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Ionic liquids based on *N*-vinyl-γ-butyrolactam: potential liquid electrolytes and green solvents

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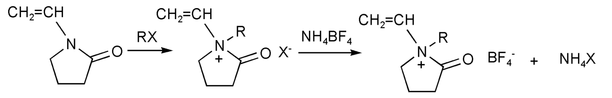
The first examples of room temperature ionic liquids, containing *N*-alkyl-*N*-vinyl-2-pyrrolidinonium (*N*-alkyl-*N*-vinyl-γ-butyrolactam) cations in combination with bromide and tetrafluoroborate anions, have been synthesized and the spectroscopic and physical characteristics of this family of ionic liquids have been investigated for intended use as liquid electrolytes and green solvents.

Over the past few years, ionic liquids (IL's) have been recognized as next generation electrolytes and green solvents and they are now used in a lot of applications.[1–5] However, several urgent questions regarding the functionalization and furthermore the coordination properties and solvent characteristics of ionic liquids still remain to be revealed.[6] Recently, MacFarlane, Forsyth and co-workers have investigated an interesting new family of room temperature molten salts, based on the *N*-alkylpyrrolidinium cation and three different anions, bis(triflioromethane sulfonyl)imide,[7,8] tetrafluoroborate[9] and dicyanamide,[10] for applications in electrolytes and solvents. They showed that lithium doped *N*-methyl-*N*-alkylpyrrolidinium bis(trifluoromethanesulfonyl)amide plastic crystal electrolytes exhibited fast ion conduction for secondary batteries.[11,12] In this work, for the design of functionalized ionic liquids, we first used the *N*-alkyl-2-pyrrolidinonium (*N*-alkyl-γ-butyrolactam) cation containing linear alkyl substituents. This lactam-based cation was then combined with bromide and tetrafluoroborate anions using two-step processes[7,14] (Scheme 1).

There are several reasons for and advantages in synthesizing the lactam-based ionic liquids. The extended vinyl (in the case of *N*-vinylpyrrolidone) and carbonyl groups present in the cation might lead to specific interactions with Li^+ ions and other metal cations that could improve their ionic conductivity. *N*-Alkylpyrrolidones are known to be highly effective and non-aqueous polar solvents hydrogen-bonded with peptides, proteins and nucleic acids and can be used for petroleum, coal and metal ore extraction processes. It is also worthy of note that the *N*-alkylpyrrolidonium cation structure in ionic liquids can improve their solvent properties and specific separation characteristics over conventional ionic liquids. Moreover, the use of alkyl pyrrolidones in the design of new ionic liquids will greatly reduce their production costs and, in case of vinylpyrrolidone, will also allow the inexpensive synthesis of the polyelectrolyte.

Details of sample preparation are provided in Notes and References.† More refluxing time was required for synthesizing the pyrrolidinonium IL's than for the pyrrolidinium one. The primary reason for longer refluxing time might be due to the fact that the basicity of pyrrolidinone is changed because the nitrogen atom conjugates its unshared electron pair with the carbonyl π electron. The IR spectra were obtained in the range 4000–650 cm^{-1} using a Perkin-Elmer 1600 series FTIR spectrometer.



Scheme 1

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX FT 500 MHz NMR spectrometer. Thermal analysis and temperature-dependent phase behavior were examined in the range of −100 to 200 °C using a Du Pont Instrument Differential Scanning Calorimeter. Transition temperatures were recorded at the peak maximum of thermal transition. All the salts were found to have sufficiently low melting points. The thermal properties of ionic liquids prepared in this work are summarized in Table 1. The ethyl derivative (C_2VPnBr) showed a relatively high melting point compared to the butyl derivative (C_4VPnBr), but for the derivatives with tetrafluoroborate anion the increase of alkyl chain length decreased the melting point below room temperature up to the dodecyl derivative and then increased the corresponding melting point. Some molten salts exhibit a number of multiphase transitions (polymorphism) in the crystalline and liquid-crystalline states, possibly including plastic crystal phases, which are able to support substantial conductivity in their crystalline lattices *via* hopping between lattice vacancies.[11] Two IL's of *N*-ethyl-*N*-vinyl-2-pyrrolidinonium bromide (C_2VPnBr) and *N*-dodecyl-*N*-vinyl-2-pyrrolidinonium tetrafluoroborate ($C_{12}VPnBF_4$) showed evidence of multiple solid phases with solid–solid thermal transition around 5 and −29 °C, respectively. The plastic crystal phases of pyrrolidinium compounds consume a large fraction of total entropy of melting and they become highly conducting.[11–13]

The conductivities of pyrrolidinonium salts also appeared to be high. The conductivity data of these salts measured by standard impedance spectroscopy method are presented in Fig. 1 as a function of temperature for four IL's. All these pyrrolidonium IL's showed low glass transition temperatures. The differential scanning calorimetry (DSC) traces for the salt *N*-dodecyl-*N*-vinyl-2-pyrrolidinonium tetrafluoroborate ($C_{12}VPnBF_4$) are presented in Fig. 2 (the first and second heating). For the discussion here, only the transitions observed for the second and subsequent heating scans will be considered. This IL possessed a liquid crystalline phase that exists over the

Table 1 Thermal properties of *N*-alkyl-*N*-vinyl-2-pyrrolidonium salts[a]

Compound[b]	T_g/°C	T_c/°C	T_m/°C	T_{IV-III}/°C	T_{III-II}/°C	T_{II-I}/°C
C_2VPnBr	−54	5	32			130
C_4VPnBr	−51		13			120
C_2VPnBF_4	−58		18		75	125
C_4VPnBF_4	−44		17			
$C_{12}VPnBF_4$	−83	−29	−13	−7	−1	12
$C_{14}VPnBF_4$	−31		5			122
$C_{16}VPnBF_4$	−28		7			118

[a] T_g = glass transition temperature, T_c = crystallization temperature during warming, T_m = melting temperature of crystal-line phase, T_{IV-III}, T_{III-II}, T_{II-I} = summary of peak maximum temperatures for thermal transitions (T ± 2 °C). [b] C_2 = ethyl, C_4 = butyl, C_{12} = dodecyl, C_{14} = tetradecyl, C_{16} = hexadecyl, VPn = *N*-vinyl-2-pyrrolidinone, BF_4 = tetrafluoroborate anion.

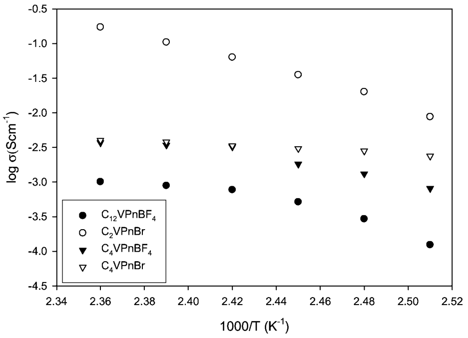


Fig. 1 Ionic conductivities as a function of temperature for four *N*-alkyl-*N*-vinyl-2-pyrrolidonium ionic liquids.

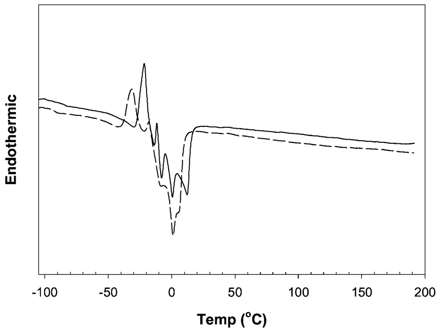


Fig. 2 Differential scanning calorimeter traces of the first (---) and second (—) heating of *N*-dodecyl-*N*-vinyl-2-pyrrolidinone tetrafluoro-borate ($C_{12}VPnBF_4$). All subsequent scans closely matched the second scan. Scan rate was 10 °C per minute.

temperature range, and the richest thermal behavior. The glass transition at −83 °C was followed by a sharp exotherm at −29 °C resulting from crystallization of the sample during warming. Continued warming eventually produced the endothermic event at −13 °C corresponding to melting. This compound, on heating from the molten state in the DSC to high temperatures, appeared to form phase IV followed by the phase nomenclature,[9] where the highest temperature crystalline phase was assigned as phase I and for subsequent decrease to 12, −1 and −7 °C as phases II, III and IV, respectively.

The *N*-alkyl-*N*-vinyl-2-pyrrolidinonium compounds exist in a liquid state at room temperature and are completely miscible with water. In particular, qualitative tests showed that inorganic copper and cobalt salts, palladium and nickel salts with organic ligands, and naphthalene were all soluble in these ionic liquids. This solubility behavior might be due to donor ligand properties of vinyl and carbonyl groups in *N*-alkyl-*N*-vinyl-2-pyrrolidinonium ionic liquids.

Electrochemical stability was analyzed by using a cyclic voltammetry (CH Instruments Electrochemical Work Station) at room temperature. A glassy carbon working electrode of 3 mm diameter was used with a platinum wire as the counter electrode and a silver wire as the reference electrode. The electrochemical stability behavior of *N*-alkyl-*N*-vinyl-2-pyrrolidinonium ionic liquids was stable to potentials ±2 V *versus* Ag/Ag$^+$. The cyclic voltammogram of $C_{12}VPnBF_4$ in Fig. 3 indicates an electrochemical window of ~4 V. A little irreversible oxidation was observed at +2 V.

In conclusion, a new family of room temperature ionic liquids based on the *N*-vinyl-γ-butyrolactam was proven to be highly conductive, electrically stable and possess a good solvent character and thus might be used for potential electrolytes and green solvents.

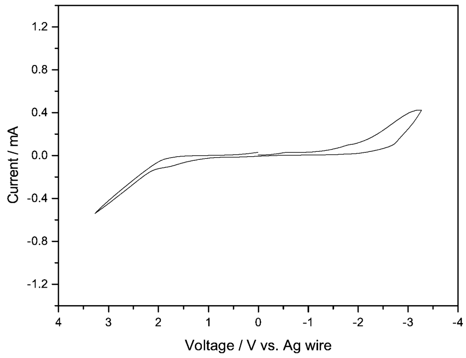


Fig. 3 Cyclic voltammogram of $C_{12}VPnBF_4$.

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Notes and references

† Representative synthesis: *N*-dodecyl-*N*-vinyl-2-pyrrolidinonium tetrafluoroborate: [$C_{12}VPnBF_4$].

N-Dodecyl-*N*-vinyl-2-pyrrolidiinonium bromide ($C_{12}VPnBr$). 11.10 g (0.1mol) *N*-vinyl-2-pyrrolidinone (Aldrich, all chemicals were used as received) was mixed with 20 g acetonitrile and 25 g (0.1 mol) 1-bromododecane was added. The mixture was stirred and refluxed under dry nitrogen for 5 days. The solvent was removed by rotary distillation and the liquid product was washed with n-hexane three times. The final product was dried under vacuum at 40 °C for more than 24 h, and 13.2 g of the product was obtained (yield 65.0%). (D_2O, δ ppm relative to TMS): 7.61-7.58 (d, H), 4.30-4.27 (t, H), 4.09-3.80 (s, H), 3.51-3.48 (t, 2H), 2.94-2.78 (t, 2H), 2.43-2.40 (t, 2H), 2.07-2.01 (m, 2H), 1.90-1.77 (t, 2H), 1.35-1.25 (d, 20H, main chain = mc), 0.85-0.83 (t, 3H). *N*-dodecyl-*N*-vinyl-2-pyrrolidinonium tetrafluoroborate ($C_{12}VPnBF_4$) silver free method.[14]

3 g (0.028 mol) of NH_4BF_4 was added to 10.1 g (0.028 mol) of $C_{12}VPnBr$ in 100 ml of acetonitrile. The mixture was stirred for 2 days, and the NH_4Br filtered from the reaction mixture. The acetonitrile filtrate contained the soluble $C_{12}VPnBF_4$; after roto-evaporation of the solvent, the $C_{12}VPnBF_4$ ionic liquid product was dried under vacuum for 24 h at 40 °C, giving a final yield of 82% (6 g). IR spectrum (film): 3120 and 3165 m, 2965 s 2885 s, 1680 s, 1575 m, 1469 s, 1380 m, 1060 vs, br (BF), 930 w, 825 w, 740 ms, 520 m. ^{13}C NMR (DMSO-d$_6$): 14.2, s, CH_3; 18.1, s, CH_2; 23.2, s. CH_2; 26.6, s, CH_2; 30.3, s, CH_2; 30.4, s, CH_2; 32.5, s, CH_2; 36.3, s, CH_2; 49.4, s, CH_2; 50.2, s, CH_2; 123.2, s, CH_2; 124.5, s, CH_2; 137.4, s, CH_2; 174.9, s, CH.

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