



The Laws Governing Ionic Liquid Extraction of Cations: Partition of 1-Ethylpyridinium Monocation and Paraquat Dication in Ionic Liquid/Water Biphasic Systems

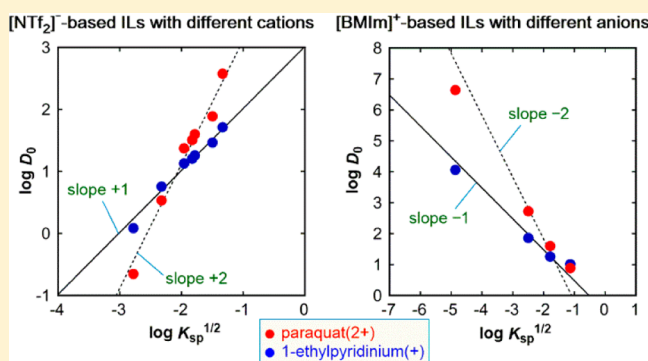
Takuya Hamamoto,^{†,‡} Miho Okai,[†] and Shoichi Katsuta^{*,†}

[†]Department of Chemistry, Graduate School of Science, Chiba University, 1-33 Yayoi-cho, Inage, Chiba 263-8522, Japan

[‡]Forensic Science Laboratory, Chiba Prefectural Police Headquarters, 1-71-1 Chuo-ko, Chuo, Chiba 260-0024, Japan

S Supporting Information

ABSTRACT: To find the laws governing the extraction of cations from aqueous solutions into hydrophobic ionic liquids (ILs), we investigated the partition of 1-ethylpyridinium monocation and paraquat (1,1'-dimethyl-4,4'-bipyridinium) dication in various IL/water biphasic systems. Ten different ILs of 1-butyl-3-methylimidazolium-based or bis-(trifluoromethanesulfonyl)amide-based salts were used. The distribution ratio of the target cations (T^{n+}) was dependent on the initial concentration in the aqueous phase and also very sensitive to the kind of IL. The behavior was quantitatively explained on the basis of a model in which the extraction goes through both the ion exchange and ion pair transfer processes, while keeping the product of the aqueous concentrations of the IL constituent ions a constant value (solubility product, K_{sp}). The distribution ratio of T^{n+} is expressed as a function of the difference between the initial and equilibrium concentrations of T^{n+} in the aqueous phase ($\Delta[T^{n+}]_w$), the aqueous solubility of IL ($K_{sp}^{1/2}$), and the cation valence n . The distribution ratio is a nearly constant value (D_0) when $\Delta[T^{n+}]_w \ll K_{sp}^{1/2}/n$ and decreases inversely proportional to the n th power of $\Delta[T^{n+}]_w$ when $\Delta[T^{n+}]_w \gg K_{sp}^{1/2}/n$. The $\log D_0$ versus $\log K_{sp}^{1/2}$ plot gives a linear relationship with a slope of $+n$ for the ILs with the same anion but different cations and that with a slope of nearly $-n$ for the ILs with the same cation but different anions. This means that the extractability dependence on the kinds of IL constituent ions is greater for the divalent cation than for the monovalent one.



INTRODUCTION

Recently, ionic liquids (ILs) have attracted much attention in various fields of chemistry owing to their novelty, environmentally friendly properties, designability, and so on. Especially, the application of ILs as extracting solvents in place of conventional organic solvents is one of the hot areas of research, because the hazardousness of organic solvents to the environment or human body can be reduced by using ILs which are almost nonvolatile and nonflammable.^{1–6} The solvent extraction with ILs has been widely applied for various chemical species, ranging from metals to biological molecules.^{2,4–12}

Enormous variations of ILs have been produced by changing the combination of cation and anion. Therefore, understanding the relationships between the kind of the IL constituent ions and the extraction property is extremely important for the application of ILs to solvent extraction. In our previous studies,^{13,14} the distribution of picrate (2,4,6-trinitrophenolate) anion in various IL/water biphasic systems was investigated in detail. For analysis of the results, we proposed an extraction model that the target anion in the aqueous phase is extracted together with the IL constituent cation in the aqueous phase or

extracted by exchange with the IL constituent anion in the IL phase. On the basis of this model, we obtained theoretical equations relating the distribution ratio (D) of the target anion to the amount of the extracted target anion, by which the partition behaviors of the anion in various IL/water biphasic systems were successively explained. In addition, we clarified that a main factor governing the distribution ratio of the target anion is the aqueous solubility of IL, i.e., the square root of the aqueous solubility product of IL (K_{sp}). On the other hand, for the IL extraction of cations, no theoretical and quantitative descriptions of the extraction behaviors have been established, except for the mechanistic studies concerning metal ion extraction with ILs in the presence of extractants.^{15–20}

The purpose of this study is to find the laws that govern the extraction of cations from water to ILs; the target cations are 1-ethylpyridinium monocation and paraquat (1,1'-dimethyl-4,4'-bipyridinium) dication. The reason for using them as model cations is that they are chemically stable and have both high extractability and high visible-light absorption which allow us to

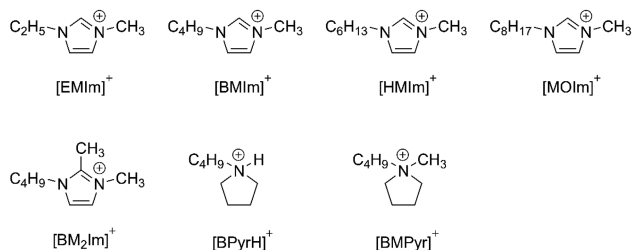
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easily measure the distribution ratio. Furthermore, paraquat is a well-known toxic herbicide frequently inspected,^{21,22} and is hardly extracted by usual nonpolar organic solvents.²³ These facts give a practical significance to the study of the extraction of paraquat with ILs. As the extraction solvents, the following 10 kinds of hydrophobic ILs are used: 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([EMIm][NTf₂]), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF₆]), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([BMIm][NTf₂]), 1-butyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)amide ([BMIm][NPF₂]), 1-butyl-3-methylimidazolium bis(nonafluorobutanesulfonyl)amide ([BMIm][NNf₂]), 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([HMIm][NTf₂]), 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)amide ([MOIm][NTf₂]), 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide ([BM₂Im][NTf₂]), 1-butylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([BPyRH][NTf₂]), and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([BMPyr][NTf₂]). The structural formulas of their constituent ions are shown in Figure 1. For some of the ILs, the aqueous solubilities were also measured to determine the K_{sp} values.

Cations:



Anions:

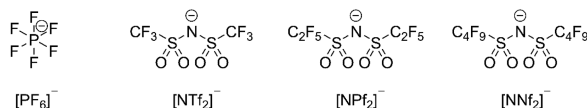


Figure 1. Structural formulas of the constituent ions of ILs and their abbreviations.

EXPERIMENTAL SECTION

Materials. [EMIm][NTf₂] of “for advanced material research” grade was purchased from Kanto Chemical Co. (Tokyo, Japan), and [BMPyr][NTf₂] of “for organic synthesis” grade was purchased from Wako Pure Chemical Industries (Osaka, Japan). They were washed three times with deionized water prior to use. [BMIm][NTf₂] was prepared by mixing aqueous solutions of [BMIm]Cl (Sigma-Aldrich Co., St. Louis, MO; ≥98.0% purity) and Li[NTf₂] (Kanto Chemical Co.; >99.7% purity) of the molar ratio 1:1.2. The IL phase separated from the aqueous phase was washed seven times with deionized water. The yield was nearly quantitative (90%). In a similar manner, [MOIm][NTf₂] was prepared from [MOIm]Cl (Wako Pure Chemical Industries; “for organic synthesis” grade) and Li[NTf₂] (97% yield), [BMIm][NPF₂] from [BMIm]Cl and Li[NPF₂] (Kishida Chemical Co., Osaka, Japan; 99% purity) (97% yield), and [BMIm][NNf₂] from

[BMIm]Cl and Li[NNf₂] (Wako Pure Chemical Industries; >97% purity) (91% yield), respectively. The purities of the products were checked by atomic absorption spectrophotometry for Li⁺ and ion-selective potentiometry for Cl⁻; mass fractions $w(\text{Li}) < 6 \times 10^{-7}$ and $w(\text{Cl}) < 1 \times 10^{-6}$ for [BMIm][NTf₂]; $w(\text{Li}) < 6 \times 10^{-9}$ and $w(\text{Cl}) < 5 \times 10^{-7}$ for [MOIm][NTf₂]; $w(\text{Li}) < 6 \times 10^{-9}$ and $w(\text{Cl}) < 4 \times 10^{-7}$ for [BMIm][NPF₂]; $w(\text{Li}) < 2 \times 10^{-7}$ and $w(\text{Cl}) < 2 \times 10^{-6}$ for [BMIm][NNf₂]. [BMIm][PF₆], [HMIm][NTf₂], [BM₂Im][NTf₂], and [BPyRH][NTf₂] were the same as previously used.^{14,24,25} Water was distilled and further deionized with a Milli-Q Lab system (Millipore, Billerica, MA). Dichloromethane (Kanto Chemical Co.; guaranteed reagent grade) was purified by distillation. Chloroform (Kanto Chemical Co.; guaranteed reagent grade) was washed three times with deionized water prior to use. Paraquat dichloride ([PQ]Cl₂) (Tokyo Chemical Industry Co.; >98.0% purity) was dried at 398 K for 3 h prior to use. 1-Ethylpyridinium chloride ([EP]Cl) (Tokyo Chemical Industry Co.; >98.0% purity), sodium picrate (Na[Pic]) monohydrate (Kanto Chemical Co.; extra-pure reagent grade), and other reagents (guaranteed reagent grade) were used as received.

Solubility Measurements. The solubilities of [EMIm][NTf₂], [BMIm][NPF₂], and [BMIm][NNf₂] in water were determined by measuring the cation concentration in the IL-saturated aqueous solutions at 298.2 ± 0.2 K by the ion pair extraction–spectrophotometric method using dichloromethane (extracting solvent) and [Pic]⁻ (ion-pairing agent).¹⁴ In dichloromethane at 298.2 ± 0.2 K, the maximum absorption wavelength (λ_{max}) and molar absorptivity (ϵ) of each ion pair were as follows: $\lambda_{\text{max}} = 367.8$ nm, $\epsilon = (1.43 \pm 0.04) \times 10^4$ cm⁻¹·mol⁻¹·dm³ for [EMIm][Pic]; $\lambda_{\text{max}} = 367.8$ nm, $\epsilon = 1.70 \times 10^4$ cm⁻¹·mol⁻¹·dm³ for [BMIm][Pic].¹³ The solubility values are summarized in Table 1, together with the literature values.^{13,14,26–29}

Partition Experiments. An aqueous solution of [EP]Cl (8.6×10^{-5} to 5.9×10^{-1} mol·dm⁻³) or [PQ]Cl₂ (1.2×10^{-5} to 4.9×10^{-2} mol·dm⁻³) and a water-saturated IL were placed in a stoppered centrifuge tube made of glass or polypropylene copolymer (PPCO); the PPCO tube was used for [PQ]Cl₂ to prevent the [PQ]²⁺ ion from adsorbing to the tube surface. The volume of the viscous IL phase was evaluated from the mass by using the densities of ILs: 1.5020 ± 0.0001 g·cm⁻³ for [EMIm][NTf₂] (wet), 1.3550 g·cm⁻³ for [BMIm][PF₆] (wet),²⁵ 1.4311 g·cm⁻³ for [BMIm][NTf₂] (wet),²⁵ 1.5117 ± 0.0001 g·cm⁻³ for [BMIm][NPF₂] (wet), 1.6111 g·cm⁻³ for [BMIm][NNf₂] (dry),³⁰ 1.370 g·cm⁻³ for [HMIm][NTf₂] (dry),³¹ 1.3276 g·cm⁻³ for [MOIm][NTf₂] (wet),³² 1.4159 g·cm⁻³ for [BM₂Im][NTf₂] (wet),¹⁴ 1.3826 g·cm⁻³ for [BPyRH][NTf₂] (wet),¹⁴ and 1.3919 g·cm⁻³ for [BMPyr][NTf₂] (wet);²⁵ the densities of water-saturated [EMIm][NTf₂] and [BMIm][NPF₂] at 298.2 ± 0.2 K were determined from three measurements for each IL with a DMA35n oscillating U-tube density meter (Anton Paar, Graz, Austria) calibrated with pure water. The volume ratio of the IL phase to the aqueous phase was adjusted from 1/25 to 1/10. The biphasic mixture in the centrifuge tube was equilibrated by stirring with a magnetic stirrer for 1 h in a water bath thermostated at 298.2 ± 0.2 K. After the two phases were completely separated by centrifugation, the tube was allowed to stand for more than 15 min in the thermostatic water bath. The concentrations of [EP]⁺ and [PQ]²⁺ in the aqueous phase were determined spectrophotometrically ($\lambda_{\text{max}} = 258.0$ nm, $\epsilon = (4.40 \pm 0.04) \times$

Table 1. Solubilities^a and Solubility Products (K_{sp}) of ILs in Water at 298.2 K and 0.1 MPa

no.	IL	mole fraction solubility	molar solubility (mol·dm ⁻³)	K_{sp} ^b (mol ² ·dm ⁻⁶)
1	[EMIm][NTf ₂]	8.38×10^{-4} (3×10^{-6}) 8.38×10^{-4} ^c	4.64×10^{-2} (1×10^{-4})	2.16×10^{-3}
2	[BMIm][PF ₆]	1.33×10^{-3} ^d 1.21×10^{-3} ^e	7.36×10^{-2} ^d	5.42×10^{-3} ^d
3	[BMIm][NTf ₂]	2.968×10^{-4} ^d 3.07×10^{-4} ^c	1.643×10^{-2} ^d	2.70×10^{-4} ^d
4	[BMIm][NPF ₂]	5.80×10^{-5} (2×10^{-7})	3.21×10^{-3} (1×10^{-5})	1.03×10^{-5}
5	[BMIm][NNf ₂]	2.468×10^{-7} (8×10^{-10})	1.366×10^{-5} (5×10^{-8})	1.867×10^{-10}
6	[HMIIm][NTf ₂]	8.62×10^{-5} ^f 9.56×10^{-5} ^c	4.77×10^{-3} ^f	2.28×10^{-5} ^f
7	[MOIm][NTf ₂]	3.00×10^{-5} ^d 3.36×10^{-5} ^c 2.5×10^{-5} ^g	1.66×10^{-3} ^d	2.76×10^{-6} ^d
8	[BM ₂ Im][NTf ₂]	1.987×10^{-4} ^f	1.100×10^{-2} ^f	1.21×10^{-4} ^f
9	[BPyrH][NTf ₂]	5.74×10^{-4} ^f	3.18×10^{-2} ^f	1.01×10^{-3} ^f
10	[BMPyr][NTf ₂]	2.69×10^{-4} ^d 2.57×10^{-4} ^h	1.49×10^{-2} ^d	2.22×10^{-4} ^d

^aValues in parentheses are standard errors. ^bCalculated as the square of solubility. ^cReference 26. ^dReference 13. ^eReference 27. ^fReference 14. ^gReference 28. ^hReference 29 (295 K).

Table 2. Aqueous Equilibrium Concentrations of IL Cation (C^+), IL Anion (A^-), and $[EP]^+$ (T^+) and Distribution Ratios (D) of $[EP]^+$ in Two IL/Water Systems^a at 298.2 K

no.	$[T^+]_{W,init}$ ^b (mmol·dm ⁻³)	$[C^+]_W$ (mmol·dm ⁻³)	$[A^-]_W$ (mmol·dm ⁻³)	$[T^+]_W$ (mmol·dm ⁻³)	$[C^+]_W \times [A^-]_W$ (mol ² ·dm ⁻⁶)	log D
IL = [EMIm][NTf ₂]						
1	0.160	45.6	46.2	0.0267	2.11×10^{-3}	1.696
2	0.800	47.3	47.0	0.129	2.22×10^{-3}	1.717
3	3.25	48.3	46.0	0.500	2.22×10^{-3}	1.735
4	13.3	52.5	42.0	2.27	2.20×10^{-3}	1.689
5	40.0	68.2	34.7	8.37	2.37×10^{-3}	1.578
6	107	92.7	25.4	31.1	2.36×10^{-3}	1.385
7	214	134	19.1	86.2	2.57×10^{-3}	1.179
IL = [BMPyr][NTf ₂]						
1	0.0864	14.8	14.6	0.0327	2.17×10^{-4}	1.215
2	0.156	14.8	14.1	0.0591	2.08×10^{-4}	1.215
3	0.800	16.0	14.9	0.299	2.39×10^{-4}	1.224
4	3.25	17.0	14.3	1.28	2.43×10^{-4}	1.188
5	9.74	19.1	12.7	4.17	2.43×10^{-4}	1.127
6	28.6	24.9	10.5	13.9	2.62×10^{-4}	1.023
7	71.4	35.1	8.16	43.5	2.86×10^{-4}	0.806
8	214	52.6	6.54	157	3.44×10^{-4}	0.564

^aThe volume ratio of the IL phase to the aqueous phase is 1/10. The data for $[EP]^+$ in the other IL/water systems are shown in Tables S1 and S2 (Supporting Information). ^bInitial concentration of $[EP]Cl$ in the aqueous phase.

$10^3 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for $[EP]^+$; $\lambda_{\max} = 256.0 \text{ nm}$, $\epsilon = (2.05 \pm 0.01) \times 10^4 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for $[PQ]^{2+}$). The concentrations of $[EP]^+$ and $[PQ]^{2+}$ in the IL phase were calculated on the basis of the mass balance, where the volume change of the IL phase due to its dissolution into the aqueous phase was taken into account based on the solubility (Table 1). The D values were calculated as the ratio of the molar concentration in the IL phase to that in the aqueous phase. The extraction of Cl^- was confirmed to be negligibly small by using a chloride ion meter.

In the case of the extraction of $[EP]^+$, the concentrations of the IL constituent ions in the aqueous phase were also investigated. The aqueous concentrations of the IL constituent cations were determined as follows. An aliquot of the aqueous phase was transferred into another stoppered glass tube, to which $Na[Pic]$ and $NaOH$ were added so that their concentrations were 5×10^{-2} and $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$,

respectively. Dichloromethane, whose volume was equal to that of the aqueous solution, was further added, and the biphasic mixture was stirred for 30 min. By this operation, both $[EP]^+$ and the IL constituent cation in the aqueous phase were quantitatively extracted as ion pairs with $[Pic]^-$ into the dichloromethane phase. As a result, the measured absorption spectrum was the superposition of the spectra of the $[EP][Pic]$ salt and the IL constituent cation- $[Pic]^-$ salt. The concentration of the IL constituent cation was calculated by considering the contribution of $[EP]^+$ ($\lambda_{\max} = 367.0 \text{ nm}$, $\epsilon = 1.70 \times 10^4 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for $[HMIIm][Pic]$; ³³ $\lambda_{\max} = 367.8 \text{ nm}$, $\epsilon = 1.72 \times 10^4 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for $[MOIm][Pic]$; ¹³ $\lambda_{\max} = 374.8 \text{ nm}$, $\epsilon = 1.69 \times 10^4 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for $[BMPyr][Pic]$; ¹³ $\epsilon = (1.13 \pm 0.07) \times 10^4 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ (at 367.0 nm), $(1.13 \pm 0.04) \times 10^4 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ (at 367.8 nm), $(1.14 \pm 0.08) \times 10^4 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ (at 374.8 nm) for $[EP][Pic]$).

The aqueous concentrations of the IL constituent anions were determined as follows. An aliquot of the aqueous phase was transferred into another centrifuge tube, to which methylene blue ([MB]Cl) and NaH₂PO₄ were added so that their concentrations were 4×10^{-4} and 4×10^{-1} mol·dm⁻³, respectively. Chloroform, whose volume was equal to that of the aqueous solution, was further added, and the biphasic mixture was stirred for 1 h. It was confirmed that the IL constituent anion in the aqueous phase was quantitatively extracted as an ion pair with [MB]⁺ into the chloroform phase. The concentration in the chloroform phase was determined spectrophotometrically ($\lambda_{\text{max}} = 652.2$ nm, $\epsilon = (6.2 \pm 0.3) \times 10^4$ cm⁻¹·mol⁻¹·dm³ for [MB][PF₆]; $\lambda_{\text{max}} = 652.2$ nm, $\epsilon = 1.20 \times 10^5$ cm⁻¹·mol⁻¹·dm³ for [MB][NTf₂];¹³ $\lambda_{\text{max}} = 652.2$ nm, $\epsilon = (1.14 \pm 0.03) \times 10^5$ cm⁻¹·mol⁻¹·dm³ for [MB][NPF₂]).

RESULTS AND DISCUSSION

As representatives, the log *D* values of the target cations ($T^{n+} = [\text{EP}]^+$ ($n = 1$) and $[\text{PQ}]^{2+}$ ($n = 2$)) with a few ILs obtained at different initial concentrations of the cations ($[T^{n+}]_{\text{W,Init}}$) are shown in Tables 2 and 3, respectively. The data obtained for

Table 3. Aqueous Equilibrium Concentrations and Distribution Ratios (*D*) of $[\text{PQ}]^{2+}$ (T^{2+}) in Two IL/Water Systems^a at 298.2 K

no.	$[T^{2+}]_{\text{W,Init}}^b$ (mmol·dm ⁻³)	$[T^{2+}]_{\text{W}}$ (mmol·dm ⁻³)	log <i>D</i>
IL = [BMIm][NTf ₂]			
1	0.0493	0.00969	1.633
2	0.123	0.0243	1.631
3	0.247	0.0496	1.620
4	0.493	0.101	1.609
5	1.23	0.269	1.576
6	2.47	0.594	1.521
7	4.93	1.40	1.422
8	12.3	5.00	1.185
9	24.7	13.5	0.939
10	49.3	31.8	0.764
IL = [BMIm][NPF ₂]			
1	0.0247	0.000428	2.757
2	0.0493	0.000915	2.729
3	0.123	0.00242	2.704
4	0.247	0.00520	2.670
5	0.493	0.0121	2.605
6	1.23	0.0445	2.432
7	2.47	0.160	2.162
8	4.93	0.694	1.791
9	12.3	4.35	1.268
10	24.7	13.4	0.930

^aThe volume ratio of the IL phase to the aqueous phase is 1/10. The data for $[\text{PQ}]^{2+}$ in the other IL/water systems are shown in Table S3 (Supporting Information). ^bInitial concentration of $[\text{PQ}]\text{Cl}_2$ in the aqueous phase.

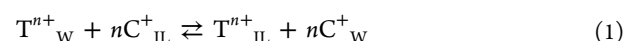
the other systems are listed in Tables S1–S3 in the Supporting Information. For a given IL, the extractability of T^{n+} , expressed by the *D* value, decreases with an increase of $[T^{n+}]_{\text{W,Init}}$ in a high $[T^{n+}]_{\text{W,Init}}$ region, whereas it is nearly constant in a low $[T^{n+}]_{\text{W,Init}}$ region. The extractability of T^{n+} is much dependent on the kind of IL used; for example, the *D* value of $[\text{PQ}]^{2+}$ with [BMIm][NNf₂] is about 20 million times greater than that with [MOIm][NTf₂] in the low $[T^{n+}]_{\text{W,Init}}$ region. In addition, the extraction selectivity between $[\text{PQ}]^{2+}$ and $[\text{EP}]^+$ is also different

with the IL used; $[\text{EP}]^+$ is more extractable than $[\text{PQ}]^{2+}$ with [BMIm][PF₆], [HMIm][NTf₂], and [MOIm][NTf₂], and the reverse is true with the other ILs. Therefore, it is obvious that the selection of the IL used is significant in the IL extraction of cations. We applied the following equilibrium theory in order to understand the above results quantitatively.

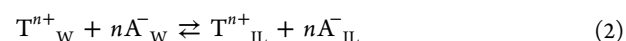
Theoretical Expression for IL Extraction of Cations.

Regarding the extraction of a target *n*-valent cation, T^{n+} , in an IL/water biphasic system, the following two equilibrium reactions can be considered.

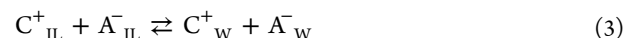
Ion exchange extraction:



Ion pair extraction:



where C^{+} and A^{-} are the IL constituent cation and anion, respectively; the subscripts “W” and “IL” represent the aqueous and IL phases, respectively. In addition, there exists the dissolution equilibrium of IL in the aqueous phase.



The equilibrium constants for eq 1 (ion exchange extraction constant, $K_{\text{ex-IE},n}$), eq 2 (ion pair extraction constant, $K_{\text{ex-IP},n}$), and eq 3 (solubility product, K_{sp}) are defined as

$$K_{\text{ex-IE},n} = [T^{n+}]_{\text{IL}} [C^{+}]_{\text{W}}^n / [T^{n+}]_{\text{W}} \quad (4)$$

$$K_{\text{ex-IP},n} = [T^{n+}]_{\text{IL}} / [T^{n+}]_{\text{W}} [A^{-}]_{\text{W}}^n \quad (5)$$

$$K_{\text{sp}} = [C^{+}]_{\text{W}} [A^{-}]_{\text{W}} \quad (6)$$

where the square brackets denote the concentration of each ion. These equations are based on the assumption of dilute solutions for C^{+} and A^{-} in the aqueous phase and for T^{n+} in both phases; the concentrations of C^{+} and A^{-} in the IL phase are not included on the right side of the equations because their activities are regarded as constant. Among these equilibrium constants, the following relationship holds.

$$K_{\text{ex-IE},n} / K_{\text{ex-IP},n} = K_{\text{sp}}^n \quad (7)$$

The K_{sp} value can be determined as the square of the solubility, assuming that ion association is negligible. The values are shown in Table 1.

When no extraction occurs, the aqueous concentrations of C^{+} and A^{-} should be both equal to $K_{\text{sp}}^{1/2}$. Upon the extraction of T^{n+} , the aqueous concentration of C^{+} increases (eq 1) and that of A^{-} decreases (eq 2). When the counteranion of T^{n+} (i.e., Cl^{-} in this study) is not involved with the extraction of T^{n+} , the following equation is derived from the charge balance in the aqueous phase

$$[T^{n+}]_{\text{W,Init}} - [T^{n+}]_{\text{W}} = ([C^{+}]_{\text{W}} - [A^{-}]_{\text{W}}) / n \quad (8)$$

where $[T^{n+}]_{\text{W,Init}}$, as mentioned above, denotes the initial concentration of T^{n+} in the aqueous phase. When $[T^{n+}]_{\text{W,Init}} - [T^{n+}]_{\text{W}}$, namely, the difference between the initial and equilibrium concentrations of T^{n+} in the aqueous phase, is represented by $\Delta[T^{n+}]_{\text{W}}$, the following equations expressing the aqueous concentrations of C^{+} and A^{-} are derived from eqs 6 and 8.

$$[C^+]_W = \{n\Delta[T^{n+}]_W + (n^2\Delta[T^{n+}]_W^2 + 4K_{sp})^{1/2}\}/2 \quad (9)$$

$$[A^-]_W = \{-n\Delta[T^{n+}]_W + (n^2\Delta[T^{n+}]_W^2 + 4K_{sp})^{1/2}\}/2 \quad (10)$$

On the other hand, D is equal to the concentration ratio of T^{n+} between the IL and aqueous phase ($D = [T^{n+}]_{IL}/[T^{n+}]_W$); hence, the following equations are derived from eqs 4 and 5.

$$\log D = \log K_{ex-IE,n} - n \log[C^+]_W \quad (11)$$

$$\log D = \log K_{ex-IP,n} + n \log[A^-]_W \quad (12)$$

Substituting $[C^+]_W$ and $[A^-]_W$ in eqs 11 and 12 by eqs 9 and 10, the following equations are obtained.

$$\log D = \log K_{ex-IE,n} - n \log\{n\Delta[T^{n+}]_W + (n^2\Delta[T^{n+}]_W^2 + 4K_{sp})^{1/2}\}/2 \quad (13)$$

$$\log D = \log K_{ex-IP,n} + n \log\{-n\Delta[T^{n+}]_W + (n^2\Delta[T^{n+}]_W^2 + 4K_{sp})^{1/2}\}/2 \quad (14)$$

Equations 13 and 14 are essentially equal to each other, because they can interconvert using eq 7.

Note that the same equations as eqs 13 and 14 can also be derived for the IL extraction of anions (T^{n-}) because we can construct the theory for the IL extraction of anions by interchanging C^+ and A^- in each equation described above. It has already been experimentally confirmed that eqs 13 and 14 hold for the distribution of a monovalent anion T^- in various IL/water biphasic systems.^{13,14}

According to eq 13 or 14, when $\Delta[T^{n+}]_W \rightarrow 0$, namely, in a dilute condition of T^{n+} , the $\log D$ value ($\log D_0$) is expressed as follows.

$$\log D_0 = \log K_{ex-IE,n} - n \log K_{sp}^{1/2} \quad (15)$$

$$\log D_0 = \log K_{ex-IP,n} + n \log K_{sp}^{1/2} \quad (16)$$

Equations 15 and 16 indicate that the $\log D$ value is constant, regardless of the value of $\Delta[T^{n+}]_W$. From eqs 15 and 16, the following equation can also be obtained.

$$\log D_0 = (\log K_{ex-IE,n} + \log K_{ex-IP,n})/2 \quad (17)$$

On the other hand, when $\Delta[T^{n+}]_W \rightarrow \infty$, the $\log D$ value ($\log D_\infty$) is expressed as follows.

$$\log D_\infty = \log K_{ex-IE,n} - n \log(n\Delta[T^{n+}]_W) \quad (18)$$

$$\log D_\infty = \log K_{ex-IP,n} + n \log K_{sp} - n \log(n\Delta[T^{n+}]_W) \quad (19)$$

Equations 18 and 19 indicate that the $\log D$ value varies in inverse proportion to the n th power of $\Delta[T^{n+}]_W$. In a graph of $\log D$ versus $\log \Delta[T^{n+}]_W$, the asymptote from eq 15 or 16 (a horizontal line) and that from eq 18 or 19 (a slope $-n$ line) have an intersection point at $\log \Delta[T^{n+}]_W = \log(K_{sp}^{1/2}/n)$.

Concentration Changes of IL Constituent Ions. For the extraction systems of $[EP]^+$ with several ILs, the concentrations of IL constituent ions, C^+ and A^- , in the aqueous phase at equilibrium were measured; the results are shown in Table 2 and Table S1 (Supporting Information). In each system, the equilibrium concentration of C^+ increases and that of A^-

decreases with an increase of the initial concentration of $[EP]^+$. Furthermore, in general, the products of the equilibrium concentrations of C^+ and A^- are nearly equal to the K_{sp} values of ILs (Table 1). These results mean that the extraction of cations with ILs always occurs through both the ion exchange extraction (eq 1) and the ion pair extraction (eq 2) holding the solubility product relationship (eq 6), similarly to the case of the extraction of anions.¹³ Exceptionally, when the initial concentration of $[EP]^+$ is high, the products of the equilibrium concentrations of C^+ and A^- are larger than K_{sp} ; the deviations are attributed to the decrease of the activity coefficients of ions in the aqueous phase associated with the increase of ionic strength. The deviations are generally remarkable (about 19–90%) when the initial concentration of $[EP]^+$ is more than 200 mmol·dm⁻³ (e.g., no. 5 and no. 6 for [BMIm][PF₆] in Table S1, Supporting Information).

Dependence of Distribution Ratio on Extracted Amount of Cations. In Figures 2 and 3, the $\log D$ values of

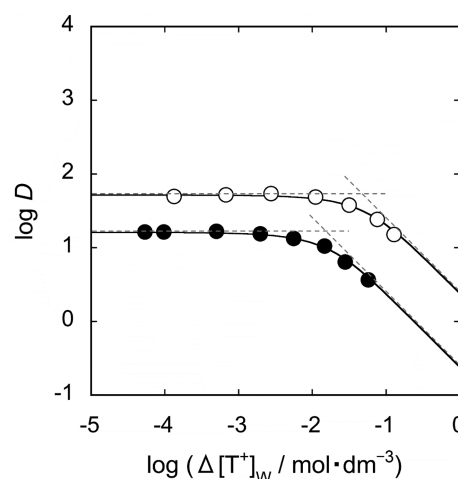


Figure 2. Distribution ratio of $[EP]^+$ as a function of the difference between the initial and equilibrium concentrations of $[EP]^+$ in the aqueous phase. The solid lines are the regression curves based on eq 13 or 14 ($n = 1$). The broken lines are the asymptotic lines based on eqs 15–18. IL: O, [EMIm][NTf₂]; ●, [BMPyr][NTf₂].

$[EP]^+$ in the [EMIm][NTf₂]/water and [BMPyr][NTf₂]/water systems and those of $[PQ]^{2+}$ in the [BMIm][NTf₂]/water and [BMIm][NPF₂]/water systems are plotted against the $\log \Delta[T^{n+}]_W$ values, respectively. When the $\log \Delta[T^{n+}]_W$ value is relatively low, i.e., the extracted amount of the target cation is small, the $\log D$ value of the cation is almost independent of $\Delta[T^{n+}]_W$. On the other hand, when the $\log \Delta[T^{n+}]_W$ value is relatively high, i.e., the extracted amount of the target cation is large, the $\log D$ value decreases with an increase of the $\log \Delta[T^{n+}]_W$ value. The decreasing degree is greater for $[PQ]^{2+}$ than for $[EP]^+$. The solid lines in these figures are the regression curves calculated from eq 13 or 14 by substituting 1 ($[EP]^+$) or 2 ($[PQ]^{2+}$) for n and using the K_{sp} values of each IL in Table 1. The correlation coefficients of these curves are 0.99 or more, indicating that the experimental results can be successfully explained by the theory presented here. The asymptote lines in the lower and higher $\log \Delta[T^{n+}]_W$ regions are indicated by broken lines in Figures 2 and 3. As expected from eqs 15 and 18 (or eqs 16 and 19), the lines have an intersection point at $\log \Delta[T^{n+}]_W \approx \log(K_{sp}^{1/2}/n)$; the $\log(K_{sp}^{1/2}/n)$ values are -1.33 ($[EP]^+$ – [EMIm][NTf₂]/water

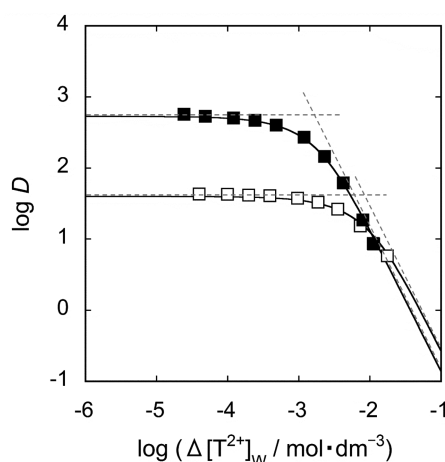


Figure 3. Distribution ratio of $[PQ]^{2+}$ as a function of the difference between the initial and equilibrium concentrations of $[PQ]^{2+}$ in the aqueous phase. The solid lines are the regression curves based on eq 13 or 14 ($n = 2$). The broken lines are the asymptotic lines based on eqs 15–18. IL: □, $[BMIm][NTf_2]$; ■, $[BMIm][NPF_6]$.

system), -1.83 ($[EP]^+ - [BMPyr][NTf_2]$ /water system), -2.09 ($[PQ]^{2+} - [BMIm][NTf_2]$ /water system), and -2.79 ($[PQ]^{2+} - [BMIm][NPF_6]$ /water system). The $K_{sp}^{1/2}/n$ value can be regarded as the upper limit of $\Delta[T^{n+}]_w$ where the D value is nearly constant independently of $\Delta[T^{n+}]_w$; therefore, the upper limit of $\Delta[T^{n+}]_w$ becomes higher for an IL of higher aqueous solubility and for a target cation of lower valence.

Dependence of Extraction Constants on IL Constituent Ions. From the data in Table 2 and Tables S1 and S2 (Supporting Information), the $K_{ex-IE,1}$ and $K_{ex-IP,1}$ values of $[EP]^+$ were determined by using eqs 13 and 14, respectively. The D_0 values of $[EP]^+$ were calculated from eq 15 or 16. The logarithmic values of $K_{ex-IE,1}$, $K_{ex-IP,1}$, and D_0 are summarized in Table 4. In the same way, $K_{ex-IE,2}$, $K_{ex-IP,2}$, and D_0 of $[PQ]^{2+}$ were determined from the data in Table 3 and Table S3 (Supporting Information). Their logarithmic values are summarized in Table 5.

Similarly to the case of the IL extraction of anions,^{13,14} the $K_{ex-IE,n}$ or $K_{ex-IP,n}$ value depends strongly on the kind of the IL constituent ion involved in the corresponding equilibrium reaction. For both $[EP]^+$ and $[PQ]^{2+}$, the $K_{ex-IE,n}$ value changes largely among the $[NTf_2]^-$ -based ILs with different C^+ , whereas the values are not different so much among the $[BMIm]^+$ -based ILs with different A^- . This is consistent with the fact that C^+ is

directly concerned with the ion exchange extraction (eq 1) and A^- is not. Similarly, the $K_{ex-IP,n}$ values depend greatly on the kind of A^- but not on the kind of C^+ , as expected from the reaction formula of the ion pair extraction (eq 2).

Regardless of the kind of target cation, the $K_{ex-IE,n}$ value with a $[NTf_2]^-$ -based IL decreases in the following C^+ order: $[EMIm]^+ > [BPyH]^+ > [BMIm]^+ > [BMPyr]^+ > [BM_2Im]^+ > [HMIIm]^+ > [MOIm]^+$. The sequence means that the IL with a more hydrophilic C^+ has a stronger ion exchange property for a cation. On the other hand, the $K_{ex-IP,n}$ value with a $[BMIm]^+$ -based IL varies with A^- as follows: $[NNF_2]^- > [NPF_6]^- > [NTf_2]^- > [PF_6]^-$. Therefore, the IL with a more hydrophobic A^- has a stronger ion pair extraction property for a cation.

Dependence of Distribution Ratio on IL Constituent Ions. The D_0 value is an upper limit of D which can be attained in a certain IL/water system, and is equal to the geometric mean of the $K_{ex-IE,n}$ and $K_{ex-IP,n}$ values, as shown in eq 17. When comparing ILs in their extraction power for a given target cation T^{n+} , the D_0 value is a useful measure. As seen from eq 16, D_0 is a linear function of $K_{ex-IP,n}$ and an n th order function of $K_{sp}^{1/2}$. For the ILs with different C^+ but the same A^- , the $\log D_0$ versus $\log K_{sp}^{1/2}$ plot should give a linear relationship with a slope of $+n$ because the $K_{ex-IP,n}$ value is insensitive to the kind of C^+ . In Figure 4, the plots of $\log D_0$ versus $\log K_{sp}^{1/2}$ are shown for the extraction of $[EP]^+$ and $[PQ]^{2+}$ with $[NTf_2]^-$ -based ILs with different C^+ . As expected above, a linear relationship with a slope of $+1$ for $[EP]^+$ and that with a slope of $+2$ for $[PQ]^{2+}$ are found. The slope values correspond to the valences of the target cations, indicating that the dependence of the D_0 value on the kind of C^+ is greater for a target cation of higher valence. As a result, the extraction selectivity between $[PQ]^{2+}$ and $[EP]^+$ differs depending on the kind of C^+ ; the IL with a more hydrophilic C^+ has a higher selectivity for $[PQ]^{2+}$ over $[EP]^+$.

Similarly, for the ILs with different A^- but the same C^+ , it is expected from eq 15 that the $\log D_0$ versus $\log K_{sp}^{1/2}$ plot gives a linear relationship with a slope of $-n$, because the $K_{ex-IE,n}$ value is insensitive to the kind of A^- . In Figure 5, the plots of $\log D_0$ versus $\log K_{sp}^{1/2}$ are shown for the extraction of $[EP]^+$ and $[PQ]^{2+}$ with $[BMIm]^+$ -based ILs with different A^- . Indeed, a linear relationship with a slope of about -1 (-0.9) for $[EP]^+$ and that with a slope of about -2 (-1.6) for $[PQ]^{2+}$ are observed. The A^- dependence of the D_0 value is greater for a target cation of higher valence, resulting in the variation of the extraction selectivity between $[PQ]^{2+}$ and $[EP]^+$ with the kind of A^- ; the IL with a more hydrophobic A^- has a higher selectivity for $[PQ]^{2+}$ over $[EP]^+$. The result that the slope

Table 4. Distribution Ratios (D_0) of $[EP]^+$ in Dilute Condition^a and Extraction Equilibrium Constants ($K_{ex-IE,1}$ and $K_{ex-IP,1}$) at 298.2 K

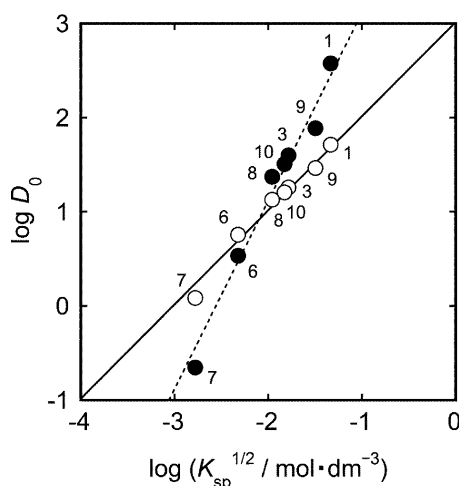
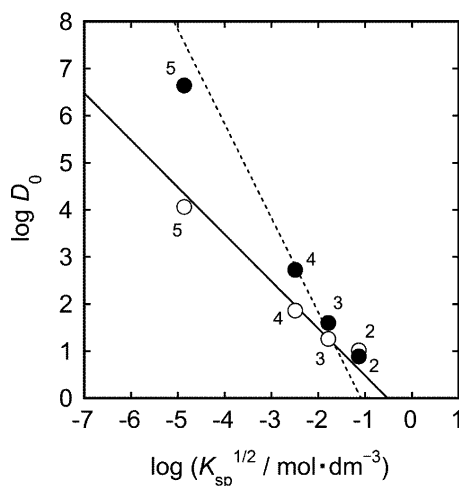
no.	IL	$\log(K_{ex-IE,1}/\text{mol}\cdot\text{dm}^{-3})^b$	$\log(K_{ex-IP,1}/\text{mol}^{-1}\cdot\text{dm}^3)^b$	$\log D_0$
1	$[EMIm][NTf_2]$	0.382 (0.010)	3.049 (0.010)	1.715
2	$[BMIm][PF_6]$	-0.119 (0.019)	2.148 (0.019)	1.014
3	$[BMIm][NTf_2]$	-0.524 (0.004)	3.044 (0.004)	1.260
4	$[BMIm][NPF_6]$	-0.630 (0.004)	4.357 (0.004)	1.864
5	$[BMIm][NNF_2]$	-0.801 (0.016)	8.928 (0.016)	4.063
6	$[HMIIm][NTf_2]$	-1.565 (0.014)	3.078 (0.014)	0.757
7	$[MOIm][NTf_2]$	-2.694 (0.009)	2.866 (0.009)	0.086
8	$[BM_2Im][NTf_2]$	-0.830 (0.002)	3.087 (0.002)	1.129
9	$[BPyH][NTf_2]$	-0.032 (0.008)	2.964 (0.008)	1.466
10	$[BMPyr][NTf_2]$	-0.619 (0.008)	3.035 (0.008)	1.208

^aIn the condition that $\Delta[T^+]_w \rightarrow 0$, where $T^+ = [EP]^+$. ^bValues in parentheses are standard errors.

Table 5. Distribution Ratios (D_0) of $[PQ]^{2+}$ in Dilute Condition^a and Extraction Equilibrium Constants ($K_{\text{ex-IE},2}$ and $K_{\text{ex-IP},2}$) at 298.2 K

no.	IL	$\log(K_{\text{ex-IE},2}/\text{mol}^2\cdot\text{dm}^{-6})^b$	$\log(K_{\text{ex-IP},2}/\text{mol}^2\cdot\text{dm}^{-6})^b$	$\log D_0$
1	[EMIm][NTf ₂]	−0.089 (0.008)	5.244 (0.008)	2.578
2	[BMIm][PF ₆]	−1.376 (0.002)	3.156 (0.002)	0.890
3	[BMIm][NTf ₂]	−1.968 (0.015)	5.169 (0.015)	1.601
4	[BMIm][NPF ₂]	−2.260 (0.011)	7.714 (0.011)	2.727
5	[BMIm][NNf ₂]	−3.086 (0.048)	16.373 (0.048)	6.643
6	[HMIIm][NTf ₂]	−4.109 (0.018)	5.177 (0.018)	0.534
7	[MOIm][NTf ₂]	−6.213 (0.027)	4.907 (0.027)	−0.653
8	[BM ₂ Im][NTf ₂]	−2.544 (0.012)	5.291 (0.012)	1.374
9	[BPyH][NTf ₂]	−1.106 (0.002)	4.885 (0.002)	1.890
10	[BMPyr][NTf ₂]	−2.145 (0.008)	5.162 (0.008)	1.509

^aIn the condition that $\Delta[T^{2+}]_w \rightarrow 0$, where $T^{2+} = [PQ]^{2+}$. ^bValues in parentheses are standard errors.

**Figure 4.** Relationship between $\log D_0$ and $\log K_{\text{sp}}^{1/2}$ for the $[\text{NTf}_2]^-$ -based IL systems. The numbers of ILs correspond to those in Tables 1, 4, and 5. The solid line is the regression line with a slope of +1 for $[\text{EP}]^+$ (○). The broken line is the regression line with a slope of +2 for $[\text{PQ}]^{2+}$ (●).**Figure 5.** Relationship between $\log D_0$ and $\log K_{\text{sp}}^{1/2}$ for the $[\text{BMIm}]^+$ -based IL systems. The numbers of ILs correspond to those in Tables 1, 4, and 5. The solid line is the regression line with a slope of −1 for $[\text{EP}]^+$ (○). The broken line is the regression line with a slope of −2 for $[\text{PQ}]^{2+}$ (●).

values are slightly larger than those expected can be attributed to some variations of the $K_{\text{ex-IE},n}$ value with the kind of A^- ; for

both target cations, the $K_{\text{ex-IE},n}$ value with a $[\text{BMIm}]^+$ -based IL decreases slightly with an increase of the size of A^- : $[\text{PF}_6]^- > [\text{NTf}_2]^- > [\text{NPF}_2]^- > [\text{NNf}_2]^-$. The higher cation exchange extractability of the IL with a smaller A^- may be explained in terms of the electrostatic interaction between A^- and T^{n+} in the IL phase.

In our previous study on the IL extraction of a picrate anion,¹⁴ the $[\text{NTf}_2]^-$ -based ILs with protic cations (such as $[\text{BPyH}]^+$), those with 1,3-dialkylimidazolium cations, and those with other aprotic cations showed different correlations in the $\log D_0$ versus $\log K_{\text{sp}}^{1/2}$ plot. The result was explained in terms of the difference in magnitude of the interactions (hydrogen bonding) of C^+ with T^- (picrate). On the other hand, in the IL extraction of cations (Figure 4), such differences with the type of C^+ are not observed (Figure 4). This shows that the interaction between C^+ and T^{n+} is weak and not an important factor governing the distribution ratio of T^{n+} .

CONCLUSION

In the extraction of mono- and divalent alkylpyridinium cations from aqueous solutions into hydrophobic ILs, the extraction is regarded as going through both the ion exchange with the IL constituent cation and the ion pair transfer with the IL constituent anion, keeping the product of the aqueous concentrations of the IL constituent ions a constant value K_{sp} . On the basis of the model, we have derived the equation expressing the distribution ratio of the target cation (T^{n+}), which is a function of $\Delta[\text{T}^{n+}]_w$ (i.e., the difference between the initial and equilibrium concentrations of T^{n+} in the aqueous phase), $K_{\text{sp}}^{1/2}$, and n . For a given T^{n+} in an IL/water system, the distribution ratio becomes a nearly constant value (D_0) when $\Delta[\text{T}^{n+}]_w \ll K_{\text{sp}}^{1/2}/n$ and decreases inversely proportional to the n th power of $\Delta[\text{T}^{n+}]_w$ when $\Delta[\text{T}^{n+}]_w \gg K_{\text{sp}}^{1/2}/n$. The remarkable solvent effects of IL on the D_0 value are also clarified: for a given T^{n+} , a higher D_0 value is attained by an IL formed by a more hydrophilic cation and a more hydrophobic anion. The IL suitable for the extraction of cations is quite different from that suitable for the extraction of anions, indicating that cation or anion selective extraction can be achieved by appropriate selection of IL. The $\log D_0$ versus $\log K_{\text{sp}}^{1/2}$ plot gives a linear relationship with a slope of $+n$ for the ILs with the same anion but different cations and that with a slope of nearly $-n$ for the ILs with the same cation but different anions. Such relationships are valid regardless of the type of the IL cation (protic or aprotic). The findings in this study enable the quantitative explanation of the extraction behavior of

cations with various ILs and also are useful for the selection of ILs to be used as the extraction solvents.

■ ASSOCIATED CONTENT

■ Supporting Information

Results of extraction of $[\text{EP}]^+$ in $[\text{BMIm}][\text{PF}_6]/\text{water}$, $[\text{BMIm}][\text{NTf}_2]/\text{water}$, $[\text{BMIm}][\text{NPF}_2]/\text{water}$, $[\text{HMIm}][\text{NTf}_2]/\text{water}$, and $[\text{MOIm}][\text{NTf}_2]/\text{water}$ systems (Table S1); results of extraction of $[\text{EP}]^+$ in $[\text{BMIm}][\text{NNf}_2]/\text{water}$, $[\text{BM}_2\text{Im}][\text{NTf}_2]/\text{water}$, and $[\text{BPyrH}][\text{NTf}_2]/\text{water}$ systems (Table S2); and results of extraction of $[\text{PQ}]^{2+}$ in $[\text{EMIm}][\text{NTf}_2]/\text{water}$, $[\text{BMIm}][\text{PF}_6]/\text{water}$, $[\text{BMIm}][\text{NNf}_2]/\text{water}$, $[\text{HMIm}][\text{NTf}_2]/\text{water}$, $[\text{MOIm}][\text{NTf}_2]/\text{water}$, $[\text{BM}_2\text{Im}][\text{NTf}_2]/\text{water}$, $[\text{BPyrH}][\text{NTf}_2]/\text{water}$, and $[\text{BMPyr}][\text{NTf}_2]/\text{water}$ systems (Table S3). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b02923.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +81-43-290-2781. Fax: +81-43-290-2874. E-mail: katsuta@faculty.chiba-u.jp.

Notes

The authors declare no competing financial interest.

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