Acid–Base Property of Ethylammonium Nitrate Ionic Liquid Directly Obtained Using Ion-selective Field Effect Transistor Electrode

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Ethylammonium nitrate (EAN) is a protic room-temperature ionic liquid and classified into an amphoteric solvent. The equilibrium constant $K_S = [EtNH_2][HNO_3]$ has directly been obtained for the first time by using an ion-selective field effect transistor (ISFET) electrode. The obtained K_S value is of $10^{-10.0}\,mol^2\,dm^{-6}$, indicating that the neutral EAN involves HNO_3 and $EtNH_2$ molecules as much as $1.0 \times 10^{-5}\,mol\,dm^{-3}$, or the pH ($= -\log[HNO_3]$) is 5 at 298 K.

Protic room-temperature ionic liquids (RTILs), simply obtained by acid–base reactions of amines or imidazolium derivatives with strong acids,[1] have recently received increasing attention as new proton conductors. The Grotthuss model established as the proton-transfer mechanism in water has also been proposed in RTILs.[2] These RTILs, prepared by mixing equimolar amounts of acid (HS_A) and base (S_B) according to the reaction, $HS_A + S_B \rightarrow S_A^- + HS_B^+$, are classified into the amphoteric solvent in view of the Brønsted acid–base concept, which may be expanded to amphoteric ionic liquids.[3] The equilibrium constant K_S, corresponding to autoprotolysis constant in amphoteric molecular solvent, as:

$$K_S = [HS_A][B], \qquad (1)$$

is thus essential for evaluation of the strength of various acids and bases in amphoteric ionic liquids as the solvent. However, directly obtained K_S values of amphoteric RTILs, as well as the acid dissociation constants in amphoteric RTILs, have not been reported yet. Yoshizawa et al.[4] have estimated the K_S value of ionic liquids of HS_B^+ and S_A^- as $\Delta pK_a = pK_a(HS_B^+) - pK_a(HS_A)$, the difference between acid dissociation constants of the respective acid and base in aqueous solution and found that the boiling point increases with increasing ΔpK_a for some protic ionic liquids. MacFarlane et al.[5] have also reported that the degree of protonation of varying anions of ionic liquids involving the *N*-methylpyrrolidinium cation well correlates to the ΔpK_a value. The ΔpK_a value corresponds to the equilibrium constant for the reaction, $S_BH^+ + S_A^- = S_B + S_AH$, in an aqueous solution, and thus the ΔpK_a value might be used as an alternative of the pK_S value of neat ionic liquids. However, the ΔpK_a values provide only a qualitative measure of the acid–base property, because, evidently, all species are hydrated in aqueous solution, and thus the ΔpK_a value must be corrected for the Gibbs energies of transfer of the related species from water to an ionic liquid to evaluate the actual pK_S value of the ionic liquid. It is not easy to evaluate the Gibbs energies of transfer, however. The direct determination of pK_S is thus indispensable for further quantitative analyses of acid–base reactions, metal-ion complexation reactions, etc. in ionic liquids.

Here, we demonstrate for the first time the direct measurements of pH and the determination of the K_S of ethylammonium nitrate (EAN), a typical amphoteric RTIL consisted of $EtNH_3^+$ and NO_3^- ions, as an example. EAN has been known as an ionic liquid at room temperature since 1914.[6] However, it has not been attracted attention for a long time, and thus detailed insights into its thermodynamic properties as a solvents[7] and intermolecular interactions[8,9] were elucidated only recently. With regard to EAN, although NO_3^- is very weak base, we expect an equilibrium according to eq 2 as:

$$EtNH_3^+ + NO_3^- \rightleftharpoons EtNH_2 + HNO_3. \qquad (2)$$

Thus, molecular HNO_3 is the strongest acid, $EtNH_2$ is the strongest base in the solution, and the pH is given by $-\log[HNO_3]$.

EAN has been prepared from aqueous ethylamine (70%) and nitric acid (69%) (Kishida Chemical, Japan) by mixing equimolar amounts of $EtNH_2$ and HNO_3 in an ice bath. The pH was adjusted to 5–6, and the solution was concentrated in vacuo at room temperature. Pale-yellow liquid EAN thus prepared was treated with activated charcoal and dried over molecular sieve 3A. The EAN finally obtained contains a small amount of excess ethylamine. Water content in EAN was checked by Karl Fisher coulometry to be less than 80 ppm, and the density was close to the reported value ($1.212\,g\,cm^{-3}$) in the literature.[9] Bis(trifluoromethanesulfonyl)imide (HTf_2N) crystals were kept in a glove box and used without further purification. Ethylamine was purified and dried by distillation. Using EAN as the solvent, an acid HTf_2N solution ($10\,mmol\,dm^{-3}$) and a base $EtNH_2$ solution (ca. $200\,mmol\,dm^{-3}$) were prepared in a glove box. The

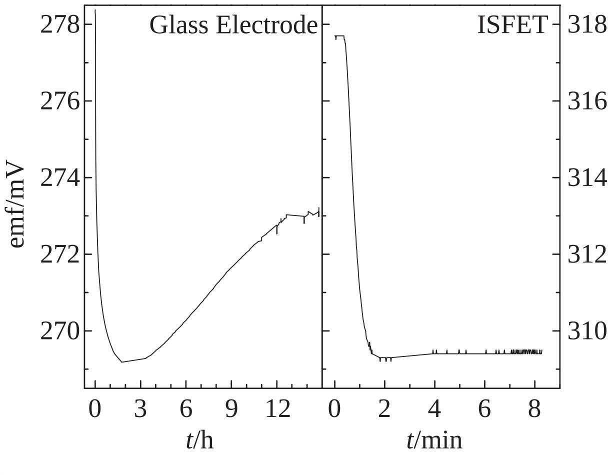

Figure 1. Time response at the emf measurement. Note that the time scale is t/h with the glass electrode and t/min with the ISFET one.

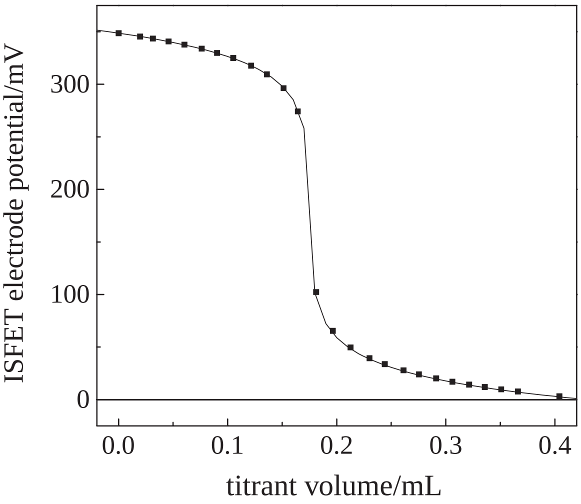

Figure 2. Potentiometric titration curve obtained by titrating an HTf_2N solution with an $EtNH_2$ solution in EAN at 298 K. The solid line shows the theoretical curve calculated using constants finally obtained.

HTf_2N solution (5 cm^3) was titrated with the $EtNH_2$ solution in a thermostated cell at 298 K. Emf measurements were carried out using a glass electrode (ORION 81-02) and an ion-selective field effect transistor (ISFET) electrode[10,11] (HORIBA 0030-10D). Izutsu et al.[10] have reported that the ISFET electrode shows an excellent Nernstian response to the pH in nonaqueous solvents. We applied the ISFET electrode for the determination of pH in EAN. As seen in Figure 1, the ISFET electrode shows a quick response, and the emf becomes constant within 0.1 mV in 5 min, whereas the glass electrode response was too slow to reach a plateau even after 12 h. Consequently, the glass electrode cannot practically be used, and we used the ISFET electrode for emf measurements in the present work.

As HTf_2N is a stronger acid than HNO_3, HTf_2N may be completely converted or leveled to HNO_3 in EAN according to the reaction, $HTf_2N + NO_3^- \rightarrow Tf_2N^- + HNO_3$. The addition of an aliquot of titrant $EtNH_2$ to the acid solution thus leads to the acid–base reaction, $HNO_3 + EtNH_2 \rightarrow NO_3^- + EtNH_3^+$, to yield solvent cations and anions of EAN. The typical titration curve is shown in Figure 2. As seen, the emf varies little in the acidic and basic regions, and a large jump is seen at a neutral point ($[HNO_3] = [EtNH_2]$), indicating that the ISFET electrode responses in the wide range of concentration of HNO_3 in EAN.

Emfs thus obtained were analyzed according to the Gran's method[12] on the basis of the Nernstian equation, $E = E^\circ + \alpha \log a_H$, where E° and α are constants and a_H denotes the activity of proton (here, HNO_3). It is found that the ISFET electrode satisfactorily obeys an ideal Nernstian response of $\alpha = 0.059$ mV/pH, and thus the titration curve is practically not affected by impurities. The pK_S value of 10.004 ($3\sigma = 0.009$) thus obtained is appreciably smaller than the $\Delta pK_a =$ ca. 12 for EAN calculated from the pK_a values of $EtNH_2$ and HNO_3 in aqueous solution reported in the literature. In order to verify the validity of the ISFET electrode, the K_S value was also determined using the hydrogen electrode. The pK_S value thus obtained is 9.83, indicating that the ISFET electrode can be satisfactorily applied to the emf measurements in ionic liquids.

The pK_S value of 10.004 does mean that neat EAN involves neutral $EtNH_2$ and HNO_3 molecules as much as 1.0×10^{-5} mol dm^{-3} at 298 K, and the pH ($= -\log[HNO_3]$) in an EAN solution varies in the range 0–10. As HNO_3 is a strong acid in water, EAN may be classified into an acidic solvent in view of the acid–base property of solvent.

In conclusion, we here demonstrate for the first time that the pK_S of an ionic liquid EAN can be directly determined using an ISFET electrode. The value is appreciably different from that estimated from the ΔpK_a calculated using pK_a of values of $EtNH_2$ and HNO_3 in aqueous solution. Acid dissociation constants of various acids and bases and stability constants of metal–ligand complexes in EAN can then be easily obtained by potentiometry using an ISFET electrode. We further expect that potentiometry using the ISFET electrode can be extended also for various ionic liquids other than EAN.

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