Chinese Chemical Letters Vol. 14, No. 6, pp 634 – 636, 2003
http://www.imm.ac.cn/journal/ccl.html

# First Binary Mixture Ionic Liquids Containing EMIMBr and IM

Li Yi DAI, Chun Yan HUA, Sheng Rong YE, Yong Kui SHAN*, Ming Yuan HE

Center for the Chemistry of Ionic Liquid, East China Normal University, Shanghai 200062

**Abstract:** A new series of binary mixture ionic liquids comprising 1-ethyl-3-methylimidozalium bromide (EMIMBr) and imidazole (IM) have been synthesized. The melting points of the ionic liquids vary with the different content of IM while they still keep satisfactory conductivity and viscosity. According to the analysis of its phase diagram, the eutectic point is about 16.5°C with the mass percentage of IM 29%.

**Keywords**: Ionic liquid, binary mixture, phase diagram.

In recent years, significant progress has been made in the application of room temperature ionic liquids[1,2,3]. An ionic liquid typically consists of organic nitrogen-containing heterocylic cations and inorganic anions. Ionic liquid gives bifunctional behavior of solvent and catalyst since the discovery of ionic liquids containing chloroaluminate ions in 1975[4] & 1982[5]. In the acidic ionic liquid, $AlCl_3$ reacting with 1, 3-dialkylimidozalium halide forms an equilibrium system containing anions $X^-$, $AlX_4^-$, $Al_2X_7^-$, $Al_3X_{10}^-$, *etc*.[6]. The physical and chemical properties can be adjusted by changing the mole fraction of $AlCl_3$. Its successful use as either solvent or catalysts has been demonstrated for a wide range of organic synthesis[7,8]. We report herein, a new series of binary mixture ionic liquids composed of 1-ethyl-3-methyl-imidozalium bromide (EMIMBr) and imidazole (IM). The binary mixture ionic liquids keep satisfactory conductivity and viscosity at relatively lower temperature. Moreover, their melting points and other properties can be tuned, depending upon the mass percentage of IM present. This provides a promising way to regulate the physical and chemical properties of ionic liquids.

EMIMBr synthesized by previous method[9] was mixed with mass% of IM from 0 to 100. As shown in **Table 1**, melting points of the salts vary over a wide range by the different proportion. It can be seen that the salt containing 30% of IM has the lowest melting point, 12~17.5°C. Obviously, the presence of IM in the ionic liquids has a tremendous effect on their melting point; basing on the further fact that the eutectic point appears when the mass% of IM up to 29 and trends to form a simple eutectic mixture (**Figure 1**), we can draw a conclusion that the melting points decrease with the increase of IM when IM% < 29 and increase with the increasing content of IM when IM% > 29.

*E-mail: shanyongkui@sina.com

**Table 1** Melting point (°C) of the binary ionic liquids

| IM% | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 60 | 70 | 90 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M.p. (°C) | 78 ~ 79 | 68 ~ 70 | 64 ~ 66 | 52 ~ 56 | 38 ~ 40 | 20 ~ 22 | 12 ~ 17.5 | 26 ~ 29 | 54 ~ 56 | 62 ~ 64 | 70 ~ 73 | 76 ~ 78 | 78 ~ 91 | 88 ~ 89 | 92 ~ 93 |

**Figure 1** Phase diagram of EMIMBr/IM

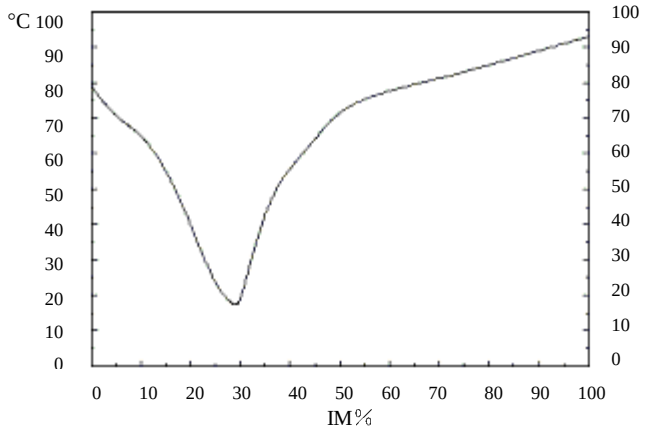


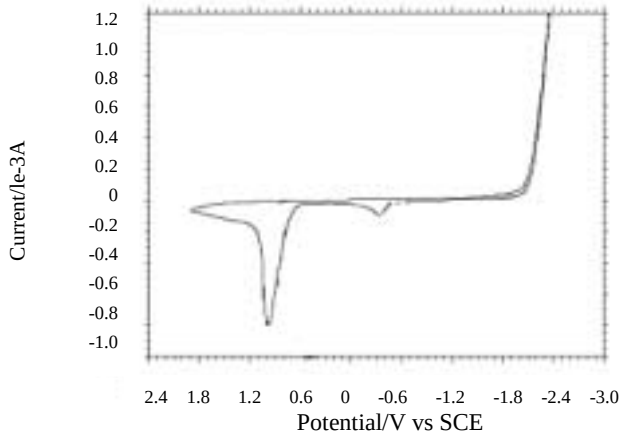

**Table 2** Conductivity ( μ S/cm) and viscosity (cP) at 60°C of certain binary ionic liquids

| IM % | 15 | 20 | 25 | 30 | 35 | 40 |
|---|---|---|---|---|---|---|
| Conductivity ($\times 10^3$ μ S/cm) | 2.2 | 2.4 | 2.8 | 2.7 | 3.0 | 3.2 |
| Viscosity (cP) | - | 24.0 | 16.5 | 13.0 | 14.0 | 15.5 |

The conductivity and viscosity were determined at 60°C by normal methods (see **Table 2**). All mixtures investigated have the similar conductivity ($10^3$ μ S/cm) just as EMIMBr. It is in the range from $2.2\times10^3$ μ S/cm to $3.2\times10^3$ μ S/cm. However, how much IM exists has no noticeable effect on their conductivity although there is a little increase in conductivity with the increasing IM%. **Table 2** reveals the changing tendency of the viscosity which is in accordance with that of melting point; when IM% equals to about 30, this binary ionic liquid possesses simultaneously the lowest melting point and smallest viscosity (13.0 cP).

**Figure 2** shows one of typical cyclic voltammograms of the binary systems (IM%= 40) at scan rate of 50 mV/s. This experiment was carried out under the condition without water or oxygen. As it can be seen from **Figure 2**, there is no current peak on the reduction process. But the oxidation process is irreversible, there being two peaks in the –0.3 V and +1.0 V region. In order to identify the ascription of two peaks, KBr was added to the substrate, resulting in the strengthened current at –0.3 V. And it was observed that the peak at +1.0 V overlapped completely with that of pure IM in the buffer solution (HAc-NaAc, pH= 5.0). In all probability, peak at –0.3 V was due to the oxidation of $Br^-$ and peak at +1.0 V was ascribable to the presence of IM.

**Figure 2** Typical cyclic voltammograms of the binary ionic liquids




## Acknowledgments

Supported by the State Key Basic Program (NO. G2000048) and the Foundation of Shanghai Science and Technology Development (01JC14002).

## References

1. D. B. Zhao, M. Wu, Y. Kou, E. Z. Min, *Catal. Today*, **2002**, *2654*, 1.
2. H. Olivier-Bourbigou, L. Magna, *J. Mol. Catal. A: Chem.*, **2002**, *182-183*, 419.
3. T. Welton, *Chem. Rev*., **1999**, *99*, 2071.
4. H. L. Chum, V. R. Koch, L. L. Miller, R. A. Osteryoung, *J. Am. Chem. Soc.*, **1975**, *97*, 3264.
5. J. S. Wilkes, J. A. Levisky, R. A. Wilson, C. L. Hussey, *Inorg. Chem.*, **1982**, *21*, 1236.
6. P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.*, **2000**, *39*, 3772.
7. Y. Chauvin, H. Olivier, C. N. Wyrvalski, L. C. Simon, R. F. de Souza, *J. Catal*., **1997**, *165*, 275.
8. F. G. Sherif, World Patent WO 98/03454, **1998**; F.G. Sherif, WO 99/03163, **1999**.
9. P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.*, **1996**, *35*, 1168.

Received 22 July, 2002