# 리튬 이온성 액체 혼합물의 전해질로써의 응용

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# Applications of the IL's and Li salts mixture to electrolytes

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## Introduction

These last few years, ionic liquids (IL's) were recognized as next generation of electrolytes and green solvents and they are now implicated in a lot of applications [1,2,3,4,5]. However, several urgent questions regarding the functionalization and furthermore the coordination properties and solvent characterictics of ionic liquids still remain to be revealed6. Recently, MacFarlane, Forsyth and co-workers have investigated an interesting series of a new family of room temperature molten salts, based on the N-alkylpyrrolidinium cation and three different anions of the bis (triflioromethane sulfonyl) imide [7,8], tetrafluoroborate9 and dicyanamide10 for applications in electrolytes and solvents

## Experimental

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]

There are several advantages and reasons to synthesize the lactam-based ionic liquids. The extended vinyl (in case of N-vinylpyrrolidone) and carbonyl groups present in 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 are extraction processes. It must be, however, 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 for designing new ionic liquids will also greately reduce their production costs and, in case of vinylpyrrolidone, it becomes also possible to synthesize its cheap polyelectrolyte.

Sample preparative details are provided in Notes and References. More refluxing time was required for synthesizing the pyrrolidinonium IL's than 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 of 4000-650 $cm^{-1}$ using a Perkin-Elmer 1600 series FTIR spectrometer.

The 1H and 13C 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 by Du Pont Instrument Differential Scanning Calorimeter.

## Results and Disscussion

The ethyl derivative ($C_2VPnBr$) showed relatively high melting point than 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 of 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 vacancies11. 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 the 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 conductive[11,12,13].

The conductivities of pyrrolidinonium salts appeared to be also high. The conductivity data of these salts measured by standard impedance spectroscopy method were presented in Fig. 2 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 ($C_{12}VPnBF_4$) were presented in Fig.1 (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 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 nomenclature9, where the highest temperature crystalline phase was assigned as phase I and for subsequent decrease to -7, -1 and 12 °C as phases II, III and IV, respectively.

The N-alkyl-N-vinyl-2-pyrrolidinonium compounds exist as 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 voltametry (CH Instruments Electrochemical Work Station) at room temperature. A glassy carbon with diameter 3 mm was used as the working electrode, a platinium 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 voltammagram of $C_{12}VPnBF_4$ in Fig. 3 indicates an electrochemical window of ~4 V. The 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.

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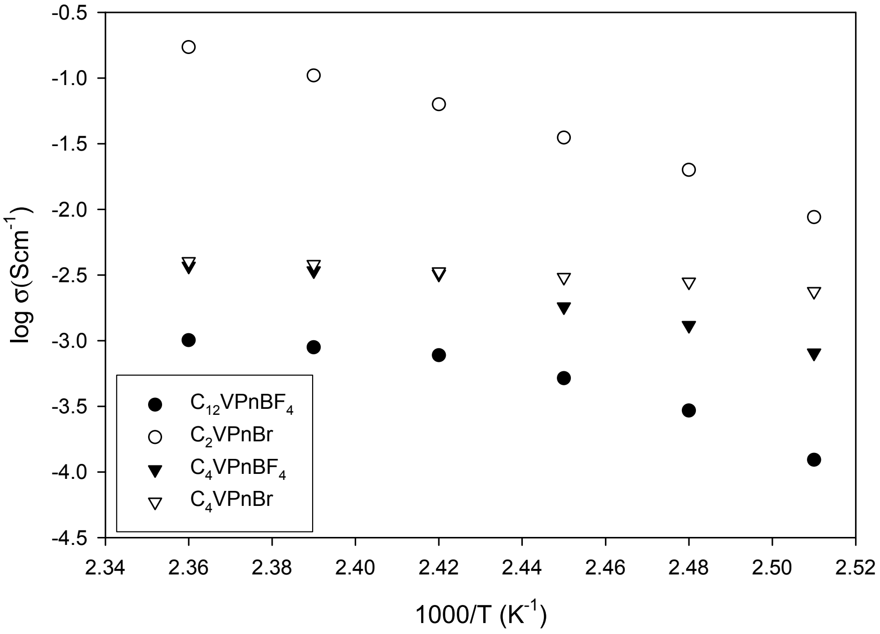

**Fig. 1** Ionic conductivities as a function of temperature for four N-alkyl-N-vinyl-2-pyrrolidonium ionic liquids.

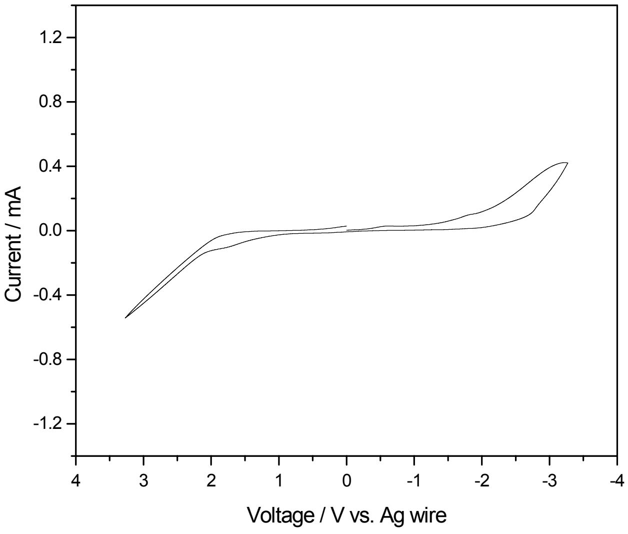

**Fig. 3** Cyclic voltammogram of $C_{12}VPnBF_4$.