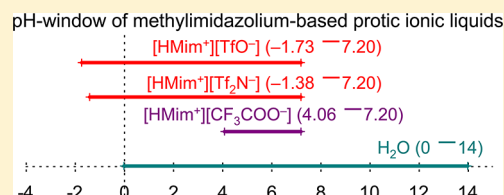


Acid–Base Property of *N*-Methylimidazolium-Based Protic Ionic Liquids Depending on AnionRyo Kanzaki,<sup>\*,†</sup> Hiroyuki Doi,<sup>‡</sup> Xuedan Song,<sup>§</sup> Shota Hara,<sup>‡</sup> Shin-ichi Ishiguro,<sup>‡</sup> and Yasuhiro Umehayashi<sup>\*,§</sup><sup>†</sup>Graduate School of Science and Engineering, Kagoshima University, 1-21-35, Korimoto, Kagoshima 890-0065, Japan<sup>§</sup>Graduate School of Science and Technology, Niigata University, 8050, Ikarashi 2-no-cho, Nisi-ku, Niigata 950-2181, Japan<sup>‡</sup>Department of Chemistry, Faculty of Sciences, Kyushu University, 6-10-1, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

**ABSTRACT:** Proton-donating and ionization properties of several protic ionic liquids (PILs) made from *N*-methylimidazole (Mim) and a series of acids (HA) have been assessed by means of potentiometric and calorimetric titrations. With regard to strong acids, bis(trifluoromethanesulfonyl) amide (Tf<sub>2</sub>NH) and trifluoromethanesulfonic acid (TfOH), it was elucidated that the two equimolar mixtures with Mim almost consist of ionic species, HMim<sup>+</sup> and A<sup>−</sup>, and the proton transfer equilibrium corresponding to autoprotolysis in ordinary molecular liquids was established. The respective autoprotolysis constants were successfully evaluated, which indicate the proton-donating abilities of TfOH and Tf<sub>2</sub>NH in the respective PILs are similar. In the case of trifluoroacetic acid, the proton-donating ability of CF<sub>3</sub>COOH is much weaker than those of TfOH and Tf<sub>2</sub>NH, while ions are predominant species. On the other hand, with regard to formic acid and acetic acid, protons of these acids are suggested not to transfer to Mim sufficiently. From calorimetric titrations, about half of Mim is estimated to be proton-attached at most in the CH<sub>3</sub>COOH–Mim equimolar mixture. In such a mixture, hydrogen-bonding adducts formation has been suggested. The autoprotolysis constants of the present PILs show a good linear correlation with dissociation constants of the constituent acids in an aqueous phase.



## ■ INTRODUCTION

Protic ionic liquids (PILs) are a subclass of room-temperature ionic liquids (RTILs) and are composed of onium salts. Ethanolammonium nitrate<sup>1</sup> and ethylammonium nitrate<sup>2</sup> (EAN) have been reported to be molten salts at room temperature, and currently they are recognized to be typical PILs. PILs are made with neutralization of a Brønsted acid HA and a base B.



Nowadays, various PILs of wide-ranging cation and anion are available.<sup>3–6</sup> Because of a dissociable hydrogen on the onium cation, PILs are expected as new solvents for acid–base reaction media<sup>7–10</sup> and as proton conductors in fuel cells.<sup>11–15</sup> In many cases, strong acids are chosen for a proton source of PILs. As the acidity of any strong acids in a solution is leveled by the conjugate acid of the solvent, one of the features of PILs is that the strong acid HA must exist as an acidic form in acidic PILs. Thus, the proton donating ability of HA in PILs has a significant meaning in PILs' chemistry as acid–base reaction media. Hence, the efforts have been made to clarify the acid–base property of PILs. We can find typical work of spectroscopy quantifying the PILs acidity by using solvatochromic dyes.<sup>16</sup> Gilbert et al. have shown the acidity level of various acids in several protic/aprotic ionic liquids by evaluating Hammett acidity function  $H_0$ .<sup>17,18</sup> They proposed the acidity order of  $\text{HPF}_6 > \text{HBF}_4 > \text{Tf}_2\text{NH} > \text{TfOH}$  ( $\text{Tf}_2\text{N}^-$  = bis-(trifluoromethanesulfonyl)amide,  $\text{TfO}^-$  = trifluoromethanesul-

fonate), which agrees well with the tendency in the gas phase acidity.<sup>19,20</sup> Direct measurement approaching  $\text{p}K_a$  of some bases in RTILs have been carried out by Barhdadi et al.<sup>21</sup>

Owing to the proton donating and accepting abilities of  $\text{HB}^+$  and  $\text{A}^-$ , respectively, PILs are considered as amphoteric solvents. In this context, the following equilibrium corresponds to an autoprotolysis, which is practically a characteristic reaction in amphoteric solvents.



The products HA and B are, respectively, the conjugate acid and base of the solvent ionic species, and hence, are the practical proton donating and accepting species in PILs. If we consider a PIL as an amphoteric solvent, the equilibrium constant  $K_s = [\text{HA}][\text{B}]$  (square brackets are used for representing the species molarity as an ordinary way throughout this paper) corresponds to an autoprotolysis constant, from which a degree of ionization by reaction 1 is estimated. And also, as is well established,  $K_s$  is a parameter concerning with acid–base properties such as a pH-window and a pH-scale.<sup>22</sup> Although one of the best ways to evaluate  $K_s$  is direct pH measurement, it is quite difficult because a usual glass electrode is practically unavailable in PILs. For an alternative of  $K_s$ , Angell et al. have proposed an index

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$\Delta pK_a^{23}$  or a “proton free energy level”<sup>24,25</sup> for PILs. They have defined  $\Delta pK_a$  as  $\Delta pK_a = pK_a(HB^+) - pK_a(HA) = -\log [HA][B]/[HB^+][A^-]$ , where  $pK_a(HB^+)$  and  $pK_a(HA)$  represent the respective acid dissociation constants of  $HB^+$  and  $HA$  in an aqueous phase. It has been demonstrated that  $\Delta pK_a$  is relevant to the predicted boiling points of PILs that may reflect an ionic character of PILs.<sup>23</sup> MacFarlane et al., have also shown a relationship between  $\Delta pK_a$  and  $^1H$  NMR chemical shift of the *N*-methyl group in a series of *N*-methylpyrrolidinium-based PILs.<sup>3</sup> Bautista-Martinez et al., have also shown a parameter  $\Delta V_{gap}$ , a potential gap between acidic and basic saturated conditions in PILs determined by cyclic voltammetry, and they found a positive correlation between  $\Delta V_{gap}$  and  $\Delta pK_a$ .<sup>26</sup> However, it is well-known that the  $pK_a$  values considerably depend on the solvent because the solvation free energy is frequently comparable to the gas phase acidity itself, especially in the charged species such as  $HB^+$  or  $A^-$ . In addition, when  $HA$  is a strong acid, it is impossible to evaluate the essential  $pK_a$  values in an aqueous phase due to the leveling effect.

Hence, it can be said that  $\Delta pK_a$  is clearly distinguishable from  $pK_s$  ( $= -\log K_s$ ). Recently, we demonstrated the direct pH measurement in EAN and its aqueous mixtures, and have successfully determined  $pK_s$  value of EAN with appropriate electrodes such as  $Pt(H_2)$  and the IS-FET (ion selective field effect transistor).<sup>27,28</sup> In fact, the  $pK_s$  value 9.83 is significantly different from  $\Delta pK_a$  of 12.0. Moreover, the reaction entropy of autoprotolysis in EAN is large and positive, while the corresponding reaction entropy in water is large and negative.<sup>29</sup> The fact suggests that reaction entropy for the autoprotolysis plays completely different role in PILs and molecular liquids; that is, it enhances autoprotolysis in Gibbs free energy in PILs, while it reduces in molecular solvents. Thus,  $pK_s$  is an essential thermodynamic quantity of PILs, even though  $\Delta pK_a$  is practically useful as a measure of the acid–base property of the PIL without direct measurements.

In the present study, to shed more light to the solvent acid–base nature of PILs, we investigated a series of PILs made from *N*-methylimidazole (Mim) and five acids with a wide variety of acidities from strong acids to weak ones by direct potentiometric and calorimetric titrations. We demonstrated that the acidity of two widely used strong acids, TfOH and  $Tf_2NH$ , are practically similar in these PILs, and that the acidity of trifluoroacetic acid is much weaker than TfOH and  $Tf_2NH$ . In addition, we found that the mixtures of Mim and acetic acid and formic acid are not essentially ionic liquids.

## EXPERIMENTAL SECTION

**Reagents.** Methylimidazole (Nippon Synthetic Chemical Industry, >99.99%) was used after distillation under reduced pressure. Liquid acids, TfOH (Central Glass, >99.5%), trifluoroacetic acid (Kishida Chemical, 99%), acetic acid (Kishida Chemical, 99.7%), and formic acid (Kishida Chemical, >98%), were purified by distillation.  $Tf_2NH$  (Morita Chemical Industries) was used without further purification. Mim was added by driplets into an aqueous solution containing equimolar  $HA$  in an ice bath. The prepared compounds were dried in vacuo for several weeks at room temperature. The water contents of these final products were determined by the Karl Fisher method to be typically less than 1 mol % (400 ppm). The elemental analyses suggest negligible impurities perturbing the target acid–base reaction. Density of the sample liquid was measured using a vibration tube densimeter (Kyoto

Electronics, DA-310) at the temperature of carrying out potentiometric titration.

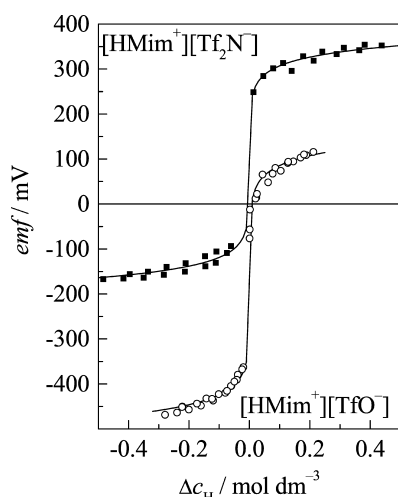
**Potentiometric Titration.** A sample of 4–6 g was set into a glass vessel with a water jacket in which the thermostatted fluid was circulated. Then the temperature was elevated to melt solid samples and thermostatted at 325 K ( $Tf_2NH$ -Mim), 367 K (TfOH-Mim), or 338 K ( $CF_3COOH$ -Mim) within a temperature fluctuation of 0.01 K. A known amount of the corresponding  $HA$  is added to prepare an acidic solution into the sample. A  $Pt(H_2)$  electrode was immersed into the sample solution. An Ag/AgCl reference electrode was separated from the sample with a double-junction salt bridge. The cell for emf (electromotive force) measurement is represented as: Ag/AgCl | 0.1 mol  $dm^{-3}$  NaCl (aq) ||  $CH_3COOH$  + Mim || sample solution |  $Pt(H_2)$ . The reference electrode was kept at room temperature (298 K) except for the immersed tip in the sample. To achieve stable emf measurement, various salt bridges were tested. Finally, we found that the  $CH_3COOH$  + Mim equimolar mixture was the best among others, thus, it was used as a salt bridge in common, though contamination from the bridge may occur to some extent. A more adequate salt bridge is needed for more accurate and stable emf measurements in PIL solutions, as well as those in aqueous ones.<sup>30</sup> Hydrogen gas was bubbled in the sample. After the equilibrium emf was attained, the sample was directly titrated by liquid Mim in the vessel. The cell showed quick response (<5 min for stabilization) and gave satisfactorily stable emf ( $3\sigma < 0.1$  mV) in each titration point except for around the neutralization point.

**Calorimetric Titration.** Calorimetric measurements were carried out for the liquid samples at 298 K ( $HA = CH_3COOH$  or  $HCOOH$ ). Fully automatic titration and data acquisition system with a twin-type isoperibol calorimeter (Tokyo Riko, Co. Ltd.) was used. A liquid Mim or  $HA$ -Mim mixture (30  $cm^3$ ) was placed in a Teflon vessel inserted in a thermostatted aluminum block at  $25 \pm 0.1$  °C with a fluctuation  $\pm 0.0001$  °C in an air bath. In the vessel, aliquots of  $HA$  were added from an autoburet (APB-S10, Kyoto Electronics) and the heats generated were determined from the temperature profile detected by doubled thermistors in the vessels on the basis of Newton’s law of cooling. The thermal conductivity in Newton’s law and the heat capacity of the cell were calibrated at each titration point with known Joule heat generated by a standard resistance. The titrations of the opposite direction (Mim added into a neat  $HA$  or a mixture) were also carried out through the entire composition range. The measured heats ranged from 0 to 45 J, with an average  $3\sigma$  of 0.4 J.

## RESULTS AND DISCUSSION

**Strong Acids.** As the  $H_0$  value of pure TfOH is much more negative ( $-14.1^{31-33}$  or  $-13^{34}$ ) than pure  $H_2SO_4$ , TfOH is a widely used superacid as a proton donating compound for acid-catalyzed reactions.  $Tf_2NH$  has attracted attention as its stronger gas-phase acidity than TfOH.<sup>19,20</sup> However, the acidity order of the two acids is ambiguous because it depends on the solvent.<sup>35,36</sup> In some cases, much more negative  $pK_a$  of TfOH (actually  $H_0$ ) than that of  $Tf_2NH$  ( $\sim -4$ ) has been employed.<sup>3,23,33</sup> We compare here the acidity by directly observed  $K_s$  in the PILs of common base.

Figure 1 shows potentiometric titration curves in  $HMim^+A^-$  ( $A^- = Tf_2N^-$  or  $TfO^-$ ).  $\Delta c_H$  represents the excess molarity of acid species  $HA$ ;  $\Delta c_H = [HA] - [Mim]$ . As described in the Experimental Section, initially acidic solutions containing excess acid ( $\Delta c_H > 0$ ) were titrated with Mim. By adding a titrant, the



**Figure 1.** Potentiometric titration curves in  $\text{HMim}^+\text{Tf}_2\text{N}^-$  (closed squares) and  $\text{HMim}^+\text{TfO}^-$  (opened circles).

emf was gradually decreased with decreasing  $\Delta c_{\text{H}}$  and suddenly dropped at around the equivalence point ( $[\text{HA}] = [\text{Mim}]$ ). Then, it slowly decreased again by further addition of Mim. This observation indicates that the  $\text{Pt}(\text{H}_2)$  electrode responds to  $[\text{HA}]$  in both PILs. The obtained neutralization curves may be likely to usual ones observed in aqueous solutions, suggesting that the equilibrium of autoprotolysis should be established in these PILs. The large emf jumps indicate that both PILs have rather large  $\text{p}K_{\text{S}}$  values.

If we assume a Nernstian response of the Pt electrode to  $[\text{HA}]$  in the PILs, the observed emf  $E_i$  at the  $i$ -th titration point can be represented as

$$E_i = E^{\circ'} + 2.303RT/F \log[\text{HA}]_i \quad (3)$$

where  $E^{\circ'}$  and  $T$  denote the apparent standard potential of the cell and temperature, respectively.  $E^{\circ'}$  is a constant involving the activity coefficient of acid in the PIL,  $\gamma_{\text{H}}$ . Supposing that  $K_{\text{S}} = [\text{HA}][\text{Mim}]$  holds,  $[\text{HA}]$  can be calculated from  $K_{\text{S}}$  and  $\Delta c_{\text{H}}$  at each titration point. It should be noted that to prepare completely neutral PILs is practically impossible, so that the excess acid (either positive or negative) in the prepared sample PIL  $\delta_{\text{HA}}$  have to be taken into consideration of  $\Delta c_{\text{H}}$ . Thus,  $E^{\circ}$  and  $\text{p}K_{\text{S}}$ , as well as  $\delta_{\text{HA}}$ , are optimized to minimize the error square sum  $U = \sum (E_{i,\text{obs}} - E_{i,\text{calc}})^2$  in which  $E_{i,\text{obs}}$  and  $E_{i,\text{calc}}$  stand for the calculated and observed emfs in the  $i$ -th titration point, respectively. Finally, obtained values are listed in Table 1, and the calculated curves, using the refined values, are shown with solid lines in Figure 1. As it can be seen in this figure, the calculated curves reproduce well each series of experimental

**Table 1.** Obtained Parameters

acid	$T$ (K)	density (g $\text{cm}^{-3}$ )	$\text{p}K_{\text{S}}$ ( $\text{HA}$ ) <sup>a</sup>	$\text{p}K_{\text{S}}$	$E^{\circ'}$ or $E^{\circ'*}$ (mV)
$\text{Tf}_2\text{NH}$	325	1.5948		8.58 (0.10)	372 (5)
$\text{TfOH}$	367	1.3376		8.93 (0.09)	153 (5)
$\text{CF}_3\text{COOH}$	338	1.3445	0.5	3.14 (0.07)	-361 (3)
$\text{HCOOH}$	298	1.1322	3.764	-1.4 <sup>b</sup>	
$\text{CH}_3\text{COOH}$	298	1.0712	4.756	-1.4 <sup>b</sup>	

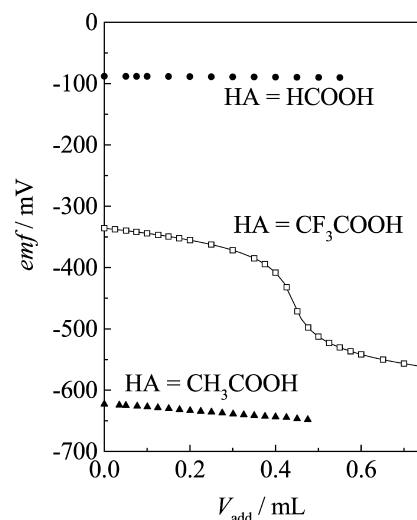
<sup>a</sup>Acid dissociation constant in aqueous phase. <sup>b</sup>Estimated at equimolar mixture by calorimetric titration (see text). The numbers in parentheses refer to three standard deviations.

points; therefore, the respective  $\text{p}K_{\text{S}}$  value can be satisfactorily determined.

According to the evaluated  $\text{p}K_{\text{S}}$  value in  $\text{HMim}^+\text{Tf}_2\text{N}^-$ , the concentrations of neutral species,  $[\text{Tf}_2\text{NH}]$  and  $[\text{Mim}]$ , can be estimated to be  $5.1 \times 10^{-5} \text{ M}$  ( $\text{M} = \text{mol dm}^{-3}$ ) at the equivalence point ( $\Delta c_{\text{H}} = 0$ ). On the other hand, the concentrations of ions,  $[\text{HMim}^+]$  and  $[\text{Tf}_2\text{N}^-]$ , are practically equal to  $c_{\text{PIL}} = 1000d/M_{\text{W}}$ , where  $d$  and  $M_{\text{W}}$  are the density of the PIL and the formula weight of  $\text{HMim}^+\text{Tf}_2\text{N}^-$ , respectively. The  $c_{\text{PIL}}$  value is 4.9 M; thus, the ionic species evidently exist in much excess than the neutral species. Similarly,  $[\text{TfOH}] = [\text{Mim}] = 3.4 \times 10^{-5} \text{ M}$  in  $\text{HMim}^+\text{TfO}^-$  at  $\Delta c_{\text{H}} = 0$ , where  $c_{\text{PIL}} (= [\text{HMim}^+] = [\text{TfO}^-]) = 5.8 \text{ M}$ . Consequently, it can be said that the equimolar mixtures of these strong acids and Mim almost completely consist of ions in practical means.

#### Potentiometric Titrations in PILs of Weak Acids.

Although  $\text{CF}_3\text{COOH}$  is classified as a weak acid due to a positive  $\text{p}K_{\text{a}}$  (0.5),  $\text{CF}_3\text{COOH}$  is acidic enough to be almost completely dissociated in an aqueous solution. The potentiometric titration curve in  $\text{HMim}^+\text{CF}_3\text{COO}^-$  is shown in Figure 2. An emf jump observed at the neutralization point means the



**Figure 2.** Potentiometric titration curves in  $\text{HMim}^+\text{CF}_3\text{COO}^-$  (opened squares) and the mixtures of  $\text{CH}_3\text{COOH}$ –Mim (closed triangles) and  $\text{HCOOH}$ –Mim (closed circles). The solid lines are guides to the eye.

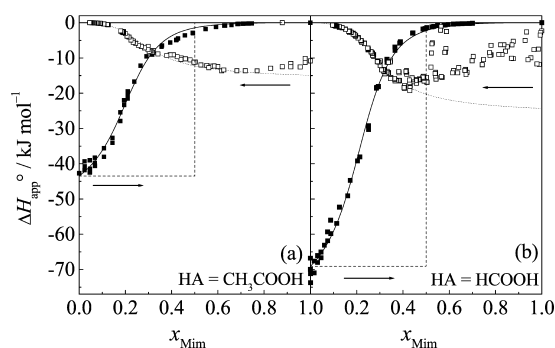
mixture mostly composed of  $\text{HMim}^+$  and  $\text{CF}_3\text{COO}^-$ . However, in comparison with  $\text{HMim}^+\text{TfO}^-$  and  $\text{HMim}^+\text{Tf}_2\text{N}^-$ , the emf drop was more moderate or much Mim was required to invert from acidic to basic solution; this indicates much more neutral species exist at an equivalence point than those in  $\text{HMim}^+\text{TfO}^-$  or  $\text{HMim}^+\text{Tf}_2\text{N}^-$ . Thus, as the significant amount of neutral species coexists, the theoretical curve in Figure 2 drawn with a solid line was calculated by using  $K_{\text{S}}^* = x_{\text{HA}} \cdot x_{\text{Mim}} / (x_{\text{A}^-} \cdot x_{\text{HMim}^+})$ , instead of  $K_{\text{S}}$ , and  $E = E^{\circ'*} + 2.303 F/RT (\log x_{\text{HA}} / c_{\text{PIL}})$ , where  $x_j$  denotes the molar fraction of component  $j$  ( $j = \text{HA}, \text{Mim}, \text{A}^-$ , and  $\text{HMim}^+$ ,  $\text{A}^- = \text{CF}_3\text{COO}^-$ ).  $K_{\text{S}}^*$  and  $E^{\circ'*}$  were then obtained similarly by minimizing  $U$ .  $E^{\circ'*}$  is different definition from  $E^{\circ'}$  in the strict sense, while the  $E^{\circ'*}$  value can be numerically compared with  $E^{\circ'}$ . For the purpose of comparison,  $K_{\text{S}}^*$  is converted to  $\text{p}K_{\text{S}}$  by  $\text{p}K_{\text{S}} = -\log K_{\text{S}}^* - 2 \log c_{\text{PIL}}$ . The final values are listed in Table 1. As shown,  $\text{p}K_{\text{S}}$  for  $\text{HMim}^+\text{CF}_3\text{COO}^-$  are significantly smaller than those for PILs consisting of strong acids. The concentrations of neutral



species at  $\Delta c_{\text{H}} = 0$  are calculated by using  $K_{\text{S}}^*$  to be 0.036 M. Although this value is much larger than that for  $\text{HMim}^+\text{Tf}_2\text{N}^-$  and  $\text{HMim}^+\text{TfO}^-$  the ionic species are still much excess ( $c_{\text{PIL}} = 6.9$  M) over the neutral species in  $\text{HMim}^+\text{CF}_3\text{COO}^-$ , and hence, the equimolar mixture practically consists of ions. The smaller  $pK_{\text{S}}$  value than that in  $\text{HMim}^+\text{Tf}_2\text{N}^-$  and  $\text{HMim}^+\text{TfO}^-$  indicates the proton donating ability of  $\text{CF}_3\text{COOH}$  in  $\text{HMim}^+\text{CF}_3\text{COO}^-$  is obviously much weaker than that of  $\text{Tf}_2\text{NH}$  and  $\text{TfOH}$ .

$\text{CH}_3\text{COOH}$  and  $\text{HCOOH}$  are much weaker acids than  $\text{CF}_3\text{COOH}$  in an aqueous phase. In a dilute aqueous solution of equimolar  $\text{CH}_3\text{COOH}$  and Mim, according to  $pK_{\text{S}}$ s, 94% of either is ionized to form  $\text{CH}_3\text{COO}^-$  and  $\text{HMim}^+$ , respectively. However, as shown in Figure 2, no practical emf jump near the equivalence point was observed in the potentiometric titrations, which indicates the proton transferred ionic species is never predominant and neutral species may considerably exist. Depending on the medium, some proton transfer patterns from  $\text{CH}_3\text{COOH}$  to Mim have been proposed. In nonpolar solvents such as chloroform, an incomplete proton transfer and a hydrogen-bonding adduct formation like  $\text{CH}_3\text{COO}^- \cdots \text{H}^+ \cdots \text{Mim}$  has been suggested.<sup>37,38</sup> In a vapor phase at a higher temperature, a hydrogen-bonded  $\text{CH}_3\text{COOH} \cdots \text{Mim}$  was proved by Raman spectroscopy.<sup>39</sup> According to ab initio calculations, the potential energy surface of  $\text{H}^+$  between imidazole-N and O of  $\text{CH}_3\text{COO}^-$  was revealed to depend on the dielectric constant, that is,  $\text{H}^+$ -N distance of 1.05–1.1 Å is a single potential well in a gas phase while another potential well at  $\text{H}^+$ -O distance of 1–1.05 Å appears in a medium of higher dielectric constants.<sup>40</sup> All of these facts strongly support our findings.

**Calorimetric Titrations in PILs of Weak Acids.** In the mixtures of Mim and weak acids ( $\text{HA} = \text{CH}_3\text{COOH}$  or  $\text{HCOOH}$ ) calorimetric titrations have been carried out. The heat generated by adding aliquots of HA or Mim to the solution successively,  $q_{\text{add}}$  was recorded at an each titration point. Figure 3 shows the apparent molar reaction enthalpy



**Figure 3.** Calorimetric titration curves in (a)  $\text{CH}_3\text{COO}^-$ -Mim and (b)  $\text{HCOOH}$ -Mim mixtures in apparent reaction enthalpy  $\Delta H_{\text{app}}^0$ . The closed and opened symbols denote the titration by Mim and HA, respectively. The arrows indicate the direction of the titration.

defined as  $\Delta H_{\text{app}}^0 = -q_{\text{add}}/m_{\text{add}}$  as a function of the molar ratio of Mim in the mixture after each addition of the titrant  $x_{\text{Mim}}$ , where  $m_{\text{add}}$  is the number of moles of HA or Mim added at an each titration point. At the beginning of addition of Mim into HA (shown with the closed squares in Figure 3), the  $\Delta H_{\text{app}}^0$  was significantly large and negative for both  $\text{CH}_3\text{COOH}$  and  $\text{HCOOH}$ . The extrapolated value of  $\Delta H_{\text{app}}^0$  toward  $x_{\text{Mim}} = 0$ ,  $\Delta H_{\text{app},0}^0$  was  $-43$  kJ/mol for  $\text{CH}_3\text{COOH}$  and  $-69$  kJ/mol for

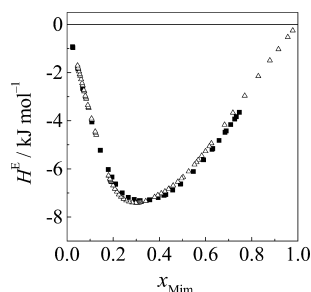
$\text{HCOOH}$ , respectively.  $\Delta H_{\text{app}}^0$  was then increased immediately with increasing  $x_{\text{Mim}}$ , and approached to zero at around  $x_{\text{Mim}} = 0.5$  via the value of  $\Delta H_{\text{app},0}^0/2$  at around  $x_{\text{Mim}} = 0.25$ . On the other hand,  $\Delta H_{\text{app}}^0$  for addition of  $\text{CH}_3\text{COOH}$  into Mim (shown with the open squares in Figure 3) at  $x_{\text{Mim}} = 1$  was about  $-10$  kJ/mol.  $\Delta H_{\text{app}}^0$  was then kept almost unchanged down to  $x_{\text{Mim}} = 0.5$ , then increased to reach zero with decreasing  $x_{\text{Mim}}$ . The  $\Delta H_{\text{app}}^0$  value for the addition of  $\text{HCOOH}$  at  $x_{\text{Mim}} > 0.5$  was rather scattered, probably due to a decarbonylation and a decarboxylation of  $\text{HCOOH}$ .<sup>41</sup> We, thus, no longer discuss about the results of  $\text{HCOOH}$  titration into Mim.

$\Delta H_{\text{app},0}^0$  for  $\text{CH}_3\text{COOH}$  was 26 kJ/mol less negative than  $\Delta H_{\text{app},0}^0$  for  $\text{HCOOH}$ . This gap in  $\Delta H_{\text{app},0}^0$  is greater than that in their dissociation enthalpies in water; small and similar values of  $\pm 1$  kJ/mol have been reported for both  $\text{CH}_3\text{COOH}$  and  $\text{HCOOH}$ .<sup>42</sup> We can consider that the addition of a small amount of Mim into neat HA involves the following processes: (1) isolation of monomeric HA and Mim as possible reactants into the gas phase, (2) proton transfer reaction from HA to Mim in the gas phase, and (3) solvation of the possible products of  $\text{A}^-$  and  $\text{HMim}^+$  by neat HA. The enthalpic cost for process (1) of  $\text{HCOOH}$  is rather larger relative to that of  $\text{CH}_3\text{COOH}$  due to a larger heat of vaporization and cohesive energy density.<sup>43</sup> From the gas phase experiments, the difference between  $\text{CH}_3\text{COOH}$  and  $\text{HCOOH}$  in the dissociation enthalpies (5.9 kJ/mol<sup>44</sup>) are much smaller than the gap in  $\Delta H_{\text{app},0}^0$ . Therefore, the unexpectedly larger  $\Delta H_{\text{app},0}^0$  for  $\text{CH}_3\text{COOH}$  than that for  $\text{HCOOH}$  should be associated with process (3). That is,  $\text{HCOOH}$  has a significantly large dielectric constant in comparison to  $\text{CH}_3\text{COOH}$ , owing to a large dipole moment, and has large solvation energy for the charged solutes, so that process (3) is enthalpically more favorable in  $\text{HCOOH}$  than in a less polar  $\text{CH}_3\text{COOH}$ .

Similarly,  $\Delta H_{\text{app},1}^0$  represents the extrapolated  $\Delta H_{\text{app}}^0$  value at  $x_{\text{Mim}} = 1$  in the titration of  $\text{CH}_3\text{COOH}$  into neat Mim. Comparing  $\Delta H_{\text{app},1}^0$  with  $\Delta H_{\text{app},0}^0$  for  $\text{CH}_3\text{COOH}$ -Mim system,  $\Delta H_{\text{app},1}^0$  was significantly less negative than  $\Delta H_{\text{app},0}^0$ . We can also consider the respective processes (1–3) corresponding to those mentioned above. If we assume that the same proton transfer reaction occurs in both titrations, independent from the titration direction, the processes (1) and (2) are common. It should be noted that process (3) involves cavity formation to embed solutes.  $\text{CH}_3\text{COOH}$  is a highly ordered solvent of hydrogen bonding. Nishi et al. revealed  $\text{CH}_3\text{COOH}$  is an associated liquid, mainly due to the chain-like self-association.<sup>45–48</sup> On the other hand, Mim $\cdots$ Mim interaction should arise from dipole–dipole interaction. In fact, endothermic mixing of Mim and nonpolar solvents such as normal alkanes has also been reported.<sup>49,50</sup> The experimental fact that  $\Delta H_{\text{app},1}^0$  was significantly less negative than  $\Delta H_{\text{app},0}^0$ . This suggests that larger endothermic enthalpy for the cavity formation in neat Mim than that in neat  $\text{CH}_3\text{COOH}$  and solvation by Mim to the product ions is significantly weaker than that by  $\text{CH}_3\text{COOH}$ . Possible interpretation may be that the hydrogen bonding among the solvent  $\text{CH}_3\text{COOH}$  molecules is kept both in the cavity formation and in the solvation in neat  $\text{CH}_3\text{COOH}$ . For more detailed discussion, however, spectroscopic investigations are needed.

In the middle composition range, one of the common features of the titration curves given in  $\Delta H_{\text{app}}^0$  is that it becomes the value of  $\Delta H_{\text{app},0}^0/2$  or  $\Delta H_{\text{app},1}^0/2$  at  $x_{\text{Mim}} < 0.5$ . In these ranges of solvent composition, the heat of mixing also

significantly contributes in  $\Delta H_{\text{app}}^\circ$ . We depict the calorimetric titration data in excess enthalpy of mixing,  $H^E$  ( $H^E = \Sigma q_{\text{mix}} / \Sigma m_j$ ). As shown in Figure 4, the titration curves evaluated with



**Figure 4.** Excess enthalpy of mixing of  $\text{CH}_3\text{COOH}$  and Mim. The closed and opened symbols denote the titration by Mim and  $\text{CH}_3\text{COOH}$ , respectively.

a different titration direction were practically the same with each other, which suggest that no hysteretic behavior was found in calorimetric titrations. Therefore, all the processes involved in the mixing should be fast, and the species distribution in the mixture never depends on titration direction but only on the solvent composition. As clearly shown in Figure 4, the  $H^E$  curves are asymmetric with a minimum of 7.3–7.4 kJ/mol at  $x_{\text{Mim}} = 0.30\text{--}0.32$ . It indicates that stoichiometric aggregates or adducts seems to be formed in the mixture. In addition, the minimum at  $x_{\text{Mim}} = 0.30\text{--}0.32$  suggests that an adduct formation of  $\text{Mim}:\text{CH}_3\text{COOH} = 1:2$ . Similar results have also been reported in mixtures of  $\text{C}_2\text{H}_5\text{COOH}$ –triethylamine<sup>51</sup> and  $\text{CH}_3\text{COOH}$ –*N*-methylpyrrolidine.<sup>52</sup> In such mixtures, the transport properties, such as viscosity and ionic conductivity, show a maximum at the component of carboxylic acids excess region. Orzechowski et al., have proposed an adduct formation of  $\text{C}_2\text{H}_5\text{COOH}:\text{triethylamine} = 2:1$ , together with a 1:1 hydrogen-bonding adduct and dissociated free ionic species.<sup>51</sup> The minimum  $H^E$  value was about  $-13$  kJ/mol at about  $x_{\text{triethylamine}} = 0.33$ . Less negative  $H^E$  for  $\text{CH}_3\text{COOH}$ –Mim than that for  $\text{C}_2\text{H}_5\text{COOH}$ –triethylamine implies that  $\text{CH}_3\text{COO}^-$  and  $\text{HMim}^+$  may not exist as free ions, but hydrogen bonding adducts should be plausibly formed also in  $\text{CH}_3\text{COOH}$ –Mim mixture, and the bonding energy is smaller than those formed in  $\text{C}_2\text{H}_5\text{COOH}$ –triethylamine. In addition, according to ab initio calculation in a gas phase, the stabilization energy of  $\text{CH}_3\text{COOH}\cdots\text{Mim}$  hydrogen-bonding adduct formation is 53.46 kJ/mol.<sup>39</sup>

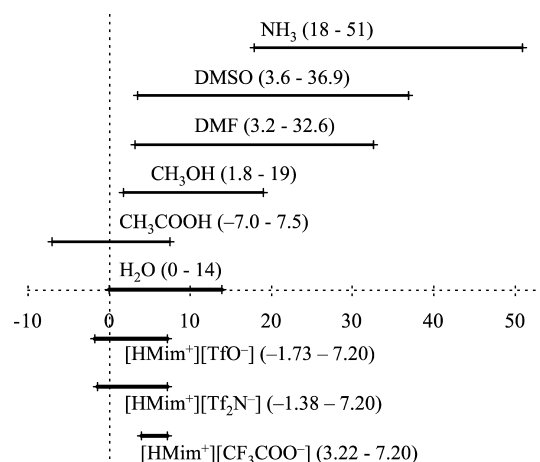
Finally, we discuss titration curves in  $\Delta H_{\text{app}}^\circ$  here again to estimate the ionization ratio (or degree of proton transfer) from the calorimetric data. As aforementioned, titration curve for Mim titration into the acids approached zero in  $\Delta H_{\text{app}}^\circ$  at around  $x_{\text{Mim}} = 0.5$ , while the titration curve of the inverted direction converged to zero at  $x_{\text{Mim}} = 0.2$ . The latter suggests that heat, except the proton transfer reaction, such as the heat of mixing and dilution, considerably contributes in  $\Delta H_{\text{app}}^\circ$ . Therefore, we discuss only the calorimetric titration curves for Mim titration into the acids. We first consider calorimetric titration curves for simple strong acid and base neutralization. In this case, the values in  $\Delta H_{\text{app}}^\circ$  should be kept constant until the equivalence point, and then they suddenly turn off (go to zero) at the equivalence point. Typical titration curves for such strong acid and base titration are shown by a dashed line in Figure 3. It should be noted that the constant  $\Delta H_{\text{app}}^\circ$  values

until the equivalence point equal to the proton transfer enthalpy for the strong acid and base. Here, let us compare the titration curves for Mim and  $\text{CH}_3\text{COOH}$  or  $\text{HCOOH}$  systems with those for simple strong acid and base neutralization.  $\Delta H_{\text{app}}^\circ$  for Mim and  $\text{CH}_3\text{COOH}$  or  $\text{HCOOH}$  are always less negative than the dashed line at the composition range below the equivalence point, indicating that Mim protonation may partially occur in the mixture. The protonation ratio of Mim is defined by  $\alpha_{\text{Mim}} = m_{\text{HMim}} / (m_{\text{HMim}} + m_{\text{Mim}})$ , where  $m_j$  is the number of moles of respective species  $j$  in the mixture. If we assume the observed heat contains only that for the proton transfer reaction  $\alpha_{\text{Mim}}$  could be estimated from the total heat generated until the titration point, as follows:

$$\alpha_{\text{Mim}} = \frac{\int_0^{x_{\text{Mim}}} \Delta H_{\text{app}}^\circ dx_{\text{Mim}}}{x_{\text{Mim}} \Delta H_{\text{app},0}^\circ} \quad (4)$$

Based on eq 4,  $\alpha_{\text{Mim}}$  at  $x_{\text{Mim}} = 0.5$  is estimated to be 0.43 for  $\text{CH}_3\text{COOH}$ –Mim and 0.45 for  $\text{HCOOH}$ –Mim. The formally obtained  $\text{p}K_s$  values from  $K_s = \{(1 - \alpha_{\text{Mim}}) c_{\text{PIL}}\}^2$  are  $-1.3$  for  $\text{CH}_3\text{COOH}$ –Mim and  $-1.4$  for  $\text{HCOOH}$ –Mim, respectively. The values are similar with each other despite a significantly different  $\Delta H_{\text{app},0}^\circ$  and  $\Delta \text{p}K_a$  in an aqueous phase. Although such an estimation is rather rough, however, it is worth pointing out that, at most, a half of Mim or some extent is proton-attached to be ionized in the equimolar mixtures of  $\text{CH}_3\text{COOH}$  or  $\text{HCOOH}$ .

**Acid–Base Property of the PILs.** The  $\text{p}K_s$  values generally corresponds the practical pH-range (0 to  $\text{p}K_s$ ) for the respective solvent. Figure 5 represents the pH range or a

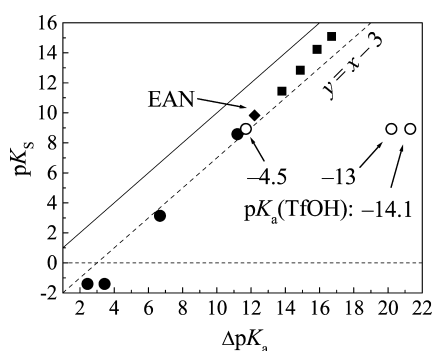


**Figure 5.** pH-windows in various solvents, including PILs, shown by a common pH scale<sup>22</sup> (DMF = *N,N*-dimethylformamide, DMSO = *N,N*-dimethylsulfoxide).

pH-window<sup>22</sup> of several solvents. For molecular solvents, each window with a width of  $\text{p}K_s$  is arranged by placing their left-end at  $-\log \gamma_{\text{t,H}}$ : the transfer activity coefficient of  $\text{H}^+$  from water to the solvent.<sup>53</sup> Therefore, these windows lie on the universal pH-scale or, in other words, solutions of identical pH in this scale have an identical  $\text{H}^+$  activity. By using this diagram, we can easily compare the acidity and basicity of solutions beyond the solvents. Here, we attempt to arrange the pH-windows of the present PILs. However,  $\gamma_{\text{t,H}}$  from water to the respective PIL is not available at the present stage. Though rough, the pH-windows are arranged according to the basicity because the conjugate base of the present PILs is Mim in common. Thus,

pH-windows of the PILs are arranged by placing their right-end at  $\text{pH} = \text{p}K_{\text{a}}(\text{HMim}^+)$ . We, of course, recognize that it is quite a rough estimation because  $\gamma_{\text{t,Mim}}$ , as well as the temperature dependence in  $\text{p}K_{\text{S}}$ , are not taken into account. Nonetheless, we emphasize Figure 5 is practically useful. With regard to  $\text{HMim}^+\text{Tf}_2\text{N}^-$  and  $\text{HMim}^+\text{TfO}^-$ , the negative leftmost values and much smaller rightmost values than 14 indicate these PILs are possibly classified into acidic solvents. It should be emphasized that the gap in the leftmost values (0.35) is significantly smaller than that in the gas phase acidity of  $\text{Tf}_2\text{NH}$  and  $\text{TfOH}$ ; that for  $\text{Tf}_2\text{NH}$  is about 55 kJ/mol smaller, which corresponds to more acidic of 10 in pH unit at 298 K, than that for  $\text{TfOH}$ .<sup>19,20</sup> This suppression arises from a large solvation free energy of the species, HA and  $\text{A}^-$ , as well as Mim and  $\text{HMim}^+$  in PIL. Watanabe et al. proposed a parameter ionicity as a measure of the ion–ion interaction in RTILs.<sup>54,55</sup> Watanabe's ionicity is larger in  $\text{C}_4\text{mim}^+\text{Tf}_2\text{N}^-$  ( $\text{C}_4\text{mim}^+$ : 1-butyl-3-methylimidazolium) than that in  $\text{C}_4\text{mim}^+\text{TfO}^-$ , indicating that  $\text{C}_4\text{mim}^+$  is more strongly interacting with  $\text{TfO}^-$  than  $\text{Tf}_2\text{N}^-$  in these RTILs. Therefore,  $\text{HMim}^+$  should be stabilized extensively in  $\text{HMim}^+\text{TfO}^-$  than in  $\text{HMim}^+\text{Tf}_2\text{N}^-$ . This may lead to increasing  $\text{p}K_{\text{S}}$  in  $\text{HMim}^+\text{TfO}^-$ . The solvation effect on HA also varies its acidity, while it cannot be separated from that on Mim. Thus, the ion–ion interaction and the solvation of ions in PILs play a key role in the acidity and basicity of PILs as solvents. In the case of  $\text{HMim}^+\text{CF}_3\text{COO}^-$ , the pH-window lies completely inside that of water.

In Figure 6, directly obtained autoprotolysis constant  $\text{p}K_{\text{S}}$  is plotted against  $\Delta\text{p}K_{\text{a}}$ , together with those for  $\text{EAN}^{27}$  and a



**Figure 6.** Relationship between  $\Delta\text{p}K_{\text{a}}$  and  $\text{p}K_{\text{S}}$  in the present PILs. The closed diamonds are for  $\text{EAN}^{27}$  and a series of PILs composed of a ternary ammonium with 2-hydroxyethyl group(s).<sup>56</sup>

series of PILs composed of ammonium with a 2-hydroxyethyl group(s) as a cation.<sup>56</sup> We employed  $-4$  for  $\text{p}K_{\text{a}}$  of  $\text{Tf}_2\text{NH}$  in water to calculate  $\Delta\text{p}K_{\text{a}}$ , as heretofore used.<sup>3,23,33</sup> As shown,  $\text{p}K_{\text{S}}$  of PILs have a good correlation with  $\Delta\text{p}K_{\text{a}}$ ; plots for  $\text{HMim}^+\text{Tf}_2\text{N}^-$ ,  $\text{HMim}^+\text{CF}_3\text{COOH}$ ,  $\text{Mim}-\text{CH}_3\text{COOH}$ , and  $\text{Mim}-\text{HCOOH}$ , as well as  $\text{EAN}$ , almost fall on a straight line with a slope of unity. Furthermore, data for the PILs consisting of a cation with a 2-hydroxyethyl group(s) also practically fall on the same line. On the other hand, plots for  $\text{HMim}^+\text{TfO}^-$  were rather scattered, depending on the employed values of  $\text{p}K_{\text{a}}$  for  $\text{TfOH}$  in an aqueous solution. If we here adopt  $\text{p}K_{\text{a}} = -4.5$  for  $\text{TfOH}$  in the aqueous solution, the plot locates near the above-mentioned straight line. Figure 6 possibly implies that the acid–base property of PILs can be approximately predicted from  $\text{p}K_{\text{S}}$  of the constituent ions in an aqueous phase. However, it would not always be true. Further investigations

such as thermodynamics of acid-dissociation of solutes in PILs are required and are now going on.

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### Notes

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