

Simple amphiphilic liquid crystalline *N*-alkylimidazolium salts. A new solvent system providing a partially ordered environment†

Ching K. Lee, Hsin W. Huang and Ivan J. B. Lin*

Department of Chemistry, Fu-Jen Catholic University, Hsinchuang, Taipei 242, Taiwan.
E-mail: Chem1001@fujens.fju.edu.tw; Fax: +886-2-29023209

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Easily accessible liquid crystals of 1-alkylimidazolium salts having a bilayer structure, are good solvents providing a partially ordered reaction environment.

Molecular thermotropic liquid crystals, which have been extensively studied and documented, are usually molecules composed of an extended rigid aromatic core and terminal flexible alkyl chains. Ionic liquid crystals (ILCs), which have been less well studied^{1–6} in comparison to neutral LCs, are amphiphiles having a hydrophilic cationic or anionic head group and hydrophobic long alkyl chains. A classic example of an ILC is an alkali metal soap, in which the anion possesses a negatively charged head group with a long alkyl chain. However, ILCs with positively charged mesomorphic cations, such as alkylammonium,¹ alkyl phosphonium,^{1b,d,2} *N*-alkylpyridinium³ and *N,N*-dialkylimidazolium^{3a,b,4} salts have also been reported. These cationic amphiphiles have many interesting properties and are potentially useful as synthetic membranes,⁵ antimicrobial agents,⁶ gellators^{7,1b,d} NLO⁸ and surfactants,⁹ to name a few.

Recently ionic liquids (ILs) have been considered as a new generation of green solvents for organic reactions.¹⁰ ILs not only provide solvent properties different from any other organic solvent, but can also be recycled very easily. Furthermore, ILs possessing liquid crystal properties further provide a partially ordered environment and may give a better selectivity for organic reactions. A few examples of liquid crystalline ionic liquids of imidazolium salts have been reported.^{4,3b,c} In this paper we report the mesomorphic behavior of a new series of 1-alkylimidazolium salts prepared simply by the addition of acids to 1-alkylimidazoles (Scheme 1). In order to appraise the usefulness of this system as a solvent, we have begun a study of the Diels–Alder condensation. A stereoselectivity different from that of the known reactions has been found.

1-Alkylimidazoles‡ were synthesized according to the literature methods.¹¹ 1-Alkylimidazolium salts ($n = 10, 12, 14, 16, 18$) were prepared by adding a slight excess of concentrated acids dropwise to the 1-alkylimidazoles. Salts with the formula [R-imH][NO₃], [R-imH]Cl·H₂O and [R-imH][BF₄] were obtained after recrystallization from THF or CH₂Cl₂–hexane. Anhydrous chloride salts were obtained by heating the hydrated samples at 140 °C under vacuum for 3 h. Under such conditions, no decomposition has been observed as evidenced by ¹H NMR spectroscopy. The completeness of the dehydration has been confirmed by thermal gravimetric analysis. The chemical shift of the NH proton depends on the anion. With an alkyl chain length of $n = 14$, the chloride salt has the lowest chemical shift at 16.0 ppm, the nitrate salt has 15.5 ppm and the [BF₄][–] salt has the highest chemical shift at 12.3 ppm. A similar trend is observed for the 2-CH protons (Cl[–], 9.4; [NO₃][–], 9.2; [BF₄][–], 8.7 ppm). These trends may reflect the strength of the H-

bonding between the respective protons and anions and have been reported.¹²

In research on the packing of charged surfactant molecules, studies of the crystal structures of imidazolium based salts are rare.^{3b,4a} Therefore, the molecular structure of [C₁₄H₂₉-imH][NO₃] was determined by single crystal X-ray diffraction and is shown in Fig. 1. 1-Alkyl chains are parallel to the imidazole planes. The nitrate planes are also parallel to the imidazole planes. Interdigitation of alkyl chains forms a bilayer lamellae with a repeating layer distance of 16.9 Å. Each bilayer is further linked with anions through hydrogen bonds.

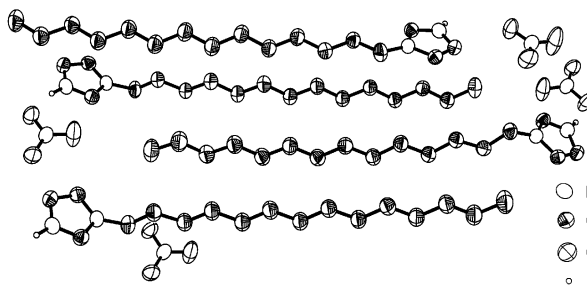
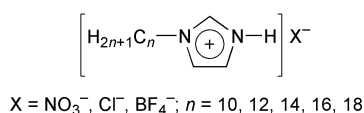


Fig. 1 ORTEP drawing of [C₁₄H₂₉-imH][NO₃] (50% thermal ellipsoids), hydrogens being omitted for clarity (except for N–H).

The liquid crystal properties of 1-alkylimidazolium salts were examined by optical polarized microscopy and differential scanning calorimetry. The nitrate salts with $n = 14, 16$ and 18 exhibit liquid crystal behavior. Characteristic focal conic fan and oily streak textures with spontaneous homeotropic phenomena are observed during the process of heating and cooling, suggesting a lamellar SmA mesophase (Fig. 2). The chloride and tetrafluoroborate salts also show SmA mesophases. The Cl[–] salt of $n = 10$ is a rt ILC and for the salt of $n = 12$, the process of crystallization needs several days when cooling to rt. The [BF₄][–] salt with $n = 12$ exhibits monotropic liquid crystal properties. In general, the temperature range of mesophase increases with increasing chain length (Fig. 3). Among the three different anions of [C_{*n*}H_{2*n*+1}-imH]X (X = Cl[–], [NO₃][–],



Fig. 2 The fan texture of the mesophase of [C₁₄H₂₉-imH][NO₃] at 70 °C.



Scheme 1 *N*-alkylimidazolium salts.

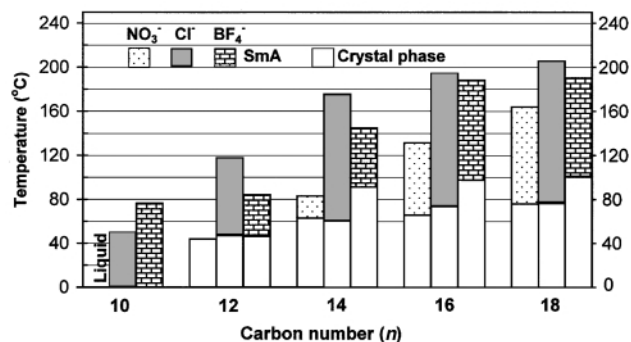


Fig. 3 The phase transition diagram of $[C_nH_{2n+1}imH]X$ from DSC at $10\text{ }^\circ\text{C min}^{-1}$. (X = Cl, BF_4^- , second heating step; X = NO_3^- , first heating step; X = BF_4^- , monotropic; X = Cl, $n = 10$ and X = NO_3^- , $n = 14$ from POM). For clarity the crystal to crystal phase transitions are not shown.

$[BF_4]^-$), the chloride salts have the widest temperature range of mesophase. This result may reflect the strength of H-bonding between the cation and the chloride anion. The nitrate salt of $n = 12$ and chloride salts of $n = 10, 12, 14$ exhibit lyotropic behavior in water, acidic water and THF. For example, both the nitrate and chloride salts of $n = 12$ in H_2O (>20% by weight concentration) are liquid crystals having a fan texture with a spontaneous homeotropic behavior at rt.

To demonstrate the effect of the lamellar phase on the stereoselectivity of Diels–Alder reactions, a preliminary condensation reaction¹³ of cyclopentadiene (0.063 g, 0.3 mmol) with diethyl maleate (0.024 g, 0.3 mmol) in an ionic liquid crystalline solvent system (a mixture of 0.42 g of $C_{12}H_{25}im$ and 0.15 mL of 12 M HCl) at rt was examined. Optical observation indicated that under these reaction conditions the reaction mixture retained the lamellar mesophase structure. The selectivity of *exo/endo* product was 54:46. A parallel reaction carried out in EtOH, gave an *exo/endo* ratio of 12:88. This preference for *exo* over *endo* product in the ionic liquid crystalline solvent is different from that observed when the reaction is carried out in EtOH and, in those earlier studies, simple ionic liquids,^{13c,d} water^{13a–c} or organic solvents.^{13a–c} This result indicates that the lamellar mesophase has a strong influence on the selectivity of the reaction product.

In summary, we prepared a new series of thermotropic liquid crystalline 1-alkyl-substituted imidazolium salts. The chloride salts of $n = 10, 12, 14$ and the nitrate salts of $n = 12$ also exhibit lyotropic properties. The thermotropic and special lyotropic properties possessed by this series of ILCs make them alternative solvents for organic reactions, such as Diels–Alder condensations, and metal-catalyzed reactions.

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Notes and references

† Crystal data for $[C_{14}H_{29}imH][NO_3]$: $C_{17}H_{33}N_3O_3$, $M = 303.44$, triclinic, $a = 8.962(3)$, $b = 19.793(18)$, $c = 22.363(7)$ Å, $\alpha = 99.606(17)$, $\beta = 92.371(18)$, $\gamma = 98.307(18)^\circ$, $V = 3862(2)$ Å³, $T = 298$ K, space group $P1$,

$Z = 10$, $\mu = 0.090$ mm⁻¹, $\sigma_{\text{calcd}} = 1.305$ mg m⁻³, $1.52 < \theta < 25.00$. Of 16247 reflections measured, 13442 were unique. Data were collected on a Siemens P4 diffractometer with graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) in ω scan mode. The structure was solved by direct methods and refined (based on F^2 using all independent data) by full matrix least squares methods (Siemens SHELXTL V. 5.03). All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms, located by Fourier difference synthesis, were isotropically refined with a common thermal parameter. R values are reported for $R1 = 0.0505$ (based on observed data, $I > 2\sigma$) and $wR2 = 0.1390$ (based on all data). CCDC 182/1768. See <http://www.rsc.org/suppdata/cc/b0/b004462h/> for crystallographic files in .cif format. ¹H-NMR (ppm, CDCl₃, 25 °C): 0.87 (t, ³J = 7 Hz, -CH₃, 3H), 1.25–1.32 (m, -CH₂, 22H), 1.87 (m, -CH₂, 2H), 4.28 (t, ³J = 7 Hz, -NCH₂, 2H), 7.11 (s, CH, 1H), 7.40 (s, -CH, 1H), 9.36 (s, -CH, 1H), 15.53 (s, -NH, 1H). Anal. Calcd. for $C_{17}H_{33}N_3O_3$: C 62.35; H 10.16; N 12.83. Found: C 62.17; H 10.14; N 12.76%.

‡ 1-Alkylimidazolium nitrates ($n = 10, 12, 14, 16, 18$) were prepared by adding a slight excess of concentrated nitric acid dropwise to the 1-alkylimidazoles at 0 °C in ether. Immediate white precipitates formed when $n = 12, 14, 16, 18$. The nitrate salt with $n = 10$ is a liquid, which was purified by successive washing with ether followed by vacuum drying. Chloride salts ($n = 10, 12, 14, 16, 18$) were prepared by using concentrated hydrochloric acid as the acid source. Tetrafluoroborate salts ($n = 10, 12, 14, 16, 18$) were prepared by adding excess of tetrafluoroboric acid (32% in water) to 1-alkylimidazoles in water–THF.

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