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The Influence of the Acidity of Ionic Liquids on Catalysis

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In the past 20 years, the concept of ionic liquids (ILs) have been extensively applied in the fields of chemistry, materials, and life sciences.^[1] Undoubtedly, the ionic liquids composed of quaternary ammonium cations and anions, such as BF_4^- , PF_6^- , Cl^- , and NTf_2^- , have been the backbone of this area since imidazolium cation ionic liquids were synthesized by Zaworotko et al. and were brought into catalysis and synthesis by Seddon, Rogers, Welton, Wasserscheid, and others.^[2] Thousands of reactions have been performed in these ionic liquids and many of them exhibited better behavior than organic solvents.^[3] Normally, the fine performance of these ionic liquids was attributed to the specific ionic environment of the ionic liquid. Nevertheless, the acidity of the air- and moisture-stable ionic liquids and its effect on catalysis is an interesting topic. As it is well known, a large amount of organic reactions can be catalyzed or promoted by an acid environment.^[4] During our investigation of the function of ionic liquids in catalysis, especially air- and moisture-stable ones, we found that these ILs normally exhibit weak acidity in the presence of a small amount of water. That means the interpretations about the function of air- and moisture-stable ionic liquids in catalytic reactions are possibly wrong because the presence of trace amount of water is not avoidable in reality. Herein, we present our results on the study of acidity of air- and moisture-stable ionic liquids and their activity in some known acid-catalyzed reactions. We hope these results could be helpful for researchers in this area to reconsider the influence of the acidity of air- and moisture-stable ionic liquids on catalysis and also in other fields.

At the initial stage, the acidity of ionic liquids–water with different cations and anions were measured with a pH meter. The concentration of ionic liquid in water was 0.1 M. The operation was performed with methods given in the Annual Book of American Society for Testing and Materials Standards (ASTM) with slight modification.^[5]

As shown in Figure 1, ionic liquid–water mixtures with BF_4^- anions were all acidic. Interestingly, the acidity of the ionic liquids could be tuned via substituted alkyl variation. The pH value of EMIm BF_4 ionic liquid reached 3.44(0.03) but the pH value of BMIm BF_4 and HMIm BF_4 were 4.27(0.14) and 6.61(0.03)

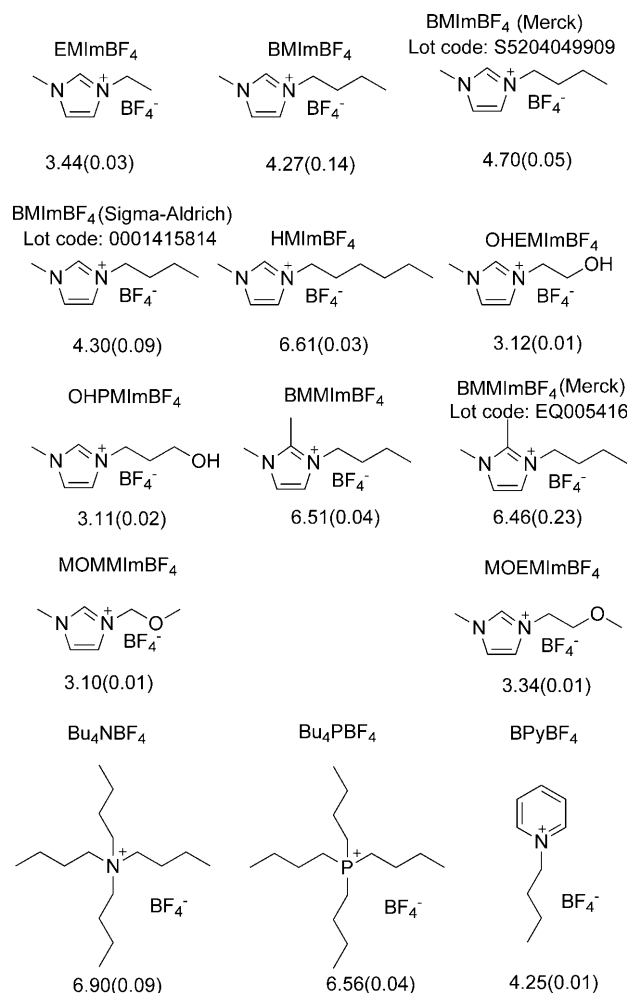


Figure 1. pH values of the aqueous phase of ionic liquids with BF_4^- as anion (0.1 M). The numbers in the parentheses are the values of the standard deviation.

respectively. BMIm BF_4 ionic liquids purchased from Merck (lot code: S5204049909) and Sigma-Aldrich (lot code: 0001415814) were also measured for comparison. Under the same condition, their pH values were 4.70(0.05) and 4.30(0.09), respectively, which are exactly the same as the acidity of the ionic liquids that we synthesized. The incorporation of an hydroxyl group would further enhance the acidity of ionic liquids with BF_4^- anion. The pH value reached 3.12(0.01) and 3.11(0.02) with hydroxyethyl or hydroxypropyl groups. The substitution of the C2 position with a methyl group weakens the acidity of this kind of ionic liquid. For the ionic liquid BMMIm BF_4 , the pH value was 6.51(0.04). This was almost the same as that with the ionic liquid from Merck, that is, 6.46(0.23) (lot code: EQ005416). For ionic liquids with tetrabutyl ammonium and tetrabutyl phosphonium cations, the IL solutions were close to

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neutral. The pH values were 6.90(0.09) and 6.56(0.04). Similar acidity was observed for an ionic liquid with butyl pyridinium cation, that is, 4.25(0.01). Therefore, the acidity of ionic liquids with BF_4^- anion could be finely tuned via cation variation in the pH value range of 3.0–7.0.

For another commonly employed ionic liquid, BMImPF₆, an interesting result was also obtained (Figure 2). The pH value of its solution was 7.16(0.04), although it is normally considered

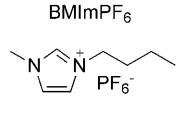
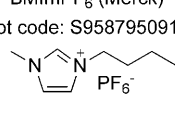
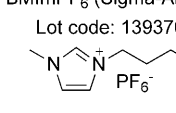
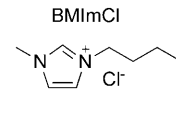


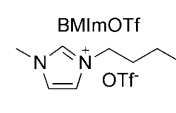

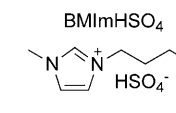
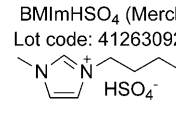
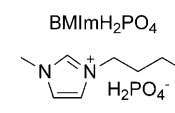
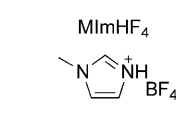
 BMImPF ₆ 7.16(0.04)	 BMImPF ₆ (Merck) Lot code: S9587950917 6.30(0.10)	 BMImPF ₆ (Sigma-Aldrich) Lot code: 1393707 6.55(0.08)
 BMImCl 6.98(0.13)	 BMImN(CN) ₂ 6.98(0.05)	 BMImNO ₃ 6.11(0.01)
 BMImOTf 7.07(0.04)	 BMImClO ₄ 6.21(0.18)	 BMImHSO ₄ 1.45(0.01)
 BMImHSO ₄ (Merck) Lot code: 412630928 1.37(0.05)	 BMImH ₂ PO ₄ 3.00(0.01)	 MImHBF ₄ 2.65(0.01)

Figure 2. pH values of the aqueous phase of ionic liquids with 1-butyl-3-methylimidazolium as cation (0.1 M).

to be more easily hydrolyzed than BMImBF₄. Similar results were obtained when applying BMImPF₆, purchased from Merck, that is, 6.30(0.10) (Lot code: S9587950917) and Sigma-Aldrich, that is, 6.55(0.08) (lot and filling code: 1393737 and 30909232). Other ionic liquid solutions with varied anions such as BMImCl, BMImN(CN)₂, BMImOTf, and BMImClO₄ were close to neutral except for the weak acidity exhibited by the ionic liquid BMImNO₃, that is, 6.11(0.01). In the end, ionic liquids with HSO₄[−] and H₂PO₄[−] anions were also measured. The pH values for ionic liquids with HSO₄[−] anion were 1.45(0.01) and 1.37(0.05) (Merck EQ412630928), and for the H₂PO₄[−] anion the value was 3.00(0.01). At the same time, the pH value of ionic liquid with protonized imidazole and BF₄[−] anion was 2.65(0.01).

By comparing the pH values of ionic liquid solutions discussed above, it could be concluded that the acidity of ionic liquids with BF₄[−] anions is comparable with the acid-functionalized ionic liquids BMImH₂PO₄ and MImHBF₄. Conversely, ionic liquids with PF₆[−] are more stable and result in neutral aqueous solutions. Therefore, ionic liquids with PF₆[−] anions are more stable in water at room temperature.

More importantly, our further explorations suggested an interesting rule for the acidity of ionic liquids containing different amounts of water (i.e., 1%–99%). Detailed experiments

were performed using the ionic liquid BMImBF₄. The variation of the pH value versus the ionic liquid concentration is shown in Figure 3. The pH value changed remarkably when its content was lower than 10%, and then a platform appeared at

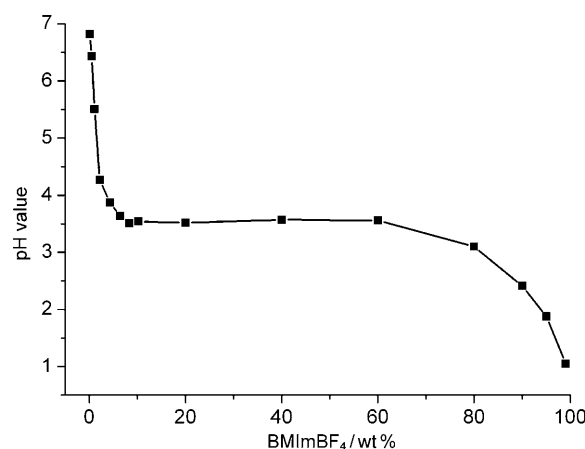


Figure 3. Variation of pH values with the concentration of BMImBF₄ in water.

10–80 wt %. Surprisingly, the acidity of the ionic liquid solution again decreased dramatically when its content was higher than 80 wt %. The pH value of samples that contained 99 wt % ionic liquid (1 wt % water in the ionic liquid) sharply decreased to 1.05(0.43). Although this result is not as accurate as the samples contain more water, it does suggest the formation of a strong acid environment in the air- and water-stable ionic liquid. Under real reaction conditions, the presence of water completely can never be completely excluded, and thus all the reactions performed in ionic liquids with BF₄[−] anions progress in a strongly acidic environment. This phenomenon was also observed for ionic liquids BPyBF₄ and BMImPF₆. The pH value of these two ionic liquids containing 1 wt % H₂O decreased to 4.34 and 1.40. However, the pH value of an ionic liquid containing stable ClO₄[−] anion was the same as the corresponding 0.1 M aqueous solution (i.e., 6.38).

A similar phenomenon was observed when using acetic acid instead of the ionic liquid BMImBF₄ (Figure 4). Although not as obvious as the system with BMImBF₄, the two turning points also appeared with 10 wt % and 80 wt % acetic acid. However, the pH value was < 0 when the acetic acid concentration was > 90% and was not detectable by the pH meter. Therefore, the acidity of acetic acid above 90% was not measured. These results indicate that the ionic liquid BMImBF₄ behaves similarly to a weak acid in water.

However, it is also possible that this critical point appears due to the inability of the pH meter to operate in highly concentrated ionic liquid–water systems. Therefore, a simple but effective method is the use of a pH indicator to check the changes in acidity of the ionic liquid–water mixture. Here, thymol blue was chosen because of its suitable pH transition interval (pH 1.2–2.8, pK_a = 1.65).^[6] A color transition point was observed at exactly > 80 wt % ionic liquid (Figure 5).

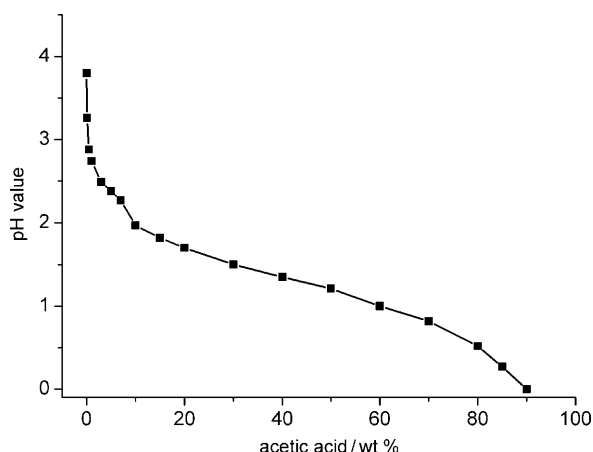


Figure 4. Variation of pH values with the concentration of acetic acid in water.

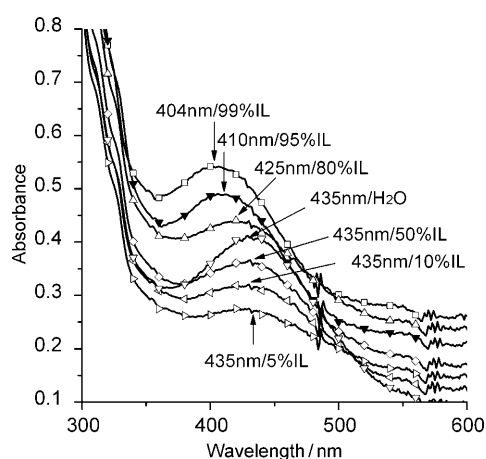
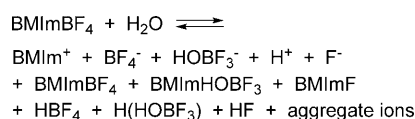


Figure 5. UV/Vis absorbance of thymol blue-BMImBF₄-H₂O.

The main absorption peak of thymol blue is at approximately 435 nm in pure water and BMImBF₄/water solutions with up to 80 wt% ionic liquid. If the BMImBF₄ concentration is above 80 wt%, an obvious blue-shift of the UV absorbance is observed. The absorption wavelength for an BMImBF₄ ionic liquid containing 1 wt% water shifted to 404 nm. This trend agrees with the results obtained by using the pH meter. It strongly indicates the existence of an exact critical point in the pH value/hydrogen ion activity.

The acidity of the ionic liquids with BF₄⁻ should be due to the hydrolysis of the anion, which can be hydrolyzed into H⁺ and HOBF₃⁻ (Scheme 1).^[7] Other species produced through deep hydrolysis are less prevalent; HOBF₃⁻ is the dominating species.^[7a] The presence of species such as BMIm⁺, BF₄⁻,



Scheme 1. Possible species in BMImBF₄-H₂O.

HOBF₃⁻, F⁻, BMImBF₄, BMImHOBF₃, BMImF, HBF₄, H(HOBF₃), and HF provides a buffer function for the ionic liquid-water system.

Based on the results discussed above, a reconsideration of the effect of these ionic liquids on catalytic reactions is necessary. Three typical acid-catalyzed reactions were chosen as model reactions to compare the catalytic activity of some typical ionic liquids. The first reaction is the acetalization reaction of *p*-chloride-benzaldehyde and propylene glycol (Table 1).^[8]

Table 1. Acetalization of *p*-chloride-benzaldehyde and propylene glycol catalyzed by ionic liquids.

Entry	Ionic liquid	Conv. ^[b] [%]	Sel. ^[c] [%]
1	OHEMImBF ₄	> 99	> 99
2	BMImBF ₄	95	> 99
3	BMImPF ₆	9	> 99
4	BMImCl	5	> 99

[a] Reaction conditions: *p*-chloride-benzaldehyde (2 mmol, 280 mg), propylene glycol (10 mmol, 760 mg), ionic liquid (1 mL), 40 mL pressure tube (Sigma-Aldrich), 50 °C, 4 h, Ar. [b] Conversion of *p*-chloride-benzaldehyde, obtained by GC-MS analysis. [c] Selectivity to 2-phenyl-1,3-dioxane, obtained by GC-MS analysis.

The results are in complete agreement with the acidity order of the ionic liquids. For the acidic ionic liquids (OHE)MImBF₄ and BMImBF₄ the conversions were 99% and 95%, respectively, with 99% selectivity. When the ionic liquids BMImPF₆ and BMImCl were applied, the conversions were < 10%.

Another acid-catalyzed reaction, the etherization of benzyl alcohol and *tert*-butyl alcohol,^[9] was performed (Table 2). The conversion with ionic liquid OHEMImBF₄ was 60%, with 95% selectivity. When the reaction was carried out in the ionic liquid BMImBF₄, the conversion was 23% and the selectivity was > 99%. When the reaction was performed in the ionic liquid BMImPF₆, no desired product was detected, and the benzyl alcohol was completely converted into dibenzyl ether and the *tert*-butyl alcohol was converted into olefins of varied

Table 2. Etherization of benzyl alcohol and *tert*-butyl alcohol.^[a]

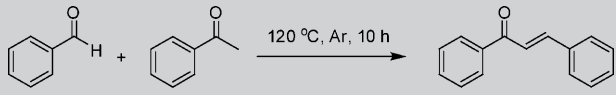
Entry	Ionic liquid	Conv. ^[b] [%]	Sel. ^[c] [%]
1	OHEMImBF ₄	60	95
2	BMImBF ₄	23	> 99
3	BMImPF ₆	> 99	0
4	BMImCl	0	0

[a] Reaction conditions: benzyl alcohol (2 mmol, 216 mg), *tert*-butyl alcohol (10 mmol, 740 mg), ionic liquid (1 mL), 40 mL pressure tube (Sigma-Aldrich), 120 °C, 10 h, Ar. [b] Conversion of benzyl alcohol, obtained by GC-MS. [c] Selectivity to benzyl *tert*-butyl ether, obtained by GC-MS.

structure. No reaction occurred in the presence of BMImCl. The peculiar activity of the ionic liquid BMImPF₆ is due to the instability of PF₆⁻ at elevated temperature. After the reaction, a hydrofluoric acid mist was observed and the pH value of the reaction system was 0.72 with the addition of 5 mL water. The reaction performed in the ionic liquid BMImPF₆ was really catalyzed by hydrofluoric acid, emitted by the hydrolysis of BMImPF₆. For the ionic liquid BMImBF₄, the pH value of the reaction mixture was 2.12 when the same method as with BMImPF₆ was used, which was not far from the acidity measured at room temperature (i.e., 3.51). These results suggest that an ionic liquid with BF₄⁻ is stable enough at 120 °C. More importantly, the acidity exhibited by BMImBF₄ could be regarded as one of the properties of an ionic liquid with BF₄⁻ anion, which is a balanced and stable system.

The condensation of benzaldehyde and acetophenone to chalcone^[10] was also used as a test reaction with the same ionic liquids (Table 3). All of the ionic liquids behaved similarly as in the etherization reaction. The conversions with ionic liq-

Table 3. Condensation reaction between benzaldehyde and acetophenone.^[a]

			
Entry	Ionic liquid	Conv. ^[b] [%]	Sel. ^[c] [%]
1	OHEMImBF ₄	> 99	> 99
2	BMImBF ₄	95	> 99
3	BMImPF ₆	> 99	> 99
4	BMImCl	0	0

[a] Reaction conditions: acetophenone (2 mmol, 240 mg), benzaldehyde (10 mmol, 1060 mg), ionic liquid (1 mL), 40 mL pressure tube (Sigma-Aldrich), 120 °C, 10 h, Ar. [b] Conversion of acetophenone, obtained by GC-MS. [c] Selectivity to chalcone, obtained by GC-MS.

uids containing BF₄⁻ anion were >99% and 95%, with >99% selectivity, but no conversion was detected when using BMImCl. When using BMImPF₆ the conversion and selectivity were also >99%, but it is difficult to define this as a BMImPF₆-catalyzed reaction because of the decomposition into hydrofluoric acid, as discussed earlier in the etherization reaction.

In conclusion, the acidity of some air- and moisture-stable ionic liquids was explored and a preliminary study of its effect on catalytic reactions was performed. Ionic liquids with BF₄⁻ as anion can be defined as a system that behaves as a weak acid and maintains stability up to 120 °C involving water. Ionic liquids with PF₆⁻ as anion are more stable than an IL containing BF₄⁻ anions at room temperature, but decompose remarkably at 120 °C. The activity of these ionic liquids in some traditional acid-catalyzed reactions is also in good agreement with the acidity order obtained in this work. Therefore, the influence of air- and moisture-stable ionic liquids on catalytic reactions, and also on their applications in other fields, should be reconsidered.

Experimental Section

General Information: All ionic liquids used were synthesized in our laboratory or purchased from Sigma-Aldrich or Merck. The ¹H NMR purity of all ionic liquids was >99%. All the ionic liquids were treated under vacuum at 80 °C for 8 h before use. The halide (Cl⁻ or Br⁻) contents of the ionic liquids were all <500 ppm, measured by Mettler Toledo Seven Multi instrument, except BMImH₂PO₄ (1.5 wt%). The water contents were measured by Karl Fischer coulometer (Metro 831 KF coulometer). Normally, the water content was <300 ppm, but <700 ppm was measured for hydroxyl-functionalized ionic liquids, 27819 ppm for BMImHSO₄, and 2282 ppm for BMImH₂PO₄. The pH value was measured with a pHS-25 pH meter (ShangHai Precision & Scientific Instrument). The pH meter was calibrated by a standard buffer solution with pH value 4.00 before use. UV/Vis measurements were performed with an Agilent 8453 instrument. The catalytic reactions were analyzed by GC-MS (6890–5973).

General procedure for the measurement of pH values of ionic liquid–water: Ionic liquid (2 mmol) and distilled water (20 mL) were added to a glass vessel (30 mL). After being shaken for 2 min and placed for 30 min, the pH value of the aqueous phase was measured. All the measurements were repeated three times and the average pH value and standard deviation were given.

General procedure for pH value measurement of BMImBF₄ or AcOH/H₂O with varied concentrations: For the pH value of BMImBF₄–H₂O, a series of samples including 0.1 wt%, 0.5 wt%, 1.0 wt%, 2.0 wt%, 8.0 wt%, 10 wt%, 15 wt%, 95 wt%, and 99 wt% BMImBF₄ were prepared and measured in triplicate. For other points, the pH was measured continuously by the addition of different amounts of water into 15 wt% sample. The operation was also performed in triplicate. A similar operation was performed for the pH value measurement of AcOH/H₂O solution. However, a suitable amount of acetic acid was added into water for the continuous measurement of samples containing 15–90 wt% acetic acid because the pH value of AcOH–H₂O solution was <0 when the concentration of acetic acid was >90 wt%, which could not be measured by the pH meter.

General procedure for the acetalization of *p*-chloride-benzaldehyde and propylene glycol: *p*-Chloride-benzaldehyde (2 mmol, 280 mg), propylene glycol (10 mmol, 760 mg), and ionic liquid (1 mL) were added into a 40 mL pressure tube, which was flushed with Ar for 5 min after which time the reaction was performed at 50 °C for 4 h under magnetic stirring.

General procedure for the etherization of benzyl alcohol and *tert*-butyl alcohol: benzyl alcohol (2 mmol, 216 mg), *tert*-butyl alcohol (10 mmol, 740 mg), and ionic liquid (1 mL) were added to a 40 mL pressure tube, which was flushed with Ar for 5 min and reacted at 120 °C for 10 h under magnetic stirring.

General procedure for the condensation reaction between benzaldehyde and acetophenone: Acetophenone (2 mmol, 240 mg), benzaldehyde (10 mmol, 1060 mg), and ionic liquid (1 mL) were added to a 40 mL pressure tube, which was flushed with Ar for 5 min and reacted at 120 °C for 10 h under magnetic stirring.

Acknowledgements

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Keywords: anions • acidity • catalysis • cations • ionic liquids

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