Evidence for Hydrogen Bonding in Solutions of 1-Ethyl-3-methylimidazolium Halides, and its Implications for Room-temperature Halogenoaluminate(III) Ionic Liquids

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Multinuclear NMR spectroscopy and conductivity measurements showed that the 1-ethyl-3-methylimidazolium cation, [emim]$^+$, not only forms strong hydrogen bonds (using all three ring protons H^2, H^4 and H^5) with halide ions in polar molecular solvents (*e.g.* ethanenitrile) and ionic liquids, but that it exists in a quasi-molecular state, [emim]X, in non-polar solvents (*e.g.* trichloro- and dichloromethane), showing a conventional aromatic stacking phenomenon.

Over the past ten years the perception of the ability of the 1-ethyl-3-methylimidazolium cation, [emim]$^+$,[1,2] to enter into hydrogen bonds with halide ions has developed from not possible,[3] through controversial,[4] to widely accepted.[5,6] However, the strongest evidence for these claims has always rested upon solid-state X-ray crystallographic determinations of the structures of both [emim]$^+$ [4,7] and [edmim]$^+$ (edmim = 1-ethyl-2,3-dimethylimidazolium) salts.[8] A number of first-class solution studies have been reported,[5,6,9] yet no incontrovertible evidence has yet been presented that the [emim]$^+$ cation is capable of forming hydrogen bonds in solution. Proton NMR spectra of room-temperature [emim]Cl–$AlCl_3$ ionic liquids are known to be very composition dependent, particularly in the basic regime.[3,10] In particular, the H^2 proton is very sensitive, moving significantly upfield with increasing acidity. This has been widely interpreted in terms of a stacked oligomeric model[3,5] in which anions and cations alternate, the anions being associated with the imidazolium ring both directly above and below its plane. Nevertheless, a ^{1}H NMR study[11] of several imidazole and imidazolium derivatives in CD_2Cl_2 has shown that the chemical shift of the H^2 proton was sensitive to the nature of the anion present, and hydrogen bonding between discrete ion pairs was postulated to explain this result. We thus decided to undertake a definitive study of the NMR characteristics of [emim]X (X = Cl, Br or I) in molecular solvents, free of the aporia associated with ionic liquids. We demonstrate here, using principally the techniques of multinuclear NMR spectroscopy and conductivity measurements, that [emim]$^+$ not only forms strong hydrogen bonds (using all three ring protons H^2, H^4 and H^5) with halide ions in polar molecular solvents (*e.g.* ethanenitrile, MeCN) and ionic liquids, but that it exists in a quasi-molecular state, [emim]X, in non-polar solvents (*e.g.* $CHCl_3$ and CH_2Cl_2), showing a conventional aromatic stacking phenomenon.

Experimental

NMR Studies.—Deuterium oxide (99%) was distilled *in vacuo* before use; CD_3CN and CD_2Cl_2 were distilled from calcium hydride under dry dinitrogen. Samples of [emim]X (X = Cl, Br or I) were weighed and solutions of them in CD_3CN and CD_2Cl_2 were prepared in a glove-box through which dry dinitrogen was passed. The preparation of the ionic liquids was as previously described.[12]

Proton and ^{13}C NMR spectra were recorded using tetramethylsilane as the external reference, at 360.13 and 90.55 MHz, respectively, ^{35}Cl NMR spectra using 2 mol dm^{-3} aqueous KCl as a reference at 35.29 MHz and ^{127}I NMR spectra using 2 mol dm^{-3} aqueous KI as the reference at 72.08 MHz. All NMR spectra were recorded at 303 K.

Conductance Measurements.—Solution preparation. Conductivity water was obtained from the Centre for Medical Research (University of Sussex); it had been purified by reverse osmosis in a Millipore Milli RO 60 system followed by passage through a Millipore Milli Q Super C system (consisting of two ion-exchange cartridges and an Organex-Q cartridge). It was used without further purification.

Aqueous solutions were prepared by weighing samples of [emim]Cl into volumetric flasks in a Faircrest glove-box with an atmosphere of dry dinitrogen, removing the sample from the box, and adding water. Only 'A'-grade volumetric flasks were used.

Ethanenitrile and dichloromethane were twice distilled from calcium hydride under an atmosphere of dry dinitrogen. The distillate was transferred to a Faircrest glove-box, through which dry dinitrogen was passed. Solutions were prepared inside this glove-box.

Calibration and background conductivities of solvents. All conductivity measurements were made at 25 °C, with continuous stirring of the solution, using a Philips PW9506 digital conductivity meter. The cell, fitted with platinum electrodes, was calibrated using aqueous 10^{-3} mol dm^{-3} KCl solutions. Background conductivities were measured for all solvents (H_2O, 1.8; MeCN, 2.0; CH_2Cl_2, 1.4 μS cm^{-1}).

Synthesis of 1-*Ethyl*-3-*methylimidazolium Halides.*—The 1-ethyl-3-methylimidazolium halides [emim]X (X = Cl, Br or I) are white, crystalline solids at room temperature. The iodide was first prepared by the addition of iodoethane to a solution of 1-methylimidazole in dry ethanenitrile.[13] Preparation of the salts by the addition of the appropriate halogenoethane to a solution of 1-methylimidazole in dry benzene has been reported.[14] However, although the bromide and iodide salts were successfully isolated as solids, [emim]Cl was originally reported as a liquid.[14]

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The salt [emim]Cl was successfully prepared as a solid by the reaction of 1-methylimidazole with chloroethane in a pressure vessel at 70 °C.[2] Subsequently, both [emim]Br[15] and [emim]I[4] have been prepared by direct combination of the halogenoethane and 1-methylimidazole. The crude products from these preparations were recrystallised from solution in ethanenitrile by the addition of ethyl ethanoate.

The principal difference between the previous successful preparations[2,14] of the [emim]X (X = Cl, Br or I) salts and those reported here is the method of recrystallisation. Ethyl ethanoate was used as a co-solvent in the recrystallisation to ensure that all of the unreacted 1-methylimidazole was removed from the product. However, removal of ethyl ethanoate from the product proved to be difficult, and leads to the formation of discoloured ionic liquids. Therefore, the final recrystallisation was from ethanenitrile alone.

Chloride. 1-Methylimidazole (20 cm^3, 0.36 mol) was distilled *in vacuo* from potassium hydroxide (1 g) directly into a dry pressure vessel fitted with a Rotaflo greaseless tap and a B19 Quickfit ground-glass socket. Chloroethane (70 cm^3, 0.43 mol) was added by distillation *in vacuo* from phosphorus(v) oxide (1 g) while the pressure vessel was maintained at −78 °C. The pressure vessel was then sealed, transferred to a vacuum line and further evacuated whilst being maintained at −196 °C for 1 h. It was then sealed, placed inside a steel bomb, and heated in an electric furnace at 76 °C for 72 h. After this time two immiscible layers had formed; when cooled to −13 °C a white precipitate formed. The pressure vessel was opened in a fume cupboard, and the excess of chloroethane allowed to evaporate through a drying tube containing calcium chloride. When the evaporation was nearly complete the solid was dissolved in dry, hot ethanenitrile (50 cm^3) and the mixture filtered using standard Schlenk techniques. Dry ethyl ethanoate (100 cm^3) was added to the filtrate. The mixture was left overnight at −13 °C and the resulting precipitate isolated by Schlenk filtration. The solid was redissolved in a minimum of ethanenitrile (20 cm^3) and the mixture filtered. The filtrate was cooled at −13 °C for 48 h. The resulting precipitate was isolated by Schlenk filtration, dried *in vacuo* for 36 h and transferred to the dry-box. The yield was 36.5 g (69.2%) (Found: C, 48.70; H, 7.45; N, 18.70. Calc. for $C_6H_{11}ClN_2$: C, 49.15; H, 7.55; N, 19.10%).

Bromide. 1-Methylimidazole (35 cm^3, 0.63 mol) was distilled *in vacuo* from potassium hydroxide (1.5 g) into a round-bottomed flask (250 cm^3) fitted with a side arm. Bromoethane (90 cm^3, 0.69 mol) was added by distillation *in vacuo* from phosphorus(v) oxide (1 g). The mixture was heated under reflux under dry nitrogen for 2 h and left to cool overnight. The resulting white solid was dissolved in hot ethanenitrile (50 cm^3) and the solution was filtered under dry dinitrogen. Dry ethyl ethanoate (100 cm^3) was added to the filtrate and the mixture cooled to −13 °C. The resulting precipitate was isolated by Schlenk filtration and recrystallised from a minimum of ethanenitrile (20 cm^3). The resulting white precipitate was isolated by Schlenk filtration, dried *in vacuo* for 36 h, and transferred to the dry-box. Yield: 69.3 g (57.6%) (Found: C, 38.90; H, 5.70; N, 13.80. Calc. for $C_6H_{11}BrN_2$: C, 37.70; H, 5.80; N, 14.65%).

Iodide. 1-Methylimidazole (25 cm^3, 0.45 mol) was distilled *in vacuo* from potassium hydroxide (1 g) directly into a round-bottomed flask (250 cm^3) fitted with a side arm. Iodoethane (60 cm^3, 0.49 mol) was added by distillation *in vacuo* from phosphorus(v) oxide. Heat was evolved and the solution became pale yellow. The solution was heated under reflux, under dry dinitrogen, for 2 h. After this time two immiscible layers had formed, the upper of which became a yellow solid on cooling to room temperature. The lower layer was removed by Schlenk filtration and the solid was dissolved in dry ethanenitrile (40 cm^3) and then recrystallised by addition of dry ethyl ethanoate (80 cm^3). This recrystallisation procedure was repeated twice before the white precipitate was finally recrystallised from a minimum of hot, dry ethanenitrile (20 cm^3) whilst protecting the product from light. The solid was dried *in vacuo* for 36 h and transferred to the dry-box. Yield: 63.0 g (79.7%)(Found: C, 30.05; H, 4.70; N, 11.20. Calc. for $C_6H_{11}IN_2$: C, 30.25; H, 4.65; N, 11.75%).

Results and Discussion

Proton NMR Spectra of [emim]Cl–$AlCl_3$ *Ionic Liquids.*—The ^1H NMR spectra of the [emim]Cl–$AlCl_3$ ionic liquids are well known,[3,16,17] and clearly demonstrate the dependence of the chemical shifts of the protons H^5, H^4, H^2, CH_2CH_3 and NCH_3 on the composition of the ionic liquid. The implications of this behaviour for interionic interactions in the ionic liquids will be discussed later. However, the unambiguous assignment of the H^5 and H^4 protons has not yet been established.

Using an acidic composition [apparent mole fraction of $AlCl_3$, $X(AlCl_3) = 0.60$] as a typical example, the ^1H NMR signals of H^5, H^4 and H^2 are broadened under the influence of the ring nitrogens; hence, the H^2 signal (δ 7.64) is unresolved in the spectra. An expanded spectrum of the [emim]Cl–$AlCl_3$ ionic liquid shows the H^5 and H^4 signals resolved into two asymmetric triplets (δ 6.70 and 6.66), which result from a doublet of doublets in which the innermost lines coalesce. Close examination of the H^2 signal reveals that it is broad and non-Lorentzian in shape, suggesting that the H^2 proton is coupled with the other ring protons. Upon irradiation of the H^2 proton of [emim]I[13] the H^5 and H^4 signals become doublets, confirming that the H^2 proton is indeed coupled with the other ring protons.

Irradiation of the protons of the *N*-methyl group of an ionic liquid [$X(AlCl_3) = 0.60$] leads to an enhancement of the most downfield signal (H^2) of 3%. Of the signals attributed to the other ring protons (H^5 and H^4), the upfield signal is enhanced by 2% whilst the downfield signal shows only very slight enhancement (< 1%). The nuclear Overhauser effect (NOE) is such that the decoupling of a signal leads to enhancement of signal intensities with those nuclei which are closest (through space) showing the greatest effect.[18] Therefore, the assignments of H^4 to the upfield signal and H^5 to the downfield signal are thus confirmed.

Conductivity of Solutions of [emim]Cl.—The conductivities, κ, of solutions of [emim]Cl in water, ethanenitrile and dichloromethane were measured at 25 °C. Their molar conductivities, Λ_m, were calculated from equation (1), where *c* is the molar concentration.[19] Equation (2) gives a common form of

$$\Lambda_m = K/c \qquad (1)$$

$$\Lambda_m = (\Lambda_m)_0 - \alpha c^{\frac{1}{2}} \qquad (2)$$

the Onsager limiting law, where $(\Lambda_m)_0$ is the limiting molar conductivity and α is the Onsager coefficient, and was used to fit the experimental data by a conventional least-squares linear-regression procedure, as shown in Fig. 1. The limiting conductance of the solutions at infinite dilution and the molar conductance at a concentration of 10^{-3} mol dm^{-3} are presented in Table 1.

Table 1 Limiting and molar conductances of solutions of [emim]Cl

Solvent	$(\Lambda_m)_0$/S cm^2 mol^{-1}	Λ_m*/S cm^2 mol^{-1}
Water	111 ± 4	109 ± 4
MeCN	168 ± 4	164 ± 4
CH_2Cl_2	2.4 ± 0.3	1.6 ± 0.3

* At 10^{-3} mol dm^{-3}.

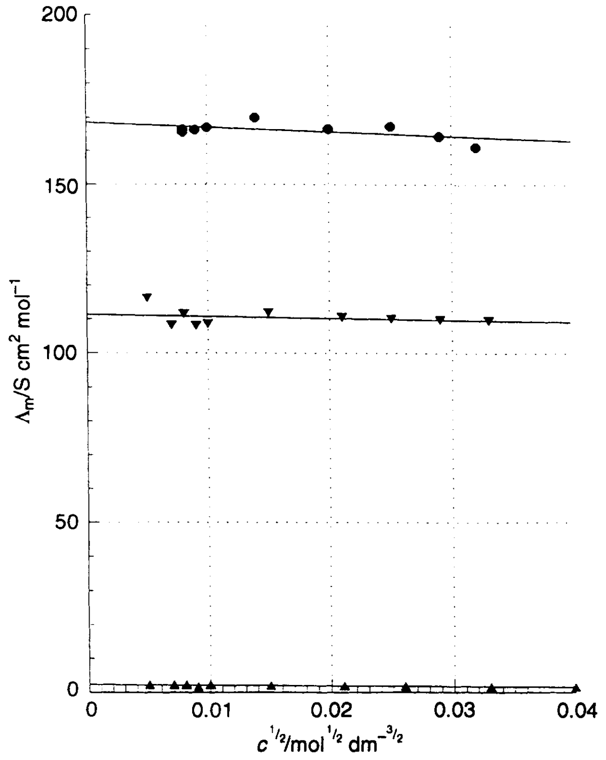

Fig. 1 Molar conductivity of [emim]Cl as a function of $c^{\frac{1}{2}}$ in MeCN (●), water (▼) and CH_2Cl_2 (▲)

The values of $(\Lambda_m)_0$ for solutions of [emim]Cl in water lie within the range found for tetraalkylammonium salts (95–122 S cm^2 mol^{-1}),[19] and unambiguously and unsurprisingly identifying the solution species as a 1:1 electrolyte. The values for solutions in ethanenitrile also lie within the range found for tetraalkylammonium salts (162–196 S cm^2 mol^{-1}),[20,21] again identifying the solution species as a 1:1 electrolyte. The difference in the slope of the plots in Fig. 1 of the conductance of [emim]Cl in water and ethanenitrile [gradient(water)/gradient(MeCN) = 0.39] indicates that cation–anion association is greater in solutions in ethanenitrile than in aqueous solutions. Hence, the solvation of [emim]Cl in ethanenitrile can be described by the equilibrium between the solved ion pair and the solvated unassociated ions, equation (3).

$$([\text{emim}]^+\cdots\text{Cl}^-)_{\text{MeCN}} \rightleftharpoons ([\text{emim}]^+)_{\text{MeCN}} + (\text{Cl}^-)_{\text{MeCN}} \quad (3)$$

Values of $(\Lambda_m)_0$ for tetraalkylammonium salts in dichloromethane could not be found in the literature, and so $(\Lambda_m)_0$ for tetraethylammonium chloride was measured [$(\Lambda_m)_0 = 28 \pm 2$ S cm^2 mol^{-1}; Λ_m (10^{-3} mol dm^{-3}) = 26 ± 2 S cm^2 mol^{-1}]. The value of $(\Lambda_m)_0$ for solutions of [emim]Cl in dichloromethane is significantly lower than that for tetraethylammonium chloride, indicating that the solution species is not a 1:1 electrolyte, but probably contains non-conducting quasi-molecular ion pairs.

Proton and ^{13}C *NMR Spectra of* [emim]X (X = Cl, Br *or* I) *in* 2 mol dm^{-3} *Solution*.—The ^{1}H and ^{13}C NMR spectra of the [emim]X (X = Cl, Br or I) salts were recorded in $CDCl_3$; these spectra show a distinct concentration dependence which will be discussed later. The spectra reported in this section were recorded using 2 mol dm^{-3} solutions of the salts. The ^{1}H and ^{13}C NMR spectra are presented in Tables 2 and 3, respectively. Assignments of these spectra follow those found in the [emim]Cl–$AlCl_3$ ionic liquids, and are in accord with those found in the literature.[3,13,22]

Table 2 Proton NMR spectral data (360.13 MHz; 2 mol dm^{-3}, $CDCl_3$; 303 K) for [emim]X (X = Cl, Br or I)

	X				
Parameter	Cl	Br	$\Delta\delta^{Cl}$*	I	$\Delta\delta^{Cl}$*
$\delta(CH_2CH_3)$	1.39	1.34	0.05	1.30	0.09 triplet
δ(NMe)	3.93	3.88	0.05	3.82	0.09 singlet
$\delta(CH_2CH_3)$	4.24	4.20	0.04	4.13	0.09 quartet
$\delta(H^4)$	7.69	7.61	0.08	7.46	0.23 singlet
$\delta(H^5)$	7.72	7.67	0.05	7.51	0.21 singlet
$\delta(H^2)$	10.20	9.86	0.34	9.56	0.64 singlet
$^3J(CH_2CH_3)$/Hz	7.29	7.22		7.30	
$^3J(CH_2CH_3)$/Hz	7.31	7.20		7.28	

* $\Delta\delta^{Cl} = \delta(\text{Cl}) - \delta(\text{X})$.

Table 3 The ^{13}C-{^{1}H} NMR spectral data (90.55 MHz; 2 mol dm^{-3}, $CDCl_3$; 303 K) for [emim]X (X = Cl, Br or I)

	X				
Parameter	Cl	Br	$\Delta\delta^{Cl}$*	I	$\Delta\delta^{Cl}$*
$\delta(CH_2CH_3)$	15.37	14.76	0.61	14.32	1.05
δ(NMe)	36.26	35.73	0.53	35.72	1.15
$\delta(CH_2CH_3)$	44.93	44.25	0.68	43.92	1.01
$\delta(C^4)$	121.74	121.30	0.44	120.90	0.84
$\delta(C^5)$	123.51	122.90	0.61	122.41	1.10
$\delta(C^2)$	137.38	135.69	1.69	134.56	2.82

* $\Delta\delta^{Cl} = \delta(\text{Cl}) - \delta(\text{X})$.

The imidazolium ring proton H^2 is shifted downfield under the influence of the two nitrogen atoms of the ring. The protons H^5 and H^4 are shifted less under the influence of only one neighbouring nitrogen atom. The spectrum of [emim]I in D_2O[13] shows a broad singlet for the H^2 signal and a multiplet integrating to two protons, attributed to the H^5 and H^4 protons. In addition, irradiation of the H^2 signal results in a simplified multiplet for the H^{5,4} signal, showing that H^2 is coupled to H^5 and H^4, and that H^5 and H^4 are not equivalent. Irradiation of the NMe signal (see above) of a [emim]Cl–$AlCl_3$ ionic liquid shows that the H^4 signal is upfield of that of H^5.

The different values of the chemical shifts for the analogous protons in each of the three salts (as shown by $\Delta\delta^{Cl}$) suggest that there is significant cation–anion interaction in solution in $CDCl_3$. This is most pronounced at the proton H^2, but detectable at H^5 and H^4.

The ^{13}C NMR spectra of the salts (Table 3) show qualitatively similar behaviour to the ^{1}H NMR spectra, although changes are much less pronounced. Chemical shifts particularly indicate the acidity of the C^2 site.

Proton NMR Spectra of Solutions of [emim]X (X = Cl, Br *or* I) *in* CD_3CN.—The ^{1}H NMR chemical shift data for solutions of [emim]X (X = Cl, Br or I) in CD_3CN are presented in Figs. 2 and 3. These data show qualitatively similar behaviour for each halide. It can be seen that, when compared to the ring protons, there is negligible change in the chemical shifts of the methyl and ethyl protons of the cation. The H^2 signal [Fig. 2(*a*)] shows a marked change in chemical shift to higher field as the solution is made more dilute (after a smaller change to lower field at high concentrations). The H^5 [Fig. 2(*b*)] and H^4 signals (not illustrated, but essentially identical to H^5) show a similar but less-pronounced behaviour. This is also true, but to a very much lesser extent, for the CH_2CH_3 and NMe signals [Fig. 3(*a*)]. The signal for the CH_2CH_3 protons [Fig. 3(*b*)], which are the most remote from the imidazolium ring, at higher concentrations moves to lower field as the solutions are made more dilute, then changes very little at low concentrations.

The ^{1}H NMR data show that cation–anion interactions

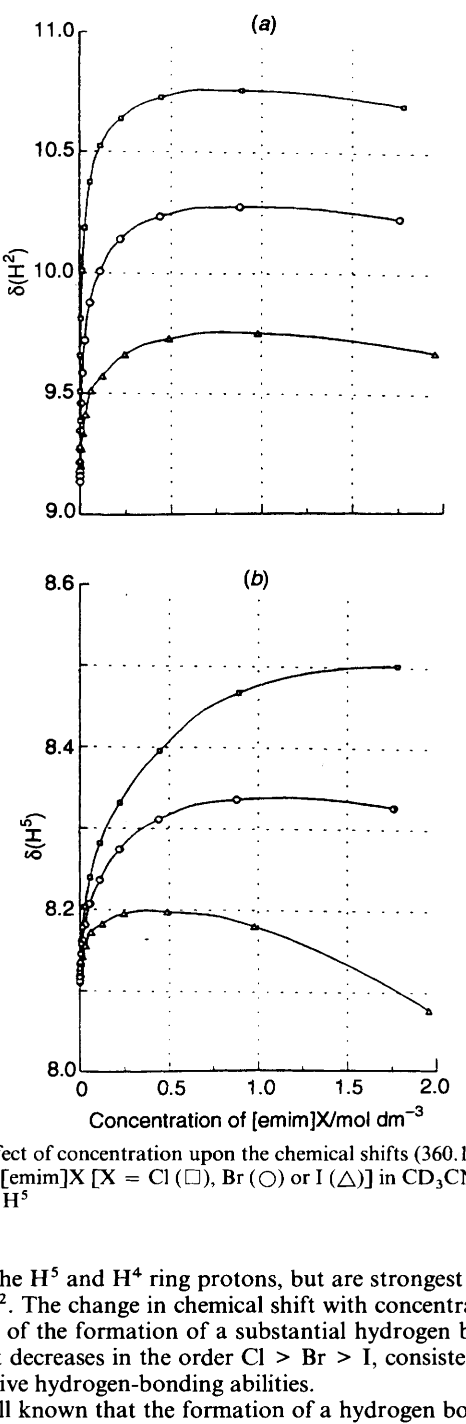

Fig. 2 Effect of concentration upon the chemical shifts (360.13 MHz, 303 K) for [emim]X [X = Cl (□), Br (○) or I (△)] in CD_3CN for (*a*) H^2 and (*b*) H^5

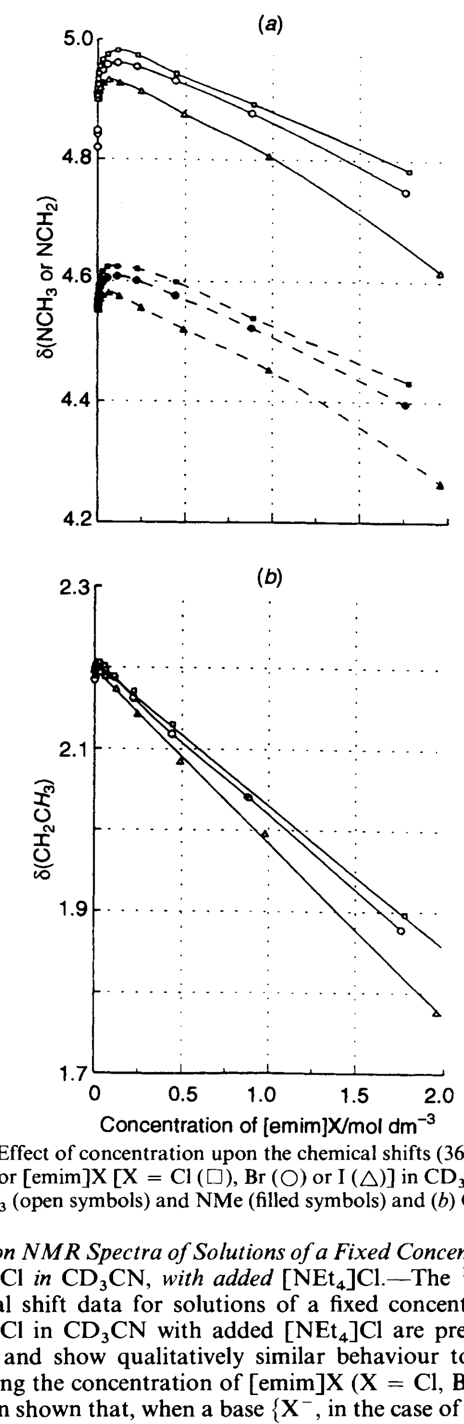

Fig. 3 Effect of concentration upon the chemical shifts (360.13 MHz, 303 K) for [emim]X [X = Cl (□), Br (○) or I (△)] in CD_3CN for (*a*) CH_2CH_3 (open symbols) and NMe (filled symbols) and (*b*) CH_2CH_3

occur at the H^5 and H^4 ring protons, but are strongest for the proton H^2. The change in chemical shift with concentration is indicative of the formation of a substantial hydrogen bond.[23] The effect decreases in the order Cl > Br > I, consistent with their relative hydrogen-bonding abilities.

It is well known that the formation of a hydrogen bond will cause a proton chemical shift to move to lower field.[18] The solution species present may be described by equation (3). Although, at low temperatures, the hydrogen- and non-hydrogen-bonded protons may show separate signals,[24] more usually only one signal is seen. The chemical shift of the signal is the population-weighted mean of the chemical shifts of the hydrogen- and the non-hydrogen-bonded protons.[23] When the cation–anion interaction is weak, as the conductivity data (see above) demonstrate is the case for [emim]Cl in ethanenitrile, equilibrium (3) is very sensitive to changes in solute concentration. As the solution becomes more dilute, the right-hand side is more favoured, the population of the more-shielded proton increases and the signal moves upfield. This is the behaviour observed for the H^2 and, to a lesser extent, for the H^4 and H^5 signals of [emim]X (X = Cl, Br or I) in CD_3CN. The behaviour of the CH_2CH_3 and NMe signals is best attributed to changes in electronic distribution in the cation.

Proton NMR Spectra of Solutions of a Fixed Concentration of [emim]Cl *in* CD_3CN, *with added* $[NEt_4]Cl$.—The ^1H NMR chemical shift data for solutions of a fixed concentration of [emim]Cl in CD_3CN with added $[NEt_4]Cl$ are presented in Fig. 4, and show qualitatively similar behaviour to that on increasing the concentration of [emim]X (X = Cl, Br or I). It has been shown that, when a base {X^-, in the case of [emim]X (X = Cl, Br or I)} is in excess, this behaviour is indicative of hydrogen-bond formation.[25] As the concentration of the Cl^- ion is increased, the population of the more deshielded proton is increased and the signal moves downfield. It is also noted that the range of chemical shifts found is similar to that for the [emim]Cl–$AlCl_3$ ionic liquids (see above).

*Chlorine-*35 *NMR Studies of Solutions of* $[NEt_4]Cl$ *in* CD_3CN.—It has been reported that at low concentrations (< 1 mol dm^{-3}) the ^{35}Cl NMR chemical shifts of solutions of $[NEt_4]Cl$ in water and ethanenitrile show little dependence on the concentration of the salt.[26,27] In order to reaffirm this under our experimental conditions, the ^{35}Cl NMR spectra of solutions of $[NEt_4]Cl$ in CD_3CN have been recorded. This demonstrates [Fig. 5(*a*)] that the effect of concentration, in a given solvent, on the chemical shift of a fully solvated unassociated chloride ion is negligible. The linewidth changes

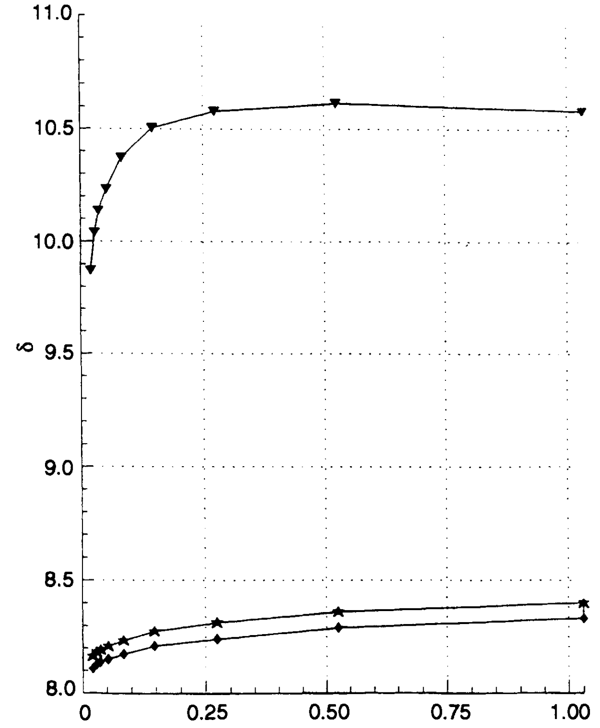

Fig. 4 Proton NMR (360.13 MHz, 303 K) chemical shifts of solutions of a fixed concentration of [emim]Cl in CD_3CN (0.0201 mol dm^{-3}), with added $[NEt_4]Cl$, as a function of the chloride-ion concentration for H^2 (▼), H^5 (★) and H^4 (◆)

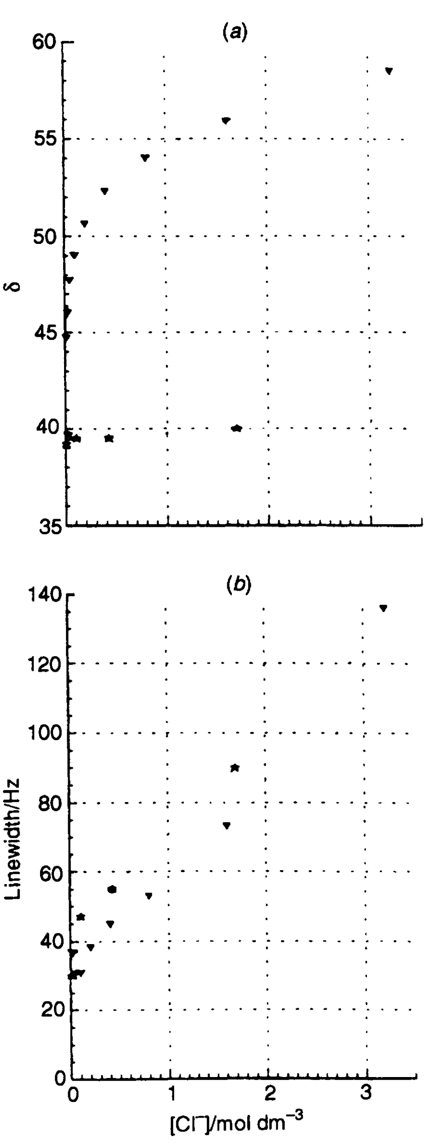

Fig. 5 Effect of concentration on (*a*) the ^{35}Cl chemical shift (35.29 MHz, 303 K) and (*b*) the linewidth for [emim]Cl (▼) or $[NEt_4]Cl$ (★) in CD_3CN

[Fig. 5(*b*)] show that the nuclear relaxation becomes slower as the solution becomes more dilute, as expected.

Chlorine-35 *NMR Spectra of Solutions of* [emim]Cl *in* CD_3CN.—The ^{35}Cl NMR chemical shift data for solutions of [emim]Cl are presented in Fig. 5(*a*). The dissociation of [emim]Cl in CD_3CN is described by equilibrium (3), and dilution of the solution is accompanied by a change in ^{35}Cl chemical shift to higher field, indicating that hydrogen bonds are being broken. Examination of Fig. 5(*a*) also suggests that the chemical shift at infinite dilution will be close to that of $[NEt_4]Cl$. It is well known[28] that the breaking of a hydrogen bond causes ^{35}Cl NMR chemical shifts to move upfield. As the hydrogen bond is broken, the electron density of the chloride ion becomes more located around the ion itself, and so its nucleus becomes more shielded.

The changes in the linewidth of the ^{35}Cl NMR signals [Fig. 5(*b*)] of solutions of [emim]Cl in CD_3CN shadow those of $[NEt_4]Cl$ in CD_3CN; hence it may be deduced that the same mechanisms are involved (*i.e.* viscosity/mobility).[28]

Chlorine-35 *NMR Spectra of Solutions of a Fixed Concentration of* [emim]Cl *in* CD_3CN, *with added* $[NEt_4]Cl$.—The ^{35}Cl NMR chemical shift data for solutions of a fixed concentration of [emim]Cl in CD_3CN, with added $[NEt_4]Cl$, are presented in Fig. 6, and demonstrate a marked downfield change in chemical shift as the concentration of chloride ion is reduced. As chloride ion is added to the solution, equilibrium (3) moves to the left, as indicated by the ^1H NMR results [see Fig. 5(*a*)], increasing the population of the deshielded ^{35}Cl nuclei. However, there is a concomitant increase in the chloride concentration, and so the increase in the population of the more shielded unassociated solvated ion is greater than that of the ion-paired $^{35}Cl^-$ ion. Hence, the ^{35}Cl NMR signal of the solution moves upfield as $[NEt_4]Cl$ is added. The change in the linewidth of the ^{35}Cl signal is again indicative of changes in physical, rather than chemical, phenomena.

Iodine-127 *NMR Spectra of Solutions of* [emim]I *in* CD_3CN.—To ensure that the effect of changing concentration on halogen chemical shifts is not restricted to ^{35}Cl NMR measurements, and to establish that the weaker hydrogen-bond acceptor, I^-, behaves in the same way as Cl^-, the ^{127}I NMR spectra of solutions of [emim]I in CD_3CN were recorded, and are presented in Fig. 7. As with ^{35}Cl NMR chemical shifts, the ^{127}I chemical shifts move to higher field with dilution of the solutions. This behaviour indicates, again, that the equilibrium between a hydrogen-bonded ion pair and unassociated solvated ions is the dominant factor in the dissolution of [emim]X (X = Cl, Br or I) in ethanenitrile (*cf.* ref. 27).

Proton NMR Spectra of Solutions of [emim]X (X = Cl, Br *or* I) *in* CD_2Cl_2.—The ^1H NMR chemical shift data for solutions of [emim]X (X = Cl, Br or I) in CD_2Cl_2 are presented in Fig. 8. The spectra of all three salts show qualitatively similar behaviour, although quantitative differences are seen. The ^1H chemical shifts of the methyl and ethyl protons of the cation show little dependence on the concentration of the solution in CD_2Cl_2. In contrast to the behaviour in CD_3CN, the H^2 proton

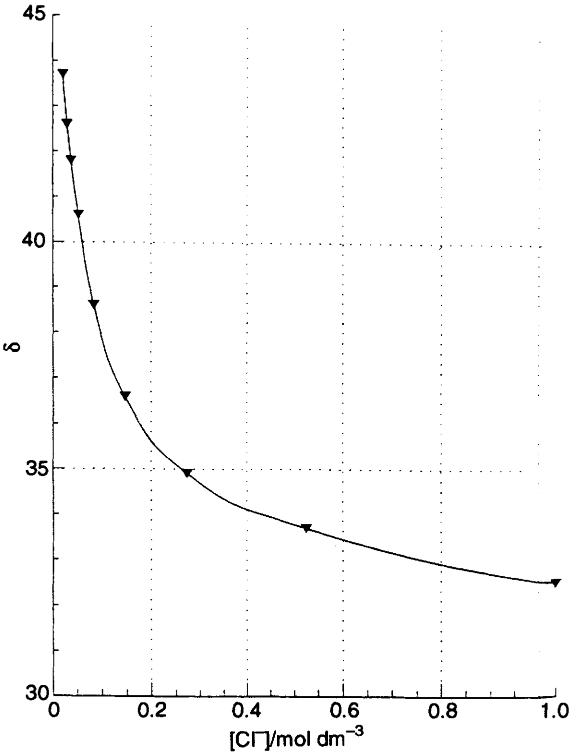

Fig. 6 Chlorine-35 NMR (35.29 MHz, 303 K) chemical shifts of solutions of a fixed concentration of [emim]Cl in CD_3CN (0.0201 mol dm^{-3}), with added $[NEt_4]Cl$, as a function of the chloride-ion concentration

signal moves downfield and the unresolved $H^{4,5}$ proton signal moves upfield as the solution is diluted (Fig. 8). Moreover, the solution is essentially non-conducting (Fig. 1). This suggests a system in which the imidazolium rings are so strongly hydrogen-bonded to the halide ions that they form a quasi-molecular species, [emim]X. These then stack parallel to each other (in the manner of conventional neutral aromatic systems in a low relative permittivity medium) with the H^2 proton inside, and the H^5/H^4 protons outside, the shielding cone of the neighbouring ring (Fig. 9). The existence of such a stacking phenomenon has recently been confirmed in the solid state, as it was observed in the crystal structure of $[edmim]Cl{\cdot}H_2O$.[29]

The evidence for stacking will now be considered in more detail. The effects of magnetic anisotropy of conjugated systems in NMR spectroscopy are well known:[30] the ^1H NMR signal of benzene is significantly downfield of that of ethane. This behaviour has been attributed, classically, to the formation of an electronic ring current in the π orbitals, which produces a secondary magnetic field which opposes the applied magnetic field, so increasing the field outside the ring and deshielding the benzene protons.[31] This is a general effect, and is demonstrated in heterocyclic compounds such as pyridine, although the electronegativity of the ring nitrogen and its lone pairs reduce the symmetry of the induced magnetic field so that the 2,6-protons are more deshielded than the 4-protons, which in turn are more deshielded than the 3,5-protons.[32]

The ring-current effect also operates within a conjugated ring, decreasing the magnetic field which gives rise to the high-field chemical shifts of internal protons such as are seen in the ^1H NMR spectra of some porphyrins.[33] The ^1H NMR spectra of 1,4-polymethylenebenzenes demonstrate that this behaviour extends beyond the plane of the ring, since the methylene protons which lie close to the benzene ring and above it experience a strong upfield shift.[34] This effect may also be intermolecular, as is demonstrated by the effect of adding benzene to NMR samples in non-aromatic solvents to produce shifts to high field.[35] The effects of ring currents may be visualised as shielding cones above and below the plane of the ring.[36]

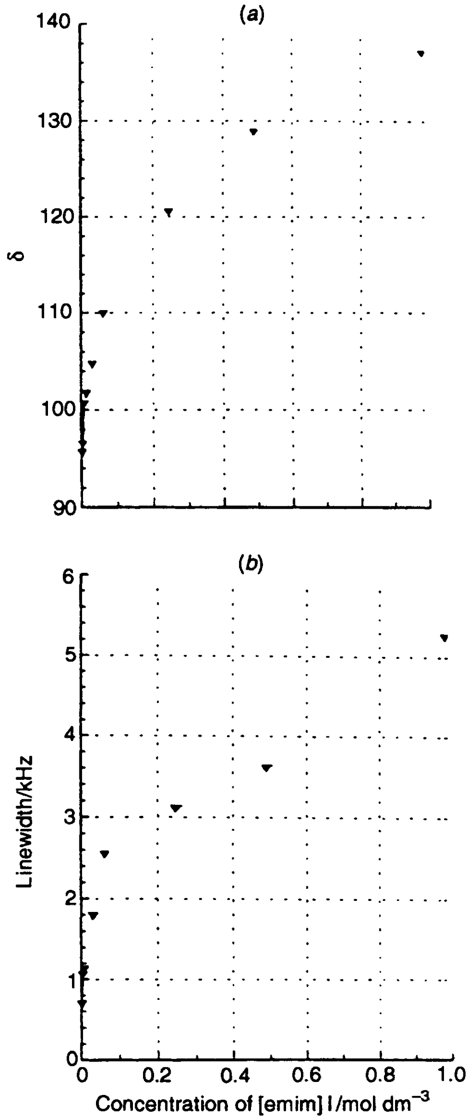

Fig. 7 Effect of concentration on (a) the ^{127}I chemical shift (72.08 MHz, 303 K) and (b) the linewidth for [emim]I in CD_3CN

The crystal structure of [emim]I[4] reveals that the imidazolium ring is conventionally aromatic and, therefore, capable of sustaining a ring current. It is the effects of this ring current which are observed in the NMR chemical shift data of solutions of [emim]X (X = Cl, Br or I) in CD_2Cl_2. At high concentration, the discrete [emim]X (X = Cl, Br or I) ion pairs are in close proximity to each other, and protons which lie inside the shielding cone of the imidazolium ring of neighbouring ion pairs experience an upfield chemical shift, whilst protons which lie outside the shielding cone (but close to the ring) experience a downfield chemical shift. As the solution is diluted, the separation of neighbouring ion pairs becomes greater, and the intermolecular ring-current effects diminish. Therefore, with dilution, the chemical shifts of protons lying inside the shielding cone of neighbouring ion pairs move downfield and protons lying outside the shielding cone (but close to the ring) move upfield. This identifies the H^2 proton as lying inside, and the H^5 and H^4 protons as lying outside, the shielding cone of neighbouring ion pairs. All other protons are sufficiently distant from the ring that the ring-current effects are negligible.

This suggests a model for the structure of [emim]X (X = Cl, Br or I) in CD_2Cl_2 in which the imidazolium rings are arranged

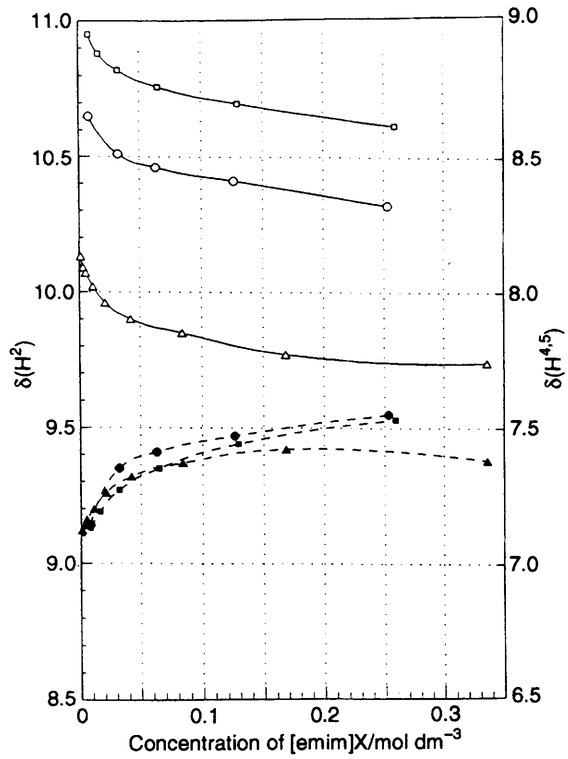

Fig. 8 Effect of concentration upon the chemical shifts (360.13 MHz, 303 K) for [emim]X [X = Cl (□), Br (○) or I (△)] in CD_2Cl_2 for H^2 (open symbols) and $H^{4,5}$ (filled symbols)

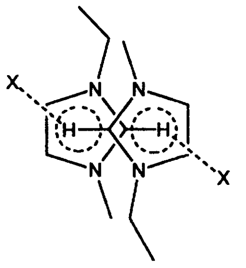

Fig. 9 Proposed structure for the stacks of quasi-molecules of [emim]X in solution in dichloromethane

in a stack with the rings parallel and staggered (Fig. 9). This type of stacking behaviour is seen in the crystal structure of imidazolium dihydrogenphosphate,[37] in which columns of stacked imidazolium rings, with any two adjacent rings related by a centre of symmetry (staggered), are seen.

It should be noted that the stacking of [emim]X (X = Cl, Br or I) ion pairs in CD_2Cl_2 is not the same as the oligomeric stacks of alternating cations and anions in the model of the [emim]Cl–$AlCl_3$ ionic liquids proposed by Wilkes and co-workers.[3] The large anion sandwiched between two rings would prevent the rings from coming close enough for intermolecular ring-current effects to be seen.

Chlorine-35 *NMR Spectra of Solutions of* [emim]Cl *in* CD_2Cl_2.—The ^{35}Cl NMR data for [emim]Cl in CD_2Cl_2 are presented in Fig. 10. The ^{35}Cl NMR chemical shifts show a marked change as the solution is diluted. Although some evidence for ring-current effects in ^{13}C NMR spectroscopy has been reported,[38–40] it is rarely unambiguous.[41,42] Some contribution from ring-current effects is possible, but another mechanism must also be in operation to explain the large effects seen.

The change in ^{35}Cl chemical shifts of solutions of [emim]Cl from lower to higher field with decreasing concentration (Fig. 10) is best explained as an association–dissociation phenomenon. When at high concentration the Cl^- ion of one ion pair is brought into close contact with the positive charge of the imidazolium ring of the neighbouring ion pair this leads to a downfield influence on its chemical shift. As the solution is diluted this 'dimer' dissociates and the chemical shift moves upfield.

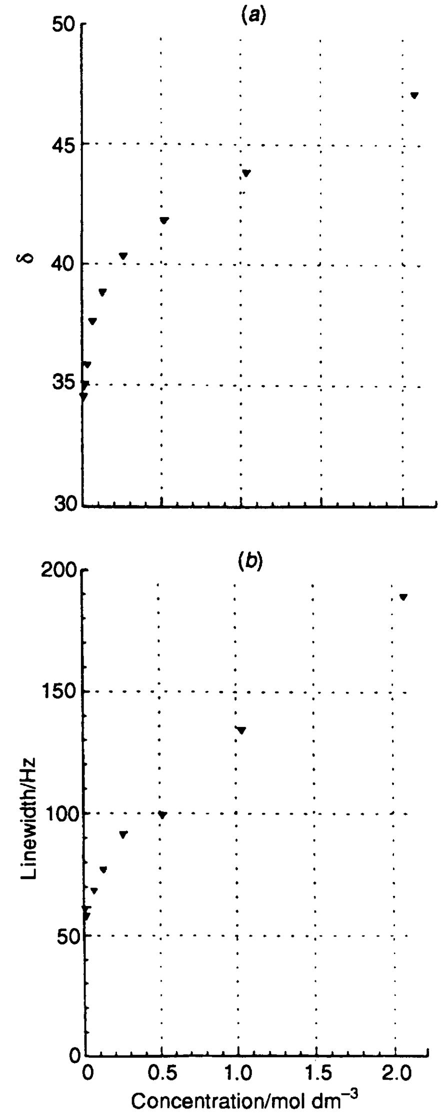

Fig. 10 Effect of concentration on (*a*) the ^{35}Cl chemical shift (35.29 MHz, 303 K) and (*b*) the linewidth for [emim]Cl in CD_2Cl_2

Table 4 Proton NMR (360.13 MHz, 303 K) chemical shift data for solutions of [emim]Cl in D_2O

	c/mol dm⁻³	
δ	2.0	0.005
H^2	8.63	8.65
$H^{5,4}$	7.35	7.38
CH_2CH_3	4.09	4.16
NMe	3.76	3.82
CH_2CH_3	1.35	1.43

Iodine-127 *NMR Spectra of Solutions of* [emim]I *in* CD_2Cl_2.—The ^{127}I NMR data for solutions of [emim]I in CD_2Cl_2 are presented in Fig. 11. The effect of dilution on the ^{127}I NMR chemical shifts is qualitatively similar to the

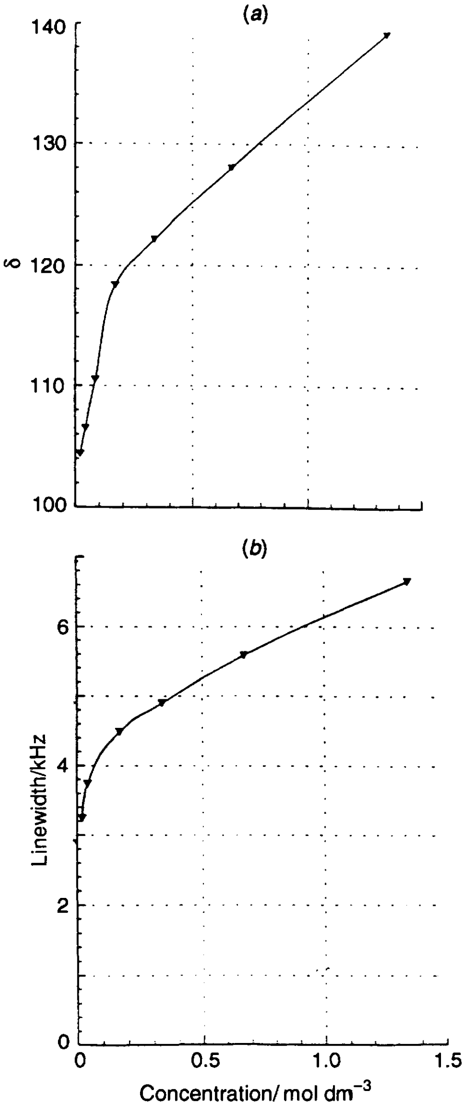

Fig. 11 Effect of concentration on (*a*) the ^{127}I chemical shift (72.08 MHz, 303 K) and (*b*) the linewidth for [emim]I in CD_2Cl_2

Table 5 Proton NMR integrals for solutions of [emim]Cl in D_2O and CD_3CN

	Solution		
Proton	D_2O	D_2O + NaOD	CD_3CN
H^2	0.89	0.05	1.0
$H^{5,4}$	1.92	0.13	2.0
CH_2CH_3	2.0	2.0	2.0
NCH_3	3.0	3.0	3.0
CH_2CH_3	3.0	3.0	3.0

behaviour of ^{35}Cl NMR chemical shifts of solutions of [emim]Cl in CD_2Cl_2, indicating that the I^- ion lies outside the shielding cone of neighbouring imidazolium rings, and close to the plane of the imidazolium ring in the $[emim]^+ \cdots I^-$ ion pair. This is in agreement with the crystal structure of [emim]I.[4]

Proton NMR Spectra of [emim]Cl *in* D_2O.—The ^1H NMR chemical shifts of 2.0 and 0.005 mol dm^{-3} solutions of [emim]Cl in D_2O are presented in Table 4. The change in chemical shift of the proton signals is negligible, indicating that there is little interaction between the cation and anion in aqueous solutions. The strong hydrogen-bonding ability of water ensures that the cations and anions of [emim]Cl remain solvent-separated, irrespective of concentration. The proton integrals for a 2.0 mol dm^{-3} solution of [emim]Cl are compared to those of the same solution with added NaOD (Table 5). All ring protons exchange with deuterium in both solutions, but the degree of exchange is significantly greater when the solution is made basic. Deuterium exchange is faster for the proton H^2 than for H^5 and H^4. Hence, it may be concluded that all protons of the imidazolium ring are acidic, and that H^2 is more acidic than H^4 and H^5.

Conclusion

There can be no doubt that the combined evidence of conductivity measurements and multinuclear NMR spectroscopy overwhelmingly argues that all three of the ring protons are involved in hydrogen bonding with halide anions. Both ^1H chemical shift and deuterium-exchange data clearly demonstrate the acidity of the imidazolium ring protons, a prerequisite of hydrogen bonding. The conductivity data and multinuclear NMR chemical shift data in ethanenitrile demonstrate that the dissolved salt is in equilibrium between hydrogen-bonded and solvent-separated forms, while those in dichloromethane show that only the associated form is present. The position that 'no hydrogen bonding is possible' is no longer tenable.

The implications of these observations for the structure of basic ionic liquids is clear. They must now be considered not as statistical aggregates of anions and cations, but as a three-dimensional network of anions and cations, linked by a network of fragile hydrogen bonds; each cation will be hydrogen bonded to three anions, *via* H^2, H^5 and H^4, and their affinity for Cl^- will be much greater than that for $[AlCl_4]^-$.

Acknowledgements

We are indebted to the BP Venture Research Unit for their generous funding of this research, and to the Lloyds of London Tercentenary Foundation for a fellowship (to T. W.).

References

1 C. L. Hussey, *Adv. Molten Salt Chem.*, 1983, **5**, 185.
2 J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263.
3 A. A. Fannin, jun., L. A. King, J. A. Levisky and J. S. Wilkes, *J. Phys. Chem.*, 1984, **88**, 2609.
4 A. K. Abdul-Sada, A. M. Greenway, P. B. Hitchcock, T. J. Mohammed, K. R. Seddon and J. A. Zora, *J. Chem. Soc., Chem. Commun.*, 1986, 1753.
5 K. M. Dieter, C. J. Dymek, jun., N. E. Heimer, J. W. Rovang and J. S. Wilkes, *J. Am. Chem. Soc.*, 1988, **110**, 2722.
6 C. J. Dymek, jun., and J. J. P. Stewart, *Inorg. Chem.*, 1989, **28**, 1472.
7 C. J. Dymek, jun., D. A. Grossie, A. V. Fratini and W. W. Adams, *J. Mol. Struct.*, 1989, **213**, 25.
8 A. K. Abdul-Sada, S. Al-Juaid, A. M. Greenway, P. B. Hitchcock, M. J. Howells, K. R. Seddon and T. Welton, *Struct. Chem.*, 1990, **1**, 391.
9 S. Tait and R. A. Osteryoung, *Inorg. Chem.*, 1984, **23**, 4352.
10 J. S. Wilkes, C. L. Hussey and J. R. Sanders, *Polyhedron*, 1986, **5**, 1567.
11 S. A. Lapshin, A. Yu. Chervinskii, L. M. Litvinenko, V. A. Dadali, L. M. Kapkan and A. N. Vdovichenko, *Zh. Org. Khim.*, 1985, **21**, 357.
12 A. K. Abdul-Sada, A. M. Greenway, K. R. Seddon and T. Welton, *Org. Mass Spectrom.*, 1993, **28**, 759.
13 R. F. Borne, H. Y. Aboul-Enein and J. K. Baker, *Spectrochim. Acta, Part A*, 1972, **28**, 393.
14 B. K. M. Chan, N.-H. Chang and M. R. Grimmel, *Aust. J. Chem.*, 1977, **30**, 2005.
15 J. R. Sanders, E. H. Ward and C. L. Hussey, *J. Electrochem. Soc.*, 1986, **133**, 325, 1526.
16 J. S. Wilkes, J. A. Levisky, J. L. Pflug, C. L. Hussey and T. B. Scheffler, *Anal. Chem.*, 1982, **54**, 2378.
17 A. G. Avent, P. A. Chaloner, M. P. Day, K. R. Seddon and T. Welton, in *Proceedings of the Seventh International Symposium on Molten*

Salts, The Electrochemical Society, Pennington, NJ, 1990, PV 90-17, p. 98.
18 J. W. Akitt, *N.M.R. and Chemistry: An Introduction to the Fourier Transform—Multinuclear Era*, 2nd edn., Chapman and Hall, London, 1983.
19 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
20 J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, 1965, **87**, 2529.
21 A. C. Harkness and H. M. Daggett, *Can. J. Chem.*, 1965, **43**, 1215.
22 J. S. Wilkes, J. S. Frye and G. F. Reynolds, *Inorg. Chem.*, 1983, **22**, 3870.
23 M. Nakano, N. I. Nakano and T. Higuchi, *J. Phys. Chem.*, 1967, **71**, 3954.
24 H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, 1970, **74**, 961.
25 R. Mathur, E. D. Becker, R. B. Bradley and N. C. Li, *J. Phys. Chem.*, 1963, **67**, 2190.
26 C. H. Langford and T. R. Stengle, *J. Am. Chem. Soc.*, 1969, **91**, 4014.
27 T. R. Stengle, Y.-C. E. Pan and C. H. Langford, *J. Am. Chem. Soc.*, 1972, **94**, 9037.
28 C. Hall, G. L. Haller and R. E. Richards, *Mol. Phys.*, 1969, **16**, 377.
29 A. Elaiwi, P. B. Hitchcock, K. R. Seddon and T. Welton, unpublished work, 1989.
30 C. W. Haig and R. B. Mallion, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1980, **13**, 303.
31 L. Pauling, *J. Chem. Phys.*, 1936, **4**, 673.
32 W. G. Schneider, H. J. Bernstein and J. A. Pople, *Can. J. Chem.*, 1957, **35**, 1487.
33 E. D. Becker and R. B. Bradley, *J. Chem. Phys.*, 1959, **31**, 1413.
34 J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, 1957, **79**, 846.
35 A. D. Buckingham, T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.
36 C. E. Johnson, jun., and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.
37 R. H. Blessing and E. L. McGaudy, *J. Am. Chem. Soc.*, 1972, **94**, 4034.
38 T. D. Alger, D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, 1966, **88**, 5397.
39 A. J. Jones, P. J. Garratt and K. P. C. Vollhart, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 241.
40 B. M. Trost and W. B. Herdle, *J. Am. Chem. Soc.*, 1976, **98**, 4080.
41 R. H. Levin and J. D. Roberts, *Tetrahedron Lett.*, 1976, **2**, 135.
42 H. Günther, H. Schmickler, H. Königshofen, K. Recker and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 243.

Received 21*st June* 1994; *Paper* 4/03777D