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ROYAL SOCIETY OF CHEMISTRY

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DOI: 10.1039/C5GC01913C

Journal Name

ARTICLE

Brønsted Acidity of Bio-Protic Ionic Liquids: The Acidic Scale of [AA]X Amino Acid Ionic Liquids

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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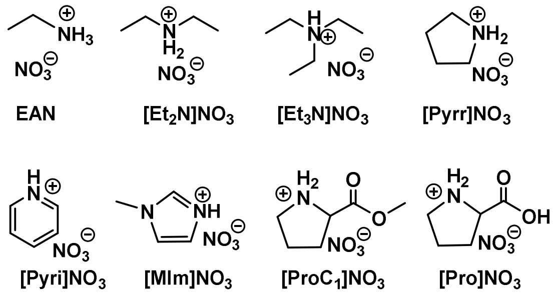
Amino acid ionic liquids (AAILs) [AA]X based on amino acid cations are a kind of typical “bio-base” protic ionic liquids (PILs), which are supposed to be acidic ionic liquids. The Brønsted acidity of [AA]X PILs at room temperature were systematically studied for the first time. Acid dissociation constants (pK_a) of [AA]X were determined by potentiometric titration method. The first acid dissociation constants (pK_{a1}) are from 1.98 to 2.42. The actual pH values of [AA]X (0.010 mol·L^{-1}) obtained from pH meter are from 2.26 to 2.44 which are slightly higher than the calculated pH values according to the above experimental pK_{a1}. The Hammett method performed on UV/Vis spectra with *p*-nitroaniline as the indicator was used to determine the acid strength of [AA]X. Their H_0 values (0.010 mol·L^{-1}) are in the range from 2.10 to 2.44. Various frameworks of amino acid cations and five anions (including nitrate (NO_3^-), chloride (Cl^-), perchlorate (ClO_4^-), trifluoromethanesulfonate (OTf^-) and trifluoroacetate (TfA^-) anions) were used to investigate the cationic and anionic effect on the acidity of AAILs. The Brønsted acidity of AAILs depends on the cationic structure, the type of anion and the concentration of [AA]X. In addition, the theoretical pK_{a1} were studied by the cluster-continuum model using density functional theory (DFT) method. The experimental and theoretical results showed that [AA]X PILs have stronger Brønsted acidity than that of the common PILs prepared by one-pot syntheses.

Introduction

Green chemistry is devoted to solve environment problem and achieve sustainable development.[1] The ideal goal of green chemistry is to reduce or delete the production of contaminants at the source with low energy consumption and low cost. The development of green chemistry is closely related to ionic liquids (ILs) because that they create a cleaner and more sustainable chemistry.[2] ILs have received much attention in recent years owing to their neglectable vapour pressures, strong solubilities, high thermal stabilities and designable structures, etc.[3] With the development of study, ILs are now considered not only as important alternative green media (solvents) and high efficiency catalysts, but as a new type of multifunctional materials for energy, industry, and medicine applications.[4]

Protic ionic liquids (PILs) are an important subset of ILs. Most of them can be easily obtained by one-step protonation reactions without any by-product. They show great potential in many applications such as catalysis, biomass energy, biology, fuel cell and so on.[5] Recently, PILs in nature were found by Davis et al., which may play specific biological roles.[6] A distinct characteristic of PILs is their supposed Brønsted acidity. Thus some PILs have been used as acidic catalysts and solvents for catalytic reactions.[7] A representative instance is that PIL [HMIm]Cl has been used in the industrially landmark BASIL process by BASF.[8] Acid catalysis is the most imperative process in the chemical industry, which can be applied to whole value chain.[9] While the use of strong inorganic acid and the waste involved brings out a series of environmental problems.[7] Therefore PILs are considered as feasible acidic catalysts with green and recoverable feature.

As more attention is paid to “fully green” or “bio-base” ILs,[10] some biorenewable natural compounds have been employed as precursors for the preparation of ILs in a cost-saving and clean way.[11] Among these natural compounds, amino acids are the most abundant natural source containing enough tunable structures. In 2005, amino acid ionic liquids (AAILs) ([AA]X and [AAE]X) were reported as bio-protic ionic liquids (bio-PILs).[11b]



Scheme 1 Structures of PILs.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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DOI: 10.1039/C5GC01913C

[AA]X can be produced via one-pot classic acid-base neutralization without any by-product or complicated post-processing. In addition, they are of low cost and can be produced in significant quantities. AAILs have been found to be potential solvents, catalysts, and chiral selectors.[12]

The scale of acidity is a key impact for the utilization of acidic catalysts.[9] However, the known acidity level of one-pot synthetic PILs, including bisulfate salts, is low.[13] Compared with other PILs, [AA]X PILs are carboxylic group (–COOH) functionalized PILs which may have considerable acidity due to their cationic structures.[14] (Scheme 1) But up to now, the acidic scale of AAILs has not been studied systematically.

In this work, detailed study about the Brønsted acidity of [AA]X PILs with different amino acid cations and anions were studied by experimental and theoretical methods. Their acid dissociation constants (pK_a) in water were determined by potentiometric titration method at ambient temperature. The actual Brønsted acidities in water solutions were confirmed by pH meter. Their Brønsted acidity strengths were also determined using Hammett acidity function method performed on UV/Vis spectra. To better understand the dissociation of AAILs in water, their acid dissociation constants (pK_a) in water solutions were calculated by density functional theory (DFT) method.

Results and discussion

The acidic abilities of various AAILs were investigated based on their molecular structures, because natural amino acids exhibit diverse chemistries by virtue of their different functional side-chain groups. Being convenient for study, protonated glycinium ([Gly]$^+$) was choose as the fundamental amino acid cation ([AA]$^+$) framework. Then the AAILs were assorted into 3 groups: 1st group, [AA]$^+$ with neutral side chains (glycinium ([Gly]$^+$), alaninium ([Ala]$^+$), phenylalaninium ([Phe]$^+$), asparaginium ([Asn]$^+$), serinium ([Ser]$^+$), threoninium ([Thr]$^+$), valinium ([Val]$^+$), isoleucinium ([Ile]$^+$), leucinium ([Leu]$^+$), prolinium ([Pro]$^+$)); 2nd group, [AA]$^+$ with acidic side chains (histidinium ([His]$^{2+}$), argininium ([Arg]$^{2+}$), lysinium ([Lys]$^{2+}$), asparticium ([Asp]$^+$)); and 3rd group, *N*-alkylated [AA]$^+$ (glycinium ([Gly]$^+$), sarcosinium ([Sar]$^+$), *N*,*N*-dimethyglycinium ([DMGly] $^+$), betainium ([Bet]$^+$)). Five different anions including nitrate (NO_3^-), chloride (Cl^-), perchlorate (ClO_4^-), trifluoromethanesulfonate (OTf^-) and trifluoroacetate (TfA^-) anions were studied. All [AA]X PILs were easily synthesized in water by directly acidification with corresponding acid by a one-step synthetic procedure at room temperature.

The acid dissociation constant (pK_a) is one of the most important physiochemical parameters. The determination of pK_a is of interest to a wide range of research fields. In synthetic chemistry, pK_a values are used to select reaction conditions.[15] Data collection about the acidity of ILs in water has become an important topic, since the use of aqueous media in biphasic systems is promising media for green chemistry.[16] The acid dissociation reaction of acidic ILs in water can be simplified by the expression:

$$\mathrm{HA} = \mathrm{A}^- + \mathrm{H}^+ \quad (1)$$

The acidic dissociation constant (pK_a) can be obtained by the equations:

$$K_a = \frac{a_{(\mathrm{H}^+)}a_{(\mathrm{A}^-)}}{a_{(\mathrm{HA})}} \quad (2)$$

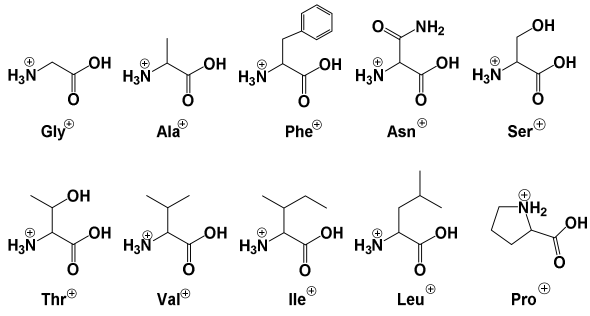
$$\mathrm{p}K_a = -\lg(K_a) \quad (3)$$

$$\mathrm{p}K_a = -\lg\left(\frac{a_{(\mathrm{H}^+)}a_{(\mathrm{A}^-)}}{a_{(\mathrm{HA})}}\right) \quad (4)$$

For a cell with a glass electrode, the cell potential has the form:

$$E = E_0 - E_g = K + \frac{RT}{F}\ln\left(a_{(\mathrm{H}^+)}\right) \quad (5)$$

where E_0 and E_g are the standard electrode potential and Donnan potential of glass electrode separately. K is a constant which is determined by the standard buffer solutions with the pH values of 4.00 ($a_{(H+)}$ = 1.00×10^{-4} mol·L^{-1}), 6.86 ($a_{(H+)}$ = 1.38×10^{-7} mol·L^{-1}) and 9.18 ($a_{(H+)}$ = 6.6×10^{-10} mol·L^{-1}), respectively. R is the gas constant, T is the absolute temperature, and F is the Faraday constant.



Scheme 2 The cationic structures of 1st group [AA]NO_3.

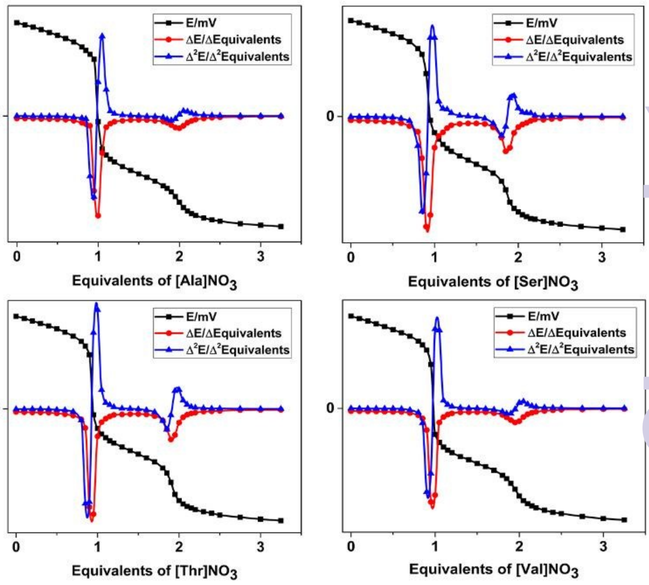


Figure 1 Potentiometric titration of 0.100 mol·L^{-1} [AA]NO_3 by KOH aqueous solution in water at 25.0(±0.1) °C.

As pK_a is defined in equation (4), the pK_a value is given by

$$\mathrm{p}K_a = K_1 - \frac{EF}{2.303RT} - \lg\left(\frac{a_{(\mathrm{A}^-)}}{a_{(\mathrm{HA})}}\right) \quad (6)$$

K_1 is a constant valued by K.

The pK_a determined by potentiometric titration method has been used to investigate the strength of Brønsted acids. Potentiometric titration curve of some 1st group [AA]X PILs (Scheme 2) are show in Figure 1. There are two abrupt points, showing that they are diprotic acids.

The potential maximum of the first derivative and the second derivative with zero as stoichiometric point were applied for the judgement of stoichiometric point, with low inaccuracy and more reliable results. pK_a values can be calculated by half stoichiometric point when $a_{(A^-)}$ equals $a_{(HA)}$, pK_a can be written as:

$$\mathrm{p}K_a = K_1 - \frac{E_{1/2}\mathrm{v}F}{2.303RT} \quad (7)$$

The pK_a values of $[AA]NO_3$ and some contrastive compounds are shown in Table 1. The pK_{a1} values of AAILs are from 2.14 to 2.42, which are much lower than those of corresponding neutral amino acids (>9.10), and even lower than that of formic acid (3.77). The low pK_{a1} may come from the –COOH group of amino acid cation. No significant differences in pK_{a1} were registered among 1st group $[AA]NO_3$, which suggested that neutral side chains on cation has no notable influence upon pK_{a1} in AAILs system unlike neutral carboxylic compounds.

Table 1 The pK_a values of AAILs and the contrastive compounds in water.

Compound	pK_{a1}	pK_{a2}
$[Gly]NO_3$	2.42(0.08)	9.88(0.19)
$[Ala]NO_3$	2.42(0.09)	9.88(0.18)
$[Phe]NO_3$	2.27(0.14)	9.24(0.14)
$[Asn]NO_3$	2.37(0.16)	9.00(0.24)
$[Ser]NO_3$	2.24(0.04)	9.08(0.04)
$[Thr]NO_3$	2.34(0.15)	9.06(0.24)
$[Val]NO_3$	2.40(0.08)	9.70(0.08)
$[Ile]NO_3$	2.42(0.06)	9.72(0.04)
$[Leu]NO_3$	2.41(0.05)	9.91(0.24)
$[Pro]NO_3$	2.14(0.07)	10.75(0.15)
$[GlyC_1]NO_3$[a]	7.65(0.12)	/
$[GlyC_1]Cl$	7.50(0.08)	/
$[AlaC_1]NO_3$[b]	7.74(0.10)	/
EAN	10.43(0.24)	/
$[Et_2N]NO_3$	10.68(0.19)	/
$[Et_3N]NO_3$	10.55(0.21)	/
$[Pyri]NO_3$	11.27(0.04)	/
$[MIm]NO_3$	7.09(0.12)	/
[αmPy]HSO_4[c]	6.0	/
[MIm]HSO_4[c]	6.9	/`
$[Et_3N]HSO_4$[c]	10.8	/
CH_3COOH[d]	4.76	/
HCOOH[d]	3.77	/
Gly[d]	9.78	/
Pro[d]	10.68	/

Condition: 0.100 mol·L^{-1}, 25.0(±0.1) °C, the data in parenthesis are the uncertainties (U). [a] [$GlyC_1$]: glycine methyl ester cation. [b] [$AlaC_1$]: alanine methyl ester cation. [c] Ref 13. [d] Ref 17.

The pK_{a2} values from protonated amine of AAILs is at the range of 9.00~10.75. The difference between two pK_a is more than 6.5, indicating that the acidity is dominated by pK_{a1}. Thus it is essential to assure the accuracy of pK_{a1} for the result. The pK_a values of common PILs are between 6.0 and 11.3. The minimum difference of the pK_a values between [AA]X PILs (pK_a) and those of common PILs is greater than 4.5, shows that the acidity of [AA]X is much stronger than those of common PILs. [AA]X PILs would be applied more extensively as relatively strong acids. The result also indicates that the notable influence upon pK_{a1} in [AA]X system unlike neutral carboxylic compounds. As a comparison, the pK_a of several typical [AAE]X AAILs were also determined with the pK_a values around 7.6. The Brønsted acidities of [AAE]X are obviously weaker than those of [AA]X PILs, and similar with some common PILs.

pH is a numeric scale used to specify acidity or alkalinity of an aqueous solution, which is important in chemistry, biology and environmental science, etc. It is the negative of the logarithm to base 10 of the activity of proton:

$$\mathrm{pH} = -\lg\left(a_{(\mathrm{H}^+)}\right) \quad (8)$$

When an acid is dissolved in water, the pH will be less than that of pure water (pH = 7) at 25 °C. The pH values can be calculated by pK_a that is a cost effective way for pH predication. The pH of a diprotic acid solution can be calculated by a general approach. The dissociation equilibria and the constant expressions are

$$\mathrm{H_2A\ (l)} = \mathrm{HA^-\ (l)} + \mathrm{H^+} \quad K_{a1} = \frac{a_{(\mathrm{H^+})}a_{(\mathrm{HA^-})}}{a_{(\mathrm{HA})}} \quad (9)$$

$$\mathrm{H_1A^-(l)} = \mathrm{HA^{2-}\ (l)} + \mathrm{H^+} \quad K_{a2} = \frac{a_{(\mathrm{H^+})}a_{(\mathrm{HA^{2-}})}}{a_{(\mathrm{HA^-})}} \quad (10)$$

In the absence of information regarding activity of [AA]X PILs in water in low concentration condition, it is assumed here that activity will be equal to the molar concentration. Choosing H_2A and H_2O as the reference proton level, the proton-condition equation (PCE) is

$$[\mathrm{H^+}] = [\mathrm{HA^+}] + 2[\mathrm{A^-}] + [\mathrm{OH^-}] \quad (11)$$

Because the solution is acidic, [OH^-] can be immediately eliminated from the PCE. Substitution of [HA^-] and [A^{2-}] with constant expression into this PCE, yields

$$[\mathrm{H^+}] = \frac{K_{a1}[\mathrm{H_2A}]}{[\mathrm{H^+}]} + 2\frac{K_{a1}K_{a2}[\mathrm{H_2A}]}{[\mathrm{H^+}]^2} = \frac{K_{a1}[\mathrm{H_2A}]}{[\mathrm{H^+}]}\left(1 + \frac{2K_{a2}}{[\mathrm{H^+}]}\right) \quad (12)$$

Thus,

$$[\mathrm{H^+}] = \left(1 + \frac{2K_{a2}}{[\mathrm{H^+}]}\right)\sqrt{K_{a1}[\mathrm{H_2A}]\left(1 + \frac{2K_{a2}}{[\mathrm{H^+}]}\right)} \quad (13)$$

This is a cubic equation for [H^+]. Because $2K_{a2}/[H^+] \ll 1$, $K_{a2}/K_{a1} < 10^{-5}$, Equation (13) can be simplified as

$$[\mathrm{H^+}] = \sqrt{K_{a1}[\mathrm{H_2A}]} \approx \sqrt{K_{a1}\left(c_{(\mathrm{H_2A})} - [\mathrm{H^+}]\right)} \quad (14)$$

Then,

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$$[\mathrm{H}^+] = \frac{-K_{a1}+\sqrt{K_{a1}+4K_{a1}c}}{2} \quad (15)$$

$$\mathrm{pH} = -\lg\left(\frac{-K_{a1}+\sqrt{K_{a1}+4K_{a1}c}}{2}\right) \quad (16)$$

The calculated pH values shown in Table 2 were obtained according to formula (16), which only depends on pK_{a1}. The pH values of 1st group [AA]X PILs are from 2.25 to 2.34, which are much lower than those of neutral amino acid solutions. [Pro]NO_3 has the strongest acidity with the lowest pK_{a1} 2.25 among 1st group [AA]X, which is close to that of HNO_3 (2.00, 0.010 mol·L^{-1}). Compared with common PILs, amino acids and acetic acid, the pH values of [AA]X are significantly lower.

The measuring pH value in solution is mainly tested by pH meter equipped with glass electrode. The pH values of [AA]X in water solutions on the concentration of 0.010 mol·L^{-1} were determined by a pH meter at 25.0(±0.1) °C. The measured pH values of 1st group [AA]X PILs in water are from 2.26 to 2.44, which are slightly higher than the calculated values. (Table 2) The ionic strength has trifling impact on pH at low concentrations. The acidity of [Pro]NO_3 is the strongest in water with pH 2.26 in 1st group [AA]X. The results are in accordance with the above results of pK_{a1}. pH values of common PILs and neutral carboxyl compound CH_3COOH and HCOOH are much higher than those of [AA]X in water solution.

The Brønsted acidity associated with Hammett acidity function of AAILs was investigated in water solutions.[18] *p*-Nitroaniline was used as indicator for the determination of Hammett acidity function by UV/Vis spectroscopy. For evaluating the Brønsted acidity of AAILs, the protonation extent of uncharged indicator bases (In) in a solution, in terms of the measurable ratio [In]/[InH^+] need to be evaluated. In a given solvent, assumed as being dissociating, the Hammett acidity function (H_0) can be expressed as the equation:

$$H_0 = \mathrm{p}K_a(\mathrm{InH}^+) + \log\left(\frac{[\mathrm{In}]}{[\mathrm{InH}^+]}\right) \quad (17)$$

Table 2 The acidity values of 1st group [AA]X and the contrastive compounds in water.

Compound	pH$_{(cal)}$	pH$_{(exp)}$	H_0^{a}
[Gly]NO_3	2.34	2.42(0.07)	2.44(0.06)
[Ala]NO_3	2.34	2.36(0.04)	2.41(0.07)
[Phe]NO_3	2.29	2.35(0.04)	/
[Asn]NO_3	2.32	2.40(0.03)	2.34(0.06)
[Ser]NO_3	2.28	2.38(0.03)	2.31(0.06)
[Thr]NO_3	2.31	2.40(0.04)	2.32(0.05)
[Val]NO_3	2.33	2.44(0.04)	2.43(0.06)
[Ile]NO_3	2.34	2.39(0.04)	2.42(0.03)
[Leu]NO_3	2.34	2.40(0.03)	2.43(0.08)
[Pro]NO_3	2.25	2.26(0.05)	2.26(0.09)
EAN	6.32	6.50(0.23)	3.04(0.01)
[Et_3N]NO_3	6.28	6.34(0.18)	3.14(0.06)
Gly	5.89	6.00(0.15)	3.02(0.14)
Pro	6.34	6.43(0.21)	3.25(0.04)

Condition: 0.010 mol·L^{-1}, 25.0(±0.1) °C, the data in parenthesis are the uncertainties (U). [a] Indicator: *p*-NA 5.0x10^{-5} mol·L^{-1}.

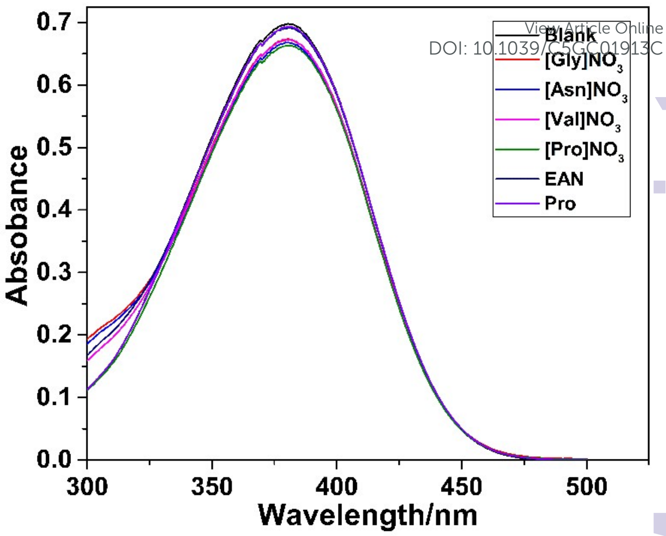

Figure 2 The UV/Vis spectra in water according to the Hammett method at 25.0(±0.1) °C. Concentrations: 0.010 mol·L^{-1}, indicator: *p*-NA 5.0x10^{-5} mol·L^{-1}.

Where pK_a(InH^+) is the pK_a value of protonated *p*-nitroaniline indicator in water solution (0.99), [In] and [InH^+] are the molar concentrations of the unprotonated and protonated forms of p-nitroaniline indicator, respectively.

The UV/Vis spectra of some AAILs in water according to the Hammett method were shown in Figure 2. An absorption peak of the unprotonated form of *p*-nitroaniline (*p*-NA) was recorded at about 380 nm. The characteristic absorption peak decreased as the acidity of the solution increased. The Hammett acidity functions (H_0) of 1st group [AA]X and the contrastive compounds in water are summarized in Table 2. The H_0 values of 1st group [AA]X are from 2.30 to 2.44, which are much lower than those of neutral amino acid solutions. [Pro]NO_3 has the strongest acidity with the lowest H_0 2.30 among 1st group AAILs. The H_0 of CH_3COOH and common PILs are higher than those of 1st group [AA]X. The results are matched with the above results of pK_{a1} and pH.

The impact of the acidic side-chain group of cations on the Brønsted acidity was studied. All of 2nd group [AA]X are triprotic acidic PILs based on their structures. (Scheme 3) Potentiometric titration curve of some 2nd group [AA]X are shown in Figure 3. Only [His]$(NO_3)_2$ shows three abrupt points at pK_a 2.01, 6.14 and 9.17, respectively. These pK_a values correspond to the dissociation of –COOH group, protonated alkylimidazolium and protonated amine separately. [Arg]$(NO_3)_2$ only take two pK_a due to the weak acid of protonated guanidine. There are only pK_{a1} but no pK_{a2} and pK_a of [Lys]$(NO_3)_2$ could be effectively detected because of the similar acidic properties of two protonated amines. As the small difference between pK_{a1} and pK_{a2} of [Asp]NO_3, the pK_a can't be obtained from potentiometric titration curve. In order to get the pK_a of [Asp]NO_3, equal molar aspartic acid (Asp) and KNO_3 aqueous solution was titrated using KOH aqueous solution to obtain pK_{a2} and pK_{a3}. And, equal molar Asp and KNO_3 in aqueous solution was titrated using HNO_3 aqueous solution by back titration method to obtain pK_{a1}. [Asp]NO_3 and [His]$(NO_3)_2$ have lower pK_a than H_3PO_4. (Table 3) Their pH$_{(cal)}$,

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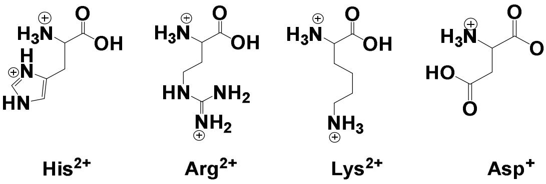
$pH_{(exp)}$ and H_0 are also lower than those of H_3PO_4. The acidity of [Asp]NO_3 and [His]$(NO_3)_2$ should be stronger than that of H_3PO_4.



Scheme 3 The cationic structures of 2nd group [AA]NO_3.

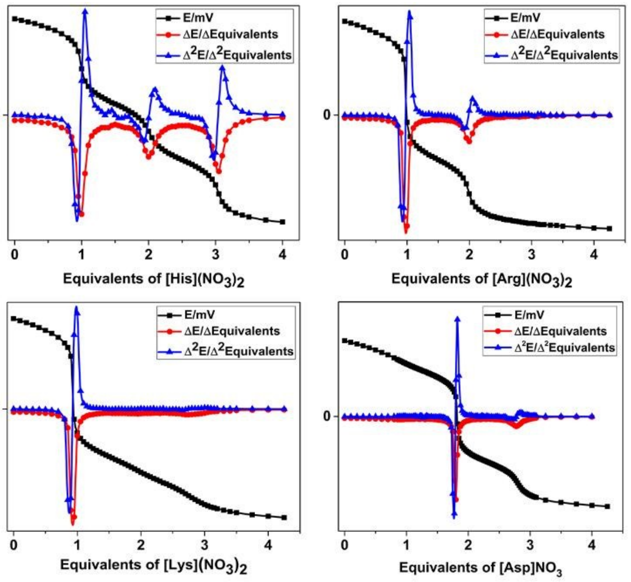


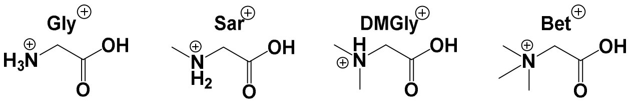
Figure 3 Potentiometric titration of 0.100 mol·L^{-1} 2nd group [AA]NO_3 by KOH aqueous solution in water at 25.0(± 0.1) °C.

Table 3 The acidity values of 2nd group [AA]X in water.

Compound	pK_{a1}	pK_{a2}	pK_{a3}	$pH_{(exp)}$	$pH_{(cal)}$	H_0
[His]$(NO_3)_2$	2.01 (0.13)	6.14 (0.08)	9.17 (0.01)	2.15 (0.02)	2.21	2.10 (0.01)
[Arg]$(NO_3)_2$	2.29 (0.12)	9.18 (0.14)	/	2.36 (0.02)	2.30	2.21 (0.01)
[Lys]$(NO_3)_2$	2.37 (0.18)	/	/	2.40 (0.02)	2.32	2.27 (0.05)
[Asp]NO_3	2.08 (0.01)	3.86 (0.02)	9.82 (0.02)	2.08 (0.02)	2.23	2.17 (0.03)
H_3PO_4	2.12	7.21	12.67	/	2.24	/

Condition: 0.010 mol·L^{-1}, 25.0(±0.1) °C, the data in parenthesis are the uncertainties (U). [a] Indicator: p-NA 5x10^{-5} mol·L^{-1}.

To obtain the effect of *N*-alkylation of cation on the Brønsted acidity, the acidities of [Gly]NO_3, [Sar]NO_3, [DMGly]NO_3 and [Bet]NO_3 were studied. Potentiometric titration curve of 3rd group [AA]X (Scheme 4) are shown in Figure 4. The pK_{a1} values of 3rd group [AA]X are from 1.98 to 2.42. The $pH_{(exp)}$ of them are from 2.26 to 2.42. The more *N*-alkyl substitutes the cation has, the lower the pK_a or pK_{a1} values of 3rd group [AA]X is. [Bet]NO_3 had the significantly lowest pK_a 1.98, $pH_{(exp)}$ 2.26 and H_0 2.17, respectively. The pH of [Bet]NO_3 is more close to the acidity of HNO_3 (2.00) under the same conditions.



Scheme 4 The cationic structures of 3rd group [AA]NO_3.

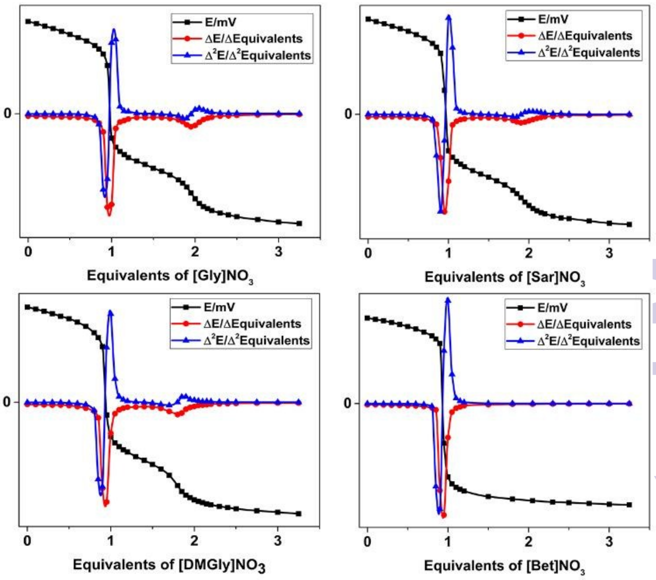


Figure 4 Potentiometric titration of 0.100 mol·L^{-1} 3rd group [AA]NO_3 by KOH aqueous solution in water at 25.0(± 0.1) °C.

Table 4 The acidity values of 3rd group [AA]X in water.

[AA]X	pK_{a1}	pK_{a2}	$pH_{(exp)}$	$pH_{(cal)}$	H_0
[Gly]NO_3	2.42 (0.08)	9.88 (0.19)	2.42 (0.02)	2.34	2.44 (0.06)
[Sar]NO_3	2.22 (0.08)	10.06 (0.08)	2.32 (0.08)	2.27	2.35 (0.01)
[DMGly]NO_3	2.18 (0.08)	10.01 (0.08)	2.32 (0.08)	2.26	2.35 (0.07)
[Bet]NO_3	1.98 (0.08)		2.26 (0.08)	2.20	2.17 (0.01)

Condition: 0.010 mol·L^{-1}, 25.0(±0.1) °C, the data in parenthesis are the uncertainties (U). [a] Indicator: p-NA 5.0x10^{-5} mol·L^{-1}.

The influence of different anions on the Brønsted acidity was also investigated. The pK_a of five kinds of [AA]X PILs with NO_3^-, Cl^-, ClO_4^-, OTf^- and TfA^- were measured by potentiometric titration method. The pK_a values were illustrated in Figure 5. [AA]ClO_4 have the strongest acidity an [AA]TfA have the weakest acidity among them. These results are consistent with the pK_a of the relative inorganic acids ($HClO_4$, –10) or organic acids (HTfA, 0.23). The stronger the acidity of the corresponding acid is, the stronger the Brønsted acidity of [AA]X PILs is.

For comparison, the $pH_{(exp)}$ and H_0 of [Pro]NO_3 and [Gly]NO_3 in water solutions at various concentrations was measured. In the spectra, a noticeable decrease of the strength of the absorption peak was found accompanied with the concentration of [Pro]NO_3 increased. (Figure 6) The pH and H reduced with the increasing of concentration. The relationship

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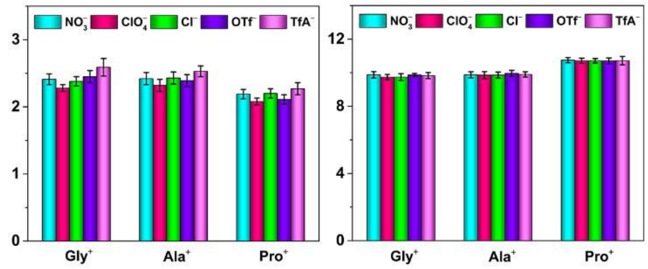

Figure 5 The experimental pK_a values of [AA]X PILs with different anions in water at 25.0 (±0.1) °C . Left: pK_{a1}; Right: pK_{a2}.

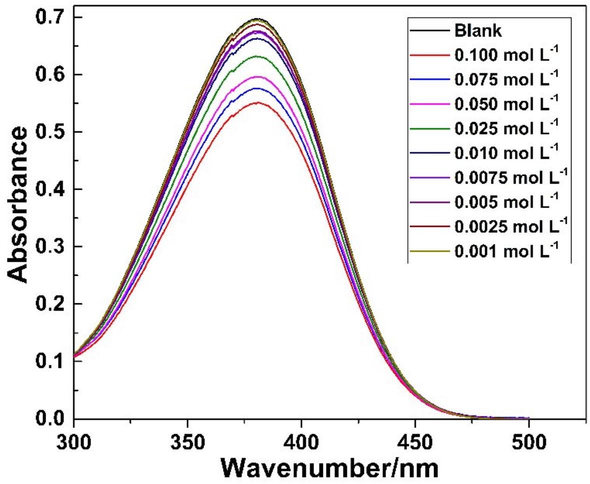

Figure 6 The UV/Vis spectra of [Pro]NO_3 with different concentrations in water according to the Hammett method at 25.0(±0.1) °C. Indicator: *p*-NA 5.0×10^{-5} mol·L^{-1}.

between the concentration of [Pro]NO_3 and the acidity can be obtained using the fitting equations like calculated pH by pK_a. Their fitting equation are

$$\mathrm{pH_{(exp)}} = -1.386\lg(c^{0.5}) + 0.926,\ \mathrm{R}^2 = 0.993 \quad (18)$$

$$H_0 = -1.612\lg(c^{0.5}) + 0.736,\ \mathrm{R}^2 = 0.997 \quad (19)$$

Respectively. (Figure 7) The acidity and concentration showed good relationship between 0.001 mol·L^{-1} to 0.100 mol·L^{-1}. Furthermore, good linear relationships between pH$_{(exp)}$, H_0 and pH$_{(cal)}$ were found separately. Their fitting linear equations were achieved respectively. (Figure 7)

$$\mathrm{pH_{(exp)}} = 0.993\mathrm{pH_{(cal)}} + 0.041,\ \mathrm{R}^2 = 0.999 \quad (20)$$

$$H_0 = 1.491\mathrm{pH_{(cal)}} - 0.985,\ \mathrm{R}^2 = 0.992 \quad (21)$$

Based on these, the desired pH can be obtained by choosing appropriate concentrations. pH$_{(exp)}$ and H_0 of [Gly]NO_3 solution in different concentrations have similar change like [Pro]NO_3.

The relationship between molecular or ion distribution fraction (χ) and pH is an important parameter for many applications such as extraction.[19] Clear relationship will promote the application of AAILs. The χ-pH diagrams of some [AA]X are illustrated in Figure 8. The pK_a was the point of intersection between two neighbouring curves.

The Brønsted acidity of AAILs determined by pK_{a1} of –COOH group is confirmed by above experimental data. In order to obtain a better understanding of the Brønsted acidities of [AA]X PILs, the decisive pK_{a1} of [AA]X were calculated by density functional theory (DFT) using Gaussian 09 suite of program.[20] It is verified that anion would have similar impact tendency on the acidity of [AA]X aqueous solution. Therefore, the calculated acidity of AA$^+$ could be considered as a simple

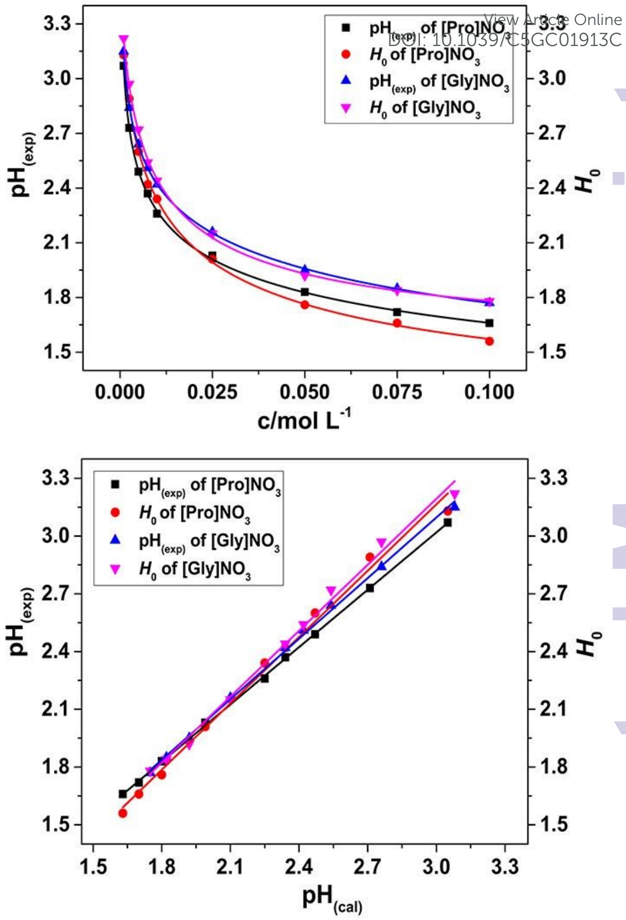

Figure 7 Top: The acidities of [Pro]NO_3 and [Gly]NO_3 at various concentrations in water at 25.0(±0.1) °C. Bottom: The fitting relationship between pH$_{(cal)}$, pH$_{(exp)}$ and H_0 of [Pro]NO_3 and [Gly]NO_3 at 25.0(±0.1) °C.

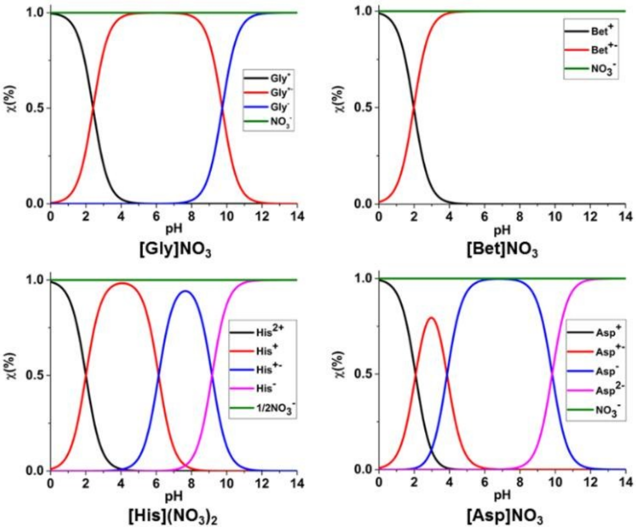

Figure 8 χ-pH profiles of AAILs.

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and approximate method for understanding the acidity of [AA]X. Relative correction factor can compensate the anionic effect. For AA^+ acids, due to the strong interaction between AA^+ and solvent water molecule, reaction can be used by equation based on the cluster-continuum model,[21]

$$AA^+(H_2O)_n + (4-n)H_2O = AA^{+-}(H_2O)_n + H_3O^+(H_2O)_3 \quad (22)$$

where the solution free energy is calculated by

$$\Delta G^*_{sol} = \Delta G^*_{sol}(AA^{+-}(H_2O)_n) + \Delta G^*_{sol}(H_3O^+(H_2O)_3) - \Delta G^*_{sol}(AA^+(H_2O)_n) - \Delta G^*_{sol}((4-n)H_2O) \quad (23)$$

that leads to the following equilibrium in equation (24),

$$K_a = \frac{[AA^{+-}(H_2O)_n][H_3O^+(H2O)_3]}{[AA^+(H_2O)_n][(4-n)H_2O]} = e^{\frac{-\Delta G^*_{sol}}{RT}} \quad (24)$$

the calculation of pK_a is then obtained from equation (25),

$$pK_a(AA^+) = \frac{-\Delta G^*_{sol}}{2.303RT} - (4-n)\lg[H_2O] \quad (25)$$

the pK_a values of [AA]X can be calculated by the simplified math formulation of pK_a,

$$pK_a(AA^+) = \frac{-\Delta G^*_{sol}}{2.303RT} - K \quad (26)$$

where *K* depends on the anions for the same *n* value. The ionic clusters $AA^+(H_2O)_n$, $AA^{+-}(H_2O)_n$, $n H_2O$ and $H_3O^+(H_2O)_3$ were optimized in gas phase at m062x/6–311++G** level. On the basis of the optimized structures, calculations with polarizable continuum model (PCM) were performed to calculated the solvation free energies of AA^+ and AA^{+-} in aqueous solution at m062x/6–311++G** level.[22] The liquidus Gibbs free energies of AA^+ and AA^{+-} were obtained from the sum of the total electronic energies of water solution and the thermal corrections to gas Gibbs free energies (G_{corr}).

The calculated values where *n* is 3 agreed well with the experimental values. The theoretical and experimental Gibbs free energies of the acid dissociation reactions and the calculated pK_{a1} values of thirteen $[AA]NO_3$ in water are summarized in Table 5. For $[AA]NO_3$, the theoretical pK_a are calculated by

$$pK_a(AA^+) = \frac{-\Delta G^*_{sol}}{2.303RT} - 0.76 \quad (27)$$

The theoretical values of [AA]X obtained are consistent with their experimental values. The pK_a value of $[Bet]NO_3$ is the lowest one in all $[AA]NO_3$, similar with our experimental results. The theoretical pK_{a1} calculation expression of $[AA]ClO_4$, [AA]Cl, [AA]OTf and [AA]TfA can be acquired by defined different K according to anion. Their expressions are

$[AA]ClO_4$: $pK_a(AA^+) = \frac{-\Delta G^*_{sol}}{2.303RT} - 0.90$ (28)

[AA]Cl: $pK_a(AA^+) = \frac{-\Delta G^*_{sol}}{2.303RT} - 0.79$ (29)

[AA]OTf: $pK_a(AA^+) = \frac{-\Delta G^*_{sol}}{2.303RT} - 0.85$ (30)

[AA]TfA: $pK_a(AA^+) = \frac{-\Delta G^*_{sol}}{2.303RT} - 0.60$ (31)

respectively. The pK_{a1} values are shown in Table 6. $[Bet]ClO_4$ possesses the lowest theoretical pK_{a1} 1.73.

Table 5 The theoretical and experimental pK_{a1} values of $[AA]NO_3$ PILs in water.

AAIL	ΔG(cal)	pK_{a1}(cal)	ΔG(exp)	pK_{a1}(exp)
$[Gly]NO_3$	18.15	2.42	13.82	2.42
$[Ala]NO_3$	18.50	2.48	13.82	2.42
$[Phe]NO_3$	18.73	2.52	12.96	2.27
$[Asn]NO_3$	18.21	2.43	13.53	2.37
$[Ser]NO_3$	19.05	2.58	12.79	2.24
$[Thr]NO_3$	18.91	2.55	13.36	2.34
$[Val]NO_3$	17.82	2.36	13.70	2.40
$[Ile]NO_3$	18.88	2.55	13.82	2.42
$[Leu]NO_3$	17.65	2.33	13.76	2.41
$[Pro]NO_3$	16.38	2.11	12.22	2.14
$[Sar]NO_3$	16.82	2.19	12.67	2.22
$[DMGly]NO_3$	15.10	1.89	12.45	2.18
$[Bet]NO_3$	15.01	1.87	11.30	1.98

Table 6 The theoretical pK_{a1} values of [AA]X PILs in water.

	ClO_4^-	Cl^-	OTf^-	TfA^-
Gly^+	2.28	2.39	2.33	2.58
Ala^+	2.34	2.45	2.39	2.64
Phe^+	2.38	2.49	2.43	2.68
Asn^+	2.29	2.40	2.34	2.59
Ser^+	2.44	2.55	2.49	2.74
Thr^+	2.41	2.52	2.46	2.71
Val^+	2.22	2.33	2.27	2.52
Ile^+	2.41	2.52	2.46	2.71
Leu^+	2.19	2.30	2.24	2.49
Pro^+	1.97	2.08	2.02	2.27
Sar^+	2.05	2.16	2.10	2.35
$DMGly^+$	1.75	1.86	1.80	2.05
Bet^+	1.73	1.84	1.78	2.03

Conclusions

[AA]X PILs as a kind of Bio-PILs with various structures synthesized by one-step protonation were proved to be relatively strong acidic PILs. The pK_{a1} of [AA]X PILs are from 1.98 to 2.42, which are much less than those of common PILs (maximum ΔpK_a 8.7). Acidic side-chain group on cation could increase the acidity of [AA]X. Moreover, the increasing acidity could be attributed to the increase of *N*-alkyl substitutes on cation. $[Bet]NO_3$ has the experimentally lowest pK_a 1.98 among the studied [AA]X. The actual pH values of [AA]X (0.010 mol·L^{-1}) obtained from pH meter are from 2.26 to 2.44. They are slightly higher than the calculated pH values according to the above experimental pK_{a1} and close to the ideal acidity of HNO_3 (2.00) under the same condition. The Hammett acidity

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H_0 values of [AA]X (0.010 mol·L^{-1}) are in the range from 2.10 to 2.44. In addition, the decisive pK_{a1} were studied using density functional theory (DFT) method. A good agreement between theoretical values and experimental values is obtained.

In summary, the theoretical and experimental results all showed that [AA]X PILs are typical moderate strong acid (pK_a 1~4). (Figure 9) Their acidity scales locate at the range between HNO_3 and HCOOH, and are very similar with that of common inorganic acid H_3PO_4. [AA]X PILs have stronger Brønsted acidity than common one-pot PILs without –COOH group on cations. The relatively strong Brønsted acidity of bio-PILs [AA]X will promote PILs to be applied widely.

Figure 9 Acidity scale of [AA]X PILs.

Experimental

General Methods: All chemicals were obtained commercially as analytical grade materials and used as received. Solvents were dried by standard procedures. [AA]X PILs were synthesized according to literature procedure by a one-step protonation reaction of an amino acid precursor with a corresponding dilute acid.[11b] The mixture of amino acid and corresponding acid was stirring in water at room temperature for 24 h, and then [AA]X was obtained in quantitative yield after drying in air and finally in vacuum. Infrared spectra (IR) were recorded on NEXUS 670 FT-IR spectrometer on KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz nuclear magnetic resonance spectrometer operating at 400 and 100 MHz, respectively, with d_6-DMSO or D_2O as locking solvent. ^1H and ^{13}C chemical shifts are reported in ppm relative to TMS. The uncertainties (U) were calculated by the equation: $U = \max\{|\bar{A} - A_i|, i = 1, 2, 3\}$; $\bar{A} = \sum_{i=1}^{3} A_i / 3$.

pK_a Determination. A stock solution (0.100 mol·L^{-1}) of [AA]X PILs was prepared in degassed water. The solution was then titrated with aqueous KOH solution (0.500 mol·L^{-1}). The electric potential (E) (±1 mV) of the solution was obtained using a Ag-AgCl/ glass combination electrode on an OHAUS STARTER 2100 pH-mV meter at 25.0(±0.1) °C. Three Standard buffer solutions with the pH value of 4.00, 6.86 and 9.18 respectively were used to measure the correlation between pH and E before determination.

pH Determination. The pH values of [AA]X PILs in water solutions (0.010 mol·L^{-1}) were measured using a calibrated glass electrode on an OHAUS STARTER 2100 pH meter at 25.0(±0.1) °C. The Standard buffer solutions with the pH value of 4.00 and 6.86 were used to calibrate the pH meter before determination.

UV/Vis Determination. Hammett acidity function of ILs was investigated on a BFRL UV-1601 UV/VIS Spectrophotometer. Samples were measured in sealed 1 mm Quartz cuvettes (Helma). The dyes of *p*-nitroaniline (Fluka, 99%) were used as indicator and molecular probe for the determination of acidity, H_0 with 5.0x10^{-5} mol·L^{-1}. Absorbance values, *A*, of indicator based on the ILs in water solutions were recorded between 300 and 500 nm in steps of 0.1 nm at 25.0(±0.1) °C. The concentrations of [AA]X PILs were 0.010 mol·L^{-1}. An appropriate amount solution was filled into vials and sealed for determination.

Computational Method. Computations were performed by the Gaussian 09 suites of programs. The geometric optimizations were carried out using the popular M06-2X analyses up to 6-311++G** basis set which including the polarizable and diffuse functions for the H atom for the descriptions of hydrogen-bonded interactions. The frequency analyses was also performed at the same level of theory. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. Single-point solvation energies were calculated at the M06-2X/6-311++G** level.

Acknowledgements

The finance support of NSFC (No. 21103116, 21303108, J1210004), FRFCU (No. 2013SCU04A12, 2015SCU04A21), and SSTIC (No. ZDSY20130331145131323) are gratefully acknowledged. We thank the Comprehensive training platform of specialized laboratory, College of chemistry, Sichuan University for instrumental measurement.

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View Article Online
DOI: 10.1039/C5GC01913C

Brønsted Acidity of Bio-Protic Ionic Liquids: The Acidic Scale of [AA]X Amino Acid Ionic Liquids

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Brønsted acidity of typical “bio-base” protic ionic liquids, [AA]X amino acid ionic liquids, were systematically studied.