

Liquid-crystalline ionic liquids

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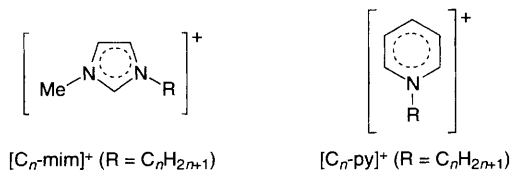
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Low-melting point salts, the basis of industrially relevant ionic liquids, exhibit smectic A mesophases over extended temperature ranges.

It is well known that organic molecules composed of a rigid and polarisable elongated core, attached to one or two aliphatic chains, often give liquid-crystal mesophases when heated.¹ In particular, when the alkyl chains are long, smectic phases tend to result due to the microphase separation of the polarisable core and the aliphatic tail portions. Smectic phases are also found in mesomorphic salts, the classic examples of which are Group 1 metal salts of carboxylic acids.²

Room-temperature chloroaluminate(III) ionic liquids are attracting much academic^{3–5} and industrial^{6–11} interest as, in addition to an extended liquid range, they exhibit super-acidity,¹² remarkable solubility properties¹³ and unique catalytic behaviour.^{7,10,11} The most widely studied systems are $\text{AlCl}_3\text{-[emim]Cl}$, $\text{AlCl}_2\text{Et-[bmim]Cl}$ and $\text{AlCl}_3\text{-[N-Bupy]Cl}$, where $[\text{emim}]^+$, $[\text{bmim}]^+$ and $[\text{N-Bupy}]^+$ are 1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium and *N*-butylpyridinium cations respectively. We have further investigated the physical properties of series of imidazolium and pyridinium salts, where the alkyl group, R, has been varied from C_2H_5 to $\text{C}_{18}\text{H}_{37}$. We report here that the salts of $[\text{C}_n\text{-mim}]^+$ and $[\text{C}_n\text{-py}]^+$ ($n = 12\text{--}18$), when associated with chloride, tetrachlorobaltate(II) or tetrachloronickelate(II) counter ions, all exhibit liquid crystalline behaviour and that the thermal stability of the resultant smectic A phase is related to the length, n , of the chain. The *N*-alkylpyridinium and 1-alkyl-3-methylimidazolium salts are therefore considered to be intermediate between the two types of liquid crystal outlined above, as they contain both an ionised, non-aliphatic portion and a short aromatic unit. The earlier work of Busico *et al.*^{14,15} and Somashekar¹⁶ forms a platform for this study.



The chloride salts were prepared by reaction at 100 °C for 7 days of 1-methylimidazole with the appropriate chloroalkane in a Carius tube sealed *in vacuo*. An analogous procedure was used for the pyridinium systems. Crystallisation was effected from ethanenitrile and the resulting salts stored under dinitrogen. The tetrachlorometalate(II) salts were prepared by heating the appropriate chloride with 0.5 equiv. of anhydrous nickel(II) chloride or cobalt(II) chloride in ethanenitrile for 3 h. Crystallisation was effected from the same solvent. All salts were checked for purity by elemental analysis, L-SIMS, IR and ¹H NMR spectroscopy (where appropriate).

The melting points and clearing points of all the salts having alkyl chain lengths of $n = 12\text{--}18$ were determined by differential scanning calorimetry (DSC) and polarising optical microscopy (below a chain length of 12 units, no liquid-crystal behaviour was observed). Thus, upon cooling from the isotropic

state, microscopy showed mesophases having homeotropic and focal conic textures consistent with a smectic A phase. An example is given in Fig. 1.

In the case of $[\text{C}_{18}\text{-py]Cl}$, two crystal-crystal transitions (72 °C, 8.55 kJ mol⁻¹; 77.6 °C, 14.7 kJ mol⁻¹) were observed by DSC before melting into the mesophase (85.6 °C, 20.51 kJ mol⁻¹). Attention is also drawn to the relatively large mesophase temperature ranges present in the chloride salts, especially those having an alkyl chain length of greater than 14 units, where the range is relatively independent of chain length. The tetrachlorometalate(II) salts, however, show a mesophase temperature range which increases monotonically with an increase in chain length (Fig. 2). This behaviour, which may be related to the z^2/r ratio for the ions (see ref. 17), is the subject of current work in our laboratories: the dependence on z^2/r is supported by the observation that, when prepared, the tetrachloroaluminate salts are liquid at room temperature. The systems presented here, which are ordered in the mesophase over large temperature ranges {e.g. for $[\text{C}_{18}\text{-py}]_2[\text{CoCl}_4]$, the

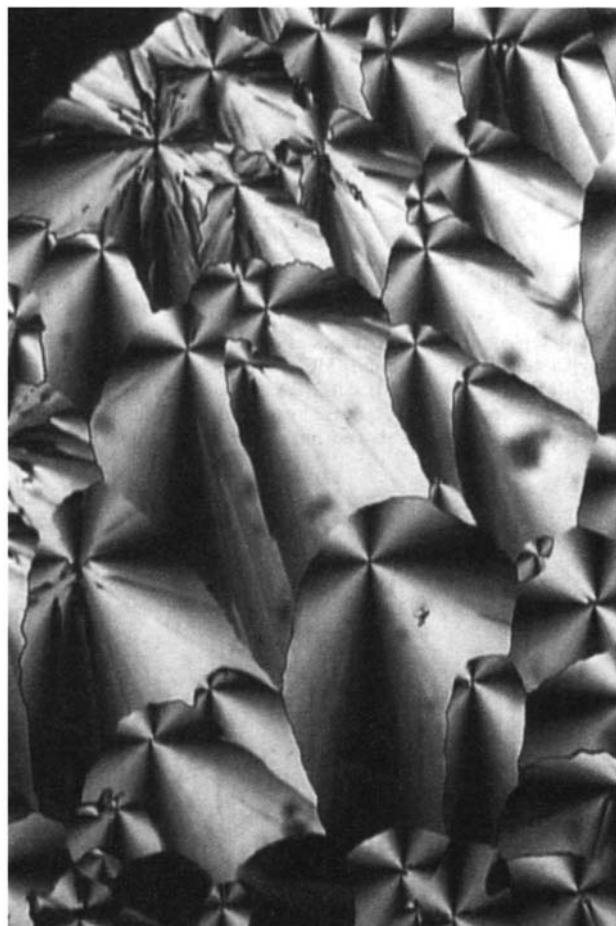


Fig. 1 Focal conic texture of $[\text{C}_{12}\text{-py}]_2[\text{CoCl}_4]$ obtained under crossed polars at magnification 180 \times

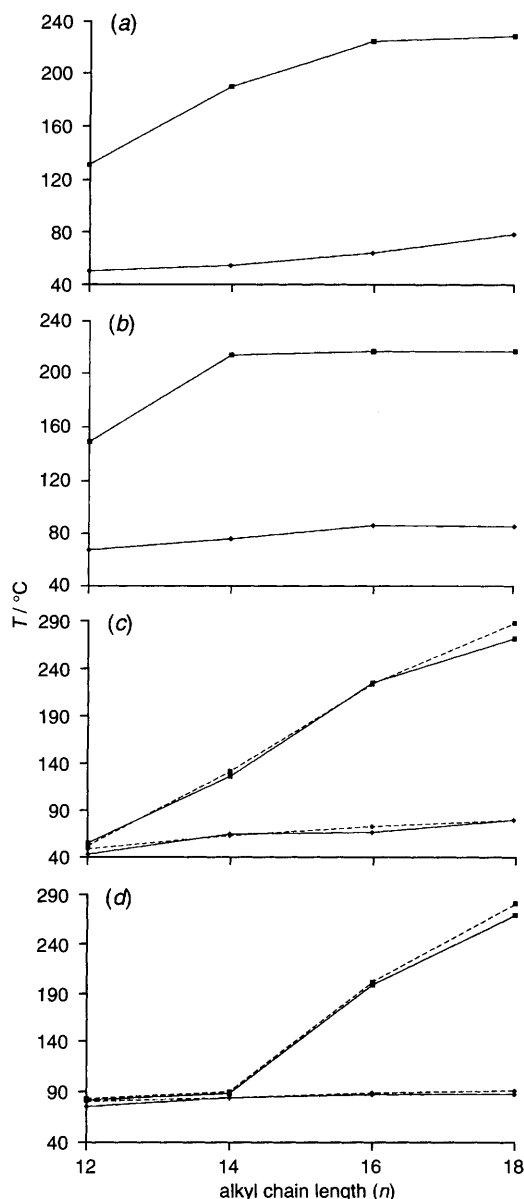


Fig. 2 Mesophase temperature ranges of (a) the $[C_n\text{-mim}]\text{Cl}$ salts, (b) the $[C_n\text{-py}]\text{Cl}$ salts, (c) the $[C_n\text{-mim}]_2[\text{MCl}_4]$ ($M = \text{Co}, \text{Ni}$) salts, and (d) the $[C_n\text{-py}]_2[\text{MCl}_4]$ ($M = \text{Co}, \text{Ni}$) salts. (■) Indicates clearing point values, (◆) indicates melting point values; in (c) and (d), solid lines indicate tetrachloronickelate(II) and dashed lines indicate tetrachlorocobaltate(II) salts.

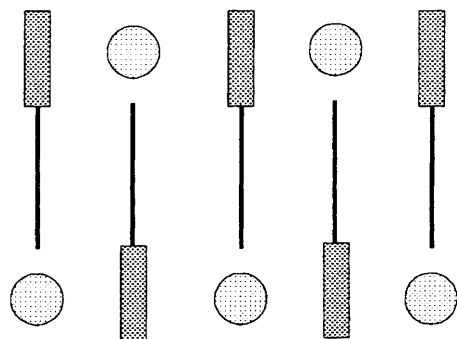


Fig. 3 The interdigitated structure proposed for the smectic phase of the salts in this work (organic moieties represented by rectangles; alkyl chains by black lines; counter ions by circles)

smectic A phase is stable over 188°C) and allow facile synthetic variation, may be suitable for use as organised media in polymer formation.¹⁸

From the work of Guillon,^{19,20} we would suggest that the structure shown in Fig. 3 is that present in the mesophase. In this arrangement, the anions are positioned between the aromatic rings in an interdigitated structure, necessary to fill the space resulting from the large size of the chlorometalate(II) anions.

In conclusion, these salts do indeed display liquid-crystalline properties over extended temperature ranges. They allow facile synthetic variation in the length of the alkyl substituents, and therefore the design of liquid crystals with predictable mesogenic characteristics. The use of liquid-crystal solvents can have a profound effect on the course of chemical reactions²¹ on account of their inherently ordered nature (*i.e.* the solvent performs a catalytic rôle). This phenomenon, coupled with the large mesophase temperature ranges of the systems presented here, results in a promising new family of solvents with many exciting potential applications.

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Footnotes:

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