Physicochemical and Acid-base Properties of a Series of 2-Hydroxyethylammonium-based Protic Ionic Liquids

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Physicochemical properties such as a thermal behavior, ionic conductivity, viscosity and density, and acid-base properties of a new class of 2-hydroxyethylammonium-based protic ionic liquids (PILs) have been investigated. Thirty-six potential PILs were surveyed to find 32 salts with a melting point below 373 K. Among them, $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ (Et , C_2H_5 ; $n = 0 - 3$) and $[(\text{EtOH})_2\text{EtNH}^+][\text{X}^-]$ ($\text{X} = \text{TFS}$, trifluoromethanesulfonate; TFSA , bis(trifluoromethanesulfonyl)amide; NO_3) were studied in terms of the Walden plots, molar volume and auto-protolysis reaction for effect of the number of 2-hydroxyethyl groups introduced in the cations and for dependence of the anion nature, respectively. With regard to $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$), the ion-ion interactions between cation-anion and cation-cation were enhanced with increasing the number of the 2-hydroxyethyl groups. In addition, the auto-protolysis constant K_s value for $[(\text{EtOH})_2\text{EtNH}^+][\text{TFSA}^-]$ is smaller than that for TFS^- based PIL, indicating that HTFSA behaves as a stronger acid than HTFS in the respective PIL. On the other hand, in $[(\text{EtOH})_2\text{EtNH}^+][\text{NO}_3^-]$, the emf jump was rather small, which suggests that the proton of HNO_3 does not easily transfer to $(\text{EtOH})_2\text{EtN}$ in the liquid state.

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Introduction

Room-temperature ionic liquids (RTILs) have been receiving much attention as new functionalized solvents in various fields of chemistry due to their unique properties.¹⁻⁴ RTILs can be classified into two categories like ordinary non-aqueous solvents, *i.e.*, aprotic (APILs) and protic (PILs) ones. PILs can be simply prepared by mixing a Brønsted acid HA and a Brønsted base B to yield $[\text{HB}^+][\text{A}^-]$ by proton transfer.⁵⁻⁷ The auto-protolysis constant K_s ($= [\text{B}][\text{HA}]$) for the spontaneous auto-protolysis reaction in ionic liquids, $\text{HB}^+ + \text{A}^- \rightleftharpoons \text{B} + \text{HA}$, can be a measure of the acid and base property of the $[\text{HB}^+][\text{A}^-]$ ionic liquid. However, it is quite difficult to determine K_s directly because of the practical unavailability of an ordinary glass electrode in PILs. Instead, $\Delta\text{p}K_a$ has been proposed by Angell *et al.*,⁸⁻¹⁰ which is defined as the difference between the acid dissociation constants K_a for HA and HB^+ in the respective aqueous solution. Gilbert *et al.* determined the Hammett acidity functions H_0 of many RTILs using UV-visible spectroscopy.¹¹⁻¹³ On the other hand, MacFarlane *et al.* have shown that the proton transfer of HB^+ to A^- proceeds in the pyrrolidinium based ionic liquids (smaller $\text{p}K_s$), though the $\Delta\text{p}K_a$ value is 5.7, which means significant amount of neutral species [B] and [HA] exist in equilibrium.¹⁴ Recently, we have reported the $\text{p}K_s$ value of

ethylammonium nitrate $[\text{EtNH}_3^+][\text{NO}_3^-]$ ionic liquid by a direct potentiometry with the IS-FET (ion selective field effective transistor) and $\text{Pt}(\text{H}_2)$ electrodes.^{15,16} Actually, the $\text{p}K_s$ values of 10.004 with the IS-FET electrode and 9.83 with $\text{Pt}(\text{H}_2)$ one, respectively, are significantly different from the $\Delta\text{p}K_a$ value of 11.93. It is thus important to determine $\text{p}K_s$ values of ionic liquids directly.

From environmental and biological viewpoints, bio-compatible ionic liquids such as the choline-based ones of low toxicity^{17,18} are attracting more attention recently, because enzyme stability is improved.¹⁹⁻²² In addition, they act as solvents or catalysts for various organic reactions.^{23,24} Similarly, RTILs with the hydroxyl groups have CO_2 absorption,²⁵⁻²⁹ and cellulose/protein dissolution abilities.³⁰⁻³² The catalytic behavior of RTILs in the organic reactions, for instance, the yield of the product, depends on the acid-base properties of RTILs.³³⁻³⁷ In order to clarify solvent natures, one must have extensive knowledge of physicochemical and Brønsted and/or Lewis acid-base properties of ionic liquids. Experimental results for the physicochemical properties³⁸⁻⁵² and solvatochromic parameters⁵³⁻⁵⁵ of ionic liquids with the hydroxyl groups have been reported.

In this paper, we report a series of potential protic ionic liquids consisting of the cations with the 2-hydroxyethyl (EtOH) and/or the ethyl (Et) group shown in Fig. 1 to find new protic ionic liquids. Among them, the selected ones composed of the $(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+$ ($n = 0 - 3$) cations coupled with trifluoromethanesulfonate TFS^- , and $[(\text{EtOH})_2\text{EtNH}^+]$ based ionic liquids combined with three anions of TFS^- , bis(trifluoromethanesulfonyl)amide TFSA^- and nitrate NO_3^- were investigated in terms of physicochemical properties such as thermal behavior, ionic conductivity, viscosity and density,

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Fig. 1 Structures and abbreviations for the cations and the anions of potential protic ionic liquids (PILs) investigated in the present study.

and also the acid-base property of pK_s . The ion-ion interaction and the acid-base property of this new class of PILs were discussed.

Experimental

Materials

As a typical example, $[\text{Et}_3\text{NH}^+][\text{TFS}^-]$ was prepared by mixing Et_3N and HTFS as follows: Et_3N was placed in a three-necked round-bottom flask immersed in an ice bath. Under vigorous stirring, HTFS was added drop wise to the amine at a temperature below 283 K. Stirring continued for 24 h at the temperature to obtain a clear $[\text{Et}_3\text{NH}^+][\text{TFS}^-]$ PIL. Then water and residual amine/acid were evaporated under reduced pressure for 72 h at room temperature. A viscous colorless or pale-yellow liquid was collected; further drying over molecular sieves 3A followed. Water content in final samples was checked to be below 1000 ppm with the Karl-Fischer titration. Prepared ionic liquids were identified with the elemental analysis.

Potentiometric titration

A sample of 4–6 g was set into a glass vessel with a water jacket in which the thermostating fluid was circulated. Then the temperature was elevated to melt solid salts, and the sample was thermostated at 305 K ($[\text{Et}_3\text{NH}^+][\text{TFS}^-]$) and 298 K (others) with a temperature fluctuation of less than 0.1 K; this was followed by adding a known amount of the corresponding base B to prepare an alkaline solution. A $\text{Pt}(\text{H}_2)$ electrode was used,

Table 1 Screening results of potential protic ionic liquids; liquid at 298 K (●), 373 K (○), and solid at 373 K (●)

	TFS ⁻	TFSA ⁻	BF ₄ ⁻	NO ₃ ⁻
EtNH ₃ ⁺	●	○	○	○
(EtOH)NH ₃ ⁺	○	○	○	○
Et ₂ NH ₂ ⁺	○	○	●	●
(EtOH)EtNH ₂ ⁺	○	○	○	○
(EtOH) ₂ NH ₂ ⁺	○	○	○	○
Et ₃ NH ⁺	○	○	○	●
(EtOH)Et ₂ NH ⁺	○	○	○	○
(EtOH) ₂ EtNH ⁺	○	○	○	○
(EtOH) ₃ NH ⁺	○	○	○	○

coupled with an Ag/AgCl reference electrode that was separated by a salt bridge with a double-junction from the sample. The cell for electromotive force (emf) measurement is represented as:

Results and Discussion

As the first screening, a series of 36 salts were surveyed as shown in Table 1, where 4 anion species were combined with primary, secondary and tertiary ammonium cations with the 2-hydroxyethyl and/or the ethyl groups. Among them, 32 samples may solely consist of ions with a melting point below 373 K, so that they can be classified into PILs. In addition, 17 PILs were stable liquids at an ambient temperature of 298 K. We noticed that TFS^- and TFSA^- anions gave PILs combined with all of the tertiary ammonium cations tested here, and $(\text{EtOH})_2\text{EtNH}^+$ cation yielded PILs coupled with all anions examined in this study. Thus, with regard to 6 PILs: $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$) and $[(\text{EtOH})_2\text{EtNH}^+][\text{X}^-]$ ($\text{X} = \text{TFSA}$ and NO_3), physicochemical properties were investigated such as melting point T_m , density ρ , ionic conductivity κ , and viscosity η . The results are listed in Table S1 (Supporting Information) accompanied by the previously reported values for analogous PILs consisting of the cations with the 2-hydroxyethyl group(s). Hence, the substitution effect of the 2-hydroxyethyl group and the anion effect can be discussed with $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$) and $[(\text{EtOH})_2\text{EtNH}^+][\text{X}^-]$ ($\text{X} = \text{TFS}$, TFSA and NO_3) PILs, respectively.

To discuss the ion-ion interaction, the Walden plots of $\log(\Lambda/S \text{ cm}^2 \text{ mol}^{-1})$ vs. $\log(\eta/\text{poise}^{-1})$ are useful.⁵⁶ According to Angell *et al.*^{8,57} and MacFarlane *et al.*,^{14,58,59} the slope of or the deviations from the ideal Walden line could be a measure of the ion-ion interaction in ionic liquids; they generally decreased when the contact ion pair formation occurs in ordinary electrolyte solutions. The Walden plots for PILs are shown in Fig. 2 accompanied by previously reported analogous PILs of $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{X}^-]$ ($n = 0 - 3$) for comparison. As shown with a dotted line in Fig. 2, the Walden plots for $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$) exhibited a good linear relationship with the least square slope of 0.97(5). Our finding of a linear relationship with a nearly unity slope among $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$) suggests that the ion-ion interactions in these ionic liquids are similar, though the substitutions of OH groups increase. As is well accepted for ordinary molecular solvents, water and alcohols have greater electron pair accepting

Fig. 2 The Walden plots of the examined PILs of cations with 2-hydroxyethyl groups. Solid and dotted lines show the ideal Walden line and the linear least square lines among $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$), respectively. The data for $[(\text{EtOH})_2\text{EtNH}^+][\text{NO}_3^-]$ is represented with open circles because of unclear ion concentrations. 1, $[\text{Et}_3\text{NH}^+][\text{TFS}^-]$; 2, $[(\text{EtOH})\text{Et}_2\text{NH}^+][\text{TFS}^-]$; 3, $[(\text{EtOH})_2\text{EtNH}^+][\text{TFS}^-]$; 4, $[(\text{EtOH})_3\text{NH}^+][\text{TFS}^-]$; 5, $[(\text{EtOH})_2\text{EtNH}^+][\text{TFSA}^-]$; 6, $[(\text{EtOH})_2\text{EtNH}^+][\text{NO}_3^-]$; 7, $[\text{Et}_3\text{NH}^+][\text{formate}]$ (Ref. 42); 8, $[\text{Et}_3\text{NH}^+][\text{formate}]$ (Ref. 44); 9, $[\text{Et}_3\text{NH}^+][\text{methylsulfonic acid}]$ (Ref. 44); 10, $[(\text{EtOH})_3\text{NH}^+][\text{acetate}]$ (Ref. 41); 11, $[\text{Et}_3\text{NH}^+][\text{di-}n\text{-butylphosphate}]$ (Ref. 44); 12, $[(\text{EtOH})_3\text{NH}^+][\text{lactic acid}]$ (Ref. 41).

property than the others owing to their OH groups, so that they are good solvents for the anions. It is supposed that the cations with the 2-hydroxyethyl group(s) have affinity with the anions owing to not only the Coulombic force but also a hydrogen bonding interaction, and their affinity should increase as the increase of the number of the 2-hydroxyethyl groups. Thus, the indication from the Walden plots seems to be inconsistent with the electron-pair accepting property, though it has been not quantitatively evaluated for the present PILs yet. In addition, quite strange behaviors in the Walden plots were recently reported for the lithium-glyme complex quasi-ionic liquids systems.⁶⁰ It is worth pointing out that it is necessary to revisit the Walden plot as a measure of the ion-ion interaction.

With regard to $[(\text{EtOH})_2\text{EtNH}^+][\text{X}^-]$ ($\text{X} = \text{TFS}, \text{TFSA}$ and NO_3) PILs, comparison of TFS^- and TFSA^- is interesting. The viscosity for $[(\text{EtOH})_2\text{EtNH}^+][\text{TFSA}^-]$ was noticeably larger than that for $[(\text{EtOH})_2\text{EtNH}^+][\text{TFS}^-]$. Nevertheless, ionic conductivity for $[(\text{EtOH})_2\text{EtNH}^+][\text{TFSA}^-]$ was almost the same as that for $[(\text{EtOH})_2\text{EtNH}^+][\text{TFS}^-]$, and thus molar ionic conductivity for $[(\text{EtOH})_2\text{EtNH}^+][\text{TFSA}^-]$ was greater. On the other hand, the TFSA^- -based aprotic ionic liquids coupled with 1-alkyl-3-methylimidazolium have lower melting point and viscosity and greater ionic conductivity than those in the corresponding TFS^- -based ones, probably due to weaker ion-ion interaction in the TFSA^- -based one because of wider delocalization of a negative charge around the $(\text{SO}_2)_2\text{N}$ moiety.⁶¹ Therefore, as for this new class of PILs, the TFSA^- -based ones have a larger molar ionic conductivity probably due to more efficiently weakened ion-ion interaction, though the viscosity increases.

To obtain further insight into the ion-ion interaction in this class of PILs, we investigated molar volumes. Molar volume V_m

Fig. 3 The 2-hydroxyethyl group(s) number dependence of V_m , V_{intra} and V_{inter} for $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$).

at 298 K except $[\text{Et}_3\text{NH}^+][\text{TFS}^-]$ (at 305 K) was given as $V_m = M_w/\rho$ with molecular weight M_w and density ρ at the same temperature. V_m can be divided into the intra- and the inter-molecular terms, *i.e.*, $V_m = V_{\text{intra}} + V_{\text{inter}}$, where V_{intra} and V_{inter} represent the intra- and the inter-molecular molar volume, respectively.⁶² Figure 3 shows a dependence of V_m , V_{intra} , and V_{inter} on the number of the 2-hydroxyethyl groups for $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$). As is clearly shown in this figure, V_m and V_{intra} increased, but V_{inter} decreased with increasing the number of the 2-hydroxyethyl groups, suggesting the increase in V_m can be evidently attributable to that in V_{intra} . Moreover, the fact of V_{inter} decrease as the number of the 2-hydroxyethyl group(s) increases suggests that the liquid structuredness of these ionic liquids is enhanced by introducing the 2-hydroxyethyl groups. As mentioned above, the OH group has strong electron-pair accepting property, so that the increase in the number of the 2-hydroxyethyl groups may strengthen the cation-anion interaction. In addition, we can point out another possibility of the cation-cation interaction in terms of mutual hydrogen bonding against the electrostatic repulsion. Such hydrogen bonding interactions between both the cation-anion and the cation-cation were found in $[(\text{EtOH})\text{NH}_3^+][\text{NO}_3^-]$ protic ionic liquid by means of a large angle neutron scattering experiments with an empirical potential structure refinement (EPSR) analysis.⁶³

V_m and V_{inter} were plotted against V_{intra} for $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$) and $[(\text{EtOH})_2\text{EtNH}^+][\text{X}^-]$ ($\text{X} = \text{TFS}, \text{TFSA}$ and NO_3) as shown in Fig. S1 (Supporting Information). Qualitatively, linear relationships were found for both V_m and V_{inter} against V_{intra} ; the least square slopes were 1.52(3) and 0.52(3) for V_m and V_{inter} , respectively. Similar linear relationships have been found among various APILs,⁶² where the least square slopes were 1.593 and 0.594, respectively. Evidently, the smaller slope of V_{inter} for the present PILs suggests that the additional hydrogen bonding interaction with the Coulombic one significantly operates among the ions in the present PILs.

Acid-base property

The auto-protolysis constant K_s can be defined as $K_s = [(\text{EtOH})_n\text{Et}_{(3-n)}\text{N}][\text{HTFS}]$ ($n = 0 - 3$) for the auto-protolysis reaction $(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+ + \text{TFS}^- \rightleftharpoons (\text{EtOH})_n\text{Et}_{(3-n)}\text{N} + \text{HTFS}$

Fig. 4 pK_s plots vs. pK_a for $(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+$ ($n = 0 - 3$).

in these ionic liquids. pK_s ($= -\log K_s$) values for $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$) were successfully obtained by direct potentiometry using a $\text{Pt}(\text{H}_2)$ electrode. The values are listed in Table S1 (Supporting Information) and are plotted against acid dissociation constants (pK_a) for $(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+$ ($n = 0 - 3$) in the respective aqueous solution as shown in Fig. 4. Clearly, the pK_s for $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$) linearly increased with increasing the pK_a . The linear relationship between pK_s and pK_a suggests that the acidity of the composing cation contributes to the auto-protolysis reaction in this class of PILs. Based on thermodynamic cycle, a Gibbs free energy change $\Delta_r G^\circ(\text{PIL})$ for the auto-protolysis reaction in PILs can be represented as:

$$\Delta_r G^\circ(\text{PIL}) = \Delta_r G^\circ(\text{HB}^+) - \Delta_r G^\circ(\text{HTFS}) + \{\Delta_r G^\circ(\text{B}) + \Delta_r G^\circ(\text{HTFS})\} - \{\Delta_r G^\circ(\text{HB}^+) + \Delta_r G^\circ(\text{TFS}^-)\}, \quad (1)$$

where $\Delta_r G^\circ(\text{HB}^+)$ and $\Delta_r G^\circ(\text{HTFS})$ stand for the respective acid dissociation reaction in an aqueous solution and $\Delta_r G^\circ(\text{X})$ ($\text{X} = \text{B}$, HTFS , HB^+ and TFS^-) denotes solvent transfer Gibbs free energy from water to the corresponding PIL for the respective species. If the solvent transfer (the third and the fourth) terms in Eq. (1) could be neglected, the linear least square slope and intercept in Fig. 4 gave unity and the acid dissociation constant for HTFS in the aqueous solution, respectively. However, the slope and the intercept were evaluated to be 1.26(6) and 1.7(6), respectively. The slope of 1.26 is significantly different from unity and the intercept of 1.7 may be too large (more positive) for that of HTFS (one of the strongest superacids), suggesting the solvent transfer free energy is never negligible.

Here, we discuss the slope of 1.26 that is significantly greater than unity. According to Eq. (1), $\Delta_r G^\circ(\text{HB}^+)$ should directly depend on the 2-hydroxyethyl groups number, while $\Delta_r G^\circ(\text{HTFS})$ is to be constant. In addition, the third and the fourth terms also depend on the 2-hydroxyethyl groups number. It should be noted that transfer of the neutral species (produces in the auto-protolysis) from water to the respective ionic liquid could be more positive in Gibbs free energy than the corresponding transfer of the ionic ones (reactants), and the third term solely contributes to $\Delta_r G^\circ(\text{PIL})$ negatively. The slope of 1.26 means the negative contribution from the third term to $\Delta_r G^\circ(\text{PIL})$ may be superior to positive one from the fourth. This suggests that the hydrogen bonding interactions become more important

Fig. 5 Potentiometric titration curves for $[(\text{EtOH})_2\text{EtNH}^+][\text{X}^-]$ ($\text{X} = \text{TFS}$, TFSA and NO_3). Open circles and solid lines represent experimental data and the titration curves calculated by using the refined pK_s values, respectively.

relative to the Coulombic ones in these PILs when the number of the 2-hydroxyethyl groups increase, which is consistent with the discussion based on molar volume.

We also attempted to determine pK_s for $[(\text{EtOH})_2\text{EtNH}^+][\text{X}^-]$ ($\text{X} = \text{TFS}$, TFSA , and NO_3). Typical potentiometric titration curves for these PILs are shown in Fig. 5. As shown in this figure, pK_s for $[(\text{EtOH})_2\text{EtNH}^+][\text{TFS}^-]$ and $[(\text{EtOH})_2\text{EtNH}^+][\text{TFSA}^-]$ were successfully evaluated to be 12.84(8) and 14.80(9), respectively, which implies that HTFSA behaves as a stronger acid than HTFS in the respective ionic liquids. As aforementioned, HTFS is one of the strongest superacids, and HTFSA may be also strong acid, though their pK_a value in the respective aqueous solution and/or Hammett acid function H_0 is unclear currently. On the other hand, gas phase acidity of HTFS and HTFSA have been reported to be 1253.1 kJ mol^{-1} and 1198.7 kJ mol^{-1} , respectively.⁶⁴ In the gas phase, the acidity of HTFSA is noticeably stronger than HTFS. Thus, the acidity order of HTFS and HTFSA in PILs composed of $[(\text{EtOH})_2\text{EtNH}^+]$ are consistent with that in the gas phase. It should be noted that a significant difference in acidity between HTFS and HTFSA in the gas phase is rather suppressed in the PILs. In fact, the pK_s value for $[\text{C}_1\text{hIm}^+][\text{TFS}^-]$ (C_1hIm^+ , *N*-methylimidazolium) of 8.93 is larger than that for $[\text{C}_1\text{hIm}^+][\text{TFSA}^-]$ of 8.58,⁶⁵ which is opposite to the case in the $[(\text{EtOH})_2\text{EtNH}^+]$ based ionic liquids.

With regard to $[(\text{EtOH})_2\text{EtNH}^+][\text{NO}_3^-]$, an emf jump at the equivalent point was small, so that the pK_s value for this PIL could not be estimated quantitatively. Similar quite small jumps in the emf were observed for $[\text{C}_1\text{hIm}^+][\text{CH}_3\text{COO}^-]$ and $[\text{C}_1\text{hIm}^+][\text{HCOO}^-]$, which can be consistent with large negative pK_s of about -1.4 for both systems roughly estimated with calorimetric titrations.⁶⁵ Large negative pK_s means neutral species in the right hand side of the auto-protolysis reaction predominantly exist in equilibrium. Such considerable amount of neutral species formation is evident in the other acetate-based protic ionic liquids.¹⁴ It should be noted that the gas phase acidity of protonated ethylammonium EtNH_3^+ is remarkably greater than that of nitric acid HNO_3 , though, as is well known, the former is a conjugate acid of a strong base ethylamine and the latter is a strong acid in the respective aqueous solution.^{64,66-70} As well as Eq. (1), if we select gas phase as the reference state, from the corresponding thermodynamic cycle, Gibbs free energy $\Delta_r G^\circ(\text{PILs})$ for the auto-protolysis reaction in PILs $\text{HB}^+ + \text{A}^-$

$\rightleftharpoons \text{B} + \text{HA}$, can be represented as:

$$\Delta_r G^\circ(\text{PIL}) = \Delta_r G^\circ(\text{HB}^+) - \Delta_r G^\circ(\text{HA}) + \{\Delta_s G^\circ(\text{B}) + \Delta_s G^\circ(\text{HA})\} - \{\Delta_s G^\circ(\text{HB}^+) + \Delta_s G^\circ(\text{A}^-)\}, \quad (2)$$

where $\Delta_r G^\circ(\text{HB}^+)$ and $\Delta_r G^\circ(\text{HA})$ denote gas phase acidity for the respective species (in Gibbs free energy) and $\Delta_s G^\circ(\text{X})$ (X: B, HA, HB^+ and A^-) stand for solvation Gibbs free energy. Generally, even if $\Delta_r G^\circ(\text{HB}^+) - \Delta_r G^\circ(\text{HA})$ are negative, $\Delta_r G^\circ(\text{PIL})$ is positive owing to much more negative $\Delta_s G^\circ(\text{HB}^+) + \Delta_s G^\circ(\text{A}^-)$ (ion “self-solvation” in ionic liquids) overcoming negative $\Delta_s G^\circ(\text{B}) + \Delta_s G^\circ(\text{HA})$ (neutral molecule solvation). Hence, with regard to $[(\text{EtOH})_2\text{EtNH}^+][\text{NO}_3^-]$, it is unlikely that ionic solvation free energy compensates or overcomes the sum of those for gas phase reaction $\Delta_r G^\circ(\text{HB}^+) - \Delta_r G^\circ(\text{HA})$ and neutral species solvation $\Delta_s G^\circ(\text{B}) + \Delta_s G^\circ(\text{HA})$. This is probably due to the hydrogen bonding interaction operating both in $(\text{EtOH})_2\text{EtN} \cdots \text{HNO}_3$ and in $(\text{EtOH})_2\text{EtNH}^+ \cdots \text{NO}_3^-$. *Ab initio* calculations support the significant hydrogen bonding interaction of $\text{EtNH}_2 \cdots \text{HNO}_3$ both in gas phase and in a dielectric solution with the PCM (polarizable continuum model).^{71,72}

Hence, the hydrogen bonding between cation-cation and cation-anion plays essential roles in macroscopic properties of the PILs composed of cations with the 2-hydroxyethyl group(s). Large angle neutron⁶³ and X-ray^{71,73} scattering experiments with the aid of molecular simulations may provide direct structural evidences at an atomistic level, and are now going on.

Conclusions

A series of new 2-hydroxyethylammonium based salts were prepared to find 32 protic ionic liquids. Among them, 6 PILs ($[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$) and $[(\text{EtOH})_2\text{EtNH}^+][\text{X}^-]$ (X = TFS, TFSA and NO_3)) were investigated in terms of the physicochemical properties such as thermal behavior, ionic conductivity, viscosity and density, and the acid-base property of pK_s , to clarify the effect of hydroxyl groups and the anionic nature on the ion-ion interaction and the acid-base property of these new class of PILs.

With regard to $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$), the Walden plots exhibited a good linear relationship. Nevertheless, V_{inter} of $[(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+][\text{TFS}^-]$ ($n = 0 - 3$) decreased with increasing the number of the 2-hydroxyethyl groups. Moreover, the pK_s became smaller as the increase of the 2-hydroxyethyl groups with a good linear relationship with the least square slope of 1.26 against pK_a for $(\text{EtOH})_n\text{Et}_{(3-n)}\text{NH}^+$ ($n = 0 - 3$) in the respective aqueous solution. These facts suggest that the hydrogen bonding interactions become more important relative to the Coulombic ones in these PILs when the number of the 2-hydroxyethyl groups increase.

The molar ionic conductivity for $[(\text{EtOH})_2\text{EtNH}^+][\text{TFSA}^-]$ was significantly larger than that for TFS-based PIL, though its viscosity was larger. In addition, the typical potentiometric titration curves for $[(\text{EtOH})_2\text{EtNH}^+][\text{TFSA}^-]$ and $[(\text{EtOH})_2\text{EtNH}^+][\text{TFS}^-]$ were successfully obtained. The pK_s value for $[(\text{EtOH})_2\text{EtNH}^+][\text{TFSA}^-]$ is larger than that for TFS-based PIL, suggesting that HTFSA behaves as a stronger acid than HTFS in the respective ILs. This acidity order is consistent with that in the gas phase. On the other hand, in $[(\text{EtOH})_2\text{EtNH}^+][\text{NO}_3^-]$, an emf jump was small, suggesting that the comparable hydrogen bonding interaction in strength may operate both in $(\text{EtOH})_2\text{EtN} \cdots \text{HNO}_3$ and in $(\text{EtOH})_2\text{EtNH}^+ \cdots \text{NO}_3^-$.

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Supporting Information

Additional data from details of experiments, physicochemical and acid-base properties of 2-hydroxyethylammonium based ILs, and the relationships between V_{intra} and V_{m} and V_{inter} are given as Supporting Information. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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