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Synthesis and characterization on a novel series of protic pyrrolidinium surfactants

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Abstract

A novel series of protic tertiary pyrrolidinium surfactants were prepared and characterized by different techniques. These compounds show good conductivity and efficient ability to reduce surface tension. Thermogravimetric analysis proves their high thermal stability at decomposition temperatures over 250 °C. Their lyotropic and thermotropic liquid crystalline properties are also discussed.

Keywords: Protic pyrrolidinium surfactants; Liquid crystal; Conductivity; Surface tension

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Pyrrolidinium salts are generally composed of short or long tailorable alkyl chains, which could lead them to have specific physicochemical properties through structural modifications. With short alkyl chains, such salts are usually adopted as ionic liquids and plastic crystal materials [1–3], which are becoming more and more popular to substitute the traditional volatile organic solvents for applications in the area of organic synthesis, catalysis, electrochemistry, liquid/liquid extraction, and preparation of novel materials. Meanwhile, their high ionic conductivity in both solid and liquid states has been paid much attention for uses as electrolytes in lithium batteries [4], solvent-free dye-sensitized solar cells [5], and so on. With long alkyl chains, however, pyrrolidinium salts behave like surfactive 1-alkyl-3-methylimidazolium salts ([$C_n$mim]X) to show amphiphilicity [6,7]. They are attracting increased attention now for their fascinating ionic liquid crystalline properties except for good conductivity [8,9].

Most pyrrolidinium ionic liquids or surfactants contain an *N*-methyl-*N*-alkylpyrrolidinium organic cation and an anion of different types like bromide, iodide, nitrate, bis-(trifluoromethane sulfonyl)imide, tetrafluoroborate or hexafluorophosphate. On that basis, several novel protic pyrrolidinium-cations ionic liquids with short alkyl chains have been developed recently [10], which can be used as proton conducting electrolyte in fuel cells, double layer capacitors, dye-sensitized solar cell, or actuators. To our best knowledge, however, there are not reports on protic surfactive pyrrolidinium salts and their liquid crystalline behaviour.

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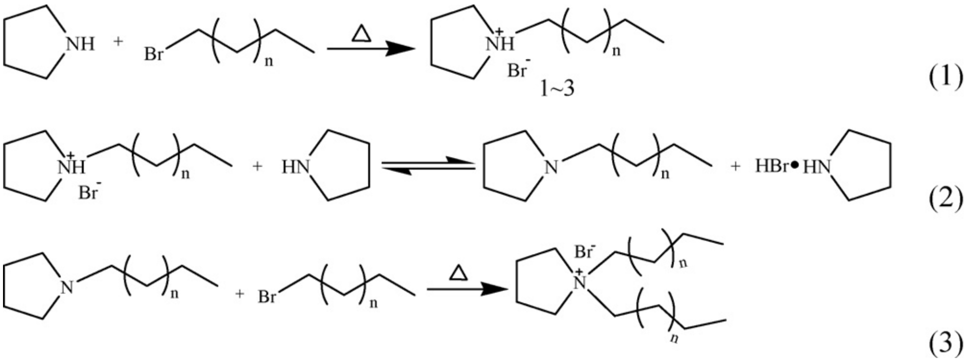

Scheme 1. Synthesis route of the protic pyrrolidinium cationic surfactants (1) and their side reactions (2 and 3). n = 9, 11, 13 for compounds **1**–**3**.

Motivated by this, we report here a range of novel protic pyrrolidinium surfactants with different chain lengths substituted on pyrrolidine ring. They were prepared by heating pyrrolidine with $C_nH_{2n+1}Br$ (n = 12, 14, 16) as outlined in Scheme 1(1). Considering that pyrrolidine is a cyclic secondary amine in nature, over-alkylation will occur in the Hofmann alkylation process and give rise to a mixture of secondary or tertiary amines, and tertiary, quaternary ammonium salts. Therefore, some side reactions will exist during the reaction of pyrrolidine with long-chain alkyl bromides as listed in Scheme 1(2 and 3). Such a process is not like a quaternisation (Menschutkin) reaction, which is usually used for the preparation of quaternary ammonium salts and no side reactions occur. To get pure protic tertiary ammonium salts, some facile and effective steps are needed. First, to prevent the Menschutkin reaction, a slight excess of pyrrolidine was employed. Then, to remove by-products, 1-alkylpyrrolidine, pyrrolidine and long-chain alkyl bromides, the produced precipitate was filtered off and washed carefully with toluene and ethyl acetate after rotary evaporation. Finally, the precipitate was recrystallized from tetrahydrofuran. Due to the well dissolution in tetrahydrofuran for reactants and by-products, like pyrrolidine hydrobromide, 1-alkylpyrrolidine, pyrrolidine, and long-chain alkyl bromides, only the product was crystallized and a white solid was obtained. After being dried in vacuo, the pure products are characterized and the NMR data of compounds **1**–**3** were listed in Ref. [12].

The obtained compounds show good conductivity, efficient ability to reduce surface tension and colorful lyotropic liquid crystalline textures in their aqueous solutions. Take *N*-dodecylpyrrolidinium bromide as an example, the conductivity of its 0.02 mol/L solution at 25 °C is 1108 μs/cm, which is similar to that of ionic liquid $[C_{12}mim][Br]$ [11], and the surface tension can be decreased to 31.5 mN/m, which is more efficient than $[C_{12}mim][Br]$ (39.4 mN/m), and sodium dodecyl sulfate (SDS) (38 mN/m). With increasing concentration, colorful fanlike lyotropic liquid crystalline texture was observed (Fig. 1a) corresponding to a hexagonal phase. The thermal behaviours of these protic pyrrolidinium surfactants are also examined by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) (Fig. 2) and polarizing optical microscopy (POM) (Fig. 1). The decomposition temperatures of all these

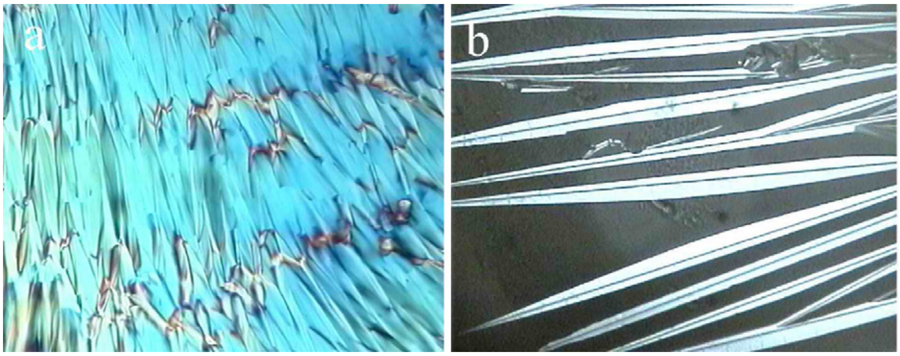

Fig. 1. Polarized optical micrographs of the representative lyotropic and thermotropic liquid crystals. (a) Fanlike texture of lyotropic liquid crystalline phase of compound **1**/H_2O systems with the composition of 50/50 wt%, 25 °C; (b) lancet-like texture of the T phase of compound **3** at 152 °C.

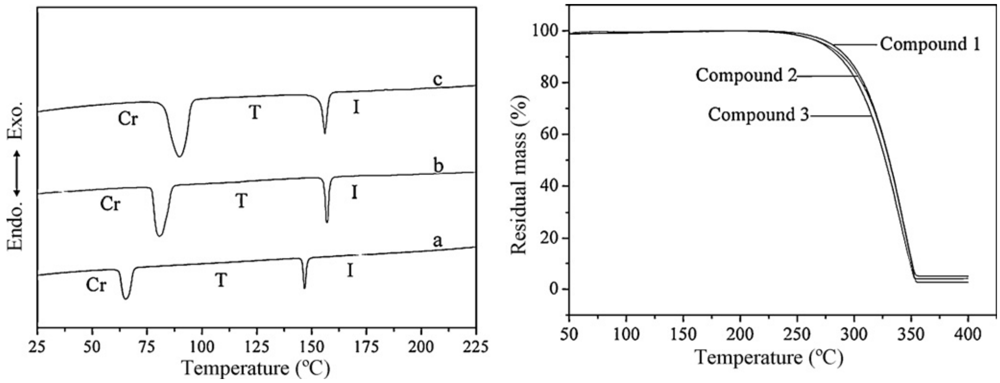

Fig. 2. DSC traces and thermograms of the pyrrolidinium salts. *Abbreviations*: Cr, crystalline phase; T, T phase; I, isotropic liquid; a–c for compounds **1**–**3**.

compounds are over 250 °C, showing high thermal stability. DSC data demonstrate that several phases existed before the melting points. The existence of thermotropic liquid crystal phases is confirmed by POM. For example, Fig. 1b shows a typical texture of thermotropic liquid crystal of *N*-hexadecylpyrrolidinium bromide corresponding to a T phase. Compared to 1-alkylimidazolium salts with the same chain length, T phase is only formed for pyrrolidinium surfactants but not for 1-alkylimidazolium salts, which mainly exhibit the SmA phase. Other protic pyrrolidinium surfactants show similar properties and the systematic studies are underway.

In summary, a series of protic *N*-alkylpyrrolidinium halide salts have been synthesized and investigated. These compounds show efficient ability to reduce surface tension as potentially useful and tunable detergents. Their good conductivity and high thermal stability allow their application as proton conducting electrolyte. They also show fascinating lyotropic and thermotropic liquid crystalline properties, which will make them adopted widely in material fields.

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[12] Compound **1** (purity >98%): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 0.86–0.89 (t, 3H; CH_3), 1.25–1.32 (m, 18H; CH_2), 1.87–1.95 (m, 2H; NCH_2CH_2), 2.05–2.12 and 2.22–2.32 (m, 4H; pyrr. H-3 and H-4), 2.73–2.82 and 2.99–3.05 (m, 4H; pyrr. H-2 and H-5); 3.79–3.83 (m, 2H; NCH_2), 11.41 (s, 1H; pyrr. NH); ESI-MS *m*/*z*: 240.3 ([M−Br−]+). Compound **2** (purity >98%): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 0.86–0.89 (t, 3H; CH_3), 1.25–1.32 (m, 22H; CH_2), 1.87–1.94 (m, 2H; NCH_2CH_2), 2.05–2.12 and 2.22–2.27 (m, 4H; pyrr. H-3 and H-4), 2.74–2.83 and 2.99–3.05 (m, 4H; pyrr. H-2 and H-5); 3.80–3.84 (m, 2H; NCH_2), 11.37 (s, 1H; pyrr. NH); ESI-MS *m*/*z*: 268.3 ([M−Br−]+). Compound **3** (purity >98%): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 0.86–0.90 (t, 3H; CH_3), 1.25–1.32 (m, 26H; CH_2), 1.87–1.94 (m, 2H; NCH_2CH_2), 2.06–2.13 and 2.17–2.28 (m, 4H; pyrr. H-3 and H-4), 2.71–2.82 and 2.98–3.05 (m, 4H; pyrr. H-2 and H-5); 3.78–3.87 (m, 2H; NCH_2), 11.58 (s, 1H; pyrr. NH); ESI-MS *m*/*z*: 296.3 ([M−Br−]+).