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FULL PAPER

The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals

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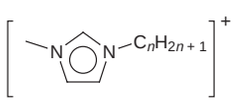
Air- and water-stable 1-alkyl-3-methylimidazolium tetrafluoroborate salts with the general formula [C_n-mim][BF_4] (n = 0–18) have been prepared by metathesis from the corresponding chloride or bromide salts. The salts have been characterised by ^{1}H NMR and IR spectroscopy, microanalysis, polarising optical microscopy and differential scanning calorimetry. Those with short alkyl chains (n = 2–10) are isotropic ionic liquids at room temperature and exhibit a wide liquid range, whereas the longer chain analogues are low melting mesomorphic crystalline solids which display an enantiotropic smectic A mesophase. The thermal range of the mesophase increases with increasing chain length and in the case of the longest chain salt prepared, [C_{18}-mim][BF_4], the mesophase range is *ca.* 150 °C.

The investigation of ambient temperature ionic liquids has largely focused on systems containing 1,3-dialkylimidazolium and *N*-alkylpyridinium organic cations and tetrachloroaluminate(III) anions.[1–4] These systems possess all the intrinsically useful characteristics of ambient temperature ionic liquids (negligible vapour pressure, wide liquidus, thermal stability, high ionic conductivity and a large electrochemical window), but they are both highly reactive to certain materials and are susceptible to moisture. Following the relatively recent reports of air-stable room temperature 1-ethyl-3-methylimidazolium based ionic liquids containing tetrafluoroborate[5] and toluenesulfonate[6] anions, a wide range of new ionic liquids have been developed incorporating many different anions[5,7,8] which demonstrate the potential specifically to tailor the properties (*i.e.* moisture stability, viscosity, miscibility with other co-solvents) of the ionic liquid. Some of these new, air- and moisture-stable ionic liquids[9] have been used as solvents for rhodium and nickel catalysed hydrogenation reactions,[10,11] electrochemical studies using the ionic liquid as both solvent and electrolyte[12,13] and in solar cell applications.[14]

The Belfast team[15] is currently investigating the wide range of properties exhibited by different ionic liquids in order to develop a database of materials which can be interrogated to obtain a desirable set of properties for a particular application or reaction. As part of this programme, we have studied the range of rheological and chemical properties exhibited by ionic liquids as a function of alkyl chain length, anion type, *etc.*, in order to develop more logical approaches to modifying their physical properties. We have demonstrated, in recent publications, that long-chain 1-alkyl-3-methylimidazolium chloride, tetrahalogenometalate[16] and hexafluorophosphate[17] salts display thermotropic smectic liquid crystalline mesomorphism over a relatively wide temperature range, increasing with increasing chain length. Related symmetrically substituted long-chain 1,3-dialkylimidazolium hexafluorophosphate salts have also been recently reported.[18] The incorporation of liquid crystalline properties into these neoteric solvents[19] promises to extend even further their range of useful solvent and catalytic properties for commercially important processes.

We report here the preparation and physical properties of 1-alkyl-3-methylimidazolium tetrafluoroborate salts with alkyl chains (C_nH_{2n+1}) varying from n = 0 to 18 (designated as [C_n-mim][BF_4] except for the commonly used [emim]$^+$ and [bmim]$^+$ for n = 2 and 4 respectively, and [H-mim]$^+$ for n = 0). The salts with short alkyl chain lengths (n = 2–10) are liquids at room temperature and form glasses on cooling to −80 °C, whereas the longer chain salts (n = 12–18) are low melting solids which display enantiotropic mesomorphism with an extensive thermotropic mesophase range. The two imidazolium salts *N*-substituted with a proton or methyl group (n = 0 and 1 respectively) are low melting crystalline solids.



[C_n-mim]$^+$, n = 0-18

Experimental

Microanalyses were performed by A.S.E.P. at the Queen's University of Belfast. All chemicals were used as received unless otherwise stated. Infrared spectra were recorded as liquid or glassy films between KBr plates using a Perkin-Elmer 1600 or Bio-Rad FTS-185 spectrometer, ^{1}H NMR spectra in propanone-d_6 solution using a Bruker WM500 spectrometer; proton chemical shifts are recorded relative to an internal TMS standard.

All the tetrafluoroborate salts with n > 3 were prepared by metathesis in aqueous solution from the respective chloride or bromide salts with either HBF_4 or $NaBF_4$; the salts with n = 1–3 were prepared using the literature method for [emim][BF_4][5] by metathesis with silver tetrafluoroborate, and [H-mim][BF_4][20] was obtained by direct reaction of 1-methylimidazole with tetrafluoroboric acid. Representative syntheses for each case are described. Analytical data are shown in Tables 1 and 2.

The melting points, clearing points and glass transition temperatures were determined by differential scanning calorimetry (Perkin-Elmer Pyris 1 DSC equipped with dinitrogen cryostatic cooling, 5–10 mg samples, 5 °C min^{-1} heating and cooling rates) and heated-stage polarising optical microscopy where appropriate (transition temperatures > 0 °C) using an Olympus BX50 microscope equipped with a Linkam TH600 hot stage and TP92 temperature controller.

The X-ray powder diffraction pattern of [C_{14}-mim][BF_4] was determined using a Siemens D5000 powder diffractometer with Cu-Kα X-rays, λ = 1.542 Å. Data were recorded from between 2 and 20° in steps of 0.05°.

Preparations

1-Methylimidazolium tetrafluoroborate, [H-mim][BF_4].[20] Tetrafluoroboric acid (11.8 cm^3, 0.092 mol, 48% solution in water) was added dropwise to stirred 1-methylimidazole (7.5 g, 0.092 mol) cooled to 0 °C in an ice-bath over 30 min. The reaction mixture was stirred for 2 h and the aqueous solvents were removed *in vacuo* to give the product as a colourless oil, which solidified on cooling. Yield 15.55 g (100%).

1-Ethyl-3-methylimidazolium tetrafluoroborate, [emim][BF_4].[5,21] Tetrafluoroboric acid (15.2 cm^3, 0.116 mol, 48% solution in water) was added slowly to a rapidly stirred slurry of silver(I) oxide (13.49 g, 0.058 mol) in water (50 cm^3) over 15 min. The reaction mixture was covered with aluminium foil to prevent photodegradation and stirred for a further hour until all the silver(I) oxide had completely reacted to give a colourless solution. A solution of 1-ethyl-3-methylimidazolium bromide (22.24 g, 0.116 mol) in water (200 cm^3) was added to the reaction mixture and stirred at room temperature for 2 h. The resulting yellow precipitate of silver bromide was removed by filtration and the solvent removed from the supernatant liquor by heating at 70 °C, initially under reduced pressure and finally *in vacuo*, to yield the tetrafluoroborate salt as a pale yellow liquid. Yield 21.36 g, 93%. IR (liquid film); $\tilde{\nu}/cm^{-1}$ 3167, 3125 (s, aromatic C–H stretch), 2990 (m, aliphatic C-H stretch), 1576 (s, sym. ring stretch) 1457 (s, sym. ring stretch), 1173 (s, sym. ring stretch) and 1052 (br s, BF_4 stretch).

1-Decyl-3-methylimidazolium tetrafluoroborate, [C_{10}-mim][BF_4]. Tetrafluoroboric acid (10.2 cm^3, 0.078 mol, 48% solution in water) was added dropwise to a cooled, rapidly stirring solution of 1-decyl-3-methylimidazolium chloride (20.2 g, 0.078 mol) in water (200 cm^3) over 10 min. The lower ionic liquid layer was collected *via* a separating funnel, dissolved in dichloromethane (300 cm^3) and washed with water (2 × 150 cm^3). The organic layer was collected, dried over anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to yield the tetrafluoroborate salt as a colourless liquid. Yield 22.55 g, 93%.

1-Methyl-3-tetradecylimidazolium tetrafluoroborate, [C_{14}-mim][BF_4]. A solution of $NaBF_4$ (6.60 g, 0.060 mol) in water (50 cm^3) was added slowly to a cooled, rapidly stirring solution of 1-methyl-3-tetradecylimidazolium chloride (19.84 g, 0.060 mol) in water (200 cm^3). The product precipitated as a waxy solid and was collected by filtration, dissolved in dichloromethane (300 cm^3) and washed with water (2 × 100 cm^3). The organic layer was collected, dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to yield the tetrafluoroborate salt which was recrystallised from methanol as a colourless powder (14.74 g, 88% yield).

The salts [C_1-mim][BF_4] and [C_3-mim][BF_4] were prepared using the method described for [emim][BF_4]; [bmim][BF_4] and [C_5-mim][BF_4] were prepared using the method for [C_{14}-mim][BF_4]. (The minimum volume of water was used to dissolve the chloride salts. The tetrafluoroborate salt did not initially separate from the aqueous phase, but was preferentially extracted by dichloromethane). The salts [C_7-mim][BF_4], [C_8-mim][BF_4] and [C_9-mim][BF_4] were prepared using the method for [C_{10}-mim][BF_4] by metathesis with HBF_4; [C_6-mim][BF_4], [C_{11}-mim][BF_4], [C_{12}-mim][BF_4], [C_{13}-mim][BF_4], [C_{15}-mim][BF_4], [C_{16}-mim][BF_4] and [C_{18}-mim][BF_4] were prepared using the method for [C_{14}-mim][BF_4] by metathesis with Na[BF_4].

Results and discussion

Synthesis of the salts

The tetrafluoroborate salts are air and water stable. In addition, it was assumed from the previously published examples, [emim][BF_4] ($n = 2$)[5,21,22] and [bmim][BF_4] ($n = 4$),[11] that their melting points should be generally lower than those of their chloride or hexafluorophosphate analogues. It was also expected that the tetrafluoroborate salts would have a greater miscibility with water than the corresponding hexafluorophosphate salts, but that they would be less hygroscopic than the chloride and bromide salts, thus placing their properties in an intermediate position between those of the $[PF_6]^-$ and Cl^- salts.

The tetrafluoroborate salts were prepared by simple metathesis reactions from the corresponding chloride or bromides. The short alkyl chain salts, [emim][BF_4] and [bmim][BF_4], had been prepared previously from the corresponding chloride salts using aqueous silver(I) tetrafluoroborate[21] or from propanone using sodium tetrafluoroborate.[11] Unfortunately, the former route can be prohibitively expensive at moderate or large scale (even when recycling of silver halide by-products is utilised) whereas, in practice, the latter method leaves appreciable amounts of chloride contamination (although the solubility of sodium chloride in propanone is only 5.5×10^{-6} mol l^{-1}, it increases significantly with only small concentrations of water and with additional dissolved salts[23]) in the ionic liquids. Recently a silver-free preparation of [emim][BF_4] using ammonium tetrafluoroborate in propanone has been described.[24]

We found that for alkyl chains longer than $n > 3$ the salts can be prepared by metathesis from the chloride or bromide salts in water followed by extraction into dichloromethane, and have developed an improved laboratory-scale metathesis and extraction route which allows a cost-effective high purity preparation of the tetrafluoroborate salts using either HBF_4 or Na[BF_4] in aqueous solution. For most of the series, the desired tetrafluoroborate salt either separates from the aqueous reaction mixture as a dense liquid ($n = 6$–10) or precipitates as a solid ($n > 10$) which can be isolated by decantation or filtration as appropriate. The water-soluble short chain salts ($n = 4$ or 5) can be extracted and purified from aqueous solution by partitioning into an organic solvent (dichloromethane is excellent on a laboratory scale). Unfortunately, for the shortest chain salts ($n < 4$), the water : CH_2Cl_2 partition coefficient is too low to permit efficient extraction of the salts from the aqueous phase and the published route using aqueous Ag[BF_4] was used to prepare $n = 1$–3. The 1-methylimidazolium salt ([H-mim][BF_4]) was synthesized by direct combination of methylimidazole and HBF_4 using a published procedure.[20] The particular method employed in each case is shown in Table 1. In all cases, except $n = 4$ and 5, the tetrafluoroborate salts were isolated with unoptimised yields of better than 85% after work-up; variation in yields represents mechanical losses during the extraction and work-up process. For $n = 4$ and 5 where the tetrafluoroborate salts have a higher solubility in aqueous media, the water : CH_2Cl_2 partition is less efficient and variable yields between 50 and 70% were obtained. For the water soluble salts ($n < 6$), testing for the presence of residual halide using silver nitrate solution gave a negative result (*i.e.* no AgCl precipitation).

1-Alkyl-3-methylimidazolium tetrafluoroborate salts ([C_n-mim][BF_4]) were prepared for $n = 0$ to 18 and characterised by a combination of ^{1}H NMR and infrared spectroscopy, microanalysis and DSC. The CHN microanalyses and ^{1}H NMR data are summarised in Tables 1 and 2, respectively. The infrared spectra for all the dialkylated salts are similar, except for an increase in aliphatic C–H stretch and bend intensities with n, and show characteristic stretching bands for the imidazolium cation and a broad, unresolved band due to the $[BF_4]^-$ anion.

The shorter chain salts are hygroscopic, although to a much lesser extent than their chloride analogues. Both miscibility with water and the hygroscopic nature of the salts decreases markedly with increasing chain length. The salts can be dried effectively by heating at 70–90 °C *in vacuo* for 6–8 h, then stored under dinitrogen in a glove-box. Karl–Fisher measurements[25] show typical water contents of dried samples to be <200 ppm.

In addition to the Karl–Fischer titration measurements, the

absence (or presence) of OH stretching absorbances in the 3500–3800 cm^{-1} region of the infrared spectra was used to monitor for the presence of water in samples, the presence of a band indicating that further drying *in vacuo* was required. In addition, for thoroughly dried samples, no broad absorption bands in the region 3000–3100 cm^{-1} which could have been ascribed to CH···F hydrogen bonding between the $[BF_4]^-$ anion and the organic cation were observed. This appears to indicate that there is no significant hydrogen bonding present, in contrast to imidazolium based ionic liquids with chloride anions.[26]

The ^{1}H NMR chemical shift of the C(2)–H protons of the tetrafluoroborate salts both in solution in propanone-d_6 and neat [C_n-mim][BF_4] (n = 2–8) are all remarkably similar and do not show the large downfield shift related to hydrogen bonding observed for the chloride salts.[26] However, there is a disparity between these observations and the confused and contradictory reports in the literature about which observations can be used to demonstrate the presence or absence of hydrogen bonding between the anions and cations in the [emim][BF_4] and [bmim][BF_4] ionic liquids. Suarez *et al.* have repeatedly reported[11,13] that [bmim][BF_4] exhibits hydrogen bonding in the liquid phase as observed from bands between 3000 and 3200 cm^{-1} in the IR spectrum, yet these IR bands are not described in the experimental section of their paper. In addition, the original communication describing, amongst other salts, [emim][BF_4] by Wilkes and Zaworotko[5] is cited as evidence for similar hydrogen bonding in related salts. However, the only reports of hydrogen bonding in this paper are in the crystal structures of the nitrate, nitrite and sulfate salts with well established, strong C–H···O hydrogen bonding in the solid state which cannot readily be compared to potential C–H···F interactions in liquid tetrafluoroborate or hexafluorophosphate[5] examples. Although it appears very likely that interactions occur (as implied by the differences in water solubility of the tetrafluoroborate and hexafluorophosphate salts), these are too weak to be seen unambiguously in the IR spectra.

The tetrafluoroborate salts were obtained as white, low-melting solids (n = 0, 1, or 11–18) or colourless to pale yellow liquids (n = 2–11). All the salts prepared are water- and air-stable under ambient conditions, and may be handled under normal laboratory conditions. The shorter chain salts (n = 0–5) are somewhat hygroscopic, but can be dried by extended heating at 70 °C under high vacuum, until no water signals are observed in the infrared spectrum around 3500 cm^{-1}. The salts were then stored under dinitrogen in a dry-box. Interestingly, in contrast to the analogous hexafluorophosphate salts, the salts with n < 6 are soluble in water, although the aqueous solubility drops rapidly through the series. Thus, while [emim][BF_4] is both hygroscopic and totally soluble in water, [C_6-mim][BF_4] is essentially insoluble in water, though water is soluble in the ionic liquid at up to 30 000 ppm[25] and the intermediate [bmim][BF_4] is completely miscible in water at room temperature, but on cooling to close to 0 °C phase separation occurs as the solubility of [bmim][BF_4] in water drops.[22]

All the tetrafluoroborate salts are soluble in propanone and in dichloromethane, but exhibit liquid clathrate formation in trichloromethane; based on observation and ^{1}H NMR measurements the clathrates have a 1 : 3 [C_n-mim][BF_4] : $CHCl_3$ ratio. We have also observed similar clathrate formation between $CHCl_3$ and hexafluorophosphate ionic liquids. It is possible that this is induced by C–H···F hydrogen bonding between the relatively acidic trichloromethane proton and the $[BF_4]^-$ or $[PF_6]^-$ anions.

Table 1 CHN Microanalytical data for the anhydrous tetrafluoroborate salts prepared. Note, for n = 0 and 1, known compounds, satisfactory analyses could not be obtained due to the hygroscopic nature of the salts

		Analysis, found (calc.) (%)		
n	Synthesis	C	H	N
2	$AgBF_4/H_2O$	35.91 (36.40)	5.67 (5.60)	13.76 (14.15)
3	$AgBF_4/H_2O$	38.91 (39.66)	6.06 (6.18)	12.92 (13.21)
4	$NaBF_4/H_2O$	42.13 (42.51)	6.86 (6.69)	12.24 (12.39)
5	$NaBF_4/H_2O$	44.71 (45.03)	7.08 (7.14)	11.44 (11.67)
6	$NaBF_4/H_2O$	45.87 (47.27)	7.53 (7.54)	10.85 (11.03)
7	HBF_4/H_2O	49.10 (49.28)	7.80 (7.89)	10.85 (10.45)
8	HBF_4/H_2O	50.96 (51.09)	8.14 (8.22)	9.58 (9.93)
9	HBF_4/H_2O	52.63 (52.72)	8.70 (8.51)	9.44 (9.46)
10	HBF_4/H_2O	54.95 (54.21)	9.05 (8.77)	8.98 (9.03)
11	$NaBF_4/H_2O$	55.24 (55.57)	9.28 (9.02)	8.51 (8.64)
12	$NaBF_4/H_2O$	56.53 (56.82)	9.32 (9.24)	8.47 (8.28)
13	$NaBF_4/H_2O$	58.19 (57.96)	9.34 (9.44)	7.87 (7.95)
14	$NaBF_4/H_2O$	58.59 (59.02)	9.87 (9.63)	7.37 (7.65)
15	$NaBF_4/H_2O$	60.13 (60.05)	10.09 (9.81)	7.23 (7.37)
16	$NaBF_4/H_2O$	60.78 (60.92)	9.77 (9.97)	7.01 (7.10)
18	$NaBF_4/H_2O$	63.01 (62.56)	10.12 (10.26)	6.83 (6.63)

Table 2 ^{1}H NMR chemical shifts δ (relative to TMS internal standard) and coupling constants J/Hz of [C_n-mim][BF_4] salts in propanone-d_6 solution (integrals and coupling constants are given in parentheses as appropriate)

n	H^2	H^4	H^5	NCH_2	NCH_3	NCH_2CH_2	Alkyl	Terminal CH_3
0	8.92 (s)	7.71 (t, J = 1.7)	7.69 (t, J = 1.7)	12.68 (1 H, br, NH)	4.09 (s)			
1	8.90 (s)	7.70 (d, J = 1.8)			4.05 (s)			
2	8.88 (s)	7.72 (d, J = 1.8)	7.65 (d, J = 1.8)	4.35 (q, J = 7.3)	4.00 (s)			1.54 (t, J = 7.3)
3	9.00 (s)	7.78 (d, J = 1.8)	7.74 (d, J = 1.8)	4.34 (t, J = 7.3)	4.07 (s)	1.99 (m, ^1J = 7.3, ^2J = 7.3)		0.99 (t, J = 7.3)
4	8.83 (s)	7.69 (d, J = 1.8)	7.63 (d, J = 1.8)	4.34 (t, J = 7.3)	4.04 (s)	1.95 (m, $^1J = {}^2J$ = 7.4)	1.41 (2 H, m, $^1J = {}^2J$ = 7.4)	0.98 (t, J = 7.4)
5	9.05 (s)	7.80 (d, J = 1.8)	7.73 (d, J = 1.8)	4.37 (t, J = 7.3)	4.06 (s)	1.97 (m)	1.38 (4 H, m)	0.92 (t, J = 7.0)
6	9.05 (s)	7.78 (d, J = 1.8)	7.72 (d, J = 1.8)	4.36 (t, J = 7.4)	4.05 (s)	1.96 (m)	1.35 (6 H, m)	0.90 (t, J = 7.4)
7	9.02 (s)	7.78 (1 H, d, J = 1.8)	7.72 (d, J = 1.8)	4.38 (t, J = 7.3)	4.07 (s)	1.98 (m)	1.32 (8 H, m)	0.91 (t, J = 7.1)
8	9.05 (s)	7.81 (d, J = 1.8)	7.75 (d, J = 1.8)	4.40 (t, J = 7.3)	4.08 (s)	1.99 (m)	1.31 (10 H, m)	0.91 (t, J = 7.3)
9	9.28 (s)	7.84 (d, J = 1.8)	7.77 (d, J = 1.8)	4.41 (t, J = 7.4)	4.04 (s)	1.99 (m)	1.32 (12 H, m)	0.91 (t, J = 7.1)
10	9.04 (s)	7.78 (s, J = 1.8)	7.72 (s, J = 1.8)	4.37 (t, J = 7.4)	4.05 (s)	1.98 (m)	1.32 (14 H, m)	0.91 (t, J = 7.0)
11	9.35 (s)	7.86 (s, J = 1.8)	7.79 (s, J = 1.8)	4.41 (t, J = 7.33)	4.09 (s)	1.99 (m)	1.32 (16 H, m)	0.91 (t, J = 7.0)
12	9.04 (s)	7.78 (s, J = 1.8)	7.72 (s, J = 1.8)	4.37 (t, J = 7.4)	4.06 (s)	1.98 (m)	1.32 (18 H, m)	0.92 (t, J = 7.0)
13	9.08 (s)	7.80 (s, J = 1.8)	7.74 (s, J = 1.8)	4.39 (t, J = 7.4)	4.07 (s)	1.99 (m)	1.32 (20 H, m)	0.92 (t, J = 6.6)
14	9.09 (s)	7.79 (s, J = 1.8)	7.74 (s, J = 1.8)	4.38 (t, J = 7.4)	4.07 (s)	1.99 (m)	1.33 (22 H, m)	0.92 (t, J = 6.8)
15	9.16 (s)	7.81 (s, J = 1.8)	7.78 (s, J = 1.8)	4.40 (t, J = 7.4)	4.09 (s)	2.00 (m)	1.34 (24 H, m)	0.93 (t, J = 7)
16	9.20 (s)	7.82 (s, J = 1.8)	7.76 (s, J = 1.8)	4.39 (t, J = 7.4)	4.09 (s)	1.98 (m)	1.33 (26 H, m)	0.92 (t, J = 7)
18	9.09 (s)	7.82 (s, J = 1.8)	7.76 (s, J = 1.8)	4.40 (t, J = 7.3)	4.09 (s)	2.00 (m)	1.33 (30 H, m)	0.92 (t, J = 7)

Table 3 Thermal data from DSC and optical microscopy observations. Transition temperatures (°C) measured from the peak positions for first order transitions (*i.e.* melting and clearing points) and transition midpoints for glass transitions from DSC; enthalpy (kJ mol^{-1}) given in parentheses

		Phase				
n	Treatment	Cr		S_A		Iso
0	Heat	·	52.4[a] (2.9)	—		·
	Cool[b]					
1	Heat	·	103.4 (9.8)	—		·
	Cool	·	73.6 (−9.6)	—		·
2	Heat	·	5.8[c] (10.1)[d]	—		·
	Cool					
3	Heat	·	−13.9[d]	—		·
	Cool					
4	Heat					
	Cool	·	−71.0[d,e]	—		·
5	Heat	·	−87.5[d]			·
	Cool	·	−88.0[d]			·
6	Heat	·	−82.4[d]	—		·
	Cool	·				·
7	Heat	·	−80.4[d]	—		·
	Cool	·	−81.9[d]	—		·
8	Heat	·	−78.5[d]	—		·
	Cool	·	−80.5[d]	—		·
9	Heat	·	−77.2[d]	—		·
	Cool	·	−80.0[d]	—		·
10	Heat	·	−4.2 (7.3)	—		·
	Cool	·	−24.7 (−12.8)	—		·
11	Heat	·	21.4 (24.7)	—		·
	Cool	·	−2.5 (−23)	—		·
12	Heat	·	26.4 (29.6)	·	38.5 (0.3)	·
	Cool	·	7.4 (−23.7)	·	37.0 (−0.2)	·
13	Heat	·	49.1 (32.2)	·	92.7 (0.5)	·
	Cool	·	17.3 (−24.1)	·	91.7 (−0.6)	·
14	Heat	·	42.4 (20.7)	·	129.5 (0.6)	·
	Cool	·	29.3 (−16.8)	·	130.0 (−0.6)	·
15	Heat	·	55.2 (33.4)	·	148.1 (0.9)	·
	Cool	·	35.0 (−23.2)	·	147.5 (−0.9)	·
16	Heat	·	49.6 (31.5)	·	182.0 (1.7)	·
	Cool	·	45.1 (−24.7)	·	172.2 (−0.8)	·
18	Heat	·	66.8 (23.8)	·	214.8 (1.0)	·
	Cool	·	64.5 (−27.6)	·	213.4 (−1.1)	·

[a] 55 °C,[20] [b] Did not crystallise on cooling. [c] 15 °C,[5] 12 °C.[21] [d] Glass transition. [e] −81 °C.[11]

The preparations of chloride-free [bmim][BF_4] and higher homologues from aqueous solution† using this low cost metathesis route with Na[BF_4] or HBF_4 permit relatively large quantities (up to kilo scale in the laboratory) of these interesting ionic liquid solvents to be prepared, which will increase the scope for the investigation of synthetic reactions using the ionic liquids as solvents. In contrast, the existing metathetic routes to [emim][BF_4] using silver salts fail under these criteria and, as has been noted by Chauvin *et al.*,[10] chloride impurities can have a major disadvantageous effect on some transition metal catalysed reactions in ionic liquid solvents. Clearly, this is the reason for the recent increase in publications of syntheses using [bmim][BF_4] in preference to [emim][BF_4] as an ionic liquid solvent. The preparation of the higher homologues described in this paper opens up new opportunities for the use of a wider range of ionic liquid solvents.

Characterisation

The melting points and mesophase clearing points (as appropriate) of the tetrafluoroborate salts are shown in Table 3 and Fig. 1. In all cases, the salts exhibited a marked tendency to supercool before crystallising or to form glasses; transition temperatures are given from DSC measurements for both heating and cooling cycles (except for the short chain salts, n = 0–4, where it proved impossible to obtain reproducible results on cooling cycles) and data are only presented for the melting transition (as indicated in Table 1). A typical DSC trace for the mesomorphic [C_{14}-mim][BF_4] salt is shown in Fig. 2 revealing the characteristically large enthalpy for the crystal (Cr)–liquid crystal transition and small enthalpy for the mesophase–isotropic (Iso) transition. Melting points and transition temperatures were also determined from heated-stage optical

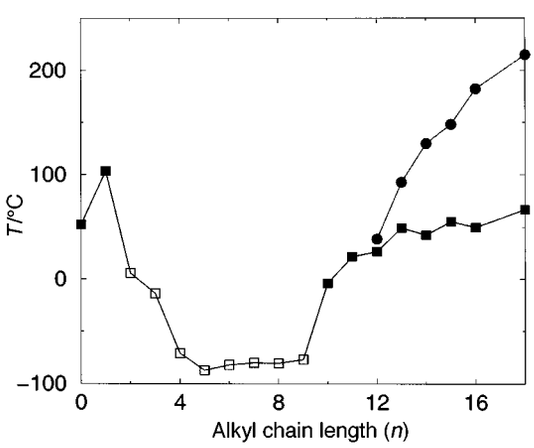


Fig. 1 Phase diagram for 1-(C_nH_{2n+1})-3-methylimidazolium tetrafluoroborate ionic liquids and liquid crystals showing the melting (closed square), glass (open square) and clearing (circle) transitions measured by DSC.

† Chloride ion concentrations determined in aqueous solution using a Cl^- ion selective electrode for the [C_n-mim][BF_4] ionic liquids (n = 2–10), prepared from the respective chloride salts, were typically below 0.2 ppm.

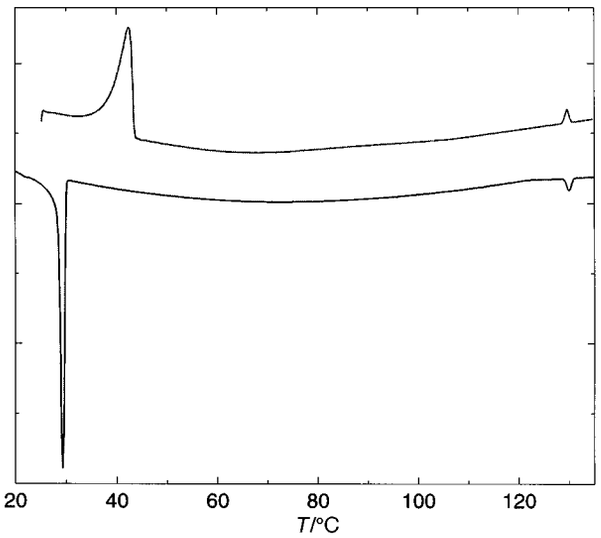


Fig. 2 The DSC trace of [C_{14}-mim][BF_4] for the second heating (upper) and cooling (lower) cycles showing the characteristically sharp Cr-S_A (smectic) and S_A-Iso transitions.

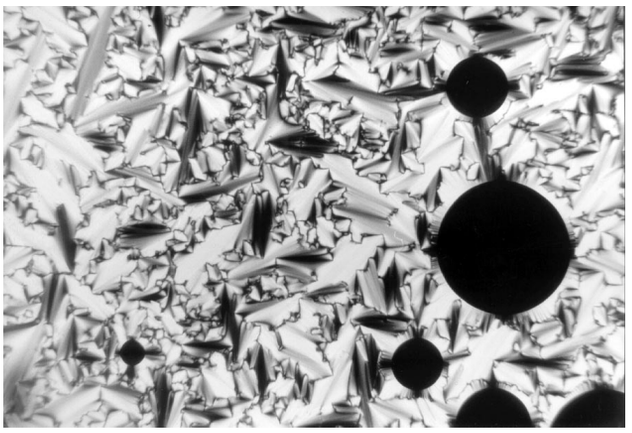


Fig. 3 The fan-like texture of the mesophase of [C_{14}-mim][BF_4] under crossed polarisers at 126 °C.

microscopy observations as appropriate. The transition temperatures measured on heating were, in all cases, within ±1 °C of the values obtained by DSC.

Thermal investigations. *Melting points.* The phase diagram for the salts as a function of chain length is illustrated in Fig. 1. Only [H-mim][BF_4], [C_1-mim][BF_4], and the salts with $n > 9$ crystallise on cooling. The ionic liquids [C_n-mim][BF_4] ($n = 2$–9) show a strong tendency to supercool, forming progressively more viscous liquids, and finally glasses, with no indication of crystallisation even on slow cooling (1 °C min^{-1}) to −170 °C. On increasing the chain length over the range $n = 0$–4 the glass transition temperatures fall progressively until a lower limit around −80 °C is reached. It is notable that for the salts with $n = 4$–9 the glass transition temperatures are all between −70 and −90 °C at a cooling rate of 5 °C min^{-1}. This T_g is very similar to the lowest glass transition points (−96 °C) observed for the [emim]Cl–$AlCl_3$ ionic liquid system at 66% $AlCl_3$ composition.[27]

Above $n = 9$, the true melting points rise quite dramatically and liquid crystalline mesomorphism is observed from $n = 12$. The salts (from $n = 10$) all supercool before crystallising; the degree of supercooling decreases with increasing chain length.

The effect on the transition behaviour from altering the alkyl chain length is continuous below $n = 10$; there is no overall difference in behaviour between the odd and even chain lengths (in contrast to the odd–even effect observed in the melting points of the mesomorphic salts described below). Hence there appears to be no advantage to be gained (in terms of solvents for potential reactions) in preparing the more expensive odd-chain length compounds in order to alter the properties.

Mesomorphism. None of the salts with $n < 12$ displayed thermotropic mesomorphism, however for $n = 12$–18 a single enantiotropic mesophase was observed on both cooling from the isotropic liquid and heating from the crystalline solid. In general, for all the mesomorphic salts, on cooling from the isotropic liquid, small *bâtonnets* first form, but rapidly disperse into a homeotropic texture (*i.e.* the optical axis is perpendicular to the slide) with birefringence only observed around air-bubbles and at the edges of the liquid. When the mesophase film is deformed, regions of focal conic and oily-streak texture are observed indicative of a layered smectic A (S_A) mesophase.[28] In addition, free standing droplets display a typical spherulitic texture. When the salts are heated between two glass microscope slides (as opposed to a more typical microscope slide and cover slip) spontaneous formation of a single homeotropic monodomain is frustrated and a fan-like texture was observed (see Fig. 3). These mesophases are miscible with those formed by the corresponding mesomorphic 1-alkyl-3-methylimidazolium and *N*-alkylpyridinium hexafluorophosphate and tetrachloronickelate salts, which had been assigned as smectic A (S_A) on the basis of the textures observed by polarised optical microscopy.[16,17] However, considering both the amphiphilic structure of the mesogen and the optical texture, this mesophase could be equally well described as an anhydrous Lα lamellar phase by analogy with the lamellar phases[29,30] formed by anhydrous soaps.[31,32] On the basis of the current observations, it is not possible to differentiate between these two descriptions of the mesophase; further small angle X-ray diffraction studies are being considered to investigate the structure of these mesophases. It is important to note that although the tetrafluoroborate salts ($n > 6$) have only low solubility in water and lyomesomorphism was not observed with any of the salts at temperatures below their respective melting points using the Lawrence penetration experiment,[33] the thermotropic mesophase displayed by all the salts with $n > 11$ was observed to swell and become more extensive on contact with water. This clearly indicates a degree of water solubility within the ionic liquid crystal mesophase and is in contrast to the hexafluorophosphate salts which show no miscibility with water and the more water soluble chloride and bromide salts which do exhibit general surfactant properties and form lyotropic mesophases in water[34] with behaviour similar to that of the analogous *N*-alkylpyridinium salts.

The melting points increase only relatively slowly with increasing ($n = 12$–18) chain length (*i.e.* from 25 to 56.4 °C) whereas the clearing temperatures show a marked dependency on the chain length (from 39.4 to 214 °C) leading to an increased thermal range of the mesophase from a modest 14.5 °C for [C_{12}-mim][BF_4] to 149 °C for [C_{18}-mim][BF_4], the longest chain compound studied. The transition temperatures and energies are shown in Table 3 and Fig. 1. A small, but significant odd–even effect was observed in the melting points; the odd chain length compounds have melting points which are increased by *ca.* 10 °C compared to those of their immediate neighbours with even length chains. This is due to the deviation of the even length chains from the linear structure of the favoured all-*trans* configuration found for odd chain lengths. It is notable that an enantiotropic mesophase is observed for the compounds with $n = 12$ and 13, in contrast to the [C_n-mim][PF_6] ionic liquid crystals[17] where mesomorphism is only observed from $n = 14$.

The phase behaviour follows the same pattern observed for the previously studied 1-alkyl-3-methylimidazolium chloride,[16] tetrachlorometalate[16] and hexafluorophosphate[17] ionic liquid crystals. Compared to the hexafluorophosphate salts, the

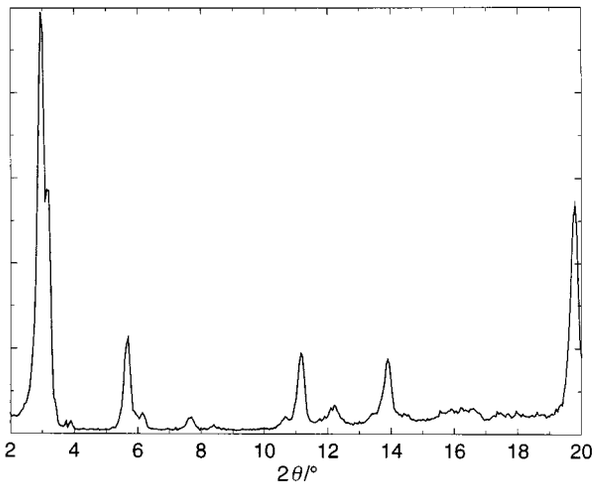


Fig. 4 Powder X-ray diffraction pattern of $[C_{14}\text{-mim}][BF_4]$ at 25 °C.

tetrafluoroborate salts display a wide thermal range of the mesophase though not as extensive as those for the chloride and tetrachlorometalate salts.[16] The enthalpy changes on melting (see Table 3) are also similar to those published for *N*-octadecylpyridinium chloride[16] and for 1-alkyl-3-methylimidazolium and 1-alkylpyridinium hexafluorophosphates,[17] and are relatively large (20–30 kJ mol^{-1}) which suggests a significant structural change on melting. In contrast, the clearing enthalpy is small and probably is solely due to weak van der Waals interactions between alkyl chains. On cooling, all the examples show extensive supercooling before crystallisation, which is typical for these imidazolium systems.

Powder X-ray diffraction studies. Although it was not possible to use variable temperature X-ray powder diffraction to study the mesophase structure of the liquid crystalline salts, the crystal powder pattern of the representative $[C_{14}\text{-mim}][BF_4]$ salt was determined at room temperature and the unit cell parameters were calculated. The salt was determined to have a triclinic space group with cell parameters $a = 7.69$, $b = 10.92$, $c = 30.23$ Å, $\alpha = 90.9$, $\beta = 102.0$, $\gamma = 88.1°$; the powder diffraction pattern is shown in Fig. 4. The unit cell parameters are consistent with an interdigitated bilayer structure, comparable to that typically observed for other long-chain imidazolium and *N*-alkylpyridinium salts. The *c* axis is long in comparison with the corresponding hexafluorophosphate salt which has a monoclinic unit cell ($c = 24.2$ Å), which is probably due to differences in the interactions between $[BF_4]^-$ or $[PF_6]^-$ with the cationic imidazolium headgroups. However, in the absence of a single crystal structure of any related tetrafluoroborate salt few conclusions can be safely drawn.

Thermogravimetric analysis. The thermal stability of representative $[bmim]^+$, $[C_{15}\text{-mim}]^+$ and $[C_{18}\text{-mim}][BF_4]$ salts was determined by thermogravimetric analysis (TGA) over the temperature range 30–500 °C under N_2, heating at 10 °C min^{-1}. In each case, the samples showed no weight loss below 250 °C. The salts $[bmim][BF_4]$ and $[C_{18}\text{-mim}][BF_4]$ show a small weight loss of 3.5 (7.9) and 7.9 wt% (24.5 g mol^{-1}) respectively between 280 and 320 °C. No further degradation was observed until the temperature reached 360 °C, from which point progressive decomposition and mass loss occurred in all three samples between 360 and 450 °C. Thus, the tetrafluoroborate ionic liquids are more thermally stable than the halide and tetrachloroaluminate(III) analogues.

Conclusion

We have described the preparation and properties of a series of tetrafluoroborate salts which are liquid or liquid crystalline at, or close to, ambient temperature. The salts described can be separated into three distinct groups on the basis of their thermal behaviour: short chain, crystalline solids with strong interactions in the solid state and relatively high melting points; intermediate ionic liquids, which have a wide liquid range (up to 400 °C) and form glasses on cooling due to the reduction of lattice energies through disruption of packing efficiencies; and mesomorphic salts which have an amphiphilic structure, long alkyl chains ($n > 11$) and properties that are governed by the microphase separation of the hydrophilic and hydrophobic components of the amphiphilic cations which induces mesophase formation and crystallisation in layered structures.

As the chain length increases the glass transition temperatures decrease rapidly due to an elongation of the molecular length, disruption of crystal packing with increased flexibility of the alkyl chains and a reduction in the lattice energy, coupled (on increasing alkyl chain) with a distinct tendency towards glass formation rather than crystallisation on cooling. The glass transition temperatures all tend towards −90 °C, which also represents the lower limit of glass formation for the [emim]Cl–$AlCl_3$ system[27] and for $[C_n\text{-mim}][PF_6]$ salts.[17] On increasing alkyl-chain length, the attractive van der Waals interactions increase and from $n = 10$ the salts start to exhibit amphiphilic character. This produces an increase in the melting point and also stabilises microphase separation of the hydrophilic ionic headgroups and hydrophobic alkyl chains which leads to increasing orientational order and the layered structure observed in the solid state. Crystalline rather than glassy solids are formed with a discontinuity in the melting points, although relative to other long-chain salts the melting points, at between 25 and 60 °C, are low. On melting the long-chain salts display a single ordered thermotropic mesophase, the clearing points increasing with chain length.

For the mesomorphic salts the variation in melting points is very small compared with the dramatic increase in clearing point with chain length. This is consistent with the behaviour observed for other alkylimidazolium salts containing *e.g.* $[NiCl_4]^{2-}$, $[CoCl_4]^{2-}$, $[PF_6]^-$ and Cl^-, although data for a complete series of alkyl chain substituents has not previously been correlated. In the case of the tetrafluoroborate salts the melting points are lower than in the previous examples. These observations follow the general, empirically observed trends for alkylimidazolium salts that the melting points decrease on changing the anion in the order $Cl^- > [PF_6]^- > [BF_4]^-$.

The liquid range of the short chain salts is exceptionally wide; the preparation of the short chain salts $[emim][BF_4]$ and $[bmim][BF_4]$ and their use as solvents for catalytic reactions and electrochemistry have previously been reported. However, difficulties in preparing pure $[emim][BF_4]$ (especially removing halide impurities) means that future work is most likely to use the longer chain homologues, especially with $[bmim]^+$ and $[C_6\text{-mim}]^+$ cations. There are interesting changes in the solvent properties of the salts with increasing chain length; for example, the transition from water miscibility to immiscibility in a progressive, controlled manner. The low melting points of the longer chain, mesomorphic salts enables access to liquid crystalline solvents with large mesophase ranges from close to ambient temperature and the potential to use these materials as ordered reaction media.

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