Distribution of 1-Alkyl-3-methylimidazolium Ions and Their Ion Pairs between Dichloromethane and Water

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The distribution behavior of the salts of a series of 1-alkyl-3-methylimidazolium cations (RMeIm⁺; R = butyl, hexyl, and octyl) with tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻), bis(trifluoromethanesulfonyl)amide (NTf₂⁻), and 2,4,6-trinitrophenolate (Pic⁻) anions has been investigated in a dichloromethane-water system at 25°C. The distribution constants (*K*_D) of the ion pairs and the transfer activity coefficients (^o*γ*^w) of the single ions were determined. For the ion pairs with a given anion, the log *K*_D value increases linearly with the number of methylene groups (*N*_{CH2}) in the cation, which can be explained by using the regular solution theory. A similar relationship was observed between log ^o*γ*^w and *N*_{CH2} for the free RMeIm⁺ ions, and the result was discussed by decomposing the transfer activity coefficient into the Born-type electrostatic contribution and the non-electrostatic one. For the free anions and their ion pairs with a given cation, the ^o*γ*^w and *K*_D values increase with increasing molar volume of the anion: *i.e.*, BF₄⁻ < PF₆⁻ < Pic⁻ < NTf₂⁻. The features of the RMeIm⁺ salts in the liquid-liquid distribution and the ion-pair formation in water are also discussed by comparing the present results with those of tetraalkylammonium salts previously reported.

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Introduction

Ionic liquids have been extensively investigated as new media for separation and sensing technologies such as solvent extraction, chromatography, electrophoresis, and electric sensors.¹⁻³ In these analytical methods, two-phase systems of hydrophobic ionic liquids and water are often used. The ionic liquid in the two-phase system dissolves partly in the aqueous phase. Therefore, the study of the aqueous solution chemistry of ionic liquids is important from the viewpoint of such analytical applications. Ionic liquid salts exist as dissociated ions and ion pairs in aqueous solution,⁴ and some of them further aggregate to form micelles.⁵⁻⁷ Recently, we have determined the ion-pair formation constants of several 1-alkyl-3-methylimidazolium salts in water under conditions where the micelle formation is negligible.⁴ The results show that the ion-pair formation constants in water are considerably different in magnitude and tendency from those in dichloromethane.⁸ The aqueous ion-pair formation is expected to be strongly affected by the hydration of ions and ion pairs. The distribution constants of solutes between a low or non-polar organic solvent and water provide useful information on the solute-water interaction. In a previous study,⁹ the distribution of tetraalkylammonium picrates was investigated in a dichloromethane-water system.

In this study, the distribution behavior of the salts of a series of 1-alkyl-3-methylimidazolium cations (RMeIm⁺; R = butyl (Bu), hexyl (Hx), and octyl (Oc)) with tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻), bis(trifluoromethanesulfonyl)amide (NTf₂⁻), and picrate (2,4,6-trinitrophenolate, Pic⁻) anions has been investigated in a dichloromethane-water system at 25°C. The salts except for the Pic⁻ salts are typical ionic liquids. The

Pic⁻ salts were used for comparison with tetraalkylammonium picrates (R₄N⁺Pic⁻). The transfer activity coefficients of the single ions and the distribution constants of their 1:1 ion pairs have been determined from analysis of the distribution data. The features of the RMeIm⁺ salts in the liquid-liquid distribution are discussed by comparing the present results with those of the R₄N⁺ ones previously reported.⁹ The aqueous ion-pair formation is also discussed based on the present experimental results.

Experimental

Reagents

The imidazolium salts used were the same as those described previously.⁸ Water was deionized with a Milli-Q Labo system (Millipore) after distillation. Dichloromethane (Kanto Chemical, GR grade) was washed with deionized water for three times. The water content of the water-saturated dichloromethane was 0.16 wt% as determined by Karl-Fischer titrations.⁹ Other reagents were of analytical grade and were used without further purification.

Distribution experiments

A two-phase system of dichloromethane and water containing a salt (5.0×10^{-5} – 8.0×10^{-3} mol dm⁻³) was equilibrated by stirring with a magnetic stirrer for 1 h in a stoppered glass tube at 25 ± 0.1°C. In the cases of hydrophobic OcMeIm⁺PF₆⁻ and all the NTf₂⁻ salts, the concentration in the aqueous phase was measured as follows. After phase separation by centrifugation, an aliquot of the aqueous phase was transferred into another stoppered glass tube, to which aqueous solutions of sodium picrate and sodium hydroxide were added in the concentrations of 0.05 and 0.01 mol dm⁻³, respectively. After pure dichloromethane was added to this tube, the two-phase mixture was stirred with a magnetic stirrer; by this operation, the

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imidazolium cation in the aqueous phase was completely extracted as an ion pair with Pic^- into dichloromethane. The Pic^- salt concentration was determined spectrophotometrically (molar absorptivity in water-saturated dichloromethane: $\lambda_{\text{max}} = 367.0 \text{ nm}$, $\varepsilon = 1.70 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for all the salts). In the case of the other salts, the salt concentration in the dichloromethane phase was measured in the following manner. An aliquot of the dichloromethane phase was transferred into a beaker and evaporated to dryness. The residue in the beaker was redissolved in water and the salt concentration was determined spectrophotometrically (molar absorptivities in water: $\lambda_{\text{max}} = 356.0 \text{ nm}$, $\varepsilon = 1.45 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for all the Pic^- salts; $\lambda_{\text{max}} = 211.5 \text{ nm}$, $\varepsilon = 4.12 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for $\text{BuMeIm}^+\text{BF}_4^-$ and $\text{BuMeIm}^+\text{PF}_6^-$; $\lambda_{\text{max}} = 211.0 \text{ nm}$, $\varepsilon = 4.21 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for $\text{HxMeIm}^+\text{BF}_4^-$ and $\text{HxMeIm}^+\text{PF}_6^-$; $\lambda_{\text{max}} = 210.5 \text{ nm}$, $\varepsilon = 4.28 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for $\text{OcMeIm}^+\text{BF}_4^-$). In both the cases, the salt concentration in the other phase was calculated from the mass balance.

Results and Discussion

Analysis of distribution data

For a salt composed of a monovalent cation (C^+) and a monovalent anion (A^-) in an organic solvent-water system, the following two equilibria of salt extraction can be considered:

where C^+A^- represents the ion pair, and the subscript “o” and “w” denote the organic and aqueous phases, respectively. In addition, the following mass balances can be considered for the aqueous and organic phases, respectively:

(Organic phase)

$$[\text{CA}]_{\text{t,o}} = [\text{C}^+\text{A}^-]_{\text{o}} + [\text{C}^+]_{\text{o}} = [\text{C}^+]_{\text{o}}(1 + K_{\text{IP,o}}[\text{A}^-]_{\text{o}}) \quad (3)$$

$$= [\text{C}^+\text{A}^-]_{\text{o}} + [\text{A}^-]_{\text{o}} = [\text{A}^-]_{\text{o}}(1 + K_{\text{IP,o}}[\text{C}^+]_{\text{o}}), \quad (4)$$

(Aqueous phase)

$$[\text{CA}]_{\text{t,w}} = [\text{C}^+\text{A}^-]_{\text{w}} + [\text{C}^+]_{\text{w}} = [\text{C}^+]_{\text{w}}(1 + K_{\text{IP,w}}[\text{A}^-]_{\text{w}}) \quad (5)$$

$$= [\text{C}^+\text{A}^-]_{\text{w}} + [\text{A}^-]_{\text{w}} = [\text{A}^-]_{\text{w}}(1 + K_{\text{IP,w}}[\text{C}^+]_{\text{w}}), \quad (6)$$

where $[\text{CA}]_{\text{t,o}}$ and $[\text{CA}]_{\text{t,w}}$ denote the total concentration of the salt in the organic phase and that in the aqueous phase, respectively; $K_{\text{IP,o}}$ and $K_{\text{IP,w}}$ are the ion-pair formation constant in the organic phase ($K_{\text{IP,o}} = [\text{C}^+\text{A}^-]_{\text{o}}/[\text{C}^+]_{\text{o}}[\text{A}^-]_{\text{o}}$) and that in the aqueous phase ($K_{\text{IP,w}} = [\text{C}^+\text{A}^-]_{\text{w}}/[\text{C}^+]_{\text{w}}[\text{A}^-]_{\text{w}}$). From Eqs. (3)–(6), the following equations are derived:

$$[\text{C}^+]_{\text{o}} = [\text{A}^-]_{\text{o}} = (-1 + \sqrt{1 + 4K_{\text{IP,o}}[\text{CA}]_{\text{t,o}}})/2K_{\text{IP,o}}, \quad (7)$$

$$[\text{C}^+]_{\text{w}} = [\text{A}^-]_{\text{w}} = (-1 + \sqrt{1 + 4K_{\text{IP,w}}[\text{CA}]_{\text{t,w}}})/2K_{\text{IP,w}}. \quad (8)$$

The ion-pair formation constant can be expressed as a function of the ionic strength (I) of each phase by using the Debye-Hückel limiting equation:

$$\log K_{\text{IP,o}} = \log K_{\text{IP,o}}^0 - 2 \times 13.3(\text{mol dm}^{-3})^{-1/2}\sqrt{I_{\text{o}}}, \quad (9)$$

$$\log K_{\text{IP,w}} = \log K_{\text{IP,w}}^0 - 2 \times 0.511(\text{mol dm}^{-3})^{-1/2}\sqrt{I_{\text{w}}}, \quad (10)$$

where the superscript ‘0’ indicates the quantity at infinite dilution and the activity coefficient of the neutral ion pair is assumed to be unity. The coefficients of the second terms on the right sides, 13.3 and 0.511, are the Debye-Hückel constants calculated as $1.82 \times 10^6(\varepsilon_r T)^{-3/2}(\text{mol dm}^{-3})^{-1/2} \text{ K}^{3/2}$, where ε_r is the dielectric constant of the solvent. An equilibrium analysis was made in the following way by using the measured concentrations, $[\text{CA}]_{\text{t,o}}$ and $[\text{CA}]_{\text{t,w}}$. Initially, the tentative $K_{\text{IP,o}}$ and $K_{\text{IP,w}}$ values were calculated from Eqs. (9) and (10) by assuming that $I_{\text{o}} = [\text{CA}]_{\text{t,o}}$ and $I_{\text{w}} = [\text{CA}]_{\text{t,w}}$, and the first approximate $[\text{C}^+]_{\text{o}}$, $[\text{A}^-]_{\text{o}}$, $[\text{C}^+]_{\text{w}}$, and $[\text{A}^-]_{\text{w}}$ values were obtained from Eqs. (7) and (8). The ionic strengths were recalculated and the second approximate values of $[\text{C}^+]_{\text{o}}$, $[\text{A}^-]_{\text{o}}$, $[\text{C}^+]_{\text{w}}$, and $[\text{A}^-]_{\text{w}}$ were obtained in a similar manner. The actual concentrations were determined by a successive approximation approach (5–9 iterations). Finally, the concentrations of the ion pair in both the phases were calculated by $[\text{C}^+\text{A}^-]_{\text{o}} = K_{\text{IP,o}}[\text{C}^+]_{\text{o}}[\text{A}^-]_{\text{o}}$ and $[\text{C}^+\text{A}^-]_{\text{w}} = K_{\text{IP,w}}[\text{C}^+]_{\text{w}}[\text{A}^-]_{\text{w}}$, and the distribution constants of the ion pairs defined as $K_{\text{D}} = [\text{C}^+\text{A}^-]_{\text{o}}/[\text{C}^+\text{A}^-]_{\text{w}}$ were obtained. The $K_{\text{ex},1}$ and $K_{\text{ex},2}$ values at infinite dilution were calculated according to the following equations:

$$K_{\text{ex},1}^0 = K_{\text{D}}K_{\text{IP,w}}^0/K_{\text{IP,o}}^0, \quad (11)$$

$$K_{\text{ex},2}^0 = K_{\text{D}}K_{\text{IP,w}}^0. \quad (12)$$

The equilibrium constants obtained for the RMeIm^+ salts are summarized in Table 1, together with the values for $\text{R}_4\text{N}^+\text{Pic}^-$.^{9,10}

The standard Gibbs energy of the extraction process of Eq. (1) is regarded as the sum of the standard Gibbs energies of transfer from the aqueous phase to the organic one for the cation and for the anion ($\Delta G^\circ_{\text{tr,w} \rightarrow \text{o}}(\text{C}^+)$ and $\Delta G^\circ_{\text{tr,w} \rightarrow \text{o}}(\text{A}^-)$, respectively). Therefore, when using the transfer activity coefficient defined as ${}^{\circ}\gamma^{\text{w}} = \exp(-\Delta G^\circ_{\text{tr,w} \rightarrow \text{o}}/RT)$, the following equation is derived:

$$K_{\text{ex},1}^0 = {}^{\circ}\gamma^{\text{w}}(\text{C}^+) {}^{\circ}\gamma^{\text{w}}(\text{A}^-). \quad (13)$$

The ${}^{\circ}\gamma^{\text{w}}$ value corresponds to the K_{D} value for a neutral solute. The ${}^{\circ}\gamma^{\text{w}}$ values for the single ions were calculated by using a literature value¹¹ of ${}^{\circ}\gamma^{\text{w}}$ for Pic^- which was determined based on the tetraphenylarsonium tetraphenylborate assumption, ${}^{\circ}\gamma^{\text{w}}(\text{Ph}_4\text{As}^+) = {}^{\circ}\gamma^{\text{w}}(\text{BPh}_4^-)$. The values of ${}^{\circ}\gamma^{\text{w}}$ and $\Delta G^\circ_{\text{tr,w} \rightarrow \text{o}}$ are summarized in Table 2.

Distribution constants of ion pairs

The log K_{D} values are generally positive, indicating that the ion pairs are more soluble in dichloromethane than in water. For the ion pairs with a given anion, the log K_{D} value increases linearly with the number of methylene groups (N_{CH_2}) in the alkyl chain R of the RMeIm^+ ion. The increment of the log K_{D} value with a methylene group ($\Delta_{\text{CH}_2} \log K_{\text{D}}$) is 0.45 for $\text{RMeIm}^+\text{Pic}^-$, 0.54 for $\text{RMeIm}^+\text{BF}_4^-$, 0.56 for $\text{RMeIm}^+\text{PF}_6^-$, and 0.54 for $\text{RMeIm}^+\text{NTf}_2^-$. The $\Delta_{\text{CH}_2} \log K_{\text{D}}$ values for the RMeIm^+ salts of BF_4^- , PF_6^- , and NTf_2^- are equal to each other and are greater than the value for $\text{RMeIm}^+\text{Pic}^-$. $\text{RMeIm}^+\text{Pic}^-$ is similar to $\text{R}_4\text{N}^+\text{Pic}^-$ in the $\Delta_{\text{CH}_2} \log K_{\text{D}}$ value ($\Delta_{\text{CH}_2} \log K_{\text{D}} = 0.47$ for $\text{R}_4\text{N}^+\text{Pic}^-$).⁹

The log K_{D} value of a neutral solute (s) can be expressed by the following equation:⁹

$$\log K_{\text{D}}(\text{s}) = \frac{V_{\text{m,s}}}{2.30} \left\{ \frac{1}{V_{\text{m,o}}} - \frac{1}{V_{\text{m,w}}} + \frac{(\delta_{\text{w}} - \delta_{\text{o}})(\delta_{\text{w}} + \delta_{\text{o}} - 2\delta_{\text{s}})}{RT} \right\}$$

Table 1 Equilibrium constants for organic salts in a dichloromethane-water system at 25°C (molar scale)

Cation	Anion	$\log(K_{\text{IP,w}}^0/\text{mol}^{-1} \text{ dm}^3)^{\text{a}}$	$\log(K_{\text{IP,o}}^0/\text{mol}^{-1} \text{ dm}^3)^{\text{b}}$	$\log K_{\text{D}}^{\text{c}}$	$\log K_{\text{ex,1}}^0^{\text{d}}$	$\log(K_{\text{ex,2}}^0/\text{mol}^{-1} \text{ dm}^3)^{\text{e}}$
BuMeIm ⁺	Pic ⁻	$0.790 \pm 0.004^{\text{f}}$	$5.102 \pm 0.007^{\text{g}}$	2.45 ± 0.02	-1.86	3.24
	BF ₄ ⁻	$0.71 \pm 0.03^{\text{f}}$	$5.58 \pm 0.01^{\text{g}}$	-0.32 ± 0.04	-5.19	0.39
	PF ₆ ⁻	$0.80 \pm 0.02^{\text{f}}$	$5.18 \pm 0.01^{\text{g}}$	1.36 ± 0.03	-3.03	2.16
	NTf ₂ ⁻	$0.90 \pm 0.02^{\text{f}}$	$5.063 \pm 0.006^{\text{g}}$	2.76 ± 0.01	-1.40	3.66
HxMeIm ⁺	Pic ⁻	$1.01 \pm 0.02^{\text{f}}$	$5.114 \pm 0.006^{\text{g}}$	3.35 ± 0.05	-0.75	4.36
	BF ₄ ⁻	$0.78 \pm 0.03^{\text{f}}$	$5.55 \pm 0.02^{\text{g}}$	0.79 ± 0.05	-3.98	1.57
	PF ₆ ⁻	$0.87 \pm 0.02^{\text{f}}$	$5.156 \pm 0.006^{\text{g}}$	2.50 ± 0.03	-1.78	3.37
	NTf ₂ ⁻	$0.99 \pm 0.02^{\text{f}}$	$5.066 \pm 0.007^{\text{g}}$	3.90 ± 0.03	-0.18	4.89
OcMeIm ⁺	Pic ⁻	$1.21 \pm 0.01^{\text{f}}$	$5.11 \pm 0.01^{\text{g}}$	4.26 ± 0.06	0.36	5.47
	BF ₄ ⁻	$0.80 \pm 0.03^{\text{f}}$	$5.51 \pm 0.02^{\text{g}}$	1.86 ± 0.06	-2.85	2.66
	PF ₆ ⁻	$0.91 \pm 0.02^{\text{f}}$	$5.141 \pm 0.008^{\text{g}}$	3.61 ± 0.02	-0.62	4.52
	NTf ₂ ⁻	$1.13 \pm 0.01^{\text{f}}$	$5.049 \pm 0.003^{\text{g}}$	4.93 ± 0.02	1.01	6.06
Me ₄ N ⁺	Pic ⁻	$0.42 \pm 0.01^{\text{h}}$	$5.01 \pm 0.01^{\text{i}}$	$-0.14 \pm 0.03^{\text{i}}$	-4.73^{i}	0.28^{i}
Et ₄ N ⁺	Pic ⁻	$0.547 \pm 0.007^{\text{h}}$	$4.10 \pm 0.02^{\text{j}}$	$1.69 \pm 0.05^{\text{i}}$	-1.86^{i}	2.24^{i}
			$4.14 \pm 0.03^{\text{j}}$			
Pr ₄ N ⁺	Pic ⁻	$0.771 \pm 0.007^{\text{h}}$	$3.96 \pm 0.02^{\text{j}}$	$3.58 \pm 0.03^{\text{i}}$	0.39^{i}	4.35^{i}
			$4.08 \pm 0.02^{\text{j}}$			
Bu ₄ N ⁺	Pic ⁻	$1.033 \pm 0.008^{\text{h}}$	$3.82 \pm 0.06^{\text{j}}$	$5.52 \pm 0.03^{\text{i}}$	2.73^{i}	6.55^{i}
			$4.04 \pm 0.02^{\text{j}}$			

a. Ion-pair formation constant in water at infinite dilution, determined by capillary electrophoresis. b. Ion-pair formation constant in dichloromethane at infinite dilution, determined by conductometry. c. Distribution constant of ion pair; average and standard deviation of 10 – 22 measurements. d. Extraction constant defined by Eq. (1), calculated from $\log K_{\text{ex,1}}^0 = \log K_{\text{D}} + \log K_{\text{IP,w}}^0 - \log K_{\text{IP,o}}^0$. e. Extraction constant defined by Eq. (2), calculated from $\log K_{\text{ex,2}}^0 = \log K_{\text{D}} + \log K_{\text{IP,w}}^0$. f. Ref. 4. g. In dry solvent; Ref. 8. h. Ref. 10. i. In water-saturated solvent; Ref. 9. j. In dry solvent; Ref. 9.

Table 2 Single-ion transfer activity coefficients and standard Gibbs energies of transfer from water (w) to dichloromethane (o) at 25°C (molar scale)^a

Ion	$\log {}^{\circ}\gamma^{\text{w}}$	$\Delta G_{\text{tr,w} \rightarrow \text{o}}^{\circ}/\text{kJ mol}^{-1}$
BuMeIm ⁺	-1.18 ^b	6.7
HxMeIm ⁺	-0.07 ^b	0.4
OcMeIm ⁺	1.04 ^b	-5.9
Me ₄ N ⁺	-4.05 ^c	23.1
Et ₄ N ⁺	-1.18 ^c	6.7
Pr ₄ N ⁺	1.07 ^c	-6.1
Bu ₄ N ⁺	3.41 ^c	-19.5
Pic ⁻	-0.68 ^d	3.9
BF ₄ ⁻	$-3.94 \pm 0.06^{\text{e}}$	22.5 ± 0.4
PF ₆ ⁻	$-1.74 \pm 0.10^{\text{e}}$	9.9 ± 0.6
NTf ₂ ⁻	$-0.12 \pm 0.10^{\text{e}}$	0.7 ± 0.6

a. Based on the Ph₄AsBPh₄ assumption. $\Delta G_{\text{tr,w} \rightarrow \text{o}}^{\circ} = -RT \ln {}^{\circ}\gamma^{\text{w}}$.

b. Calculated from $\log {}^{\circ}\gamma^{\text{w}}(\text{C}^+) = \log K_{\text{ex,1}}^0 - \log {}^{\circ}\gamma^{\text{w}}(\text{A}^-)$ for the Pic⁻ salts.

c. Ref. 9.

d. Ref. 11.

e. Average and standard deviation of the $\log {}^{\circ}\gamma^{\text{w}}(\text{A}^-)$ values determined for the three RMeIm⁺ salts as $\log {}^{\circ}\gamma^{\text{w}}(\text{A}^-) = \log K_{\text{ex,1}}^0 - \log {}^{\circ}\gamma^{\text{w}}(\text{C}^+)$. Individual data of $\log {}^{\circ}\gamma^{\text{w}}(\text{A}^-)$: -4.01 for BuMeIm⁺BF₄⁻, -3.91 for HxMeIm⁺BF₄⁻, and -3.89 for OcMeIm⁺BF₄⁻; -1.84 for BuMeIm⁺PF₆⁻, -1.71 for HxMeIm⁺PF₆⁻, and -1.66 for OcMeIm⁺PF₆⁻; -0.22 for BuMeIm⁺NTf₂⁻, -0.11 for HxMeIm⁺NTf₂⁻, and -0.02 for OcMeIm⁺NTf₂⁻.

$$+ \frac{E_{\text{o,s}} - E_{\text{w,s}}}{2.30RT}, \quad (14)$$

where the first term, $(V_{\text{m,s}}/2.30)\{V_{\text{m,o}}^{-1} - V_{\text{m,w}}^{-1} + (\delta_{\text{w}} - \delta_{\text{o}})(\delta_{\text{w}} + \delta_{\text{o}} - 2\delta_{\text{s}}/RT)\}$, is derived from the regular solution theory,^{12,13} and $V_{\text{m,x}}$ and δ_{x} denote the molar volume and solubility parameter of a compound x, respectively. The $E_{\text{x,s}}$ term represents the energy

Fig. 1 Distribution constants of ion pairs as a function of solute molar volume. Ion pairs: Δ , RMeIm⁺BF₄⁻; $\diamond$, RMeIm⁺PF₆⁻; $\square$, RMeIm⁺NTf₂⁻; $\circ$, RMeIm⁺Pic⁻ (R = Bu, Hx, and Oc); $\bullet$, R₄N⁺Pic⁻ (R = Me, Et, Pr, and Bu). The data for R₄N⁺Pic⁻ are cited from Ref. 9.

for specific interaction between a solute s and a solvent x which can not be dealt with using the regular solution theory (dipole-dipole interaction, hydrogen bonding, etc.). Thus, the $E_{\text{o,s}} - E_{\text{w,s}}$ value indicates the relative strength of the specific solute-solvent interaction in the organic phase as compared to that in the aqueous phase. Equation (14) describes quantitatively the distribution behavior of the R₄N⁺Pic⁻ ion pairs between dichloromethane and water by using an empirical δ_{w} value, 36.2 MPa^{1/2}.⁹

In Fig. 1, the $\log K_{\text{D}}$ values of the ion pairs are plotted against their molar volumes, $V_{\text{m,s}}$, which are calculated as the sum of the molar volumes of the constituent ions. Experimental values^{6,14-17} of the ionic molar volumes in water are listed in Table 3, where the data for Pic⁻ and NTf₂⁻ have been obtained in this study through density measurements of aqueous solutions of Na⁺Pic⁻

Table 3 Molar volumes in water, van der Waals volumes, and van der Waals radii for ions

Ion	$V_m/\text{cm}^3 \text{ mol}^{-1}$ (25°C)	$V_{\text{vdw}}/\text{cm}^3 \text{ mol}^{-1}$	$r_{\text{vdw}}/10^{-8} \text{ cm}$
BuMeIm ⁺	140.7 ^a	91.1 ^b	3.31 ^b
HxMeIm ⁺	170.7 ^a	111.4 ^b	3.53 ^b
OcMeIm ⁺	201.3 ^a	131.7 ^b	3.74 ^b
Me ₄ N ⁺	83.6 ^c	56.6 ^c	2.82 ^c
Et ₄ N ⁺	143.7 ^c	96.9 ^c	3.37 ^c
Pr ₄ N ⁺	207.5 ^c	137.4 ^c	3.79 ^c
Bu ₄ N ⁺	271.2 ^c	178.0 ^c	4.13 ^c
Pic ⁻	138.6 ^d	95.1 ^b	3.35 ^b
BF ₄ ⁻	49.7 ^e	29.5 ^b	2.27 ^b
PF ₆ ⁻	66.4 ^f	42.4 ^b	2.56 ^b
NTf ₂ ⁻	146.1 ^g , 148.2 ^d	90.8 ^b	3.30 ^b

a. Obtained by subtracting the limiting apparent molar volumes (V_m^0) in water at 25°C of Br⁻ from that of RMeImBr. The V_m^0 values are 30.2 cm³ mol⁻¹ for Br⁻ (Ref. 14), 170.86 cm³ mol⁻¹ for BuMeIm⁺Br⁻ (Ref. 15), 200.9 cm³ mol⁻¹ for HxMeIm⁺Br⁻ (Ref. 6), and 231.5 cm³ mol⁻¹ for OcMeIm⁺Br⁻ (Ref. 6).

b. Ref. 8.

c. Ref. 9.

d. Calculated from the apparent molar volumes of Na⁺Pic⁻ (131.9 ± 1.3 cm³ mol⁻¹) and Li⁺NTf₂⁻ (141.8 ± 1.9 cm³ mol⁻¹) in the aqueous solutions of 0.10 mol kg⁻¹ at 25°C determined in this work. The V_m^0 values of Na⁺ (-6.7 cm³ mol⁻¹; Ref. 14) and Li⁺ (-6.4 cm³ mol⁻¹; Ref. 14) were used in the calculation.

e. Ref. 14.

f. Ref. 16.

g. Obtained by subtracting the V_m^0 value of Li⁺ from that of Li⁺NTf₂⁻ (139.7 cm³ mol⁻¹; Ref. 17).

and Li⁺NTf₂⁻ with a pycnometer. A good linear relationship is observed between $\log K_D$ and $V_{m,s}$ for a series of the RMeIm⁺ ion pairs with a given anion. This result means that an additional methylene group does not produce any appreciable change in δ_s and $E_{o,s} - E_{w,s}$ in Eq. (14). As seen from the molar volumes of the RMeIm⁺ ions (Table 3), the volume contribution of a methylene group is constant ($V_{m,\text{CH}_2} = 15.2$ cm³ mol⁻¹). Therefore, a linear relationship holds between $\log K_D$ and N_{CH_2} as described above. The same is true for the R₄N⁺Pic⁻ salts, where $V_{m,\text{CH}_2} = 15.9$ cm³ mol⁻¹.⁹ The δ_s and $E_{o,s} - E_{w,s}$ values were calculated from the slope and intercept of the $\log K_D$ and $V_{m,s}$ plot, respectively, where $\delta_s = 20.3$ MPa^{1/2},¹⁸ $V_{m,o} = 64.5$ cm³ mol⁻¹,¹⁸ and $V_{m,w} = 18.1$ cm³ mol⁻¹ (calculated from the density)¹⁹ were used. The values obtained are summarized in Table 4, together with the literature values for R₄N⁺Pic⁻.^{9,10}

The δ_s values for RMeIm⁺BF₄⁻, RMeIm⁺PF₆⁻, and RMeIm⁺NTf₂⁻ are equal to each other and are smaller than that of RMeIm⁺Pic⁻. The smaller δ_s values for the fluorine-containing ion pairs seem reasonable because it is known that fluorinated organic compounds generally have low solubility parameters, due to the low polarizability of the fluorine atom.¹³ According to Eq. (14), the slopes of the $\log K_D$ and $V_{m,s}$ plots generally increase with decreasing δ_s . Therefore, the greater $\Delta_{\text{CH}_2} \log K_D$ values for the fluorine-containing ion pairs are attributed to the smaller δ_s values, as compared to RMeIm⁺Pic⁻. The δ_s value of RMeIm⁺Pic⁻ is close to that of R₄N⁺Pic⁻, which is responsible for the similar $\Delta_{\text{CH}_2} \log K_D$ values of these ion pairs.

Recently, the heats of vaporization (ΔH_{vap}) of RMeIm⁺ salts as ion pairs were determined by using a line-of-sight mass spectrometric technique at 25°C.²⁰ The solubility parameters calculated from the equation $\delta = \{(\Delta H_{\text{vap}} - RT)/V_m\}^{1/2}$ are 21.2,

Table 4 Solubility parameters and solute-solvent interaction energy terms in Eq. (14) (ion pair) and Eq. (16) (cation) at 25°C

Ion pair	$\delta_s/\text{MPa}^{1/2}$	$(E_{o,s} - E_{w,s})/\text{kJ mol}^{-1}$
RMeIm ⁺ Pic ⁻	19.8	-33.6 ± 0.1
RMeIm ⁺ BF ₄ ⁻	18.7	-40.8 ± 0.6
RMeIm ⁺ PF ₆ ⁻	18.5	-36.2 ± 0.8
RMeIm ⁺ NTf ₂ ⁻	18.7	-42.5 ± 2.2
R ₄ N ⁺ Pic ⁻	19.7, ^b 19.4 ^c	-39.0 ± 0.2 ^{d,e}
Cation (i)	$\delta_s/\text{MPa}^{1/2}$	$(E_{o,i} - E_{w,i})/\text{kJ mol}^{-1}$
RMeIm ⁺	19.8	-9.8 ± 0.3
R ₄ N ⁺	19.5 ^d	-13.4 ± 0.9 ^d

a. Uncertainty is less than 0.2 MPa^{1/2}.

b. Determined from the solubilities of Bu₄N⁺Pic⁻ in hexane and tetradecane; Ref. 10.

c. Determined from the distribution constants of R₄N⁺Pic⁻ in *m*-xylene-water system; Ref. 10.

d. Ref. 9.

e. Recalculated using the V_m value of Pic⁻ determined in this work.

20.5, 20.2, 25.0, and 24.5 MPa^{1/2} for BuMeIm⁺NTf₂⁻, HxMeIm⁺NTf₂⁻, OcMeIm⁺NTf₂⁻, OcMeIm⁺BF₄⁻, and OcMeIm⁺PF₆⁻, respectively. These δ values are greater than those determined from Eq. (14) based on the regular solution theory. Such discrepancies are reasonable because the solubility parameters from ΔH_{vap} include the contributions from all the forces between the ion pairs such as London dispersion, dipole-dipole, and hydrogen bonding, whereas those determined in this study represent mainly the contribution from the dispersion forces to which the regular solution theory is applicable. The difference between the δ value from ΔH_{vap} and that from Eq. (14) is particularly large for the BF₄⁻ and PF₆⁻ salts, suggesting that the forces other than dispersion play important roles in the ion pair-ion pair interactions of these salts.

The $E_{o,s} - E_{w,s}$ values are all negatively large, reflecting the much stronger solute-solvent specific interaction for the ion pairs in the aqueous phase than in the organic phase. The absolute value of $E_{o,s} - E_{w,s}$, which can be a measure of the specific interaction in water, varies in the order, RMeIm⁺NTf₂⁻ $\approx$ RMeIm⁺BF₄⁻ > RMeIm⁺PF₆⁻ $\approx$ RMeIm⁺Pic⁻. Additionally, the absolute value of $E_{o,s} - E_{w,s}$ is smaller for RMeIm⁺Pic⁻ than for R₄N⁺Pic⁻, suggesting that the RMeIm⁺ ion pair has weaker specific interaction with water than the R₄N⁺ one.

According to Eq. (14), the fact that the K_D value of RMeIm⁺NTf₂⁻ is greater than that of RMeIm⁺BF₄⁻ is attributed only to the larger molar volume of the former, because these ion pairs are equal both in δ_s and in $E_{o,s} - E_{w,s}$. The $\log K_D$ values of RMeIm⁺PF₆⁻ are greater than those expected from the relationships between $\log K_D$ and $V_{m,s}$ for RMeIm⁺BF₄⁻ and RMeIm⁺NTf₂⁻ (Fig. 1). This is attributed to the difference in $E_{o,s} - E_{w,s}$ because there is no difference in the δ_s values of these ion pairs. When comparing RMeIm⁺Pic⁻ and R₄N⁺Pic⁻ having similar molar volumes, one finds that the K_D values is obviously greater for the former (Fig. 1); this is also attributed to the difference in $E_{o,s} - E_{w,s}$.

For a given cation, the K_D value of the ion pair always increases in the following anion order: *i.e.*, BF₄⁻ < PF₆⁻ < Pic⁻ < NTf₂⁻. This indicates that the K_D value is greater for the anion having a larger molar volume (Table 3). It should be noted that the order of the molar volume in water is slightly different from that of the van der Waals volume (BF₄⁻ < PF₆⁻ < NTf₂⁻ < Pic⁻), showing that the void space between the ion and the solvent (water) molecules is larger for NTf₂⁻ than for Pic⁻. In addition,

Fig. 2 Transfer activity coefficients of RMeIm⁺ and R₄N⁺ ions (A), those calculated based on the Born equation (B), and non-electrostatic terms in the transfer activity coefficients (C) plotted as a function of solute molar volume. Cation: ○, RMeIm⁺ (R = Bu, Hx, and Oc); ●, R₄N⁺ (R = Me, Et, Pr, and Bu). The data for R₄N⁺Pic⁻ are cited from Ref. 9.

no linear relationship is observed for the $\log K_D$ vs. $V_{m,s}$ plot for the ion pairs of a given cation with different anions. This is because the δ_i and $E_{o,s} - E_{w,s}$ values of the ion pair vary with the kind of the anion (Eq. (14)).

As shown in Eq. (12), the ion pair extraction constant ($K_{ex,2}^0$) is a product of $K_{IP,w}^0$ and K_D . It can be seen from the equilibrium constants in Table 1 that the alkyl-chain length dependence of the $K_{ex,2}^0$ value, BuMeIm⁺ < HxMeIm⁺ < OcMeIm⁺, is almost completely determined by that of the K_D value. The same is true for the anion dependence. The $K_{ex,2}^0$ values of RMeIm⁺Pic⁻ are much greater than those of R₄N⁺Pic⁻ when the cations have similar molar volumes; for example, $\log K_{ex,2}^0 = 5.47$ for OcMeIm⁺Pic⁻ (V_m (OcMeIm⁺) = 201.3 cm³ mol⁻¹) and 4.35 for Pr₄N⁺Pic⁻ (V_m (Pr₄N⁺) = 207.5 cm³ mol⁻¹). Although both the $K_{IP,w}^0$ and K_D values make positive contributions to the higher ion-pair extractability of RMeIm⁺ as compared to that of R₄N⁺, the contribution of K_D is more dominant. From the above, it can be said that the cation and anion dependences of the ion-pair extractability predominantly reflect those of the distribution of the ion pair.

Transfer activity coefficients of ions

Similarly to the $\log K_D$ value, the sign of the $\log {}^\circ\gamma^w$ value indicates the relative affinity of the ion to the different solvents. The negative value means that the ion is more strongly solvated in water than in dichloromethane, and the positive value means the opposite. The $\log {}^\circ\gamma^w$ value of the RMeIm⁺ ion increases linearly with N_{CH_2} from the negative value for BuMeIm⁺ to the positive one for OcMeIm⁺. An increment of the $\log {}^\circ\gamma^w$ value with a methylene group is 0.56, which is equal to those for RMeIm⁺BF₄⁻ (0.54), RMeIm⁺PF₆⁻ (0.56), and RMeIm⁺NTf₂⁻ (0.54), but greater than that for RMeIm⁺Pic⁻ (0.45). On the other hand, the $\log {}^\circ\gamma^w$ values of the anions are all negative. The $\log {}^\circ\gamma^w$ value varies in the order BF₄⁻ < PF₆⁻ < Pic⁻ < NTf₂⁻, which is the same order as that observed for the K_D values of their ion pairs with RMeIm⁺. Additionally, it was found that there is a good correlation between the $\log {}^\circ\gamma^w$ values and the standard ion-transfer potentials between nitrobenzene and water²¹ for the cations and anions, respectively.

The $\log {}^\circ\gamma^w$ values for the RMeIm⁺ ions show a good linear relationship with the molar volumes of the cations (Fig. 2(A)). The transfer of an ion between an organic solvent and water is often discussed by using the Born equation for electrostatic solvation energies.²² For a monovalent ion (i), the Born

expression of the transfer activity coefficient (${}^\circ\gamma_{Born}^w$) is

$$\log {}^\circ\gamma_{Born}^w(i) = \frac{e^2}{2.30kT \times 8\pi\epsilon_0 r_i} \left(\frac{1}{\epsilon_{r,w}} - \frac{1}{\epsilon_{r,o}} \right), \quad (15)$$

where k , e , r_i , and ϵ_0 are the Boltzmann's constant, the elementary electric charge, the radius of i, and the permittivity of vacuum, respectively. The $\log {}^\circ\gamma_{Born}^w$ values for the cations were calculated from Eq. (15), where $\epsilon_{r,w} = 78.3$,¹⁹ $\epsilon_{r,o} = 8.94$,²³ and $r_i = r_{vdw}$ (van der Waals radius, Table 3) were used. The $\log {}^\circ\gamma_{Born}^w$ values are shown in Fig. 2(B). The molar volume dependence of $\log {}^\circ\gamma_{Born}^w$ is not linear and is much less steep than that of the actual $\log {}^\circ\gamma^w$ value. We now express the non-electrostatic contribution, $\log {}^\circ\gamma^w - \log {}^\circ\gamma_{Born}^w$, by using an expression similar to that for the $\log K_D$ value of an electrically neutral solute (Eq. (14)):

$$\log {}^\circ\gamma^w(i) - \log {}^\circ\gamma_{Born}^w(i) = \frac{V_{m,i}}{2.30} \times \left\{ \frac{1}{V_{m,o}} - \frac{1}{V_{m,w}} + \frac{(\delta_w - \delta_o)(\delta_w + \delta_o - 2\delta_i)}{RT} \right\} + \frac{E_{o,i} - E_{w,i}}{2.30RT}, \quad (16)$$

where V_i and δ_i are the molar volume and solubility parameter of the ion i, respectively; $E_{s,i}$ is the energy of specific interaction between the ion i and the solvent x, other than the Born-type interaction. The plot of $\log {}^\circ\gamma^w - \log {}^\circ\gamma_{Born}^w$ vs. $V_{m,s}$ for the RMeIm⁺ ions is shown in Fig. 2(C). A good linear correlation is observed for all the cations. The linearity indicates that the δ_i and $E_{o,i} - E_{w,i}$ values for the cations are constant regardless of the alkyl-chain length. The values of δ_i and $E_{o,i} - E_{w,i}$ are shown in Table 4. The solubility parameter of the RMeIm⁺ ions is equal to that of the ion pairs with Pic⁻, and greater than those of the other ion pairs with the fluorinated anions. The $E_{o,i} - E_{w,i}$ value of the cations is negative, similarly to the case of the ion pairs; however, the absolute value is much smaller than those of the ion pairs, indicating that the specific interaction with water of the RMeIm⁺ ions is rather weak, except for the Born-type electrostatic interaction. It follows from this that the anion-water interactions or dipole (ion pair)-dipole (water) interactions make an important contribution in the specific interaction of the ion pairs with water. In addition, it is found that the alkyl-chain length dependence of the $\log {}^\circ\gamma^w$ value of RMeIm⁺ is governed by the non-electrostatic ion-solvent interactions which can be

Fig. 3 Difference between logarithmic ion-pair formation constants in water and dichloromethane as a function of reciprocal van der Waals radius of the cation. The symbols are the same as those in Fig. 1. The data for $R_4N^+Pic^-$ are cited from Ref. 9.

explained based on the regular solution theory. The above results are almost the same as those observed for the R_4N^+ ions.⁹ The δ_i value of $RMeIm^+$ is nearly equal to that of R_4N^+ . The $E_{o,i} - E_{w,i}$ value, however, is larger for $RMeIm^+$ than for R_4N^+ , indicating that the specific interaction with water is weaker for $RMeIm^+$. This is probably due to charge delocalization on the imidazolium ring. The difference in the $E_{o,i} - E_{w,i}$ value between $RMeIm^+$ and R_4N^+ is smaller than that in the $E_{o,s} - E_{w,s}$ value between the ion pairs $RMeIm^+Pic^-$ and $R_4N^+Pic^-$. It thus appears that the dehydration of the ions in the aqueous ion pairing process is greater for the $RMeIm^+$ salts than for the R_4N^+ ones, as the result of the stronger cation-anion interaction for the $RMeIm^+$ salts.⁸

Difference between ion-pair formation constants in water and dichloromethane

The ion-pair formation constants of the $RMeIm^+$ salts in water ($K_{IP,w}^0$) are much smaller than those in dichloromethane ($K_{IP,o}^0$) (Table 1). This can be explained in terms of the permittivity of water being much greater than that of dichloromethane based on the electrostatic association model. However, the difference in the cation dependence between $K_{IP,w}^0$ ($BuMeIm^+ < HxMeIm^+ < OcMeIm^+$) and $K_{IP,o}^0$ ($BuMeIm^+ \approx HxMeIm^+ \approx OcMeIm^+$) can not be explained by this model. Such a solvent effect on the ion-pair formation is discussed by considering the following relationship among the ion-pair formation constants, the transfer activity coefficients of the ions, and the distribution constant of the ion pair.⁹

$$\log K_{IP,w}^0 - \log K_{IP,o}^0 = \log {}^o\gamma^w(A^-) + \log {}^o\gamma^w(C^+) - \log K_D(C^+A^-). \quad (17)$$

Applying Eqs. (14)–(16), Eq. (17) can be rewritten as

$$\begin{aligned} \log K_{IP,w}^0 - \log K_{IP,o}^0 = & \log {}^o\gamma^w(A^-) \\ & + \frac{e^2}{2.30kT \times 8\pi\epsilon_0 r_C} \left(\frac{1}{\epsilon_{r,w}} - \frac{1}{\epsilon_{r,o}} \right) + \frac{V_{m,C}}{2.30} \\ & \times \left\{ \frac{1}{V_{m,o}} - \frac{1}{V_{m,w}} + \frac{(\delta_w - \delta_o)(\delta_w + \delta_o - 2\delta_C)}{RT} \right\} + \frac{E_{o,C} - E_{w,C}}{2.30RT} \\ & - \frac{V_{m,CA}}{2.30} \left\{ \frac{1}{V_{m,o}} - \frac{1}{V_{m,w}} + \frac{(\delta_w - \delta_o)(\delta_w + \delta_o - 2\delta_{CA})}{RT} \right\} \end{aligned}$$

$$- \frac{E_{o,CA} - E_{w,CA}}{2.30RT}, \quad (18)$$

where the subscript C and CA denote the cation C^+ and the ion pair C^+A^- , respectively. When $\delta_C \approx \delta_{CA}$ and $V_{m,CA} \approx V_{m,C} + V_{m,A}$, the sum of the third and fifth terms on the right side of Eq. (18) is approximately equal to $-(V_{m,A}/2.30)\{1/V_{m,o} - 1/V_{m,w} + (\delta_w - \delta_o)(\delta_w + \delta_o - 2\delta_C)/RT\}$, where $\delta_C = \delta_C$ or δ_{CA} . Furthermore, when the values of δ_C , $E_{o,C} - E_{w,C}$, and $E_{o,CA} - E_{w,CA}$ are constant regardless of the cation species, the following equation is valid for a given anion:

$$\log K_{IP,w}^0 - \log K_{IP,o}^0 \approx \frac{e^2(\epsilon_{r,w}^{-1} - \epsilon_{r,o}^{-1})}{2.30kT \times 8\pi\epsilon_0} \times \frac{1}{r_C} + \text{const.} \quad (19)$$

This equation means that the cation dependence of the $\log K_{IP,w}^0 - \log K_{IP,o}^0$ value is determined by that of the Born-type electrostatic solvation of the cation in the solvents. In Fig. 3, the $\log K_{IP,w}^0 - \log K_{IP,o}^0$ values are plotted against the reciprocal van der Waals radius of the cation. For the $RMeIm^+Pic^-$ salts, the plot shows a good linear relationship with a slope, -1.2×10^{-7} cm, which is in complete agreement with the theoretical value of the slope from Eq. (19), -1.21×10^{-7} cm. This result shows that Eq. (19) is valid for $RMeIm^+Pic^-$ because the $RMeIm^+$ cations and the $RMeIm^+Pic^-$ ion pairs have the same value of solubility parameter (Table 4). If one regards the cation dependence of the $K_{IP,o}^0$ value as a standard, the anomalous cation dependence of the $K_{IP,w}^0$ value can be attributed to the effect of electrostatic solvation of the cation in the high dielectric solvent water. Although the same holds true for $R_4N^+Pic^-$ (Fig. 3),⁹ the increment of the $\log K_{IP,w}^0$ value with each methylene group in the cation is obviously greater for $RMeIm^+Pic^-$ than for $R_4N^+Pic^-$.⁴ According to Eq. (19), this fact is related to the difference between these salts in the alkyl-chain length dependence of the $\log K_{IP,o}^0$ value; the $K_{IP,o}^0$ value of $R_4N^+Pic^-$ decreases with increasing alkyl-chain length, whereas that of $RMeIm^+Pic^-$ is almost constant.⁸

Linear relationships between $\log K_{IP,w}^0 - \log K_{IP,o}^0$ and $1/r_{vdw}$ are also observed for $RMeIm^+BF_4^-$, $RMeIm^+PF_6^-$, and $RMeIm^+NTf_2^-$ (Fig. 3), but the slopes (-3.5×10^{-8} , -4.3×10^{-8} , and -7.0×10^{-8} cm, respectively) are considerably less steep than that expected from Eq. (19). This is because the solubility parameters of these ion pairs are smaller than those of the cations. In this case, we can consider the following equation derived from Eq. (18):

$$\begin{aligned} \log K_{IP,w}^0 - \log K_{IP,o}^0 = & \frac{V_{m,C}}{2.30} \\ & \times \left\{ \frac{1}{V_{m,o}} - \frac{1}{V_{m,w}} + \frac{(\delta_w - \delta_o)(\delta_w + \delta_o - 2\delta_C)}{RT} \right\} + \frac{V_{m,CA}}{2.30} \\ & \times \left\{ \frac{1}{V_{m,o}} - \frac{1}{V_{m,w}} + \frac{(\delta_w - \delta_o)(\delta_w + \delta_o - 2\delta_{CA})}{RT} \right\} \\ \approx & \frac{e^2(\epsilon_{r,w}^{-1} - \epsilon_{r,o}^{-1})}{2.30kT \times 8\pi\epsilon_0} \times \frac{1}{r_C} + \text{const.} \quad (20) \end{aligned}$$

The plots of the left side of Eq. (20) vs. $1/r_{vdw}$ of the cation showed linear relationships with slopes of -1.5×10^{-7} , -1.7×10^{-7} , and -1.7×10^{-7} cm for $RMeIm^+BF_4^-$, $RMeIm^+PF_6^-$, and $RMeIm^+NTf_2^-$, respectively. These slope values are comparable with the theoretical value (-1.21×10^{-7} cm).

The $\log K_{IP,w}^0$ value of $RMeIm^+Pic^-$ is greater than that of $R_4N^+Pic^-$ when the cation are similar in size; for example, $\log K_{IP,w}^0 = 1.21^7$ for $OcMeIm^+Pic^-$ ($r_{vdw}(OcMeIm^+) = 3.74 \times 10^{-8}$

cm) and 0.77^{10} for $\text{Pr}_4\text{N}^+\text{Pic}^-$ ($r_{\text{vdw}}(\text{Pr}_4\text{N}^+) = 3.79 \times 10^{-8}$ cm). According to Eq. (18), the difference in $\log K_{\text{IP,w}}^0$ between $\text{RMeIm}^+\text{Pic}^-$ and $\text{R}_4\text{N}^+\text{Pic}^-$ is approximately equal to the sum of the differences in $\log K_{\text{IP,o}}^0$ and in $\{(E_{\text{o,C}} - E_{\text{w,C}}) - (E_{\text{o,CA}} - E_{\text{w,CA}})\}/2.30RT$, because the solubility parameters for RMeIm^+ , R_4N^+ , and their picrates are nearly equal to one another. The $\{(E_{\text{o,C}} - E_{\text{w,C}}) - (E_{\text{o,CA}} - E_{\text{w,CA}})\}/2.30RT$ value is a little smaller for $\text{RMeIm}^+\text{Pic}^-$ (4.2) than for $\text{R}_4\text{N}^+\text{Pic}^-$ (4.5), which does not contribute to the greater $\log K_{\text{IP,w}}^0$ value for $\text{RMeIm}^+\text{Pic}^-$. On the other hand, the $K_{\text{IP,o}}^0$ value is much greater for $\text{RMeIm}^+\text{Pic}^-$ than for $\text{R}_4\text{N}^+\text{Pic}^-$; for example, $\log K_{\text{IP,o}}^0 = 5.11^8$ for $\text{OcMeIm}^+\text{Pic}^-$ and 4.08^9 for $\text{Pr}_4\text{N}^+\text{Pic}^-$. The cation dependence of the ion-pair formation constant in dichloromethane reflects that of the direct cation-anion interaction in the gas phase.^{8,9} It can therefore be concluded that the direct cation-anion interaction is also a major factor determining the larger aqueous ion-pair formation constants for RMeIm^+ compared to those for R_4N^+ .

Conclusion

In this study, the distribution properties of the RMeIm^+ salts in the dichloromethane-water system have been quantitatively evaluated through determination of the distribution constants of the ion pairs and the transfer activity coefficients of the constituent ions at 25°C. In each case of the cation, anion, and ion pair, there is a tendency that the solute having a larger molar volume prefers more to partition from water to dichloromethane. The alkyl-chain length dependence of the distribution constant of the ion pair can be explained as a linear function of the molar volume on the basis of the regular solution theory. The alkyl-chain length hardly gives any change in the solubility parameter of the solute and the specific solute-solvent interaction. For the cations, the factor governing the alkyl-chain length dependence of the transfer activity coefficient is not the Born-type electrostatic interaction but the non-electrostatic interaction which can be dealt with by the regular solution theory. The solubility parameters determined for the RMeIm^+ cations and their ion pairs with Pic^- are equal to each other, and those for the ion pairs with the fluorinated anions (BF_4^- , PF_6^- , and NTf_2^-) are smaller owing to the low polarizability of the fluorine atoms.

The solubility parameter of the RMeIm^+ ions is nearly equal to that of the R_4N^+ ions, whereas the specific interaction with water is slightly weaker for the RMeIm^+ ions owing to charge delocalization on the imidazolium ring. The picrate ion pair of RMeIm^+ is even more hydrophobic than that of R_4N^+ when the cations have similar molar volumes. It is suggested that more dehydration of the ions in the aqueous ion pairing occurs for the RMeIm^+ salt than for the R_4N^+ one, as a result of the stronger cation-anion interaction for the former. The ion-pair extractability of the RMeIm^+ salt is higher than that of the R_4N^+ one when the cations are similar in size, which mainly reflects the difference in hydrophobicity of the ion pairs.

The cation dependence of the aqueous ion-pair formation constants of the RMeIm^+ salts has been discussed by using an equation derived considering the thermodynamic cycle in the dichloromethane-water system. The increase of the aqueous ion-pair formation constant with increasing alkyl-chain length of the cation is governed by the Born-type electrostatic solvation energy of the cation, which is in inverse proportion to the cation radius. On the other hand, the greater aqueous ion-pair

formation constant for $\text{RMeIm}^+\text{Pic}^-$ than for $\text{R}_4\text{N}^+\text{Pic}^-$ (when the cations are similar in size) reflects the trend in the direct cation-anion interaction, as is the case of the ion-pair formation constant in dichloromethane.

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