Talanta 83 (2010) 299–304

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Solvent effect of ionic liquids on the distribution constant of 2-thenoyltrifluoroacetone and its nickel(II) and copper(II) chelates and the evaluation of the solvent properties based on the regular solution theory

Keiji Kidani, Hisanori Imura*

Division of Material Sciences, Graduate School of Natural Science & Technology, Kanazawa University, Kanazawa 920-1192, Japan

ARTICLE INFO

Article history:
Received 11 August 2010
Received in revised form 7 September 2010
Accepted 8 September 2010
Available online 24 September 2010

Keywords:
Ionic liquids
Distribution constant
Enol fraction
Regular solution theory
Solubility parameter
4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione
Nickel(II)
Copper(II)

ABSTRACT

Distribution constants of 2-thenoyltrifluoroacetone (Htta) and its Ni(II)and Cu(II) chelates between 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_n$mimTf_2N; $n = 4$, 6, and 8) as ionic liquid (IL) and an aqueous phase were determined. The enol fraction of Htta in ILs was spectrophotometrically measured to calculate the distribution constant of the enol form ($K_{D,HE}$) of Htta. The $K_{D,HE}$ values in ILs were evaluated by comparing those in various molecular solvents such as alkanes, aromatic hydrocarbons, chlorohydrocarbons, ethers, ketones, and esters previously reported on the basis of the regular solution theory (RST). It was elucidated that the IL solutions of Htta (enol) can be taken as apparently regular solutions as expected in the organic solvents. On the other hand, the effect of ILs on the distribution constant of metal(II) chelates ($K_{D,M}$) was fairly complicated. The $Cu(tta)_2$-IL solutions behaved like the alkane and aromatic hydrocarbon solutions but the $Ni(tta)_2$-IL (C_4mimTf_2N) like ether and ketone solutions. In the Ni(II) case, some specific interactions between the Ni(II) chelate and IL was suggested. Finally, the solubility parameters of ILs were calculated using $K_{D,HE}$ by RST and were in good agreement with the literature values obtained by the enthalpy of vaporization.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Ionic liquids (ILs) are organic salts having melting points under 100 °C. Especially, IL in liquid state at room temperature are termed room-temperature ionic liquid. Unlike conventional organic solvents or molecular solvents, the ionic nature of ILs leads to their unique properties such as negligible vapor pressure and noncombustibility. Furthermore, their physicochemical properties can be finely tuned by changing the cationic and/or the anionic components. Thus various ILs have been synthesized and applied to many fields in chemistry such as analytical chemistry [1], electrochemistry [2], organic chemistry [3], and others [4].

Some ILs immiscible with water have been used as a solvent for liquid–liquid extraction of metal cations and summarized in a recent review [5]. Most different natures of the ILs from such conventional solvents for extraction as hydrocarbons, ethers, ketones, esters, and alcohols are that ILs are salts and act as liquid ion exchangers. Barnes and co-workers reported the extraction of strontium nitrate into 1-alkyl-3-methylimidazolium hexafluorophosphates with dicyclohexano-18-crown-6 [6], and Rogers and coworkers incorporated thiourea, thioether, and urea into derivatized imidazolium cations and used these functionized ILs as the extractant in the extraction of Hg^{2+} and Cd^{2+} [7].

In the use of ILs as an extraction solvent, however, the recovery or stripping of extracted species from ILs is often a severe problem because the IL phase includes the ionic extractable species as its salt and also cannot be evaporated. In addition, the loss of an IL component with the ion-exchange reaction also becomes the problem. From these problems, the use of acidic chelating extractants is designed [8–10]. Since an extractable metal chelate is formed by the acid dissociation of the extractant, the use of acidic chelating extractant is a favorable choice to achieve the recovery by simple back-extraction with acids, even if metal chelates extractable into the IL phase are not only common neutral chelates but also anionic (or cationic) ones.

Therefore, it is necessary to understand the whole extraction equilibria containing the distribution constant of an acidic chelating extractant and its metal chelate between ILs and an aqueous phase as well as the physicochemical properties of ILs for solvent extraction. At the present time, however, there are few reports dealing with the distribution constants in the IL systems on the basis of solution theory.

In this study, the distribution constants of 2-thenoyltrifluoroacetone (Htta) and its Ni(II) and Cu(II) chelates were determined using a series of ILs having different alkyl groups,

---

* Corresponding author. Tel.: +81 76 264 5694; fax: +81 76 264 6060.
E-mail addresses: imura@se.kanazawa-u.ac.jp, imura@cacheibm.s.kanazawa-u.ac.jp (H. Imura).

0039-9140/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2010.09.011

1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_n$mimTf_2N: $n = 4$, 6, and 8). The enol fraction of Htta in the IL phase was measured to discuss the solvent effect of IL on the intrinsic distribution constant of the enol form. From these results, solvent properties of IL were evaluated with the aid of the regular solution theory (RST), and the solubility parameter of the ILs was calculated using the distribution constants.

2. Experimental

2.1. Reagents

The syntheses of $C_n$mimTf_2N where n (the number of carbon atoms in the alkyl chain) = 4, 6, and 8 were performed according to the literature [11]. The ILs obtained were further purified by the active carbon treatment [12]. 2-Thenoyltrifluoroacetone (1-(2′-thienyl)-4,4,4-trifluoro-1,3-butanedione; Htta) was obtained from Dojindo Laboratories, and further purified by vacuum sublimation. A stock solution (1×10^{-3} mol dm^{-3}) of Ni(II) was prepared by diluting a standard solution for atomic absorption spectrometry purchased from Sigma-Aldrich Japan with water. Other chemicals used were of analytical or guaranteed reagent-grade. High purity deionized water (18.2 MΩ) processed by a Milli-Q system (Millipore) was used throughout this work.

2.2. Apparatus

A UV/vis spectrophotometer (JASCO model Ubest V-570i RM/DS) was used for the determination of Htta in $C_n$mimTf_2N and aqueous solutions. A Zeeman atomic absorption spectrophotometer (FAAS, Hitachi model Z-6100) was used for the determination of Ni(II) in aqueous solutions. The shaking was performed using a Taitec SR-2s shaker at 300 strokes/min. A pH meter (Horiba model F-52) equipped with a combination glass electrode (Horiba 9611-10D) was calibrated by the pH standard solutions of oxalate, phthalate, phosphate, tetraborate, and calcium hydroxide.

2.3. Procedures

2.3.1. Distribution of Htta

An aliquot (0.5 cm^3) of a $C_n$mimTf_2N solution containing 1.0×10^{-2} mol dm^{-3} Htta was shaken with a 5-cm^3 portion of an aqueous solution of 1.0×10^{-1} mol dm^{-3} (H, Na)Cl at 25 ± 1 °C for 1 h. The pH value of aqueous phases was adjusted to 1–12 with 1.0×10^{-1} mol dm^{-3} hydrochloric acid and 1.0×10^{-2} mol dm^{-3} sodium hydroxide. After the two phases were separated by centrifugation, the equilibrium concentrations of Htta in both $C_n$mimTf_2N phase and aqueous phase were measured from the absorbance at 334 and 268 nm, respectively and the distribution ratio (D_{HA}) of Htta was calculated. The equilibrium pH value in the aqueous phase was immediately measured after the phase separation.

2.3.2. Determination of enol fraction

A stock solution of 5.0×10^{-3} mol dm^{-3} Htta in benzene was prepared by dissolving it in anhydrous benzene distilled, and stored in the dark prior to experiment in order to reach keto-enol equilibration. A 0.03 cm^3 portion of the stock solution of Htta was added to $C_n$mimTf_2N (3 cm^3) which was pre-equilibrated with the aqueous solution of 1.0×10^{-1} mol dm^{-3} sodium chloride and immediately mixed. The change in absorbance of the enol form of Htta in $C_n$mimTf_2N was measured at 334 nm for 6,000 s at 25 ± 1 °C.

To determine the enol fraction of Htta in the benzene stock solution, the NMR spectrum was measured in C_6D_6. The enol fraction was calculated from the NMR signals of enol vinyl proton and the keto methylene protons [13].

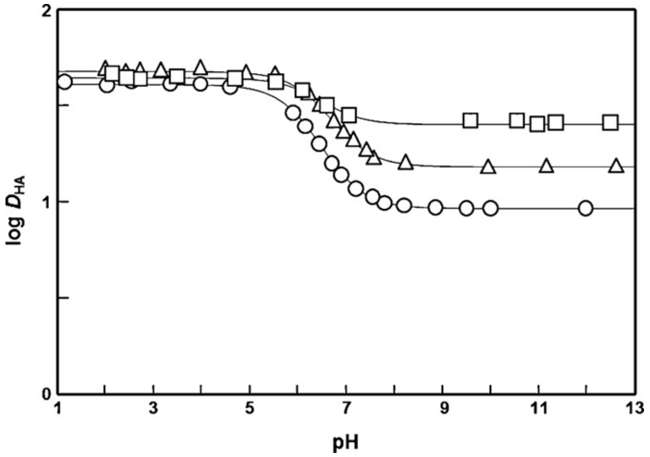

Fig. 1. Distribution ratio of Htta as a function of pH. Initial concentration of Htta, 1.0×10^{-2} mol dm^{-3}. Ionic strength, 1.0×10^{-1} mol dm^{-3} (H,Na)Cl. (○) C_4mimTf_2N; (△) C_6mimTf_2N; (□) C_8mimTf_2N.

2.3.3. Distribution of Ni(II)

A 5.0-cm^3 portion of an aqueous Ni(II) solution (1.0×10^{-5} mol dm^{-3}) containing 1.0×10^{-1} mol dm^{-3} potassium nitrate was shaken for 2 h with a 1.0 cm^3 of a C_4mimTf_2N solution of 1.0×10^{-3}–1.0×10^{-1} mol dm^{-3} Htta at 25 ± 1 °C. The pH value of aqueous phase was adjusted to 3–5 with 1.0×10^{-1} mol dm^{-3} nitric acid, 1.0×10^{-2} mol dm^{-3} acetic acid, and 1.0×10^{-2} mol dm^{-3} sodium hydroxide. After centrifugation, pH was immediately measured and the Ni(II) concentration in the aqueous phase were determined by FAAS. The Ni(II) concentration in the C_4mimTf_2N phase was determined after back-extraction into a 10-fold volume of 1 mol dm^{-3} nitric acid. The distribution ratio (D_M) of Ni(II) was calculated from the Ni(II) concentrations in both phases.

3. Results and discussion

3.1. Distribution of Htta

The distribution ratio of Htta between the $C_n$mimTf_2N ($n = 4$, 6, and 8) and the aqueous phase was investigated as a function of aqueous phase pH to determine the distribution constant of Htta. Fig. 1 shows that log D_{HA} in each $C_n$mimTf_2N system is almost constant in the lower pH region as expected because the neutral Htta species is formed and distributed between the two phases. In the medium region of pH 6–7, the log D_{HA} value decreases with increase in pH due to the dissociation of Htta in the aqueous phase and the distribution into the aqueous phase, as generally seen in the organic solvent systems. In the higher pH region in the $C_n$mimTf_2N system, however, the log D_{HA} value becomes constant again because the anionic species of tta$^-$ is transferred from the aqueous phase into the $C_n$mimTf_2N phase by ion-exchange with the Tf_2N^- anion.

Therefore, D_{HA} of Htta in the $C_n$mimTf_2N system can be written as follows:

$$D_{HA} = \frac{[\mathrm{Htta}]_{IL} + [\mathrm{tta}^-]_{IL}}{[\mathrm{Htta}] + [\mathrm{tta}^-]}, \qquad (1)$$

where the subscript IL denotes the $C_n$mimTf_2N phase. The distribution constant of Htta ($K_{D,HA}$) and the ion-exchange constant of tta$^-$ (K_{IE}) are defined by:

$$K_{D,HA} = \frac{[\mathrm{Htta}]_{IL}}{[\mathrm{Htta}]}, \qquad (2)$$

Table 1
Enol fraction and distribution constants of Htta at 25 °C.

Solvent	$\log K_{D,HA}$	f_e	$\log K_{D,HE}$	$\log K_{D,A}$[a]
C_4mimTf_2N	1.61 ± 0.05	0.43 ± 0.01	3.04 ± 0.05	0.96 ± 0.10
C_8mimTf_2N	1.68 ± 0.06	0.55 ± 0.02	3.22 ± 0.06	1.18 ± 0.12
C_8mimTf_2N	1.64 ± 0.08	0.72 ± 0.01	3.29 ± 0.08	1.40 ± 0.07
Benzene	1.62[b]	0.95 ± 0.02[c]	3.39	–

[a] Conditional constant at $(0.9–1) \times 10^{-2}$ mol dm^{-3} tta$^-$ in IL.
[b] Ref. [27].
[c] Calculated by NMR method.

$$K_{IE} = \frac{[\text{tta}^-]_{IL}[\text{Tf}_2\text{N}^-]}{[\text{tta}^-][\text{Tf}_2\text{N}^-]_{IL}}. \tag{3}$$

When $[\text{Tf}_2\text{N}^-]_{IL}$ and $[\text{Tf}_2\text{N}^-]$ can be considered as constant under the given conditions, the following equation for an apparent distribution constant of tta$^-$ ($K_{D,A}$) is given:

$$K_{D,A} = \frac{K_{IE}[\text{Tf}_2\text{N}^-]_{IL}}{[\text{Tf}_2\text{N}^-]} = \frac{[\text{tta}^-]_{IL}}{[\text{tta}^-]}. \tag{4}$$

Hence, Eq. (1) is rewritten as follows:

$$D_{HA} = \frac{K_{D,HA} + (K_{D,A}K_a/[\text{H}^+])}{1 + (K_a/[\text{H}^+])}, \tag{5}$$

where K_a is the acid dissociation constant of Htta in the aqueous phase. The values of $K_{D,HA}$, $K_{D,A}$, and K_a were calculated using a nonlinear least-squares method, and the former two distribution constants are shown in Table 1. The K_a value obtained in the C_4mimTf_2N, C_6mimTf_2N, and C_8mimTf_2N systems were 6.16, 6.43, and 6.37 respectively, which were in good agreement with the literature value ($pK_a = 6.33$ [14]). The calculated values of D_{HA} using those constants are well consistent with those of experimental data as shown in Fig. 1.

3.2. *Enol fraction of Htta in C_nmimTf_2N*

It is well known that β-diketones exist as a mixture of an enol form and a keto form in not only the aqueous but also the organic phase. The enol content, or enol fraction (f_e) greatly depends on the polarity of solvents, e.g., $f_e = 0.9–1$ in nonpolar solvents, and $f_e = 0.01–0.8$ in polar solvents. Therefore, $K_{D,HA}$ in Table 1 is the apparent distribution constant of Htta which comprises the tautomers. To elucidate the solvent effect on the distribution constant of Htta as a proton complex and its metal chelate, the distribution constant of the enol form of Htta has to be determined. Hence the tautomerism of Htta in C_nmimTf_2N was investigated.

To determine f_e of Htta in C_nmimTf_2N, the UV spectrophotometry was used. The absorption spectra of Htta in C_4mimTf_2N at different standing intervals just after the preparation of the solution are shown in Fig. 2. According to the literature [15], the peaks observed in the vicinity at 265 and 290 nm are attributed to the keto or keto hydrate form, but the peak at 340 nm to the enol form. Since the absorbance at 334 nm gradually decreases with increasing time whereas the absorbance at 269 nm increases, the transformation of the enol to the keto form takes place in the C_4mimTf_2N solution. The absorbance at 334 nm was confirmed to be due to only the enol form from the fact that this absorption band disappeared by the bromination of the enol form [16]. The time dependence of the absorbance at 334 nm is shown in Fig. 3. The absorbance of the enol form (A_t) decreases with increasing time until the tautomeric equilibrium is attained in C_4mimTf_2N since the absorption at 334 nm is due to the enol form. Consequently, the absorbance of enol form at equilibrium (A_e) was obtained. On the other hand, the enol fraction of Htta in the benzene solution, 0.95 ± 0.02, was determined by the ^{1}H NMR spectrum. This value gives the initial enol fraction in the C_4mimTf_2N solution just after the mixing with the benzene solution, i.e., the enol fraction (f_0) at $t = 0$ (t_0). As shown in an inset in Fig. 3, the tautomerization reaction obeys the pseudo-first-order equation [17], therefore, the absorbance of enol form (A_0) at t_0 can be determined by the following rate equation:

$$\log A_t = -\left(\frac{k}{2.303}\right) t + \log A_0, \tag{6}$$

where k is a rate constant for the transformation of enol to keto. The inset of Fig. 3 shows that the plots of logarithms of absorbance vs. t have a good linear relation with a coefficient of determination, $R^2 = 0.9996$. Therefore, the following equation is derived:

$$f_e = \frac{A_e f_0}{A_0}, \tag{7}$$

The f_e values obtained at equilibrium are shown in Table 1. The f_e value increases with the increase in 1-alkyl chain length. This is the decreasing order of polarity of the C_nmimTf_2N, so the f_e values

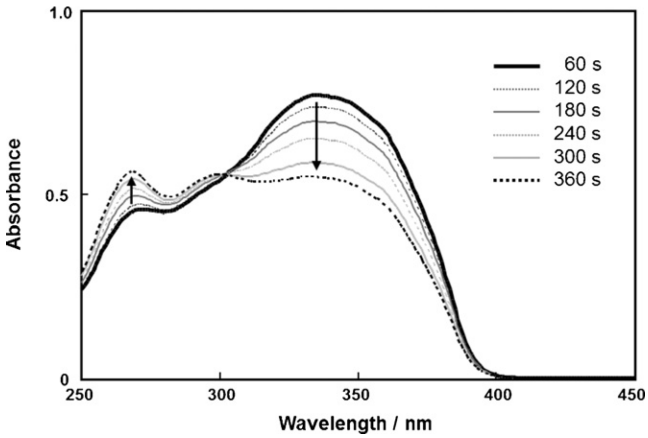

Fig. 2. Absorption spectra of Htta in C_4mimTf_2N. Concentration of Htta, 5.0×10^{-5} mol dm^{-3}.

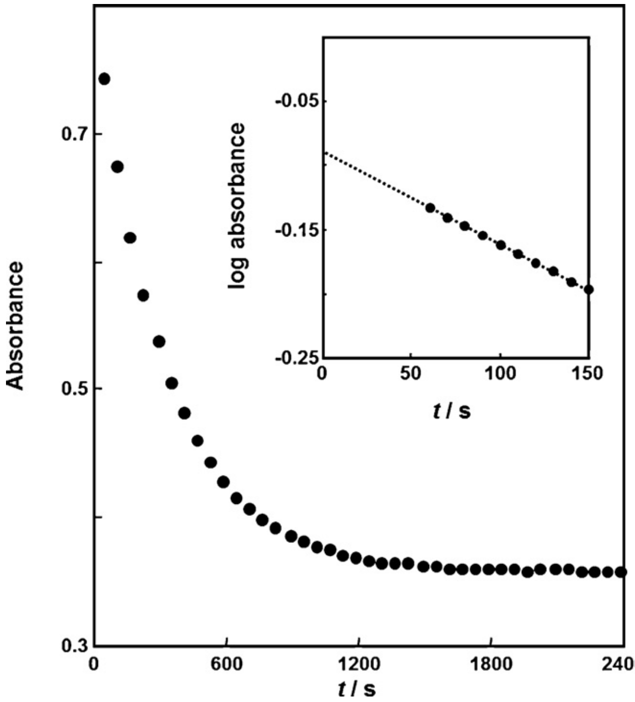

Fig. 3. Time dependence of the absorbance of enol form of Htta in C_4mimTf_2N. The inset provides a magnification showing the log absorbance of enol form as a function of t ($R^2 = 0.9996$). Concentration of Htta, 5.0×10^{-5} mol dm^{-3}. Wavelength, 334 nm.

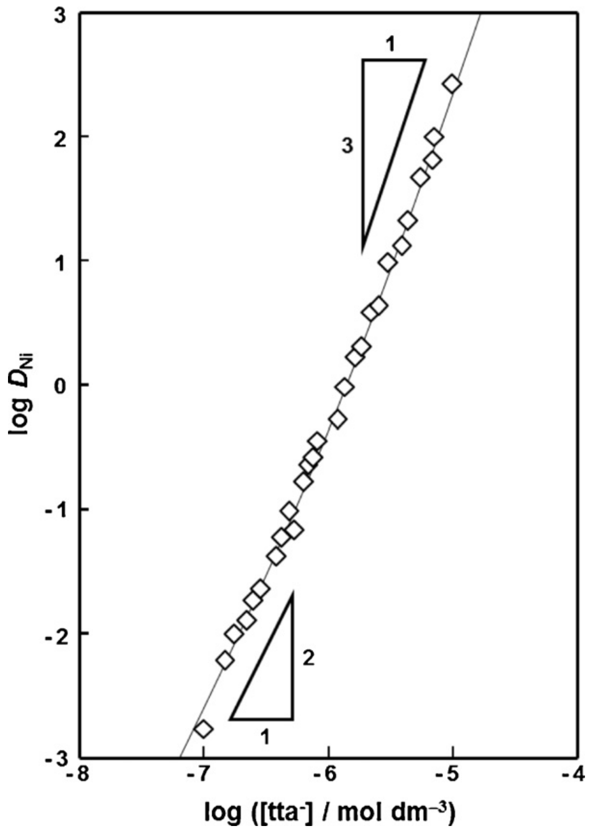

Fig. 4. Distribution ratio of Ni(II) as a function of the tta⁻ concentration in the aqueous phase in the C_4mimTf_2N system. The triangles inserted express the respective slopes. Initial concentration of Htta: 1.0×10^{-2}–1.0×10^{-3} mol dm^{-3}. pH 4.0–5.5.

become larger with the lowering in the polarity of C_nmimTf_2N. In addition, it is known that the enol fraction of Htta in an organic solvent containing water is decreased by the formation of keto hydrate, for instance, about 10% of Htta in water-saturated benzene is in keto hydrated form [15]. Therefore, the difference in the f_e values observed among C_nmimTf_2N can be explained by the difference in the polarity and the solubility of water in ILs. This method was applicable to other β-diketones such as acetylacetone and benzoylacetone.

The distribution constant of the enol form ($K_{D,HE}$) was calculated as follows:

$$K_{D,HE} = \left(\frac{f_e}{f_{aq}}\right) K_{D,HA}, \tag{8}$$

where f_{aq} (=0.016) is the enol fraction in the aqueous phase and was cited from the literature [16]. The values of $K_{D,HE}$ in the three C_nmimTf_2N systems thus obtained are shown in Table 1.

3.3. Distribution of Ni(II) chelate

Divalent metal cations can be extracted with Htta into the C_nmimTf_2N phase as neutral or anionic chelate. In our previous paper [18], Cu(II) was extracted with Htta as only a neutral chelate, but Mn(II), Co(II), Zn(II), and Cd(II) were extracted as an anionic chelate into the C_nmimTf_2N phases. Ni(II) was extracted competitively as both neutral and anionic chelates into the C_4mimTf_2N phase. To determine the distribution constant of neutral Ni(II)-tta chelate in the C_4mimTf_2N system, the extraction equilibrium was investigated in detail. The distribution ratio of Ni(II) (D_{Ni}) into C_4mimTf_2N is plotted in Fig. 4 as a function of the concentration of tta⁻ in the aqueous phase. The tta⁻ concentration was calculated using the distribution constants obtained above as follows:

$$[\mathrm{tta}^-] = \frac{[\mathrm{Htta}]_{\mathrm{ini}} K_a}{(K_{D,HA}+1)[\mathrm{H}^+] + (K_{D,A}+1)K_a}, \tag{9}$$

where $[\mathrm{Htta}]_{\mathrm{ini}}$ is the initial concentration of Htta in IL. The slope of the plots approaches to two at the lower tta⁻ concentration and to three at the higher one. This indicates that Ni(II) was extracted as $Ni(tta)_2$ and $Ni(tta)_3{}^-$ into the C_4mimTf_2N phase. Therefore, the extraction equilibrium and the extraction constant of the neutral species ($K_{ex,2}$) and the anionic species ($K_{ex,3}$) can be written as follows:

For neutral species,

$$\mathrm{Ni}^{2+} + 2\mathrm{HTTa}_{(IL)} \rightleftharpoons \mathrm{Ni(tta)}_{2(IL)} + 2\mathrm{H}^+ \tag{10}$$

$$K_{ex,2} = \frac{[\mathrm{Ni(tta)_2}]_{IL}[\mathrm{H}^+]^2}{[\mathrm{Ni}^{2+}][\mathrm{Htta}]_{IL}^2}. \tag{11}$$

For anionic species,

$$\mathrm{Ni}^{2+} + 3\mathrm{Htta}_{(IL)} + \mathrm{Tf_2N}^-_{(IL)} \rightleftharpoons \mathrm{Ni(tta)}^-_{3(IL)} + 3\mathrm{H}^+ + \mathrm{Tf_2N}^-, \tag{12}$$

$$K_{ex,3} = \frac{[\mathrm{Ni(tta)_3^-}]_{IL}[\mathrm{H}^+]^3[\mathrm{Tf_2N}^-]}{[\mathrm{Ni}^{2+}][\mathrm{Htta}]_{IL}^3[\mathrm{Tf_2N}^-]_{IL}} \tag{13}$$

When $[\mathrm{Tf_2N}^-]_{IL}$ and $[\mathrm{Tf_2N}^-]$ are constant, $K_{ex,3}$ is rewritten as follows:

$$K'_{ex,3} = \frac{K_{ex,3}[\mathrm{Tf_2N}^-]_{IL}}{[\mathrm{Tf_2N}^-]} = \frac{[\mathrm{Ni(tta)_3^-}]_{IL}[\mathrm{H}^+]^3}{[\mathrm{Ni}^{2+}][\mathrm{Htta}]_{IL}^3}. \tag{14}$$

Since none of Ni(II) was extracted in the absence of Htta in C_4mimTf_2N, D_{Ni} in this system can be written as:

$$D_{Ni} = \frac{[\mathrm{Ni(tta)_2}]_{IL} + [\mathrm{Ni(tta)_3^-}]_{IL}}{[\mathrm{Ni}^{2+}]}. \tag{15}$$

From Eqs. (9), (11), and (14), Eq. (15) can be rewritten as:

$$D_{Ni} = \frac{[\mathrm{tta}^-]^2 K_{D,HA}^2 K_{ex,2}}{K_a^2} + \frac{[\mathrm{tta}^-]^3 K_{D,HA}^3 K'_{ex,3}}{K_a^3} \tag{16}$$

According to Eq. (16), the values of $K_{ex,2}$ and $K_{ex,3}$ were determined by the nonlinear least-squares fitting of the plots in Fig. 4, and are shown in Table 2. The $\log K'_{ex,3}$ values increased with increase in the carbon number of 1-alkyl group of C_nmimTf_2N, or the hydrophobicity of IL. The similar relationship between the $\log K'_{ex,3}$ values and the carbon number of the 1-alkyl group is observed for Mn(II), Co(II), Zn(II), and Cd(II) in the C_4mimTf_2N, C_6mimTf_2N, and C_8mimTf_2N systems [18].

The distribution constant of neutral metal(II) chelate ($K_{D,M2}$) can be calculated as follows:

$$K_{D,M2} = \frac{K_{ex,2}K_{D,HA}^2}{\beta_2 K_a^2}, \tag{17}$$

where β_2 is the 1:2 chelate formation constant in the aqueous phase and the values for $Ni(tta)_2$ and $Cu(tta)_2$ are reported to be $10^{6.54}$

Table 2
Distribution constant and extraction constants for divalent metals in C_nmimTf_2N systems.

Divalent metal	Solvent	$\log K_{D,M2}$	$\log K_{ex,2}$	$\log K'_{ex,3}$
Ni	C_4mimTf_2N	4.61	−4.36 ± 0.09	−6.06 ± 0.09
	C_6mimTf_2N	–	–	−5.54 ± 0.14[a]
	C_8mimTf_2N	–	–	−4.93 ± 0.09[a]
Cu	C_4mimTf_2N	4.99	−1.32 ± 0.03[a]	–
	C_6mimTf_2N	5.09	−1.31 ± 0.04[a]	–
	C_8mimTf_2N	5.14	−1.18 ± 0.03[a]	–

[a] Ref. [18].

Table 3
Solubility parameters of $C_n$mimTf$_2$N.

Solvent	δ_{IL}[a]	$\delta_{IL,w}$	$\delta_{IL,w\,ex}$
C_4mimTf$_2$N	19.8	20.1	20.5 ± 0.7
C_8mimTf$_2$N	19.0	19.2	19.4 ± 0.7
C_8mimTf$_2$N	18.9	19.1	19.2 ± 0.7

[a] Ref. [29].

[19] and $10^{9.30}$ [20], respectively by the present authors. The values of $K_{D,M2}$ of Ni(II) and Cu(II) chelate in the $C_n$mimTf$_2$N systems are shown in Table 2. In the C_6mimTf$_2$N and C_8mimTf$_2$N systems, Ni(II) was extracted as only an anionic chelate as described previously [18].

3.4. Application of the regular solution theory

The distribution constant of enol form can be written by using a modified equation based on RST [21]:

$$\ln K_D = \frac{V_2}{RT}\{C_{ww} - C_{oo} + 2(C_{o2} - C_{w2})\} + V_2\left(\frac{1}{V_o} - \frac{1}{V_w}\right), \qquad (18)$$

where V and C stand for the molar volume and the cohesive energy density respectively, and the subscript 2, 'w', and 'o' denote the solute, water, and organic solvent, respectively. If the interaction between the solute and organic solvent molecules is mainly due to their dispersion forces, the geometric mean approximation for the cohesive energy density using the solubility parameter (δ), $C_{o2} \approx \delta_o \delta_2$, is valid. Since $C_{oo} = \delta_o^2$ from the definition, Eq. (18) can be rewritten as:

$$\frac{RT}{V_2}\left\{\ln K_D - V_2\left(\frac{1}{V_o} - \frac{1}{V_w}\right)\right\} + \delta_o^2 = 2\delta_2\delta_o + C_{ww} - 2C_{w2}. \qquad (19)$$

If water-saturated $C_n$mimTf$_2$N and organic solvents are regarded as a binary solvent mixture with water, the solubility parameter of a water-saturated solvent ($\delta_{o,w}$) can be calculated by the following equation with the conventional solubility parameter for the aqueous solution (δ_w = 35.8 MPa$^{1/2}$ calculated by RST using the distribution constant of acetylacetone [22]):

$$\delta_{o,w} = \phi_o\delta_o + \phi_w\delta_w, \qquad (20)$$

where ϕ is the volume fraction. Even if the solubility parameter of water (47.9 MPa$^{1/2}$) calculated from the vaporization enthalpy was used instead of δ_w, the $\delta_{o,w}$ values did not so much vary because the solubilities of water in organic solvents and ILs used were not so high; the solubilities in C_4mimTf$_2$N, C_6mimTf$_2$N, and C_8mimTf$_2$N were 1.58 [23], 1.07 [24], and 0.91 [24] wt%, respectively.

Plots of the left-hand side of Eq. (19) vs. the $\delta_{o,w}$ are expected to be linear, and the apparent solubility parameter of the solute (δ_2) and the interaction term with water ($C_{ww} - 2C_{w2}$) can be obtained from the slope and the intercept respectively. Fig. 5 shows the plots for the enol of Htta in $C_n$mimTf$_2$N along with those in various organic solvents systems [25–28]. The solubility parameters of $C_n$mimTf$_2$N (δ_{IL}) taken from the literature [29] and of water-saturated $C_n$mimTf$_2$N ($\delta_{IL,w}$) calculated using Eq. (20) are listed in Table 3. The molar volume of the Htta and its metal(II) chelates were taken from the literature; V_2: Htta, 160 cm^3 mol^{-1} [22]; Ni(tta)$_2$ [19] and Cu(tta)$_2$ [20], 304 cm^3 mol^{-1}. As shown in Fig. 5, in the $K_{D,HE}$ system, a good linear relationship hold for all organic solvents, and also for $C_n$mimTf$_2$N. Consequently, RST is applicable to $C_n$mimTf$_2$N systems, namely, it seems that the $C_n$mimTf$_2$N solutions of Htta (enol) can be taken as apparently regular solutions like other organic solutions. The solvent effect can be quantitatively evaluated by means of Eq. (19).

In the Ni(II) and Cu(II) chelate, the distribution constant of these chelates may be also written using Eq. (19) on the basis of RST. As shown in Fig. 6, the plots for the Cu(II) chelate in the $C_n$mimTf$_2$N

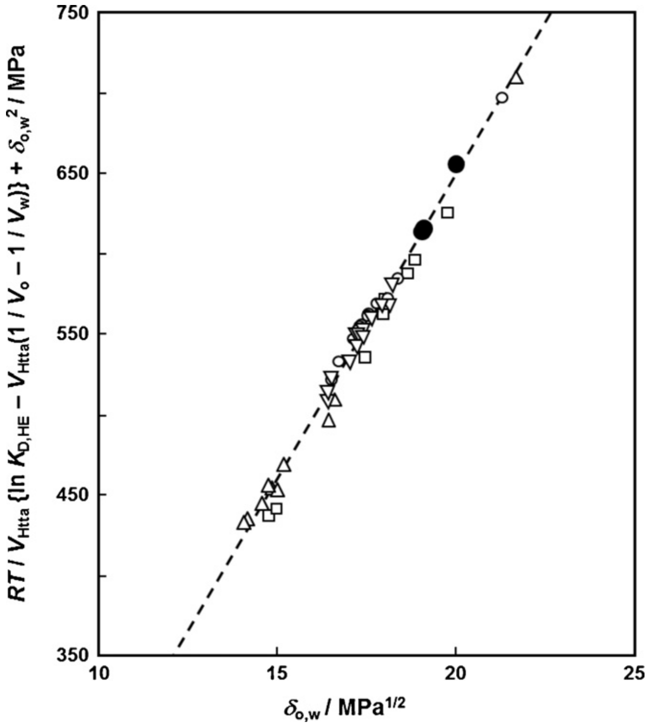

Fig. 5. Evaluation of distribution constant of the enol form with the regular solution theory. (●) $C_n$mimTf$_2$N; (□) alkanes and aromatic hydrocarbons (Ref. [27]); (○) ketones (Ref. [26]); (▽) esters (Ref. [25]); (△) ethers (Ref. [28]).

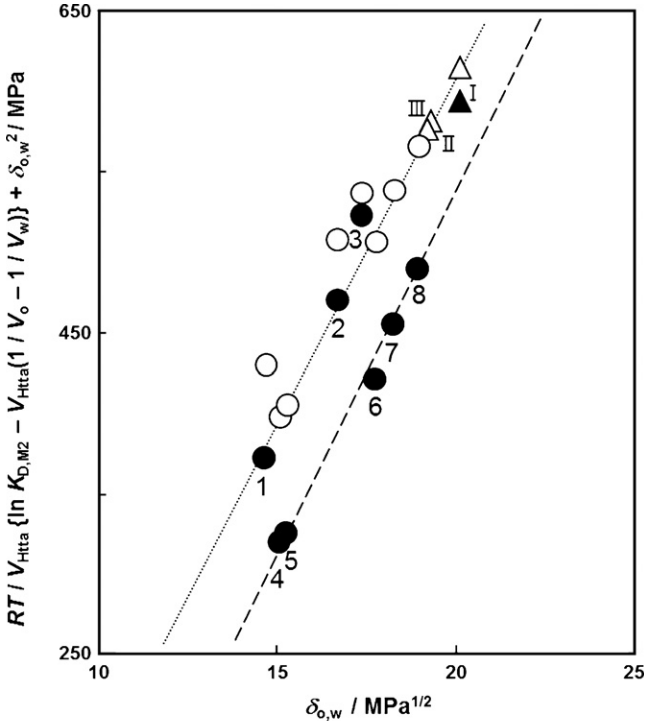

Fig. 6. Evaluation of distribution constants of Cu(tta)$_2$ and Ni(tta)$_2$ with the regular solution theory. (▲) Ni(tta)$_2$ in the C_4mimTf$_2$N system; (△) Cu(tta)$_2$ in $C_n$mimTf$_2$N systems; (●) Ni(tta)$_2$ in organic solvent systems (Ref. [19]); (○) Cu(tta)$_2$ in organic solvent systems (Ref. [19]). I, C_4mimTf$_2$N; II, C_6mimTf$_2$N; III, C_8mimTf$_2$N. 1, Dibutyl ether; 2, diisobutyl ketone; 3, methylisobutyl ketone; 4, hexane; 5, heptane; 6, carbon tetrachloride; 7, isopropylbenzene; 8, benzene.

systems are in good agreement with a straight line obtained by the non-polar organic solvent systems, whereas the plots for the Ni(II) chelate in the C_4mimTf_2N system shows the large deviation from the straight line which obeys Eq. (19). Namely, the C_nmimTf_2N solution of Cu(II) chelate can be taken as apparently regular solutions. In the Ni(II) chelate, however, a deviation is clearly observed in ethers, ketones, and C_4mimTf_2N. Since the deviations from straight lines found for dibutyl ether, diisobutyl ketone, and methylisobutyl ketone are interpreted by specific interaction, such as direct coordination of the oxygen-containing solvent to the central metal ion [30], such deviations for the Ni(II) chelate in the C_4mimTf_2N system may be ascribable to some specific interaction between Ni(II) chelate and C_4mim^+ cation or Tf_2N^- anion, i.e., solvation or coordination of C_4mimTf_2N to the hydrated Ni(II) chelate.

3.5. Calculation of the solubility parameter of IL

Since ILs have essentially null volatility, it was difficult to determine the solubility parameter of ILs from their vaporization energy. Hence various solution properties of IL such as the viscosity [31], the surface tension [32], and the bimolecular rate constant of the Diels–Alder reaction [33] have been measured to calculate δ_{IL}. However, these values show remarkably large scatter, e.g., δ_{IL} of C_4mimTf_2N calculated from the surface tension is 21.3 $MPa^{1/2}$ [32] and from the viscosity, 26.3 $MP^{1/2}$ [31]. Recently, Rebelo and co-workers showed that C_4mimTf_2N could evaporate without decomposition [34], and the vapor pressures and enthalpy of vaporization for C_nmimTf_2N were measured by some sophisticated techniques; thermogravimetric method gave 19.8 $MPa^{1/2}$ for δ_{IL} of C_4mimTf_2N [29], Knudsen-effusion method, 21.2 $MPa^{1/2}$ [35], and mass spectrometric method, 21.1 $MPa^{1/2}$ [36]. These values are relatively close each other.

In this work, the solubility parameter ($\delta_{IL,w\,ex}$) of C_nmimTf_2N saturated with water (0.10 mol dm^{-3} NaCl solution) was calculated from the $K_{D,HE}$ values of the enol of Htta using the following equation derived from Eq. (19):

$$\delta_{o,w}^2 - 2\delta_2\delta_{o,w} - (C_{ww} - 2C_{w2}) + \left(\frac{RT}{V_2}\right)\left\{\ln K_{D,HE} - V_2\left(\frac{1}{V_o} - \frac{1}{V_w}\right)\right\} = 0. \tag{21}$$

As mentioned above, δ_2 of the enol and the $C_{ww} - 2C_{w2}$ term can be obtained from the linear relationship in Eq. (19) using various organic solvents; i.e., $\delta_2 = 18.5$ $MPa^{1/2}$ and $C_{ww} - 2C_{w2} = -99.1$ MPa. The $\delta_{IL,w\,ex}$ values are calculated by Eq. (21) from the $K_{D,HE}$ value in ILs and shown in Table 3. The $\delta_{IL,w\,ex}$ values for 3 kinds of C_nmimTf_2N are in good agreement with the $\delta_{IL,w}$ values obtained from the literature values which were calculated from the enthalpy of vaporization [29]. The difference in the solubility parameter of C_nmimTf_2N having different 1-alkyl chains is mostly due to the additional van der Waals interactions and the change in the molar volume caused by 1-alkyl groups.

4. Conclusion

A spectrophotometric determination method of the enol fraction of Htta in C_nmimTf_2N used as IL was developed to calculate the exact distribution constant of the enol form of Htta between the IL and the aqueous phase. Effect of ILs on the distribution constants of the enol and its Ni(II) and Cu(II) chelates was evaluated with the aid of RST. The $K_{D,HE}$ values in the IL system well obeyed the equation derived from RST as observed in various organic solvents. Consequently, the solubility parameter of C_nmimTf_2N saturated with water could be calculated by RST. In the $Cu(tta)_2$ case, the similar result was obtained in the IL and the nonpolar organic solvent system. On the other hand, the $K_{D,M}$ value for Ni(II) in the IL largely deviated from the equation of RST which held for the nonpolar organic solvents, but showed the deviation similar to that for oxygen-containing solvents such as ethers and ketones. This may be ascribable to some specific interactions between $Ni(tta)_2$ and C_4mimTf_2N. Since there are still many unidentified characteristics of ionic liquids, it is necessary to continue such fundamental studies as solubility, distribution, and solvation.

Acknowledgement

The authors thank Dr. N. Hirayama of Department of Chemistry, Faculty of Science at Toho University for helpful discussion. This work was supported by a Grant-in-Aid for Scientific Research (C) (No.21550075) from Japan Society for the Promotion of Science (JSPS).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.09.011.

References

[1] J. McFarlane, W.B. Ridenour, H. Luo, R.D. Hunt, D.W. DePaoli, Sep. Sci. Technol. 40 (2005) 1245.
[2] J. Pernak, A. Skrzypczak, G. Lota, E. Frackowiak, Chem. Eur. J. 13 (2007) 3106.
[3] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003.
[4] J.L. Kaar, A.M. Jesionowski, J.A. Berberich, R. Moullton, A.J. Russell, J. Am. Chem. Soc. 125 (2002) 4125.
[5] Z. Li, J. Chang, H. Shan, J. Pan, Rev. Anal. Chem. 26 (2007) 109.
[6] S. Dai, Y.H. Ju, C.E. Barnes, J. Chem. Soc., Dalton Trans. (1999) 1201.
[7] A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J.H. Davis Jr., R.D. Rogers, Environ. Sci. Technol. 36 (2002) 2523.
[8] A.E. Visser, R.P. Swatolski, S.T. Griffin, D.H. Hartman, R.D. Rogers, Sep. Sci. Technol. 32 (2001) 785.
[9] N. Hirayama, M. Deguchi, H. Kawasumi, T. Honjo, Talanta 65 (2005) 255.
[10] H. Okamura, N. Hirayama, K. Morita, K. Shimojo, H. Naganawa, H. Imura, Anal. Sci. 26 (2010) 607.
[11] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156.
[12] V. Farmer, T. Welton, Green Chem. 4 (2002) 97.
[13] J.A. Pople, W.G. Schneider, H.J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, New York, 1959.
[14] T. Sekine, Y. Hasegawa, in: A.S. Kertes, Y. Marcus (Eds.), Solvent Extraction Research, Wiley-Interscience, New York, 1969, p. 289.
[15] E.I. King, W.H. Reas, J. Am. Chem. Soc. 73 (1951) 1806.
[16] J.C. Reid, M. Calvin, J. Am. Chem. Soc. 72 (1950) 2948.
[17] J.E. Meany, J. Phys. Chem. 73 (1969) 3421.
[18] K. Kidani, N. Hirayama, H. Imura, Anal. Sci. 24 (2008) 1251.
[19] N. Suzuki, S. Matsumora, H. Imura, Polyhedron 6 (1987) 497.
[20] H. Imura, N. Suzuki, Talanta 32 (1985) 785.
[21] H.M.N.H. Irving, in: J.A. Marinsky, Y. Marcus (Eds.), Ion Exchange and Solvent Extraction, Marcel Dekker, New York, 1974, p. 139.
[22] T. Wakahayashi, S. Oki, T. Omori, N. Suzuki, J. Inorg. Nucl. Chem. 26 (1964) 2255.
[23] J.M. Crosthwaite, S.N.V.K. Aki, E.J. Maginn, J.F. Brennecke, J. Phys. Chem. B 108 (2004) 5113.
[24] A. Chapeaux, L.D. Simoni, M.A. Stadtherr, J.F. Brennecke, J. Chem. Eng. Data 52 (2007) 2462.
[25] N. Suzuki, K. Akiba, T. Kanno, Anal. Chim. Acta 43 (1968) 311.
[26] T. Wakabayashi, K. Takaizumi, K. Seto, N. Suzuki, K. Akiba, Bull. Chem. Soc. Jpn. 41 (1968) 1854.
[27] K. Akiba, N. Suzuki, T. Kanno, Bull. Chem. Soc. Jpn. 42 (1969) 2537.
[28] N. Suzuki, K. Akiba, H. Asano, Anal. Chim. Acta 52 (1970) 115.
[29] H. Luo, G.A. Baker, S. Dai, J. Phys. Chem. B 112 (2008) 10077.
[30] O. Borodin, G.D. Smith, W. Henderson, J. Phys. Chem. B 110 (2006) 16879.
[31] S.H. Lee, S.B. Lee, Chem. Commun. (2005) 3469.
[32] H. Jin, B. O'Hare, J. Dong, S. Arzhantsev, G.A. Baker, J.F. Wishart, A.J. Benesi, M. Maroncelli, J. Phys. Chem. B 112 (2008) 81.
[33] K. Swiderski, A. McLean, C.M. Gordon, D.H. Vaughan, Chem. Commun. (2004) 2178.
[34] L.P.N. Rebelo, J.N.C. Lopes, J.M.S.S. Esperança, E. Filipe, J. Phys. Chem. B 109 (2005) 6040.
[35] D.H. Zaitsau, G.J. Kabo, A.A. Strechan, Y.U. Paulechka, J. Phys. Chem. A 110 (2006) 7303.
[36] J.P. Armstrong, C. Hurst, R.G. Jones, P. Licence, K.R.J. Lovelock, C.J. Satterley, I.J. Villar-Garcia, J. Phys. Chem. Chem. Phys. 9 (2007) 982.