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Synthesis, thermal and lyotropic liquid crystalline properties of protic ionic salts

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A series of protic ionic salts were synthesised by a simple acid–base reaction from various pyridine derivatives and dodecylbenzenesulfonic acid in a common organic solvent and characterised in terms of their thermal and lyotropic liquid crystalline properties using various experimental techniques. All of them exhibited lyotropic liquid crystalline phases in toluene, methanol, acetonitrile, dimethyl sulfoxide and water. Their critical concentrations for the formation of biphasic solutions and concentrations for the formation of lyotropic solutions were quite broad depending on the dielectric constants of the solvents. Their lyotropic phases were identified as lamellar phases, since their textures exhibited bâtonnets, oily streaks and mosaic textures. They can potentially be used for many organic transformations, which may have implications in green chemistry.

Keywords: protic ionic salts; lyotropic liquid crystalline textures

1. Introduction

Room temperature (RT) ionic liquids have received unabated attention as a class of novel solvents for many potential applications. These applications include, but are not limited to, green inorganic, organic and polymer syntheses, energy storage devices, separations and catalysis. The term ionic liquid is broadly used to describe a large class of low melting ionic salts that are usually liquids below 100°C. They are a unique class of organic solvents, which possess many interesting properties that include low vapour pressure, non-flammability, high thermal stability, liquid state over a broad range of temperature and solvating properties for diverse compounds including polymers (*1–6*).

The two ionic liquids originally reported were ethanolammonium nitrate (m.p. 52–53°C) and ethylammonium nitrate, both of which are also protic ionic liquids (PILs) (*7, 8*). This class of ionic liquids, usually prepared from a simple combination of a wide variety of organic amines with HBF_4, $NH(SO_2CF_3)_2$ and other acids, has rekindled interest for many researchers, since they provide additional interesting properties quite different from RT ionic liquids for many technological applications. First, they are electroactive for H_2 oxidation and O_2 reduction at a Pt electrode under non-humidifying conditions, which shows the prospect of the use of these materials for anhydrous proton conductors at elevated temperatures (*9–16*). Second, they can be used conveniently as strong Brønsted acids for many chemical transformations both in academic and industrial laboratories, since they are deemed less noxious than traditional liquid acids. Two notable transformations in organic chemistry are esterification and Diels–Alder reactions that can be carried out successfully in these PILs (*17, 18*).

In this paper, we report the convenient synthesis of a series of protic ionic salts (**1**–**4**, see Scheme 1) via simple acid–base reaction of various pyridine derivatives and dodecylbenzenesulfonic acid (DBSA) in a common organic solvent, either ether or isopropanol (see further information, available via the Multimedia link on the online article webpage). Their chemical structures were characterised by FTIR and ^1H and ^{13}C NMR spectra and elemental analyses. Their thermal and lyotropic liquid crystalline (LC) properties were studied by using various experimental techniques with the aim of understanding the structure–physical property relationships and developing novel materials based on this class of protic ionic salts.

2. Experimental

Procedures for compounds 1–4

To an ether solution of DBSA (2.04 g, 6.44 mmol) was added dropwise γ-picoline (0.5 g, 5.37 mmol). White crystals formed immediately, which were collected and washed with ether to yield 1.8 g (84%) of white compound **1**. IR (KBr, ν_{max} cm^{-1}): 3456, 3248, 3086, 2924, 2855, 1643, 1504, 1227, 1173, 1034, 1011, 810, 685, 586. ^1H NMR (400 MHz, CD_3OD, 298 K): δ 8.68 (d, J=6.8 Hz, 2H, Ar–H), 7.91 (d,

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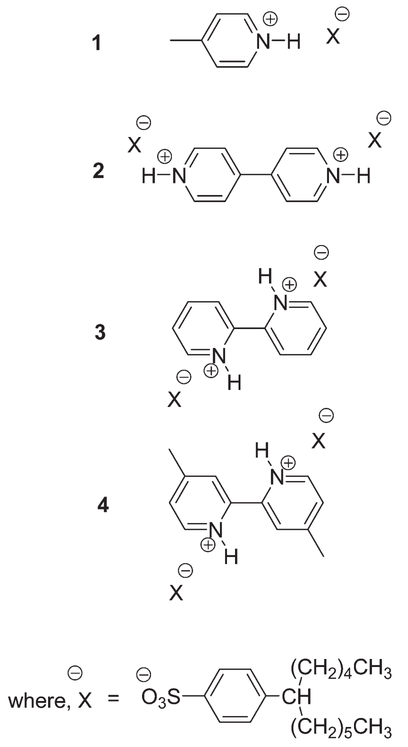

Scheme 1. Chemical structures of synthesised protic ionic salts **1**–**4**.

J=6.4 Hz, 2H, Ar–H), 7.73–7.76 (m, 2H, Ar–H DBSA), 7.19–7.25 (m, 2H, Ar–H DBSA), 2.65 (s, 3H, CH$_3$), 0.80–2.8 (m, 22H, aliphatic-H DBSA), 0.75 (t, J=7.4 Hz, 3H, CH$_3$ DBSA); the acidic proton signal was not detected due to the rapid exchange with trace amount of moisture and solvent. ^{13}C NMR (100 MHz, CD$_3$OD, 298 K): δ 151.64, 150.12, 143.91, 141.96, 129.20, 128.72, 128.66, 127.94, 127.06, 127.01, 41.09, 39.38, 38.08, 33.07, 30.76, 30.43, 28.67, 23.73, 22.81, 22.39, 21.68, 14.45. Elemental analysis: calculated (found) for $C_{24}H_{37}NO_3S$ (419.63), C 68.70 (68.78), H 8.89 (9.06), N 3.34 (3.53), S 7.64 (7.87%).

4,4′-Bipyridyl (0.5 g, 3.20 mmol) was dissolved in a minimum volume of isopropanol. An isopropanol solution of DBSA (2.4 g, 7.36 mmol) was added, upon which precipitation of compound **2** occurred immediately. The reaction mixture was stirred for half an hour to ensure that the reaction was complete. The solid product was collected, washed with ether and air-dried. Yield: 2.4 g (92%) as white crystals. IR (KBr, $\nu_{\max}$ cm^{-1}): 3456, 3248, 3094, 2924, 2855, 1628, 1466, 1381, 1227, 1165, 1119, 1026, 1003, 826, 664, 571. ^{1}H NMR (400 MHz, CD$_3$OD, 298 K): δ 9.07 (d, J=5.2 Hz, 2H, Ar–H), 8.53 (d, J=5.4 Hz, 2H, Ar–H), 7.72–7.76 (m, 4H, Ar–H DBSA), 7.20–7.25 (m, 4H, Ar–H DBSA), 0.80–2.80 (m, 44H, aliphatic-H DBSA), 0.75 (t, J=7.4 Hz, 6H, CH$_3$ DBSA); the acidic proton signal was not detected due to the rapid exchange with trace amount of moisture and solvent. ^{13}C NMR (100 MHz, CD$_3$OD, 298 K): δ 152.62, 145.24, 128.77, 128.70, 127.98, 127.07, 127.03, 41.11, 39.40, 38.08, 33.04, 30.78, 30.46, 28.80, 23.75, 22.81, 21.88, 14.47. Elemental analysis: calculated (found) for $C_{46}H_{68}N_2O_6S_2$ (809.19), C 68.28 (67.90), H 8.40 (8.70), N 3.46 (3.63), S 7.92 (8.30%).

The reaction for compound **3** was carried out using similar procedure and on an identical scale for compound **2**. When the dodecylbenzenesulfonic acid was added precipitation did not occur instantaneously. The solvent isopropanol from the reaction mixture was completely removed by rotary evaporation. Upon addition of ether a precipitate formed. The precipitate was collected and washed with ether to yield 2.45 g (94%) of an off-white compound. IR (KBr, $\nu_{\max}$ cm^{-1}): 3456, 3248, 3063, 2924, 2855, 1605, 1528, 1466, 1242, 1157, 1034, 1003, 833, 772, 687, 579. ^{1}H NMR (400 MHz, CD$_3$OD, 298 K): δ 8.88 (d, J=5.4 Hz, 2H, Ar–H 6,6′), 8.61 (d, J=8.2 Hz, 2H, Ar–H 3,3′), 8.42 (td, J=8.0, 1.6 Hz, 2H, Ar–H 4,4′), 7.89 (td, J=8.0, 1.6 Hz, 2H, Ar–H 5,5′), 7.74–7.77 (m, 4H, Ar–H DBSA), 7.20–7.26 (m, 4H, Ar–H DBSA), 0.80–2.80 (m, 44H, aliphatic-H DBSA), 0.75 (t, J=7.4 Hz, 6H, CH$_3$ DBSA); the acidic proton signal was not detected due to the rapid exchange with trace amount of moisture and solvent. ^{13}C NMR (100 MHz, CD$_3$OD, 298 K): δ 150.21, 148.70, 147.48, 144.45, 143.75, 128.76, 128.46, 127.93, 127.10, 124.77, 41.11, 39.39, 38.08, 33.08, 30.77, 30.44, 28.69, 23.76, 22.81, 21.88, 14.46. Elemental analysis: calculated (found) for $C_{46}H_{68}N_2O_6S_2$ (809.19), C 68.28 (67.88), H 8.47 (8.74), N 3.46 (3.81), S 7.92 (8.32%).

4,4′-Dimethyl-2,2′-bipyridyl (0.5 g, 2.71 mmol) and DBSA (2.04 g, 6.24 mmol) were used for the preparation of compound **4**. The set up and the isolation procedure for this compound were essentially identical to those for compound **3**. Yield 2.16 g (95%), as a white compound. IR (KBr, $\nu_{\max}$ cm^{-1}): 3456, 3248, 3078, 2924, 2855, 1628, 1528, 1458, 1373, 1227, 1165, 1119, 1039, 1011, 833, 671, 579. ^{1}H NMR (400 MHz, CD$_3$OD, 298 K): δ 8.68 (d, J=5.20 Hz, 2H, Ar–H 6,6′), 8.46 (s, 2H, Ar–H 3,3′), 7.63–7.71(m, 6H, Ar–H 5,5′ and Ar–H DBSA), 7.20–7.25 (m, 4H, Ar–H DBSA), 2.65 (s, 6H, CH$_3$ 2,2′-bipyridyl), 0.80–2.80 (m, 44H, aliphatic-H DBSA), 0.75 (t, J=7.4 Hz, 6H, CH$_3$ DBSA); the acidic proton signal was not detected due to the rapid exchange with trace amount of moisture and solvent. ^{13}C NMR (100 MHz, CD$_3$OD, 298 K): δ 150.21, 148.32, 146.62, 143.79, 128.93, 128.75, 127.96, 127.10, 125.26, 41.11, 39.39, 38.08, 33.04, 30.77, 30.44, 28.69, 23.76, 22.81, 21.88, 14.46. Elemental analysis: calculated (found) for $C_{48}H_{72}N_2O_6S_2$ (837.24), C 68.86 (68.48), H 8.67

(8.76), N 3.35 (3.49), S 7.66 (8.04%). Note that the salts **1**–**4** were prepared without the use of anhydrous solvents and a glove box.

3. Results and discussion

We successfully synthesised the PILs **1**–**4** by simple acid–base reaction of pyridine derivatives with DBSA with relatively high yields and characterised their chemical structures by various spectroscopic techniques and elemental analysis (see further information, available via the Multimedia link on the online article webpage) FTIR spectra were quite informative in identifying these salts, since they were formed from the proton transfer from DBSA to various pyridine derivatives, as evidenced from the appearance of two characteristic absorption bands at ca. 1173 and 1227 cm^{-1} for $^{-}O_3S$-DBSA instead of an absorption band at ca. 900 cm^{-1} of the –SO_3H group of DBSA. Furthermore, there was a disappearance of the out-of-plane bending mode of pyridine rings ca. at 990 cm^{-1} and a concomitant appearance of two characteristic absorption bands of pyridinium rings at ca. 1011 and 1034 cm^{-1}, demonstrating the acid–base reaction for the synthesis of these salts. A strong band associated with pyridinium C–C bonds identified as the sp^2/sp^2 C–C bond stretching frequency appeared at ca. 1643 cm^{-1} and that of the benzene ring of $^{-}O_3S$-DBSA appeared at ca. 1600 cm^{-1} (see further information, available via the Multimedia link on the online article webpage).

The thermal properties of compounds **1**–**4** were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA results revealed that all of the PILs had excellent thermal stability in the temperature range 182–272°C, the temperature at which the 5 wt % loss of each of these compounds occurred at a heating rate of 10°C min^{-1} in nitrogen. Figure 1 shows the DSC thermograms of compounds **1** and **2** obtained at heating and cooling rates of 10°C min^{-1}.

Compound **1**, which was prepared from γ–picoline (liquid) and DBSA (viscous liquid), exhibited an onset temperature of melting (T_m) at 92°C with an enthalpy change (ΔH) of 2.7 kcal mol^{-1} and a peak maximum at 96°C in the first heating cycle of its DSC thermogram. In the first cooling cycle, there was a crystallisation exotherm (T_c) at 76°C with ΔH=2.3 kcal mol^{-1}. However, both the T_m in the second heating and the T_c in the second cooling cycles of its DSC thermograms were shifted to lower temperatures with decreased enthalpy changes when

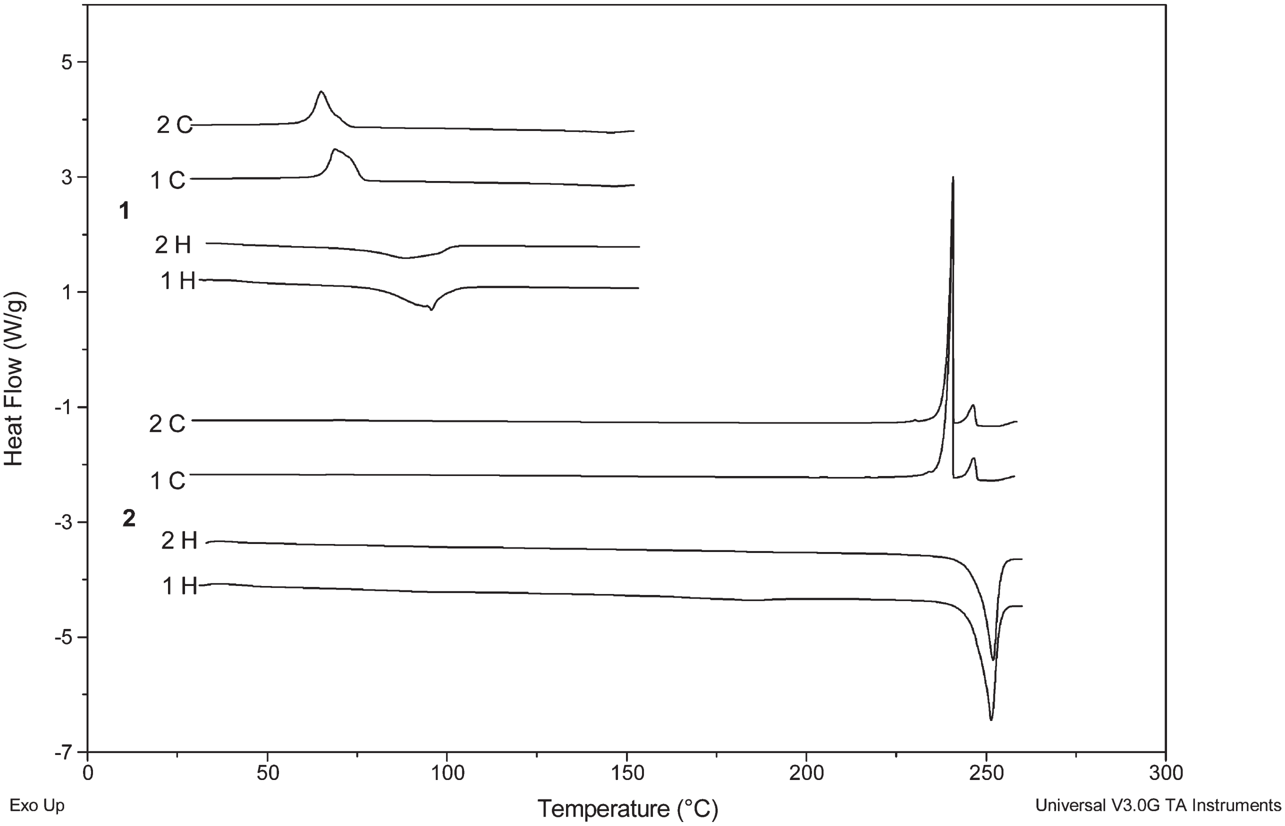

Figure 1. DSC thermograms of compounds **1** and **2** obtained at heating and cooling rates of 10°C min^{-1}.

compared with those in the first heating and cooling cycles. Apparently, it showed a broad melting endotherm when compared with that of a typical organic compound. The T_m of this salt was higher than those of γ–picoline and DBSA because of the formation of salt. The ionic salt **2**, which was prepared from 4,4′-bipyridine (m.p. 109–112°C) and DBSA, showed an indistinct endotherm at 162°C with ΔH=1.1 kcal mol^{-1} and a large endotherm at 248°C with ΔH=11.4 kcal mol^{-1} in the first heating cycle of its DSC thermogram. In the subsequent cooling cycle it exhibited a small exotherm at 248°C with small ΔH=1.0 kcal mol^{-1} and a large exotherm at 241°C with high ΔH=8.4 kcal mol^{-1}. It showed identical endotherms and exotherms in the second heating and cooling cycles, respectively.

On examining this salt (**2**) using polarising optical microscopy (POM), it was found that the large endotherm in the heating cycle was the crystal-to-liquid (T_m) transition. However, on cooling it exhibited a LC phase, which consists of thread-like or the so-called the Schlieren texture, as shown in Figure 2. On further cooling it transformed from the LC phase into a crystalline phase. The absence of supercooling of the isotropic to LC phase transition in the DSC thermogram as opposed to the supercooling that usually occurs during transformation from the LC phase to the crystalline phase of an organic compound also indicated the existence of a LC phase in this salt. The appearance of one large melting endotherm in the heating cycle and of two exotherms in the cooling cycle is the signature of a monotropic LC phase present in this salt (*19, 20*). However, it exhibited a very narrow temperature range of 7°C in the LC phase.

Salt **3**, which was prepared from 2,2′-bipyridine (m.p. 71–72°C) and DBSA, exhibited a large T_m endotherm at 120°C with ΔH=12.8 kcal mol^{-1} in the first heating cycle of its DSC thermogram. In the first cooling cycle, it exhibited a single exotherm T_c at 103°C with ΔH=11.8 kcal mol^{-1}. The DSC thermograms in the second heating and cooling cycles were essentially identical to those in the first heating and cooling cycles with the exceptions that both T_m and T_c were slightly shifted to lower temperatures with slightly reduced ΔH values. The T_m value was higher than those of 2,2′-bipyridyl and DBSA because of the ionic interactions present in this salt. Salt **4**, which was prepared from 4,4′-dimethyl-2,2′-bipyridine (m.p. 169–174°C) and DBSA, exhibited a large T_m endotherm at 114°C with ΔH=8.5 kcal mol^{-1} in the first heating cycle of its DSC thermogram. In the first cooling cycle, it exhibited a single exotherm T_c at 92°C with ΔH=7.8 kcal mol^{-1}. The T_m and T_c values, including their ΔH values, in the second heating and cooling cycles were essentially identical to those in the first heating and cooling cycles. The T_m value of **4** was much lower than that of 4,4′-dimethyl-2,2′-bipyridyl, suggesting that chemical structural modifications of organic bases and acids may lead to the development of PILs, i.e. protic ionic salts with melting transitions below 100°C (*14*).

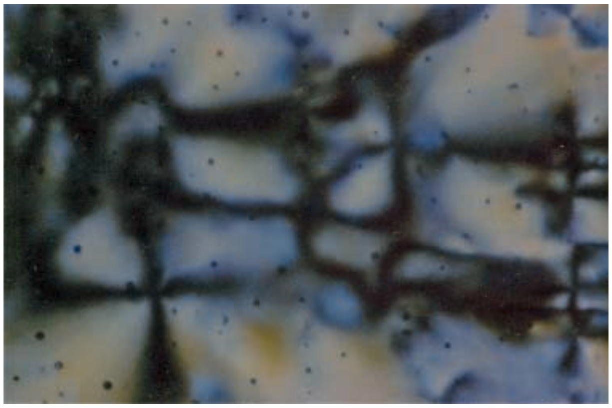

Figure 2. Photomicrograph of compound **2** taken on cooling from the isotropic liquid phase under crossed polarisers, showing a monotropic, thermotropic LC phase (magnification 400 ×).

The solubility properties of salts **1**–**4** in various non-polar and polar solvents including water were remarkable, which motivated us to explore the lyotropic LC properties in various solvents having dielectric constants in the broad range 2.4–78.4. Table 1 shows the solution properties of salt **1** in various solvents. Solution properties of other salts **2**–**4** are provided in the online supplementary material (see Tables S1–S3, which are available via the Multimedia link on the online article webpage).

When examined with POM under crossed polarisers at RT, Salt **1** exhibited an isotropic solution (dark background) at a relatively low concentration of 10 wt % in toluene, which is relatively a non-polar solvent. At intermediate concentrations it formed a biphasic solution at 20 wt % in this solvent, wherein there coexisted an anisotropic (birefringence) and an isotropic phase. This concentration is usually known as critical concentration (C^*) at which the appearance of an anisotropic phase occurs. At the higher concentration of 30 wt %, the development of fully-grown lyotropic phase occurred in this solvent. When examining the solution properties of this salt in methanol (a protic polar solvent) it exhibited an isotropic solution at concentrations as high as ca. 70 wt % because of its high solubility. Consequently, the biphasic and lyotropic solutions appeared at high concentrations of 80 and 90 wt % in this solvent. In more polar solvents such as acetonitrile and dimethyl sulfoxide, its isotropic solution, C^* and lyotropic

Table 1. Solution properties of compound **1** in solvents of varying dielectric constants (ε=2.4–78.4) at room temperature.

Solvent	Concentration/wt %	Solution properties[a]
Toluene	10	isotropic solution
(ε=2.4)	20	biphasic solution[b]
	30	lyotropic solution[c]
CH_3OH	60	isotropic solution
(ε=32.6)	69	isotropic solution
	80	biphasic solution[b]
	90	lyotropic solution[c]
CH_3CN	30	isotropic solution
(ε=37.5)	41	isotropic solution
	50	biphasic solution[b]
	70	biphasic solution[b]
	81	lyotropic solution[c]
DMSO	30	isotropic solution
(ε=48.9)	39	isotropic solution
	49	biphasic solution[b]
	70	biphasic solution[b]
	80	lyotropic solution[c]
H_2O	41	isotropic solution
(ε=78.4)	50	biphasic solution[b]
	60	biphasic solution[b]
	69	lyotropic solution[c]

[a] Observation with a polarising optical microscope between crossed polarisers at room temperature; [b] Lyotropic phase coexisting with an isotropic phase; [c] Strong shear birefringence.

solutions appeared at essentially identical concentrations of ca. 40, 50 and 80 wt % in these solvents. In water, its isotropic solution, *C** and lyotropic solutions appeared at concentrations of ca. 40, 50 and 70 wt % in this universal solvent (Table 1).

Salt **2**, a dicationic salt, exhibited a biphasic solution at concentrations as low as 1 wt % and lyotropic solution at 20 wt % in toluene. In methanol, its isotropic solution, *C** and lyotropic solutions appeared at concentrations of ca. 10, 20 and 30 wt %, which were much lower concentrations when compared with those of salt **1**. In acetonitrile, it showed a biphasic solution at a very low concentration of 1 wt % and developed a lyotropic solution at ca. 20 wt %. In DMSO, its isotropic solution, *C** and lyotropic solutions appeared at concentrations of ca. 5, 10 and 20 wt %. In water, its isotropic solution, *C** and lyotropic solutions appeared at concentrations of ca. 1, 5 and 60 wt % (see Table S1).

Salt **3**, like salt **2**, exhibited a biphasic solution at 1 wt % in toluene, but its lyotropic solution occurred at a much lower concentration 10 wt % than that of salt **2**. It showed high solubility in methanol at concentrations as high as 50 wt % to form an isotropic solution and formed a fully-developed lyotropic phase at ca. 60 wt %. In acetonitrile, its isotropic, biphasic and lyotropic solutions occurred at ca. 1, 5 and 20 wt %. In DMSO, it formed an isotropic solution at the highest concentration of 70 wt % among the solvents studied. Its lyotropic phase appeared at 80 wt %. In water, it also had high solubility up to 60 wt % at which it exhibited isotropic solution. Correspondingly, its biphasic and lyotropic solutions occurred at much higher concentrations of 70 and 80 wt %, respectively (see Table S2).

Salt **4** showed isotropic, biphasic and lyotropic solutions at ca. 1, 10 and 30 wt % in toluene. These solution properties occurred in methanol at 40, 50 and 60 wt %, which were much higher than those in toluene. In acetonitrile, its isotropic, biphasic and lyotropic solutions occurred at 1, 5 and 20 wt %, which were the lowest concentrations among the solvents studied. In DMSO and water, it had solubility as high as 50 wt %, wherein it formed isotropic solutions. Its *C** for the formation of biphasic solution in both the solvents was essentially identical at ca 60 wt %, but its concentration for the formation of lyotropic phase in water (90 wt %) was slightly higher than that in DMSO (80 wt %) (see Table S3). From these limited studies, it is difficult to correlate *C** and lyotropic concentrations for these salts in various solvents from non-polar to highly polar solvents with regard to their chemical structures. However, the formation of lyotropic phase of these salts in non-polar toluene was presumably related to the long tail hydrocarbon of DBSA counter ion present in each of these salts, since it not only increased the solubility of each of these salts in this solvent but also aided in exceeding the *C** for the formation of lyotropic phase.

The textures of lyotropic LC phases of the compounds were more or less similar to thermotropic LC phases of compounds. However, the thermotropic compounds have the advantage of being one-component systems and, hence, less complex than the lyotropic compounds that are by definition many-component systems (*21*). The lyotropic phases of the compounds in specific solvents may exhibit the various textures of nematic, hexagonal (middle) and lamellar (neat) phase. The latter two phases are originally found in many amphiphilic compounds (*21–23*). The textures observed with POM studies for all of the biphasic and lyotropic solutions of **1**–**4** in all of the solvents within the range of dielectric constants 2.4–78.4 indicated small and large bâtonnets, oily streaks and different types of polygonal arrays (often referred to as mosaic textures) (Figure 3 and Figures S1–S3, which are available via the Multimedia link on the online article webpage), all of which were indicative of a lamellar phase (*21–24*). The oily streaks appear as long individual bands with fine and well-resolved transversal striations corresponding probably to chains of focal conic groups.

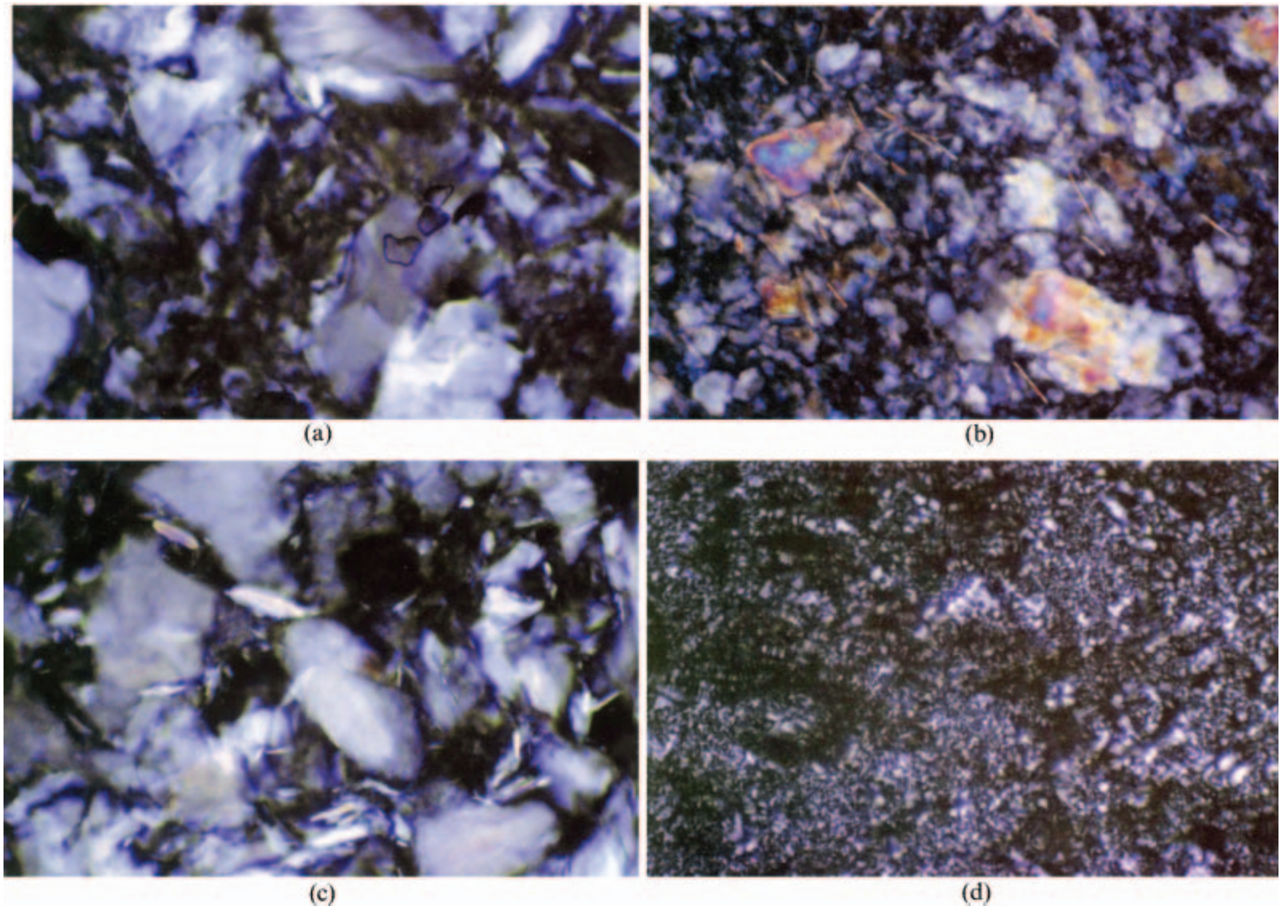

Figure 3. Photomicrographs of compound **1** at concentrations of (a) 40 wt % in toluene, (b) 90 wt % in methanol, (c) 81 wt % in acetonitrile and (d) 79 wt % in water taken at RT under crossed polarisers, exhibiting lyotropic LC phases (magnification 400 ×).

The black areas between the streaks are homeotropic regions where the optical axis of the molecules is normal to the glass surfaces (*24*).

An important feature, common to each of these salts (**1**–**4**) was that the textures of either the biphasic or lyotropic solutions were preserved on slow evaporation of various solvents from these solutions. Their basic features, i.e. threaded textures mixed with small or large bâtonnets, oily streaks and polygonal arrays, indicated that the local orientation of liquid crystal-forming units in these salts did not change when the slow evaporation of solvents occurred from either biphasic solutions or lyotropic solutions. However, they underwent a decrease in the density of threads with the simultaneous development of birefringent domains that presumably occurred because of the annihilation process between disclinations of various strengths and types. Finally, these salts underwent a time-dependent transition, from their biphasic or lyotropic solutions to a crystalline phase of spherulitic structure (*25*–*29*).

Although DSC measurements of a biphasic solution of salt **1** in DMSO (60 wt %) in sealed liquid pan produced no observable peak in the first heating and second heating cycles recorded at a heating rate of 10°C min^{-1}, its lyotropic solution (81 wt %) in this solvent produced a broad endotherm in both the heating cycles at an identical heating rate. Correspondingly, there was a broad exotherm in the each of the cooling cycles at a cooling rate of 10°C min^{-1}. However, cooling exotherms were somewhat narrower than the endotherms in the heating cycles (not shown). In conjunction with POM studies it was found that this endotherm was related to the transition from the lamellar LC phase to an isotropic solution and the exotherm was related to the appearance of lyotropic phase from an isotropic solution on cooling. The DSC measurements of a lyotropic solution of **2** in DMSO (50 wt %) also produced a broad endotherm in both the heating cycles and a relatively sharper exotherm in both the cooling cycles (see Figure S4, which is available via the Multimedia link on the online article webpage). Thermograms obtained from a lyotropic solution of salt **3** in DMSO (80 wt %) showed a broad endotherm in each of the heating cycles, but no exotherm in the each of the cooling cycles. Thermograms obtained from a lyotropic solution of salt **4** in DMSO (80 wt %) showed only an endotherm in the first heating cycle, but no endotherm in the second heating cycle. There was no exotherm in each of the cooling cycles.

4. Conclusions

We have presented an easy synthetic procedure for the preparation of a series of protic ionic salts via a simple acid–base reaction in a common organic solvent. The ionic salt **2** exhibited a monotropic LC phase in the cooling cycle; and others had T_m values in the range 114–162°C. The salts had excellent thermal stability in the temperature range ca. 180–275°C in nitrogen. They exhibited lyotropic lamellar phases in toluene, methanol, acetonitrile, dimethyl sulfoxide and water. To our knowledge, there are relatively few reports on the thermotropic and lyotropic LC properties of protic ionic salts (*30–32*). In this regard, the lyotropic LC phases of protic ionic salts reported herein represent a class of ordered solvent media at RT, which could be useful for performing many organic reactions with high selectivities and high yields. Thus, these ionic salts are potentially suitable for organic transformations, which may have green chemistry implications.

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Supplementary material

Solution properties of salts **2–4** in various solvents (Tables S1–S3), ^{1}H and ^{13}C NMR spectra of **1–4** (Figures S1–S4), photomicrographs in biphasic and lyotropic solutions of **2–4** (Figures S5–S7) and DSC thermograms of a lyotropic solution of salt **2** in DMSO (Figure S8) are provided as supplementary material, which is available via the Multimedia link on the online article webpage.

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