

# Solvent effect of ionic liquids on the distribution constant of 2-thenoyltrifluoroacetone

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

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**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)

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## Abstract

Distribution constants of 2-thenoyltrifluoroacetone (Htta) and its Ni(II) and Cu(II) chelates between 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ( $C_n\text{mimTf}_2\text{N}$ ;  $n = 4, 6, \text{ and } 8$ ) 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  $\text{Cu}(\text{tta})_2$ -IL solutions behaved like the alkane and aromatic hydrocarbon solutions but the  $\text{Ni}(\text{tta})_2$ -IL ( $C_4\text{mimTf}_2\text{N}$ ) 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.

## 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  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  [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 can not 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,

1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ( $C_n\text{mimTf}_2\text{N}$ ;  $n = 4, 6, \text{ and } 8$ ). 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  $C_n\text{mimTf}_2\text{N}$  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-Thienyltrifluoroacetone (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 ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) 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 M $\Omega$ ) 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  $C_n\text{mimTf}_2\text{N}$  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

#### *Distribution of Htta*

An aliquot ( $0.5 \text{ cm}^3$ ) of a  $C_n\text{mimTf}_2\text{N}$  solution containing  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  Htta was shaken with a  $5\text{-cm}^3$  portion of an aqueous solution of  $1.0 \times 10^{-1} \text{ mol dm}^{-3}$  (H, Na)Cl at  $25 \pm 1 \text{ }^\circ\text{C}$  for 1h. The pH value of aqueous phases was adjusted to 1 - 12 with  $1.0 \times 10^{-1} \text{ mol dm}^{-3}$  hydrochloric acid and  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  sodium hydroxide. After the two phases were separated by centrifugation, the equilibrium concentrations of Htta in both  $C_n\text{mimTf}_2\text{N}$  phase and aqueous phase were measured from the absorbance at 334 and 268 nm, respectively and the distribution ratio ( $D_{\text{HTA}}$ ) of Htta was calculated. The equilibrium pH value in the aqueous phase was immediately measured after the phase separation.

#### *Determination of enol fraction*

A stock solution of  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$  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  $0.03 \text{ cm}^3$  portion of the stock solution of Htta was added to  $C_n\text{mimTf}_2\text{N}$  ( $3 \text{ cm}^3$ ) which was pre-equilibrated with the aqueous solution of  $1.0 \times 10^{-1} \text{ mol dm}^{-3}$  sodium chloride and immediately mixed. The change in absorbance of the enol form of Htta in  $C_n\text{mimTf}_2\text{N}$  was measured at 334 nm for 6,000 s at  $25 \pm 1 \text{ }^\circ\text{C}$ .

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].

#### *Distribution of Ni(II)*

A 5.0-cm<sup>3</sup> portion of an aqueous Ni(II) solution ( $1.0 \times 10^{-5}$  mol dm<sup>-3</sup>) containing  $1.0 \times 10^{-1}$  mol dm<sup>-3</sup> potassium nitrate was shaken for 2 h with a 1.0 cm<sup>3</sup> of a C<sub>4</sub>mimTf<sub>2</sub>N solution of  $1.0 \times 10^{-3}$  -  $1.0 \times 10^{-1}$  mol dm<sup>-3</sup> Htta at  $25 \pm 1$  °C. The pH value of aqueous phase was adjusted to 3 - 5 with  $1.0 \times 10^{-1}$  mol dm<sup>-3</sup> nitric acid,  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> acetic acid, and  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> 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<sub>4</sub>mimTf<sub>2</sub>N phase was determined after back-extraction into a 10-fold volume of 1 mol dm<sup>-3</sup> 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<sub>*n*</sub>mimTf<sub>2</sub>N (*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. Figure 1 shows that log  $D_{HA}$  in each C<sub>*n*</sub>mimTf<sub>2</sub>N 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<sub>*n*</sub>mimTf<sub>2</sub>N system, however, the log  $D_{HA}$  value becomes constant again because the anionic species of tta<sup>-</sup> is transferred from the aqueous phase into the C<sub>*n*</sub>mimTf<sub>2</sub>N phase by ion-exchange with the Tf<sub>2</sub>N<sup>-</sup> anion.

Therefore,  $D_{HA}$  of Htta in the C<sub>*n*</sub>mimTf<sub>2</sub>N system can be written as follows:

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

where the subscript IL denotes the  $C_n\text{mimTf}_2\text{N}$  phase. The distribution constant of Htta ( $K_{\text{D,HA}}$ ) and the ion-exchange constant of  $\text{tta}^-$  ( $K_{\text{IE}}$ ) are defined by:

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

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

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

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

Hence, Eq. 1 is rewritten as follows:

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

where  $K_{\text{a}}$  is the acid dissociation constant of Htta in the aqueous phase. The values of  $K_{\text{D,HA}}$ ,  $K_{\text{D,A}}$ , and  $K_{\text{a}}$  were calculated using a nonlinear least-squares method, and the former two distribution constants are shown in Table 1. The  $K_{\text{a}}$  value obtained in the  $C_4\text{mimTf}_2\text{N}$ ,  $C_6\text{mimTf}_2\text{N}$ , and  $C_8\text{mimTf}_2\text{N}$  systems were 6.16, 6.43, and 6.37 respectively, which were in good agreement with the literature value ( $\text{p}K_{\text{a}} = 6.33$  [14]). The calculated values of  $D_{\text{HA}}$  using those constants are well consistent with those of experimental data as shown in Fig. 1.

### 3.2. Enol fraction of Htta in $C_n\text{mimTf}_2\text{N}$

It is well known that  $\beta$ -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  $C_n\text{mimTf}_2\text{N}$  was investigated.

To determine  $f_e$  of Htta in  $C_n\text{mimTf}_2\text{N}$ , the UV spectrophotometry was used. The absorption spectra of Htta in  $C_4\text{mimTf}_2\text{N}$  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  $C_4\text{mimTf}_2\text{N}$  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  $C_4\text{mimTf}_2\text{N}$  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,  $0.95 \pm 0.02$ , was determined by the  $^1\text{H}$  NMR spectrum. This value gives the initial enol fraction in the  $C_4\text{mimTf}_2\text{N}$  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:

$$\log A_t = - (k / 2.303) t + \log A_0, \quad (6)$$

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:

$$f_e = A_e f_0 / A_0, \quad (7)$$

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  $C_n$ mimTf<sub>2</sub>N, so the  $f_e$  values become larger with the lowering in the polarity of  $C_n$ mimTf<sub>2</sub>N. 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  $C_n$ mimTf<sub>2</sub>N can be explained by the difference in the polarity and the solubility of water in ILs. This method was applicable to other  $\beta$ -diketones such as acetylacetone and benzoylacetone.

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

$$K_{D,HE} = (f_e / f_{aq}) K_{D,HA}, \quad (8)$$

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  $C_n$ mimTf<sub>2</sub>N 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  $C_n\text{mimTf}_2\text{N}$  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  $C_n\text{mimTf}_2\text{N}$  phases. Ni(II) was extracted competitively as both neutral and anionic chelates into the  $C_4\text{mimTf}_2\text{N}$  phase. To determine the distribution constant of neutral Ni(II)-tta chelate in the  $C_4\text{mimTf}_2\text{N}$  system, the extraction equilibrium was investigated in detail. The distribution ratio of Ni(II) ( $D_{\text{Ni}}$ ) into  $C_4\text{mimTf}_2\text{N}$  is plotted in Fig. 4 as a function of the concentration of  $\text{tta}^-$  in the aqueous phase. The  $\text{tta}^-$  concentration was calculated using the distribution constants obtained above as follows:

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

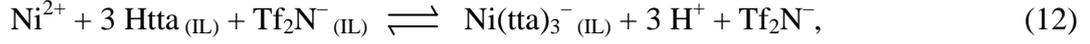
where  $[\text{Htta}]_{\text{ini}}$  is the initial concentration of Htta in IL. The slope of the plots approaches to two at the lower  $\text{tta}^-$  concentration and to three at the higher one. This indicates that Ni(II) was extracted as  $\text{Ni}(\text{tta})_2$  and  $\text{Ni}(\text{tta})_3^-$  into the  $C_4\text{mimTf}_2\text{N}$  phase. Therefore, the extraction equilibrium and the extraction constant of the neutral species ( $K_{\text{ex},2}$ ) and the anionic species ( $K_{\text{ex},3}$ ) can be written as follows:

For neutral species,



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

For anionic species,



$$K_{\text{ex},3} = \frac{[\text{Ni}(\text{tta})_3^-]_{\text{IL}} [\text{H}^+]^3 [\text{Tf}_2\text{N}^-]}{[\text{Ni}^{2+}] [\text{Htta}]_{\text{IL}}^3 [\text{Tf}_2\text{N}^-]_{\text{IL}}}. \quad (13)$$

When  $[\text{Tf}_2\text{N}^-]_{\text{IL}}$  and  $[\text{Tf}_2\text{N}^-]$  are constant,  $K_{\text{ex},3}$  is rewritten as follows:

$$K_{\text{ex},3}' = \frac{K_{\text{ex},3} [\text{Tf}_2\text{N}^-]_{\text{IL}}}{[\text{Tf}_2\text{N}^-]} = \frac{[\text{Ni}(\text{tta})_3^-]_{\text{IL}} [\text{H}^+]^3}{[\text{Ni}^{2+}] [\text{Htta}]_{\text{IL}}^3}. \quad (14)$$

Since none of Ni(II) was extracted in the absence of Htta in  $\text{C}_4\text{mimTf}_2\text{N}$ ,  $D_{\text{Ni}}$  in this system can be written as:

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

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

$$D_{\text{Ni}} = \frac{[\text{tta}^-]^2 K_{\text{D,HA}}^2 K_{\text{ex},2}}{K_{\text{a}}^2} + \frac{[\text{tta}^-]^3 K_{\text{D,HA}}^3 K_{\text{ex},3}'}{K_{\text{a}}^3}. \quad (16)$$

According to Eq.16, the values of  $K_{\text{ex},2}$  and  $K_{\text{ex},3}'$  were determined by the nonlinear least-squares fitting of the plots in Fig.4, and are shown in Table 2. The  $\log K_{\text{ex},3}'$  values increased with increase in the carbon number of 1-alkyl group of  $\text{C}_n\text{mimTf}_2\text{N}$ , or the hydrophobicity of IL. The similar relationship between the  $\log K_{\text{ex},3}'$  values and the carbon number of the 1-alkyl group is observed for Mn(II), Co(II), Zn(II), and Cd(II) in the  $\text{C}_4\text{mimTf}_2\text{N}$ ,  $\text{C}_6\text{mimTf}_2\text{N}$ , and  $\text{C}_8\text{mimTf}_2\text{N}$  systems [18].

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

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

where  $\beta_2$  is the 1:2 chelate formation constant in the aqueous phase and the values for Ni(tta)<sub>2</sub> and Cu(tta)<sub>2</sub> are reported to be 10<sup>6.54</sup> [19] and 10<sup>9.30</sup> [20], respectively by the present authors. The values of  $K_{D,M2}$  of Ni(II) and Cu(II) chelate in the C<sub>n</sub>mimTf<sub>2</sub>N systems are shown in Table 2. In the C<sub>6</sub>mimTf<sub>2</sub>N and C<sub>8</sub>mimTf<sub>2</sub>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]:

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

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 ( $\delta$ ),  $C_{o2} \approx \delta_o \delta_2$ , is valid. Since  $C_{oo} = \delta_o^2$  from the definition, Eq. 18 can be rewritten as:

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

If water-saturated C<sub>n</sub>mimTf<sub>2</sub>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 ( $\delta_w = 35.8 \text{ MPa}^{1/2}$  calculated by RST using the distribution constant of acetylacetone [22]) :

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

where  $\phi$  is the volume fraction. Even if the solubility parameter of water ( $47.9 \text{ MPa}^{1/2}$ ) calculated from the vaporization enthalpy was used instead of  $\delta_w$ , 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  $C_4\text{mimTf}_2\text{N}$ ,  $C_6\text{mimTf}_2\text{N}$ , and  $C_8\text{mimTf}_2\text{N}$  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 ( $\delta_2$ ) and the interaction term with water ( $C_{ww} - 2C_{w2}$ ) can be obtained from the slope and the intercept respectively. Figure 5 shows the plots for the enol of Htta in  $C_n\text{mimTf}_2\text{N}$  along with those in various organic solvents systems [25-28]. The solubility parameters of  $C_n\text{mimTf}_2\text{N}$  ( $\delta_{IL}$ ) taken from the literature [29] and of water-saturated  $C_n\text{mimTf}_2\text{N}$  ( $\delta_{IL,w}$ ) 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,  $160 \text{ cm}^3 \text{ mol}^{-1}$  [22];  $\text{Ni}(\text{tta})_2$  [19] and  $\text{Cu}(\text{tta})_2$  [20],  $304 \text{ cm}^3 \text{ mol}^{-1}$ . As shown in Fig. 5, in the  $K_{D,HE}$  system, a good linear relationship hold for all organic solvents, and also for  $C_n\text{mimTf}_2\text{N}$ . Consequently, RST is applicable to  $C_n\text{mimTf}_2\text{N}$  systems, namely, it seems that the  $C_n\text{mimTf}_2\text{N}$  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  $C_n\text{mimTf}_2\text{N}$  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  $C_4\text{mimTf}_2\text{N}$

system shows the large deviation from the straight line which obeys Eq. 19. Namely, the  $C_n\text{mimTf}_2\text{N}$  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  $C_4\text{mimTf}_2\text{N}$ . 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  $C_4\text{mimTf}_2\text{N}$  system may be ascribable to some specific interaction between Ni(II) chelate and  $C_4\text{mim}^+$  cation or  $\text{Tf}_2\text{N}^-$  anion, i.e., solvation or coordination of  $C_4\text{mimTf}_2\text{N}$  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  $\delta_{\text{IL}}$ . However, these values show remarkably large scatter, e.g.,  $\delta_{\text{IL}}$  of  $C_4\text{mimTf}_2\text{N}$  calculated from the surface tension is  $21.3 \text{ MPa}^{1/2}$  [32] and from the viscosity,  $26.3 \text{ MP}^{1/2}$  [31]. Recently, Rebelo and co-workers showed that  $C_4\text{mimTf}_2\text{N}$  could evaporate without decomposition [34], and the vapor pressures and enthalpy of vaporization for  $C_n\text{mimTf}_2\text{N}$  were measured by some sophisticated techniques; thermogravimetric method gave  $19.8 \text{ MPa}^{1/2}$  for  $\delta_{\text{IL}}$  of  $C_4\text{mimTf}_2\text{N}$  [29], Knudsen-effusion method,  $21.2 \text{ MPa}^{1/2}$  [35], and mass spectrometric method,  $21.1 \text{ MPa}^{1/2}$  [36]. These values are relatively close each other.

In this work, the solubility parameter ( $\delta_{\text{IL,w ex}}$ ) of  $C_n\text{mimTf}_2\text{N}$  saturated with water ( $0.10 \text{ mol dm}^{-3}$  NaCl solution) was calculated from the  $K_{\text{D,HE}}$  values of the enol of Htta using the following equation derived from Eq. 19:

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

As mentioned above,  $\delta_2$  of the enol and the  $C_{ww} - 2 C_{w2}$  term can be obtained from the linear relationship in Eq. 19 using various organic solvents; i.e.,  $\delta_2 = 18.5 \text{ MPa}^{1/2}$  and  $C_{ww} - 2 C_{w2} = -99.1 \text{ MPa}$ . The  $\delta_{IL,w \text{ ex}}$  values are calculated by Eq. 21 from the  $K_{D,HE}$  value in ILs and shown in Table 3. The  $\delta_{IL,w \text{ ex}}$  values for 3 kinds of  $C_n\text{mimTf}_2\text{N}$  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  $C_n\text{mimTf}_2\text{N}$  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  $C_n\text{mimTf}_2\text{N}$  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  $C_n\text{mimTf}_2\text{N}$  saturated with water could be calculated by RST. In the  $\text{Cu}(\text{tta})_2$  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  $\text{Ni}(\text{tta})_2$  and

C<sub>4</sub>mimTf<sub>2</sub>N. Since there are still many unidentified characteristics of ionic liquids, it is necessary to continue such fundamental studies as solubility, distribution, and solvation.

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## Figure captions

Fig.1 Distribution ratio of Htta as a function of pH.

Initial concentration of Htta,  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ . Ionic strength,  $1.0 \times 10^{-1} \text{ mol dm}^{-3}$  (H,Na)Cl.

○, C<sub>4</sub>mimTf<sub>2</sub>N; △, C<sub>6</sub>mimTf<sub>2</sub>N; □, C<sub>8</sub>mimTf<sub>2</sub>N.

Fig.2 Absorption spectra of Htta in C<sub>4</sub>mimTf<sub>2</sub>N.

Concentration of Htta,  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ .

Fig.3 Time dependence of the absorbance of enol form of Htta in C<sub>4</sub>mimTf<sub>2</sub>N.

The inset provides a magnification showing the log absorbance of enol form as a function of  $t$  ( $R^2 = 0.9996$ ).

Concentration of Htta,  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ . Wavelength, 334 nm.

Fig. 4 Distribution ratio of Ni(II) as a function of the tta<sup>-</sup> concentration in the aqueous phase in the C<sub>4</sub>mimTf<sub>2</sub>N system. The triangles inserted express the respective slopes.

Initial concentration of Htta:  $1.0 \times 10^{-2} - 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ . pH 4.0 - 5.5.

Fig. 5 Evaluation of distribution constant of the enol form with the regular solution theory.

●, C<sub>*n*</sub>mimTf<sub>2</sub>N; □, alkanes and aromatic hydrocarbons<sup>a</sup>; ○, ketones<sup>b</sup>; ▽, esters<sup>c</sup>; △, ethers<sup>d</sup>.

a: Ref.[27], b: Ref.[26], c: Ref.[25], d: Ref.[28].

Fig. 6 Evaluation of distribution constants of Cu(tta)<sub>2</sub> and Ni(tta)<sub>2</sub> with the regular solution theory.

▲, Ni(tta)<sub>2</sub> in the C<sub>4</sub>mimTf<sub>2</sub>N system; Δ, Cu(tta)<sub>2</sub> in C<sub>n</sub>mimTf<sub>2</sub>N systems;

●, Ni(tta)<sub>2</sub> in organic solvent systems<sup>a</sup>; ○, Cu(tta)<sub>2</sub> in organic solvent systems<sup>a</sup>.

I, C<sub>4</sub>mimTf<sub>2</sub>N; II, C<sub>6</sub>mimTf<sub>2</sub>N; III, C<sub>8</sub>mimTf<sub>2</sub>N.

1, Dibutyl ether; 2, diisobutyl ketone; 3, methylisobutyl ketone; 4, hexane; 5, heptane;

6, carbon tetrachloride; 7, isopropylbenzene; 8, benzene.

a: Ref.[19].

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

<b>Solvent</b>	<b>log <math>K_{D,HA}</math></b>	<b><math>f_e</math></b>	<b>log <math>K_{D,HE}</math></b>	<b>log <math>K_{D,A}^a</math></b>
<b>C<sub>4</sub>mimTf<sub>2</sub>N</b>	1.61 ± 0.05	0.43 ± 0.01	3.04 ± 0.05	0.96 ± 0.10
<b>C<sub>6</sub>mimTf<sub>2</sub>N</b>	1.68 ± 0.06	0.55 ± 0.02	3.22 ± 0.06	1.18 ± 0.12
<b>C<sub>8</sub>mimTf<sub>2</sub>N</b>	1.64 ± 0.08	0.72 ± 0.01	3.29 ± 0.08	1.40 ± 0.07
<b>Benzene</b>	1.62 <sup>b</sup>	0.95 ± 0.02 <sup>c</sup>	3.39	—

a: Conditional constant at  $(0.9-1) \times 10^{-2} \text{ mol dm}^{-3}$  in IL

b: Ref.[27]

c: Calculated by NMR method.

Table 2 Distribution constant and extraction constants for divalent metals in  $C_n\text{mimTf}_2\text{N}$  systems

Divalent metal	Solvent	$\log K_{D,M2}$	$\log K_{ex,2}$	$\log K_{ex,3}'$
Ni	$C_4\text{mimTf}_2\text{N}$	4.61	$-4.36 \pm 0.09$	$-6.06 \pm 0.09$
	$C_6\text{mimTf}_2\text{N}$	—	—	$-5.54 \pm 0.14^a$
	$C_8\text{mimTf}_2\text{N}$	—	—	$-4.93 \pm 0.09^a$
Cu	$C_4\text{mimTf}_2\text{N}$	4.99	$-1.32 \pm 0.03^a$	—
	$C_6\text{mimTf}_2\text{N}$	5.09	$-1.31 \pm 0.04^a$	—
	$C_8\text{mimTf}_2\text{N}$	5.14	$-1.18 \pm 0.03^a$	—

a: Ref.[18].

Table 3 Solubility parameters of C<sub>n</sub>mimTf<sub>2</sub>N

<b>Solvent</b>	$\delta_{\text{H}}^{\text{a}}$	$\delta_{\text{H},\text{W}}$	$\delta_{\text{H},\text{W}}^{\text{ex}}$
C <sub>4</sub> mimTf <sub>2</sub> N	19.8	20.1	20.5 ± 0.7
C <sub>5</sub> mimTf <sub>2</sub> N	19.0	19.2	19.4 ± 0.7
C <sub>8</sub> mimTf <sub>2</sub> N	18.9	19.1	19.2 ± 0.7

a: Ref.[29].

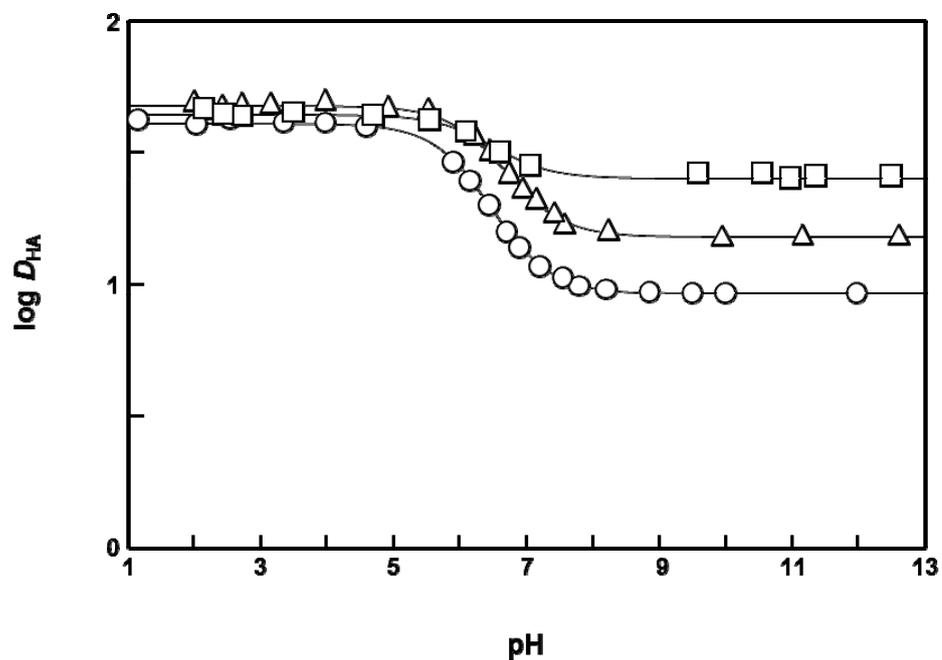


Fig.1 Distribution ratio of Htta as a function of pH.  
 Initial concentration of Htta,  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ . Ionic strength,  $1.0 \times 10^{-1} \text{ mol dm}^{-3}$  (H,Na)Cl.  
 O, C<sub>4</sub>mimTf<sub>2</sub>N;  $\Delta$ , C<sub>6</sub>mimTf<sub>2</sub>N;  $\square$ , C<sub>8</sub>mimTf<sub>2</sub>N.

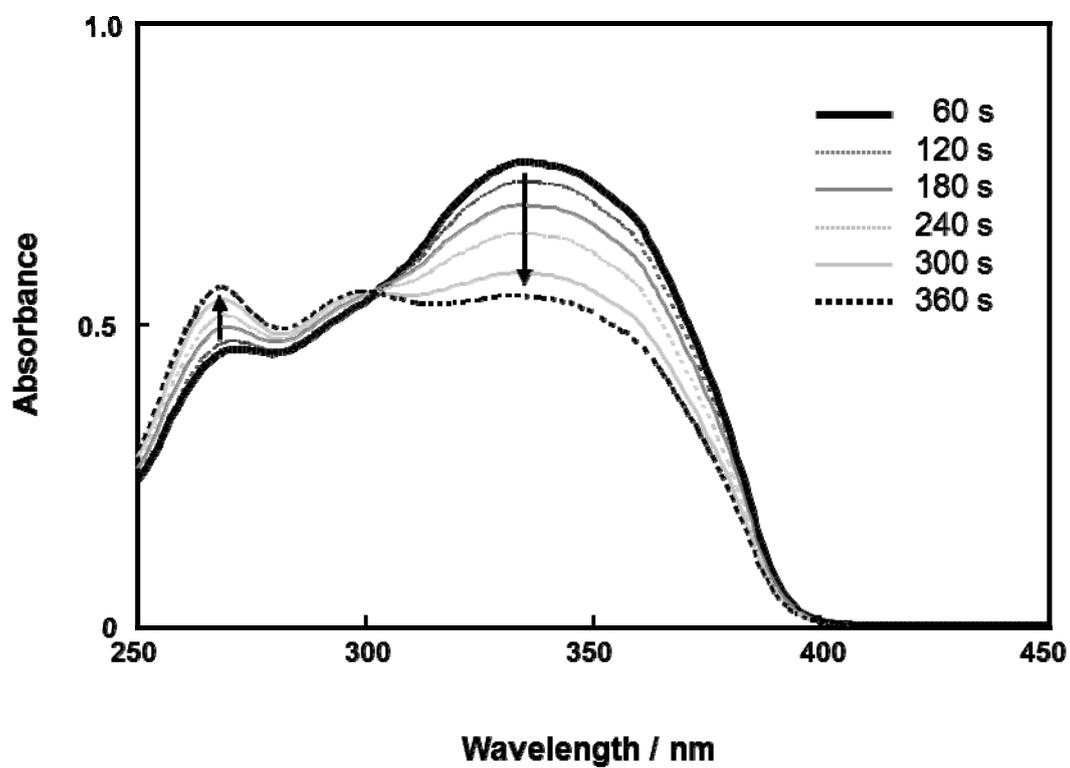


Fig.2 Absorption spectra of Htta in C<sub>4</sub>mimTf<sub>2</sub>N.  
Concentration of Htta,  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ .

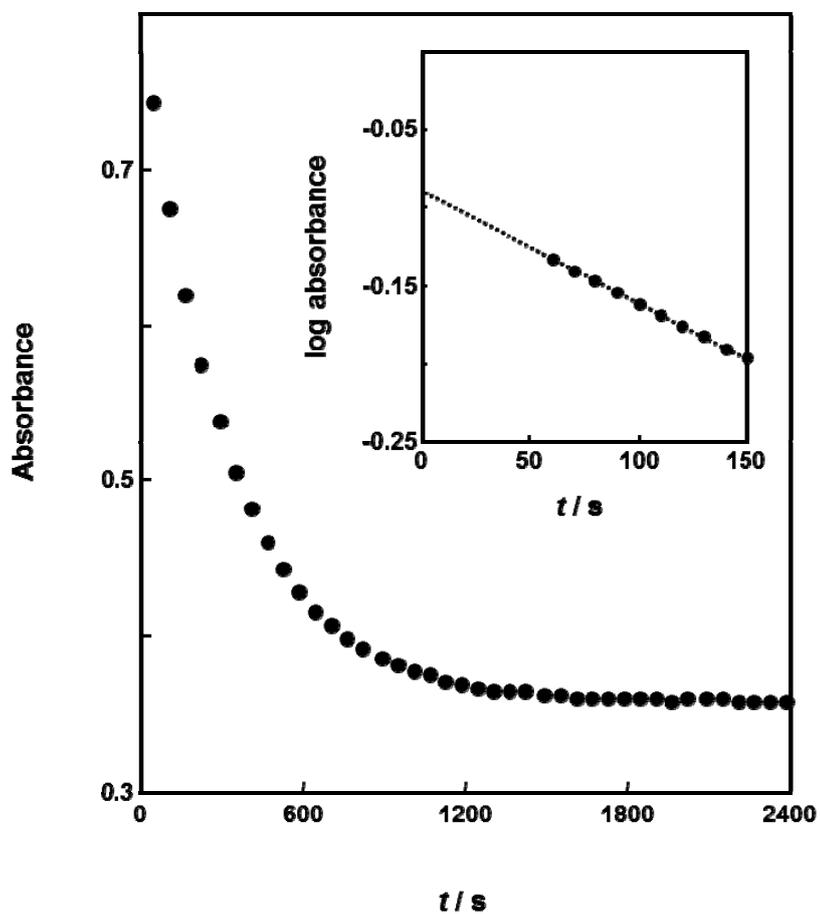


Fig.3 Time dependence of the absorbance of enol form of Htta in  $C_4mimTf_2N$ . The inset provides a magnification showing the log absorbance of enol form as a function of  $t$  ( $R^2 = 0.9996$ ). Concentration of Htta,  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ . Wavelength, 334 nm.

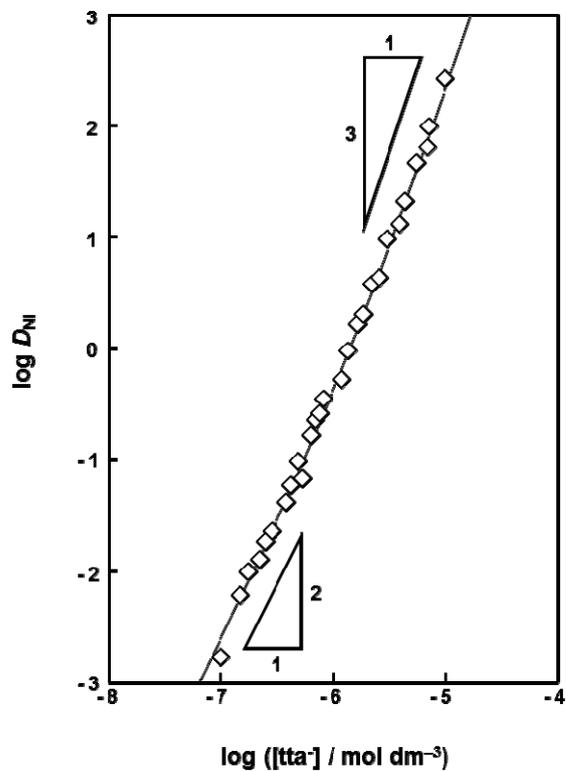


Fig.4 Distribution ratio of Ni(II) as a function of the tta<sup>-</sup> concentration in the aqueous phase in the C<sub>4</sub>mimTf<sub>2</sub>N system. The triangles inserted express the respective slopes. Initial concentration of Htta:  $1.0 \times 10^{-2}$  -  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>. pH 4.0 - 5.5.

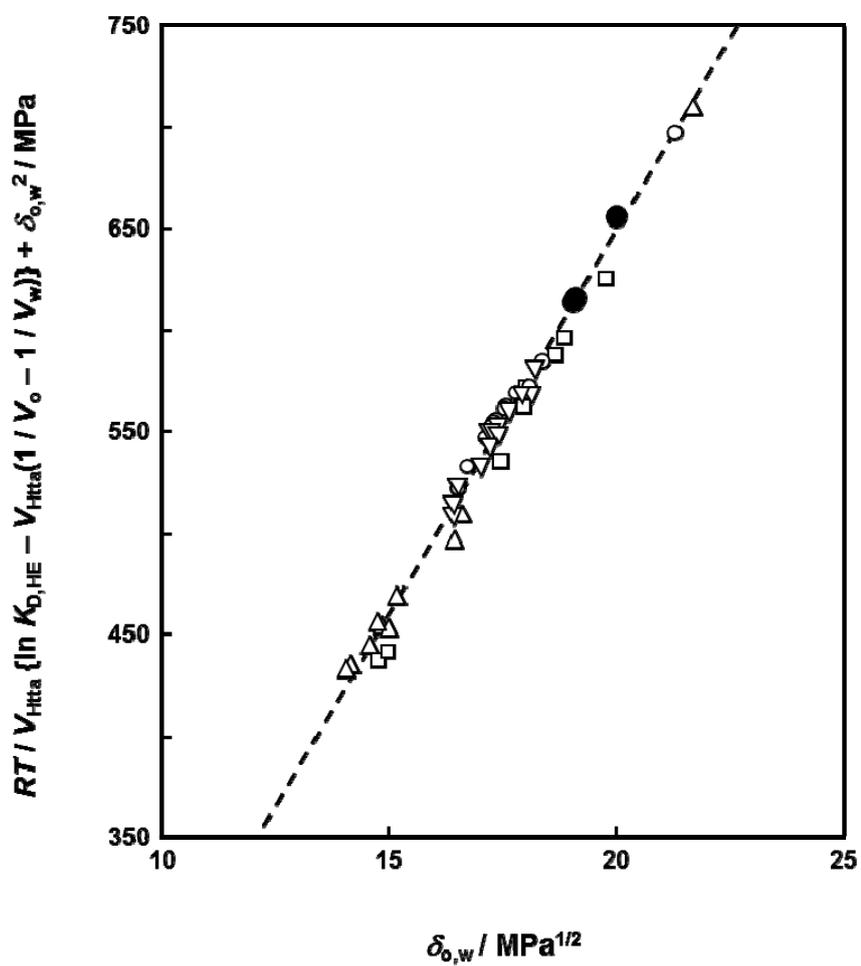


Fig. 5 Evaluation of distribution constant of the enol form with the regular solution theory.  
 ●,  $C_{11}\text{mimTf}_2\text{N}$ ; □, alkanes and aromatic hydrocarbons<sup>a</sup>; ○, ketones<sup>b</sup>; ▽, esters<sup>c</sup>; △, ethers<sup>d</sup>.  
 a: Ref.[27], b: Ref.[26], c: Ref.[25], d: Ref.[28].

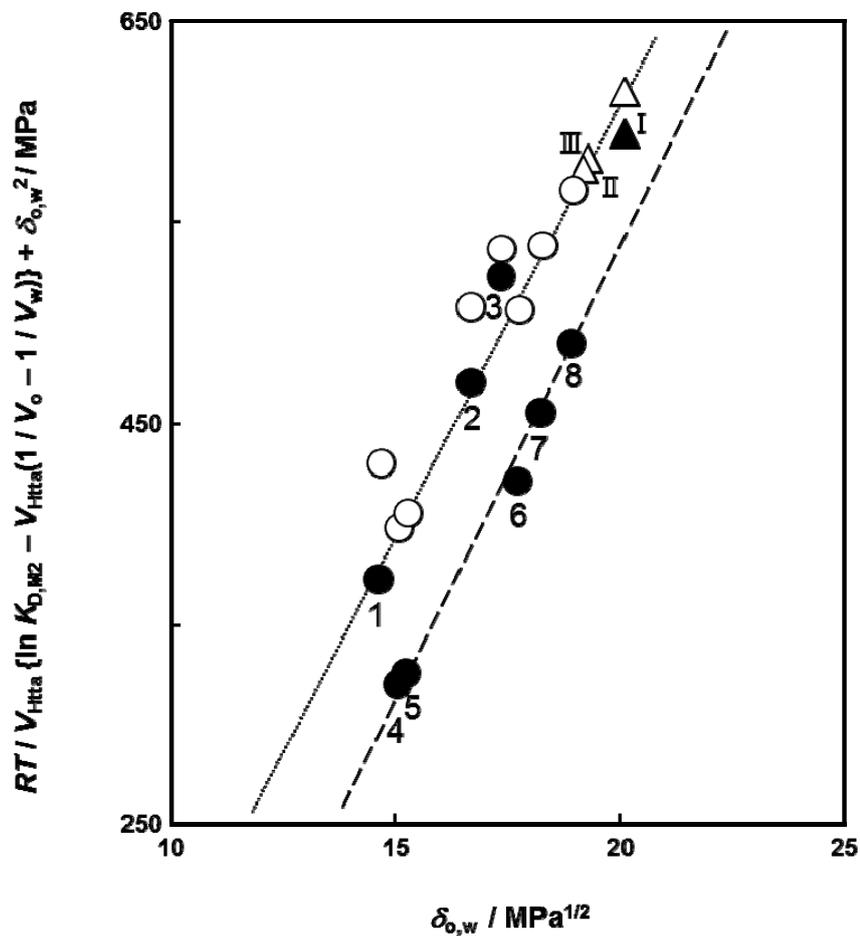


Fig.6 Evaluation of distribution constants of  $\text{Cu}(\text{tta})_2$  and  $\text{Ni}(\text{tta})_2$  with the regular solution theory.  
 ▲,  $\text{Ni}(\text{tta})_2$  in the  $\text{C}_4\text{mimTf}_2\text{N}$  system; △,  $\text{Cu}(\text{tta})_2$  in  $\text{C}_n\text{mimTf}_2\text{N}$  systems;  
 ●,  $\text{Ni}(\text{tta})_2$  in organic solvent systems<sup>a</sup>; ○,  $\text{Cu}(\text{tta})_2$  in organic solvent systems<sup>a</sup>.  
 I,  $\text{C}_4\text{mimTf}_2\text{N}$ ; II,  $\text{C}_6\text{mimTf}_2\text{N}$ ; III,  $\text{C}_8\text{mimTf}_2\text{N}$ .  
 1, Dibutyl ether; 2, diisobutyl ketone; 3, methylisobutyl ketone; 4, hexane; 5, heptane;  
 6, carbon tetrachloride; 7, isopropylbenzene; 8, benzene.  
 a: Ref.[19].

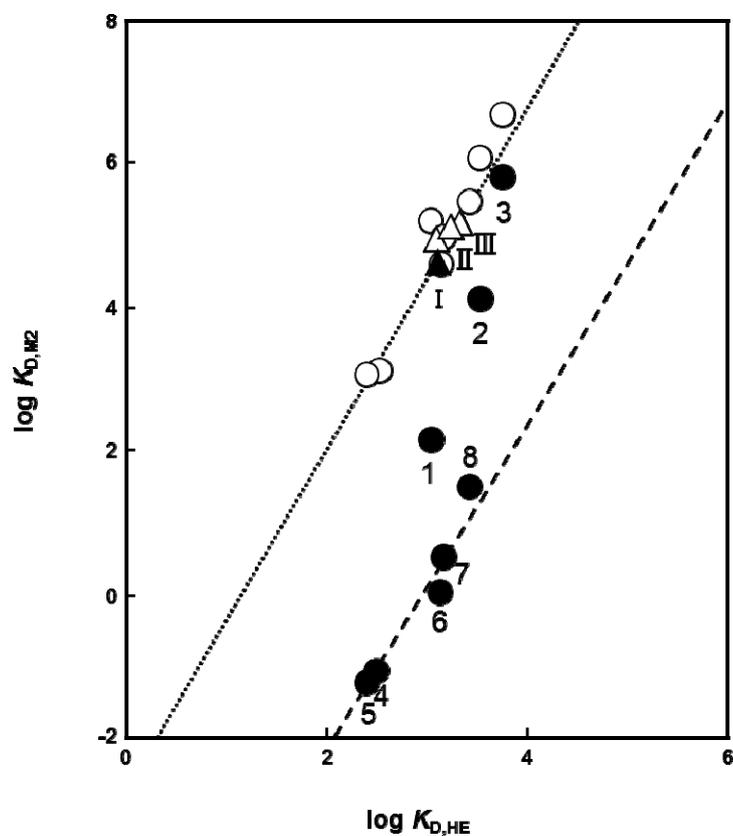


Fig. S1 Linear free energy relationship between the distribution constant of enol form and its divalent metal chelate  
 ▲, Ni(tta)<sub>2</sub> in the C<sub>4</sub>mimTf<sub>2</sub>N system. Δ, Cu(tta)<sub>2</sub> in C<sub>n</sub>,mimTf<sub>2</sub>N systems.

●, Ni(tta)<sub>2</sub> in organic solvent systems<sup>a</sup>. ○, in Cu(tta)<sub>2</sub> organic solvent systems<sup>a</sup>.

I, C<sub>4</sub>mimTf<sub>2</sub>N; II, C<sub>6</sub>mimTf<sub>2</sub>N; III, C<sub>8</sub>mimTf<sub>2</sub>N.

1, Dibutyl ether; 2, diisobutyl ketone; 3, methylisobutyl ketone; 4, hexane; 5, heptane; 6, carbon tetrachloride;  
 7, isopropylbenzene; 8, benzene.

a: Ref.[19].