Determination of the Lewis acidity of ionic liquids by means of an IR spectroscopic probe

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Pyridine and ethanenitrile can be used as molecular probes to measure the Lewis acidities of ionic liquids by monitoring the shift of IR absorption bands near 1450 cm^{-1} for pyridine and in the range 2250–2340 cm^{-1} for ethanenitrile.

Applications of acidic room temperature ionic liquids (ILs) as replacements for traditional liquid acids such as H_2SO_4 and HF have received significant attention.[1–5] While much work has focused on commercial applications, fundamental studies of the acidity–activity relationship in comparison with conventional liquid and solid acids are still rare. In fact, a well-established procedure for determination of the acidities of ILs has not yet been developed.

The most common so-called acidic ILs are composed of metal halides and quaternary nitrogen or phosphorus-containing halide salts with the apparent mole fraction of metal halides (MCl_x), x, greater than the stoichiometric neutral point. The "acidity" here refers not to Lewis acidity (as is frequently assumed), but to the acidity of an anionotropic solvent system, in which a base is a substance that liberates a characteristic anion (*e.g.* Cl^-), while an acid consumes it.[6–8] Further quantification of the acidity is defined in terms of $-\log_{10}[Cl^-]$ of ILs.[6] NMR spectroscopy ([27]Al, ^{31}P and ^{1}H) has been used to determine the form and the fraction of the anionic species,[8,9] while other techniques, for example, UV and IR spectroscopy and electrochemical methods have been used to monitor the interaction between donors and anionic species.[7,8,10,11] Unfortunately, all of these techniques suffer from disadvantages such as strong medium-specificity, little available reference information and/or difficulties in manipulation. In this communication, we demonstrate that similar to the case of solid acids, information from IR spectroscopy in the 1400–1700 cm^{-1} region for pyridine and the 2200–2400 cm^{-1} region for ethanenitrile allows the Lewis and/or Brønsted character of acidic ILs to be distinguished and the strength of Lewis acidity to be estimated. This method is easy to use and widely applicable to both liquid and solid acids, and hence allows a comprehensive comparison of different acidic systems to be performed.[†]

Pyridine has been widely used as a probe molecule for determination of the Lewis and Brønsted acidities of solid acids by monitoring the bands in the range of 1400–1700 cm^{-1} arising from its ring vibration modes.[12] The presence of a band near 1450 cm^{-1} is indicative of pyridine coordinated to Lewis acid sites, whilst a band near 1540 cm^{-1} is an indication of the formation of pyridinium ions resulting from the presence of Brønsted acidic sites. In this work pyridine was added to ionic liquids based on the [bmim][+] cation (Fig. 1). Neat pyridine (Fig. 2A (a)) shows a well-resolved single band at 1437 cm^{-1} which is essentially unchanged in the presence of the neutral IL [bmim][BF$_4$] (Fig. 2A (b)). In the presence of the Lewis acid [bmim]Cl/ZnCl$_2$ (x = 0.67), the band shifts to 1450 cm^{-1}, consistent with the coordination of pyridine at Lewis acid sites (Fig. 2A (c)). When pyridine is mixed with the acidic IL [bmim]Cl/AlCl$_3$ (x = 0.67), a similar band at 1454 cm^{-1} is observed (Fig. 2A (d)), confirming the presence of Lewis acidity,
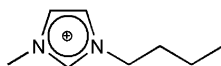
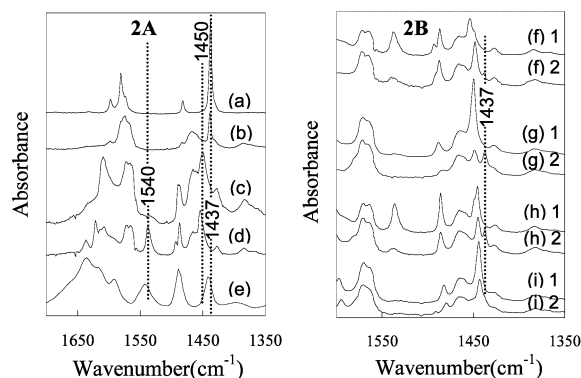**Fig. 1** Structure of the [bmim][+] cation of ionic liquids.

Fig. 2 A FT-IR spectra of (a) pure pyridine; (b) pyridine + [bmim][BF$_4$] (1:5 by vol.); (c) pyridine + [bmim]Cl/ZnCl$_2$ (x = 0.67) (1:5 by vol.); (d) pyridine + [bmim]Cl/AlCl$_3$ (x = 0.67) (1:5 by vol.); (e) pyridine + HCl solution (36 wt%). Bands at 1437 cm^{-1} in (a) and the neutral ionic liquid (b) arise from free pyridine whilst bands near 1450 cm^{-1} in (c) and (d) result from pyridine coordinated at Lewis acid sites. Bands near 1540 cm^{-1} in (d) and (e) indicate the presence of pyridinium cations formed by protonation at Brønsted acid sites. **B** FT-IR spectra of mixtures (1:5 by vol.) of pyridine + [bmim]Cl/MCl$_x$. (f) [bmim]Cl/AlCl$_3$, **1** x = 0.67, **2** x = 0.5; (g) [bmim]Cl/ZnCl$_2$, **1** x = 0.67, **2** x = 0.33; (h) [bmim]Cl/FeCl$_3$, **1** x = 0.67, **2** x = 0.5; (i) [bmim]Cl/CuCl, **1** x = 0.67, **2** x = 0.5.

but in addition another band is observed at approximately 1540 cm^{-1}, suggesting that Brønsted acid sites are also present. Traces of water may give rise to protonic species in ILs, which are highly acidic.[5] A similar band near 1540 cm^{-1}, is observed in the solution spectrum of pyridine-HCl (Fig. 2A (e)), confirming that this band does indeed result from the presence of pyridinium cations.[‡]

It can be seen in Fig. 2B that after pyridine (py:IL = 1:5 by volume) is added to ILs of the type [bmim]Cl/MCl$_x$ (with the apparent mole fraction of MCl$_x$, x, of 0.67 in each case), the wavenumber of the band corresponding to coordination at Lewis acid sites increases from 1444 cm^{-1} for [bmim]Cl/CuCl to 1446 cm^{-1} for [bmim]Cl/FeCl$_3$, 1450 cm^{-1} for [bmim]Cl/ZnCl$_2$ and 1454 cm^{-1} for [bmim]Cl/AlCl$_3$, indicating that the Lewis acidity increases in the order CuCl < FeCl$_3$ < ZnCl$_2$ < AlCl$_3$ when x = 0.67, at which point ILs have strong Lewis acidities. When x = 0.5, [bmim]Cl/MCl$_x$ (M ≠ Zn) are stoichiometrically neutral. For [bmim]Cl/ZnCl$_2$ this value is x = 0.33. At the neutral point, a free pyridine band at 1437 cm^{-1} is generally observed for each sample. The wavenumber and the intensity (relative to the band at 1437 cm^{-1}) change from 1443 (m) cm^{-1} for [bmim]Cl/CuCl, to 1445 (m) cm^{-1} for [bmim]Cl/FeCl$_3$, 1448 (m) cm^{-1} for [bmim]Cl/ZnCl$_2$ and 1448 (s) cm^{-1} for [bmim]Cl/AlCl$_3$, indicating the same order as that observed when x = 0.67 (intensities in parentheses: m = medium, s = strong). Although these variations are small, they are reproducible and we believe they are significant.

Table 1 shows the position of the band near 1450 cm^{-1}, arising from pyridine coordinated at Lewis acid sites, as a function of apparent mole fraction x in [bmim]Cl/AlCl$_3$. The acidity of an IL is determined by the nature of its anionic species,[4] so it is not surprising to see that the band at 1450 cm^{-1} remains unchanged when x increases from 0.4 to 0.55. However, it suddenly shifts to 1454 cm^{-1} with a shoulder at 1449 cm^{-1} when x increases from 0.6

Table 1 The IR bands of probes in [bmim]Cl/AlCl$_3$ with different compositions

Mole fraction of AlCl$_3$ (x)	Predominant anionic species	Pyridine[a] (cm^{-1})	Ethanenitrile[b] (cm^{-1})
$x = 0.4$	Cl$^-$, [AlCl$_4$]$^-$	1448	
$x = 0.5$	[AlCl$_4$]$^-$	1448	
$x = 0.55$	[AlCl$_4$]$^-$, [Al$_2$Cl$_7$]$^-$	1448	2333
$x = 0.6$	[AlCl$_4$]$^-$, [Al$_2$Cl$_7$]$^-$	1449	2335
$x = 0.67$	[Al$_2$Cl$_7$]$^-$	1454	2338

[a] Pyridine/ILs = 1:5, by volume. [b] ethanenitrile/ILs = 1:5, by volume.

to 0.67, at which point [Al$_2$Cl$_7$]$^-$ anions become predominant, implying that the pyridine molecular probe can differentiate between [AlCl$_4$]$^-$ and [Al$_2$Cl$_7$]$^-$ by coordination at the different acidic sites.

We have also used ethanenitrile, a weaker Lewis base than pyridine, to measure the Lewis acidities of ILs. Pure ethanenitrile shows two characteristic bands at 2292 and 2252 cm^{-1}, originating from its CN stretching vibrations. It can be seen from Fig. 3A (a)–(c) that these are essentially unchanged when ethanenitrile is added to either HCl or [bmim][BF$_4$] which have no Lewis acidity. However, the addition of ethanenitrile to [bmim]Cl/MCl$_x$ ($x = 0.67$) (Fig. 3A (d)–(g)) results in the appearance of a new band at higher wavenumber occurring at 2292 cm^{-1} for [bmim]Cl/CuCl, 2310 cm^{-1} for [bmim]Cl/FeCl$_3$, 2318 cm^{-1} for [bmim]Cl/ZnCl$_2$, and 2338 cm^{-1} for [bmim]Cl/AlCl$_3$, showing that the Lewis acidity increases in the order CuCl < FeCl$_3$ < ZnCl$_2$ < AlCl$_3$. This is the same order as that determined using pyridine. Furthermore, as shown in Fig. 3B, for [bimim]Cl/AlCl$_3$ with different apparent mole fractions, when $x \leqslant 0.5$, the band around 2330 cm^{-1} is absent. When $x > 0.5$, a monotonic blue shift of this band is observed with increasing value of x (see Table 1), corresponding to an increase in Lewis acid strength. These results are in complete agreement with those obtained using pyridine.
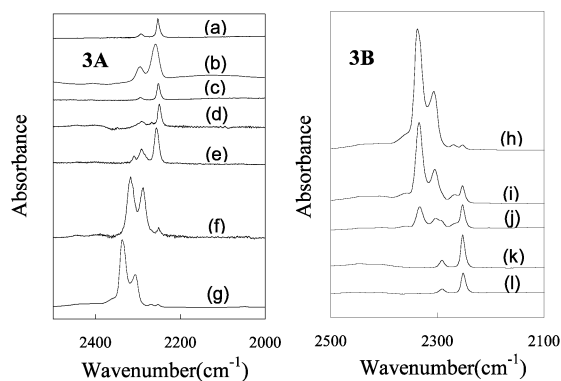
In conclusion, we have described a novel and efficient way to characterize the acidity of ionic liquids. By using pyridine and ethanenitrile as IR probe molecules, consistent results can be obtained both for testifying to the presence of Lewis acidity and for the estimation of Lewis acidic strength. Brønsted acidity, if it exists, can be simultaneously demonstrated. The resulting information about the acidic properties can be expected to shed further light on our understanding of the role of ILs in catalytic reactions. Meanwhile, considering its relatively simple nature, the method has the potential for wide application in the characterization of acidic ILs.

Notes and references

† During the course of this work, a method for the determination of Brønsted acidity in ionic liquids was reported.[13] Our method is complementary in that it provides a way of measuring the Lewis acidity.
‡ The pyridine used was dried with KOH and distilled over 5Å molecular sieves and solid KOH. Ethanenitrile was refluxed over and distilled from P$_2$O$_5$. Commercial AlCl$_3$ was mixed with Al turnings and 1 wt% NaCl and sublimed under 50 mmHg nitrogen, at least twice, until no ash-like residue was left. [bmim]Cl was dried under vacuum at 90 °C. [bmim]Cl/AlCl$_3$ was prepared by slowly mixing weighed amounts of [bmim]Cl with re-sublimed AlCl$_3$ in a glove bag under nitrogen using dry ice for cooling. ZnCl$_2$, CuCl, FeCl$_3$ were used as received. All IR samples were prepared by mixing probe liquids and ILs in a given volume ratio, and then spreading into liquid films on CaF$_2$ windows. The spectra were recorded on a Bruker Vector 22 Fourier transform infrared spectrophotometer at room temperature and repeatedly confirmed by a Nicolet Magna-IR 750 spectrometer with a resolution of 0.5 cm^{-1}.

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Fig. 3 A FT-IR spectra of (a) pure ethanenitrile; (b) ethanenitrile + HCl solution (36 wt%); (c) ethanenitrile + [bmim][BF$_4$] (1:5 by vol.); (d) ethanenitrile + [bmim]Cl/CuCl ($x = 0.67$) (1:5 by vol.); (e) ethanenitrile + [bmim]Cl/FeCl$_3$ ($x = 0.67$) (1:5 by vol.); (f) ethanenitrile + [bmim]Cl/ZnCl$_2$ ($x = 0.67$) (1:5 by vol.); (g) ethanenitrile + [bmim]Cl/AlCl$_3$ ($x = 0.67$) (1:5 by vol.). **B** FT-IR spectra of ethanenitrile + [bmim]Cl/AlCl$_3$ (1:5 by vol.): (h) $x = 0.67$; (i) $x = 0.6$; (j) $x = 0.55$; (k) $x = 0.5$; (l) $x = 0.4$. The appearance of a third band at high frequency in (d)–(g) and (h)–(l) is indicative of the presence of Lewis acid sites. The position of this band shifts to higher frequency with increasing Lewis acid strength.