammonium ions.

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