Protic Ionic Liquids

Deutsche Ausgabe: DOI: 10.1002/ange.201511328
Internationale Ausgabe: DOI: 10.1002/anie.201511328

A pH Scale for the Protic Ionic Liquid Ethylammonium Nitrate

Ryo Kanzaki, Hitoshi Kodamatani, Takashi Tomiyasu, Hikari Watanabe, and Yasuhiro Umebayashi**

Abstract: *To quantify the properties of protic ionic liquids (PILs) as acid–base reaction media, potentiometric titrations were carried out in a neat PIL, ethylammonium nitrate (EAN). A linear relationship was found between the 14 pK_a values of 12 compounds in EAN and in water. In other words, the pK_a value in EAN was found to be roughly one unit greater than that in water regardless of the charge and hydrophobicity of the compounds. It is possible that this could be explained by the stronger acidity of HNO_3 in EAN than that of H_3O^+ in water and not by the difference in the solvation state of the ions. The pH value in EAN ranges from −1 to 9 on the pH scale based on the pH value in water.*

Protic ionic liquids (PILs) function as H^+ carriers and/or reservoirs for dissociable hydrogen ions (H^+) and have several industrial applications, for example in fuel cell electrolytes. In some PILs, protons are considered to be transferred through a proton-hopping mechanism.[1] For organic syntheses, PILs exhibit the desirable properties of ionic liquids, such as a negligible volatility and thermal and chemical stability. In addition, PILs themselves can act as the catalyst in acid-catalyzed reactions, where the Brønsted/Lewis acidity of the PILs determines the reaction pathway and the catalytic activity.[2] However, few reported studies have addressed the acid–base properties of PILs.

Acid–base reactions are of general interest across the field of chemistry because the reactant is reversibly charged or can be neutralized by H^+ association or dissociation, drastically changing its reactivity or behavior. Thus the acid–base properties of PILs have attracted attention as a key characteristic of the compounds.[3] Although there are certain studies evaluating experimentally the acid–base equilibria in ionic liquids,[4] it remains difficult to compare directly the pH value in a PIL with that in water. This is mainly due to the wide pH range, from acidic to basic, caused by autoprotolysis, a unique equilibrium in amphoteric solvents such as PILs. To determine the pH value particularly in H^+-deficient solutions, the autoprotolysis constant have been already determined in some PILs.[5–8]

[*] Prof. R. Kanzaki, Prof. H. Kodamatani, Prof. T. Tomiyasu
Graduate School of Science and Engineering
Kagoshima University
1-21-35, Korimoto, Kagoshima, 890-0065 (Japan)
E-mail: kanzaki@sci.kagoshima-u.ac.jp
H. Watanabe, Prof. Y. Umebayashi
Graduate School of Science and Technology
Niigata University
8050, Ikarashi 2-no-cho, Nishi-ku, Niigata, 950-2181 (Japan)
E-mail: yumescc@chem.sc.niigata-u.ac.jp

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201511328.

The purpose of this study is to establish a pH scale that is universally applicable to protic solvents, both molecular and ionic. To do this, we determined 14 acid dissociation constants of 12 compounds in the neat PIL ethylammonium nitrate (EAN) by means of potentiometric titrations with a hydrogen electrode. EAN was described first in 1914[9] and is considered a typical PIL whose physicochemical properties are the most widely understood. Many thorough investigations, from the macroscopic[10] to the molecular level,[11] indicated that EAN provides water-like solvation conditions. As an acid–base medium, its autoprotolysis constant was experimentally determined by us[6,7] and by Letellier et al.[5] In the present study, we investigate the pH scale in EAN with respect to the unified pH scale based on water. This enables us to compare the pH values, or the H^+ activity, directly between EAN and water.

Figure 1 shows the potentiometric titration curve of acetic acid (AcOH) titrated with propylamine in EAN as the solvent. The dotted line is the calculated curve for the titration of acetic acid with NaOH in water evaluated by using the value of $pK_a = 4.76$. Clearly, the experimental titration curve is systematically shifted towards higher pH values. In addition, a less sharp jump in the pH value was detected at the neutralization point than that in water. These facts indicate that acetic acid behaves as a weak acid. A least-squares analysis was done to obtain the pK_a value ($K_a = [AcO^-][H^+]/[AcOH]$) of 5.45 ($3\sigma = 0.03$, Hamilton R factor = 0.5 %),

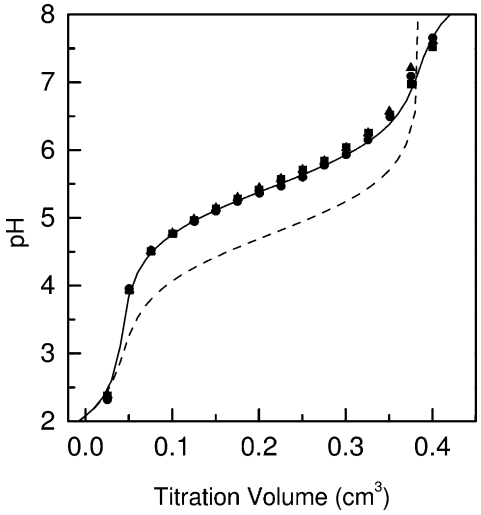

Figure 1. Typical potentiometric titration curve in EAN as the solvent, in which acetic acid is titrated with propylamine as the base. Titrations were carried out three times. The solid line is the calculated titration curve obtained using the pK_a^{EAN} value determined in this work. The dashed line is the theoretical titration curve of the same acid when the solvent is water titrating with NaOH.

 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

which is 0.69 logarithmic units greater than that in water. The solid line is the calculated curve based on the finally obtained pK_a value. As all experimental points were sufficiently reproducible, the acid dissociation equilibrium of acetic acid in EAN can be clearly described by a single equilibrium constant. Even though physicochemically predictable, this is experimentally confirmed by tracing the acid–base equilibria through the potentiometric titration.

Next, 14 pK_a values of the 12 compounds were obtained and listed in Table S1 in the Supporting Information. In all cases, the titration curves can be satisfactorily explained by one (or two) acid dissociation constants. In Figure 2, the

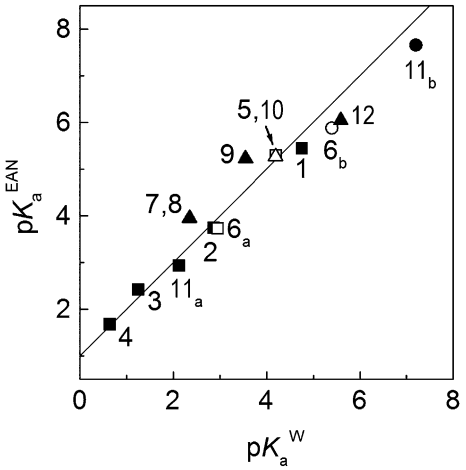

Figure 2. Relationship between acid dissociation constants in EAN (pK_a^{EAN}) and in water (pK_a^{W}). **1** = acetic acid; **2** = chloroacetic acid; **3** = dichloroacetic acid; **4** = trichloroacetic acid; **5** = benzoic acid; $\mathbf{6_a}$ and $\mathbf{6_b}$ = phthalic acid; **7** = glycin; **8** = α-alanine; **9** = β-alanine; **10** = adenine; $\mathbf{11_a}$ and $\mathbf{11_b}$ = phosphoric acid; **12** = trifluoroethylamine. See the text for the grouping of the symbols. The line indicates where $pK_a^{EAN} = pK_a^{W} + 1$.

pK_a^{EAN} value (pK_a in EAN) is plotted against pK_a^{W} (pK_a in water), where pK_a is classified into three groups. Group 1 (indicated by squares in Figure 2) reflects the dissociation of a neutral compound ($HA \rightarrow H^+ + A^-$; $HA = CH_3COOH$, $CH_2ClCOOH$, $CHCl_2COOH$, CCl_3COOH, phthalic acid, benzoic acid, and H_3PO_4). The empty symbols correspond to compounds having an aromatic ring, presumably hydrophobic. Group 2 (denoted by circles) reflects the dissociation of a monoanion ($HA^- \rightarrow H^+ + A^{2-}$; HA^- = hydrogen phthalate and $H_2PO_4^-$). Group 3 (triangles) indicate the dissociation of a cation, which includes the conjugate acid of the zwitterion ($HB^+ \rightarrow H^+ + B$ or $B^{\pm}$; B = adenine, $CF_3CH_2NH_2$; $B^{\pm}$ = glycin, α-alanine, β-alanine, respectively). When the charge on the compounds decreases by acid dissociation, the compounds of group 1 are ionized, those of group 2 become more negatively charged, and those of group 3 lose their positive charge. If the cation and anion are preferentially solvated by different species in an EAN, unlike in water, the pK_a value would be expected to show a significant change depending on the group, because the charge on the species differs from each other. In contrast, Figure 2 shows that all experimental pK_a^{EAN} versus pK_a^{W} points roughly fall on one straight line, without a systematic deviation among the groups. This suggests that the pK_a increase in EAN is mainly due to the stronger acidity of EAN compared to that of water, while the effect of solvation is negligible. For further discussion, please refer to the Supporting Information.

The line in Figure 2 indicates where $pK_a^{EAN} = pK_a^{W} + 1$. Therefore, the pK_a value in EAN is likely to be greater by one unit. A few exceptions should be pointed out, that is, the pK_a values of zwitterions are shifted slightly to higher values, and the larger pK_a values tend to shift to lower values. As a result, EAN is one pH unit more acidic than water (corresponding to ten times greater activity). This could be explained by the fact that HNO_3 is the probable form of the solvated H^+ in EAN, which behaves as a strong acid in water.

With regard to base dissociation constants (pK_b), the value is given through $pK_a + pK_b = pK_{AP}$, where K_{AP} is the autoprotolysis constant ($pK_{AP} = -\log K_{AP}$). If we assume that $pK_{AP} = 14$ in water and $pK_{AP} = 10$ in EAN (9.83 in fact)[6] for simplicity, the fact that the pK_a^{EAN} value is always one unit greater than pK_a^{W} suggests that the pK_b^{EAN} value is five units smaller than the pK_b^{W} value. This means that the basicity of EAN is 5 pH units weaker, or the activity of $C_2H_5NH_2$ (the probable active base in EAN) is weakened to 1/100 000 of that of OH^- in water. As $C_2H_5NH_2$ acts as a H^+ acceptor in a base dissociation reaction in EAN, this is acceptable because $C_2H_5NH_2$ is a weak base ($pK_a = 10.63$) in water. In conclusion, EAN is a solvent with stronger acidity and weaker basicity than water.

A common pH axis is convenient means to consider the ionization behavior of a certain acid (or base) in EAN.[12] Figure 3 shows the pH windows of EAN and water lying on

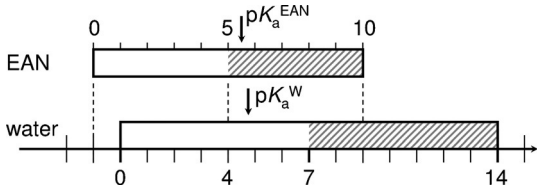

Figure 3. The pH value windows of EAN (upper) and water (lower) on the water-based pH scale. The blank and shadowed areas represent the acidic and basic regions, respectively. The arrows indicate the pK_a values in each solvent.

the water-based pH scale. The blank and shadowed areas represent acidic and basic regions, respectively. The scale on the EAN window is the pH value that is available only in EAN; in other words, the pK_a^{EAN} values are unique in EAN. The arrows indicate that $pK_a^{W} = 4.76$ for acetic acid in water and $pK_a^{EAN} = 5.45$ in EAN. The shift in the pK_a value could be explained by the arrangement of the EAN pH window on the water-based pH scale (see also a gas-based "unified pH scale"[13]). It is worth noting that the pK_a^{EAN} value is within the basic region, which indicates acetic acid acts as a slightly weak acid in EAN, like phenol in water, for example. Considered from another standpoint, the pH window characterizes the acid–base nature of the solvent. Under neutral conditions, the pH value of EAN is $pK_{AP}/2 = 5$, at the midpoint of the window. This point, however, corresponds

 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

to pH = 4 on the water-based pH scale, which is mildly acidic. Therefore, EAN can be classified as an acidic solvent, whose acidity is 3 pH units higher than that of water.

This study demonstrates that the potentiometrically determined pK_a value in a PIL is linearly related to that in water over a wide pH range. Accordingly, we align the pH window of EAN with the water-based pH scale. The pH window may help refine the conditions for using a PIL for acid-catalyzed reactions and estimate the active species under a given set of conditions. The respective edge values of the window are shown to be governed by the acidity of HNO_3 and the basicity of the $C_2H_5NH_2$ unit of EAN. Therefore, the acid–base properties of PILs can be tuned by choosing appropriate constituent ions. Although the stronger acidity of EAN compared to that of water could be attributable to the stronger H^+ activity in EAN than that in H_3O^+, the true solvation state and the structure of H^+ in EAN should be assessed at the molecular level, a discussion which is still ongoing even in water.[14]

Experimental Section

EAN was prepared from aqueous ethylamine and nitric acid.[15] The water content determined by a Karl Fisher method was 80–200 ppm. This amount of water hardly affects acid–base equilibria in an EAN–water mixture, even if it seems non-negligible in a concentration unit (a few tens $mmol\,dm^{-3}$).[7,15] Other chemicals of analytical grade (> 99%) were used without further purification. Potentiometric titrations were carried out with the electromotive force (emf) measurements by using the electrochemical cell represented as:

$$Ag/AgCl\,|\,0.1\,\text{M}\,NaCl\,(aq)\;\|\;EAN\;\|\;\text{sample EAN solution}\,|\,Pt\,(H_2)$$

where the double bars correspond to a liquid junction with a 4 G glass filter. The cell gave a satisfactorily stable emf within 5–10 min. The emf E shows the Nernstian response as:

$$E = E_0 + RT/F\ln([H^+]\,mol^{-1}\,dm^{-3})$$

where E_0 is the practical standard potential of the cell. Throughout this Communication, $pH = -\log([H^+]\,mol^{-1}\,dm^{-3})$ is used. E_0 was determined by a separate titration in advance. The value is −234 mV with a daily fluctuation of a few millivolts. At the same time, the autoprotolysis constant $K_{AP} = [HNO_3][C_2H_5NH_2]$ was also determined, which was confirmed to have a negligible fluctuation. Detailed experimental and calibration procedures are available in the Supporting Information.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number 26410157.

Keywords: acid–base catalysis · acidity · ionic liquids · pH scale · potentiometric titrations

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 6266–6269
Angew. Chem. **2016**, *128*, 6374–6377

[1] a) A. Noda, M. A. B. H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu, M. Watanabe, *J. Phys. Chem. B* **2003**, *107*, 4024–4033; b) H. Nakamoto, A. Noda, K. Hayamizu, S. Hayashi, H. Hamaguchi, M. Watanabe, *J. Phys. Chem. C* **2007**, *111*, 1541–1548; c) M. S. Miran, T. Yasuda, M. A. B. H. Susan, K. Dokko, M. Watanabe, *J. Phys. Chem. C* **2014**, *118*, 27631–27639.

[2] a) K. E. Johnson, R. M. Pagni, J. Bartmess, *Monatsh. Chem.* **2007**, *138*, 1077–1101; b) T. L. Greaves, C. J. Drummond, *Chem. Rev.* **2008**, *108*, 206–237; c) A. R. Hajipour, F. Rafiee, *Org. Prep. Proced. Int.* **2010**, *42*, 285–362; d) R. Skoda-Földes, *Molecules* **2014**, *19*, 8840–8884.

[3] a) D. R. MacFarlane, J. M. Pringle, K. M. Johansson, S. A. Forsyth, M. Forsyth, *Chem. Commun.* **2006**, 1905–1917; b) L. M. Mihichuk, G. W. Driver, K. E. Johnson, *ChemPhysChem* **2011**, *12*, 1622–1632; c) J.-P. Belieres, C. A. Angell, *J. Phys. Chem. B* **2007**, *111*, 4926–4937; d) J. Stoimenovski, E. I. Izgorodina, D. R. MacFarlane, *Phys. Chem. Chem. Phys.* **2010**, *12*, 10341–10347; e) C. A. Angell, N. Byrne, J-.P. Belieres, *Acc. Chem. Res.* **2007**, *40*, 1228–1236; f) M. Yoshizawa, W. Xu, C. A. Angell, *J. Am. Chem. Soc.* **2003**, *125*, 15411–15419; g) D. R. MacFarlane, R. Vijayaraghavan, H. N. Ha, A. Izgorodina, K. D. Weaver, G. D. Elliott, *Chem. Commun.* **2010**, *46*, 7703–7705; h) C. A. Angell, Y. Ansari, Z. Zhao, *Faraday Discuss.* **2012**, *154*, 9–27.

[4] a) J. A. Bautista-Martinez, L. Tang, J.-P. Belieres, R. Zeller, C. A. Angell, C. Friesen, *J. Phys. Chem. C* **2009**, *113*, 12586–12593; b) R. Barhdadi, M. Troupel, C. Comminges, M. Laurent, A. Doherty, *J. Phys. Chem. B* **2012**, *116*, 277–282; c) K. Fujii, K. Hashimoto, T. Sakai, Y. Umebayashi, M. Shibayama, *Chem. Lett.* **2013**, *42*, 1250–1251; d) H. Deng, X. Li, Y. Chu, J. Q. He, J. P. Cheng, *J. Org. Chem.* **2012**, *77*, 7291–7298; e) C. Mao, Z. Wang, P. J. Ji, J. P. Cheng, *J. Org. Chem.* **2015**, *80*, 8384–8389; f) Z. Wang, H. Deng, X. Li, P. J. Ji, J. P. Cheng, *J. Org. Chem.* **2013**, *78*, 12487–12493; g) F. D′Anna, S. La Marca, R. Noto, *J. Org. Chem.* **2009**, *74*, 1952–1956; h) C. Thomazeau, H. Olivier-Bourbigou, L. Magna, S. Luts, B. Gilbert, *J. Am. Chem. Soc.* **2003**, *125*, 5264–5265; i) T. Robert, L. Magna, H. Olivier-Bourbigou, B. Gilbert, *J. Electrochem. Soc.* **2009**, *156*, F115–F121.

[5] N. Benlhima, D. Lemordant, P. Letellier, *J. Chim. Phys.* **1989**, *86*, 1919–1939.

[6] R. Kanzaki, K. Uchida, S. Hara, Y. Umebayashi, S. Ishiguro, S. Nomura, *Chem. Lett.* **2007**, *36*, 684–685.

[7] R. Kanzaki, X. Song, Y. Umebayashi, S. Ishiguro, *Chem. Lett.* **2010**, *39*, 578–579.

[8] a) K. Hashimoto, K. Fujii, M. Shibayama, *J. Mol. Liq.* **2013**, *188*, 143–147; b) R. Kanzaki, H. Doi, X. Song, S. Hara, S. Ishiguro, Y. Umebayashi, *J. Phys. Chem. B* **2012**, *116*, 14146–14152; c) X. Song, R. Kanzaki, S. Ishiguro, Y. Umebayashi, *Anal. Sci.* **2012**, *28*, 469–474.

[9] V. P. Walden, *Bull. Acad. Imp. Sci. (St. Petersburg)* **1914**, *8*, 405–422.

[10] a) D. F. Evans, S.-H. Chen, *J. Am. Chem. Soc.* **1981**, *103*, 481–482; b) D. Mirejovsky, E. M. Arnett, *J. Am. Chem. Soc.* **1983**, *105*, 1112–1117; c) D. F. Evans, A. Yamauchi, R. Roman, E. Z. Casassa, *J. Colloid Interface Sci.* **1982**, *88*, 89–96; d) S. B. Velasco, M. Turmine, D. D. Caprio, P. Letellier, *Colloids Surf. A* **2006**, *275*, 50–54; e) D. K. Magnuson, J. W. Bodley, D. F. Evans, *J. Solution Chem.* **1984**, *13*, 583–587; f) M. Allen, D. F. Evans, R. Lumry, *J. Solution Chem.* **1985**, *14*, 549–560; g) M. Ammam, D. D. Caprio, L. Gaillon, *Electrochim. Acta* **2012**, *61*, 207–215.

[11] a) H. Weingärtner, A. Knocks, W. Schrader, U. Kaatze, *J. Phys. Chem. A* **2001**, *105*, 8646–8650; b) M. Halder, L. S. Headley, P. Mukherjee, X. Song, J. W. Petrich, *J. Phys. Chem. A* **2006**, *110*, 8623–8626; c) R. Hayes, S. Imberti, G. G. Warr, R. Atkin, *Phys. Chem. Chem. Phys.* **2011**, *13*, 3237–3247; d) T. L. Greaves, D. F. Kennedy, S. T. Mudie, C. J. Drummond, *J. Phys. Chem. B* **2010**, *114*, 10022–10031; e) Y. Umebayashi, W.-L. Chung, T. Mitsugi, S. Fukuda, M. Takeuchi, K. Fujii, T. Takamuku, R. Kanzaki, S.

 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Ishiguro, *J. Comput. Chem. Jpn.* **2008**, *7*, 125 – 134; f) X. Song, H. Hamano, B. Minofar, R. Kanzaki, K. Fujii, Y. Kameda, S. Kohara, M. Watanabe, S. Ishiguro, Y. Umebayashi, *J. Phys. Chem. B* **2012**, *116*, 2801 – 2803; g) R. Atkin, G. G. Warr, *J. Phys. Chem. B* **2008**, *112*, 4164 – 4166; h) K. Fumino, A. Wulf, R. Ludwig, *Angew. Chem. Int. Ed.* **2009**, *48*, 3184 – 3186; *Angew. Chem.* **2009**, *121*, 3230 – 3233; i) R. Hayes, I. Silvia, G. G. Warr, R. Atkin, *Angew. Chem. Int. Ed.* **2013**, *52*, 4623 – 4627; *Angew. Chem.* **2013**, *125*, 4721 – 4725.

[12] a) Y. Marcus, *Pure Appl. Chem.* **1983**, *55*, 977; b) K. Izutsu in *Electrochemistry in Nonaqueous Solutions*, Wiley-VCH, Weinheim **2002**, pp. 78 – 82.

[13] a) D. Himmel, S. K. Goll, I. Leito, I. Krossing, *Angew. Chem. Int. Ed.* **2010**, *49*, 6885 – 6888; *Angew. Chem.* **2010**, *122*, 7037 – 7040; b) D. Himmel, S. K. Goll, I. Leito, I. Krossing, *Chem. Eur. J.* **2011**, *17*, 5808 – 5826; c) D. Himmel, S. K. Goll, F. Scholz, V. Radtke, I. Leito, I. Krossing, *ChemPhysChem* **2015**, *16*, 1428 – 1439.

[14] a) E. S. Stoyanov, I. V. Stoyanova, C. A. Reed, *Chem. Sci.* **2011**, *2*, 462 – 472; b) D. Decka, G. Schwaab, M. Havenith, *Phys. Chem. Chem. Phys.* **2015**, *17*, 11898 – 11907.

[15] R. Kanzaki, K. Uchida, X. Song, Y. Umebayashi, S. Ishiguro, *Anal. Sci.* **2008**, *24*, 1347 – 1349.

Received: December 7, 2015
Revised: January 26, 2016
Published online: April 13, 2016

 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim