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# Thermodynamic Study of the Solvation States of Acid and Base in a Protic Ionic Liquid, Ethylammonium Nitrate, and Its Aqueous Mixtures

Ryo Kanzaki,*[1] Xuedan Song,[2] Yasuhiro Umebayashi,[2] and Shin-ichi Ishiguro[2]
[1]*Graduate School of Science and Engineering, Kagoshima University, Korimoto, Kagoshima 890-0065*
[2]*Department of Chemistry, Faculty of Sciences, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581*

(Received January 26, 2010; CL-100077; E-mail: kanzaki@sci.kagoshima-u.ac.jp)

Ethylammonium nitrate (EAN) is a typical protic ionic liquid (PIL) known for a long time. In order to investigate acid–base reaction mechanisms in PIL, thermodynamic quantities of a reaction, which corresponds to autoprotolysis in amphoteric solvents, has been determined in neat EAN. Unlike $H_3O^+$ and $OH^-$ in water, proton donor and acceptor species in EAN are both neutral; this makes acid–base reaction mechanisms in EAN distinct from that in water. EAN–water mixtures have also been studied.

Recently, protic ionic liquids (PILs) have received increasing attention as a new protic solvent.[1,2] As the composing ions of PILs have both a proton accepting and a donating ability PILs have characteristics of an amphoteric solvent. Not only as novel acid–base reaction media, PILs are expected to be candidates for fuel cell electrolytes due to excess electrochemically available protons.[2] In amphoteric solvents, autoprotolysis is a peculiar reaction, through which a proton is transferred between two solvent species to generate a conjugate acid and base of the solvent. If we consider that $A^-$ and $HB^+$, that are products of a proton transfer from Brønsted acid (HA) to base (B), are the solvent species in PILs, the following equilibrium is equivalent to autoprotolysis.

$$A^- + HB^+ \rightleftharpoons HA + B \qquad (1)$$

As HA and B practically act as the proton donor and acceptor for acid–base reaction in PILs, the acidity of HA and the basicity of B are the relevant properties of PIL as an acid–base reaction media. From this point of view, $\Delta pK_a$ is a plausible indicator to specify PILs defined as a gap of $pK_a$s, or of *proton-free energy level*, between HA and $HB^+$ in an aqueous solution.[3,4] However, acid–base reaction mechanisms in neat PILs cannot be simply extrapolated from those in an aqueous phase due to absolutely different solvent environment. In the present study, we have investigated the solvation state of HA and B by means of direct thermodynamic measurements in neat PIL, ethylammonium nitrate (EAN), which is a typical PIL known for a long time,[5,6] and EAN–aqueous mixtures. Although an anhydrous condition is preferable for electrochemical applications, EAN–water mixture is also useful as a promising reaction medium for biomolecules[7] and for understanding PILs as an extensively concentrated electrolyte solution.[8]

EAN was prepared from aqueous solutions of ethylamine and nitric acid. Details about the preparation procedure have been mentioned elsewhere.[9] The concentration of excess $HNO_3$ in the final product was separately determined by potentiometric titration. Doubly distilled water was used to prepare EAN–water mixture. Trifluoromethanesulfonic acid (HTfO) and propylamine ($C_3H_7NH_2$) were used after distillation. These compounds are completely ionized in EAN to generate equimolar $HNO_3$ and $C_2H_5NH_2$, respectively. Calorimetric neutralization measurements were carried out at 298 K by means of an online-controlled titration and data acquisition system developed in our laboratory. A basic solution (30 $cm^3$) containing ca. 10 mmol $dm^{-3}$ $C_3H_7NH_2$ was titrated with aliquots of ca. 100 mmol $dm^{-3}$ acidic HTfO solution. The heats of reaction at each titration point were determined with errors less than 0.02 J.

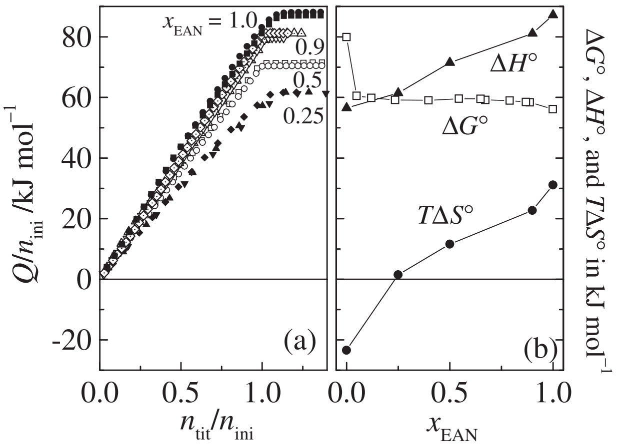

**Figure 1.** Calorimetric titration curves of neutralization in EAN and EAN–water mixture (a), and obtained $\Delta G°$, $\Delta H°$, and $T\Delta S°$ of autoprotolysis plotted against $x_{EAN}$ (b).

Calorimetric titration curves in neat EAN and EAN–water mixtures of $x_{EAN}$ (the molar fraction of EAN) = 0.25, 0.5, and 0.9 are shown in Figure 1a. In this figure, $Q/n_{ini}$ are plotted against $n_{tit}/n_{ini}$ where $Q$ is the total heat evolution to each titration point, and $n_{ini}$ and $n_{tit}$ are the moles of $C_3H_7NH_2$ in the initial solution and of the total HTfO added, respectively. As shown, $Q$ increases linearly with increasing $n_{tit}$ and then becomes constant at the equivalent point ($n_{tit}/n_{ini} = 1$). If eq 1 is taken into account, the following reaction corresponds to autoprotolysis in EAN:

$$C_2H_5NH_3{}^+ + NO_3{}^- \rightarrow C_2H_5NH_2 + HNO_3 \qquad (2)$$

The reaction enthalpy of eq 2 is given by $\Delta H_2° = \partial(Q/n_{ini})/\partial(n_{tit}/n_{ini})$ because reaction (2) is the backward reaction of a neutralization in EAN. The obtained $\Delta H_2°$ is 82.7 kJ $mol^{-1}$ (standard deviation is 0.6 kJ $mol^{-1}$), a little larger than that estimated in terms of van't Hoff plot.[10] We have already demonstrated that the product of the concentrations, $[HNO_3][C_2H_5NH_2]$, gives a constant $K_S$, similarly to the autoprotolysis constant of amphoteric solvents.[9] Thus the reaction free energy and entropy of eq 2 are obtained by $\Delta G_2° = -RT \ln K_S$ and $\Delta S_2° = (\Delta H_2° - \Delta G_2°)/T$, respectively.

**Table 1.** Reaction thermodynamic quantities at 298.15 K[a]

| $\Delta G°$/kJ mol$^{-1}$ | $\Delta H°$/kJ mol$^{-1}$ | $T\Delta S°$/kJ mol$^{-1}$ |
|---|---|---|
| $C_2H_5NH_3^+ + NO_3^- \rightarrow C_2H_5NH_2 + HNO_3$ in EAN | | |
| 54.9(3) | 83(2) | 28(2) |
| $2H_2O \rightarrow H_3O^+ + OH^-$ in water[11] | | |
| 79.9 | 55.9 | –24.1 |
| $C_2H_5NH_3^+ + NO_3^- \rightarrow C_2H_5NH_2 + HNO_3$ in water[11] | | |
| 64 | 67 | 3 |

[a] The values in parentheses refer to three standard deviations.

Here, it should be pointed out that $K_S$ generally denotes autoprotolysis constant in an amphoteric solvent, although reaction (2) does not exactly belong to *protolysis*.

Reaction thermodynamic quantities of several related reactions are summarized in Table 1. The large and positive $\Delta G_2°$ and $\Delta H_2°$ indicate the similarity of reaction (2) to autoprotolysis in water. That is, $C_2H_5NH_2$ and $HNO_3$ are minor species in EAN under neutral conditions, as well as $H_3O^+$ and $OH^-$ in pH 7 water, and this is mainly contributed by a large and positive reaction enthalpy. In contrast, $\Delta S_2°$ is large and positive while that of autoprotolysis in water is large and negative. Through reaction (2) in EAN, $C_2H_5NH_3^+$ and $NO_3^-$ are converted to $C_2H_5NH_2$ and $HNO_3$. In other words, ions are uncharged in an ionic atmosphere. As a result, the solvation is weakened and positive $\Delta S_2°$ is given. On the other hand, ions are generated by autoprotolysis in water. Ions are tightly hydrated in aqueous phase not only by the neighboring water molecules but also those in the further hydration shell. Consequently, the reaction entropy of autoprotolysis has an opposite sign between in EAN and in water. The effect of entropic term ($T\Delta S°$) on $\Delta G°$ is raised to larger than 50 kJ mol$^{-1}$ at 298 K. Note that both $\Delta H_2°$ and $T\Delta S_2°$ are significantly larger than those for the equivalent reaction in aqueous phase. Hence, it is emphasized that the acid–base properties of PILs cannot be predicted by extrapolating those for the constituent ions in aqueous phase without taking the solvation structure into account.

As mentioned in the previous paper,[9a] $H_3O^+$ acts practically as a proton donor in an EAN–water mixture. Thus, the following reaction corresponds to autoprotolysis instead of eq 2 in EAN.

$$C_2H_5NH_3^+ + H_2O \rightarrow C_2H_5NH_2 + H_3O^+ \qquad (3)$$

Figure 1b shows $\Delta G°$, $\Delta H°$, and $T\Delta S°$ of autoprotolysis of $x_{EAN}$. Note that the actual formula ascribing autoprotolysis changes depending on $x_{EAN}$. Interestingly, p$K_S$ for eq 3 (or $\Delta G_3°$) in the $x_{EAN} = 0.9$ mixture is larger than that for eq 2 in neat EAN; this means $H_3O^+$ has an apparently stronger acidity than $HNO_3$. As $HNO_3$ is a stronger acid than $H_3O^+$ in an aqueous phase, the acidity order is reversed. This can be explained by a solvation effect on the proton donor species, $H_3O^+$ and $HNO_3$. That is, positive $\Delta H_3°$ and $\Delta S_3°$ at $x_{EAN} = 0.9$ indicate the solvation structure is broken through reaction (3). However, smaller $\Delta H_3°$ and $\Delta S_3°$ than $\Delta H_2°$ and $\Delta S_2°$ indicate that the solvation of $H_2O$ is less extensively weakened when converted to $H_3O^+$ than $NO_3^-$ converted to $HNO_3$ because $H_3O^+$ is still solvated by negatively charged solvents, $NO_3^-$. $\Delta H°$ and $T\Delta S°$ are almost canceled out, but a slightly larger decrease of $T\Delta S°$ than $\Delta H°$ with decreasing $x_{EAN}$ from 1.0 to 0.9 consequently results in an apparently larger $\Delta G°$ or p$K_S$ in $x_{EAN} = 0.9$ mixture than that in neat EAN.

Both $\Delta H_3°$ and $\Delta S_3°$ decrease almost linearly with decreasing $x_{EAN}$ in parallel among the midterm EAN content. As a result, p$K_S$ is kept almost constant through a wide $x_{EAN}$ range, unlike the EAN-rich region. In addition, reaction (3) continuously stands corresponding to autoprotolysis. These facts make EAN–water mixture a good solvent for acid–base reactions with stable acid–base properties in a wide EAN–water composition. Considering that EAN is known as a hydrogen-bonding solvent showing water-like properties and is miscible with water in a regular fashion,[12] EAN and water are possibly merged by mutually exchanging hydrogen-bonding pairs without drastic change in the solvent structure. The linear changes of $\Delta H_3°$ and $\Delta S_3°$ imply the successive transition of the fraction of the solvating species on $C_2H_5NH_3^+$, $H_2O$, and $H_3O^+$ depending on $x_{EAN}$. However, we have no direct evidence. The solvent–solvent interaction and the solvation manner in EAN–water mixture should be clarified by further investigations.

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