Chinese Chemical Letters Vol. 14, No. 5, pp 523 – 524, 2003 523
http://www.imm.ac.cn/journal/ccl.html

Preparation and Characterization of New Type Ionic Liquids

Qing Hai CAI, Yong Kui SHAN*, Li Yi DAI, Bi Xia SU, Ming Yuan HE

Center for chemistry of ionic liquid, East China Normal University, Shanghai 200062

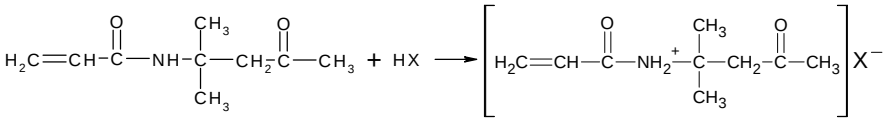
Abstract: A new type of ionic liquids containing cation of diacetone acrylamide [or N-(1,1-bismethyl-3-oxo-butyl)acrylamide] and anions such as CH_3COO^- (Ac), CF_3COO^- (TF), BF_4^-(BF), PF_6^-(PF), HSO_4^-(SO) and Cl^-(Cl) were prepared by normal neutralization. The obtained ionic liquids were identified by FT-IR and ^{1}H NMR spectroscopy. However, their properties such as melting point, conductivity, viscosity *etc.* were determined.

Keywords: Ionic liquid, diacetone acrylamide, preparation, characterization.

Ionic liquids are finding ever-expanding applications as alternative reaction media and catalysts for organic synthesis[1], solvents and extractants for separation science[2] and electrolytes for electrochemistry [3] due to their characteristics of a wide liquid range, nonvolatility, adjustability of chemical and physical properties and large windows of electrochemistry, and which display a good performance in these fields. Especially, the constraints of environment are becoming more and more stringent in recent years, thus the search for new, more versatile ionic liquids is driven by the increasing need for green and environment benign chemistry. The most recent publications are concerned with the synthesis of new ionic liquids[4], systematic investigation of their properties[5] and further applications as media and catalysts[6]. We herein report a new type of ionic liquid based on diacetone acrylamide(DA) cation and anions such as Ac, TF, BF, PF, SO and Cl, Which are of low melting point, two of them are liquid at room temperature. Diacetone acrylamide(the purity 99.1%) synthesized by literature method[7] was converted to corresponding ionic liquids(ILs) by reaction with a solution of specified acid such as HBF_4, HCl, H_2SO_4 *etc*. at room temperature(**Scheme 1**). The ILs were obtained by filtration to remove the filtrates or decantation to remove the aqueous phase from the reaction mixture. Identification of them was by FT-IR (Nicolet 670) and ^{1}H NMR(Brucker DXS 300, in D_2O). IR spectra of the ILs are basically in accord with that of DA except for DATF, DABF and DAPF with characteristic peaks of 1778.7(C=O in TF), 1168.3(C-F in TF), 1081(B-F in BF) and 843.4 cm^{-1} (P-F in PF). ^{1}H NMR spectra of them are almost the same, and basically consistent with that of DA, except for 2.05 ppm representing the hydrogens in Ac (^{1}H NMR of the ILs: 6.18, 6.20, 6.17, 5.60~5.80, 3.15, 2.23, 1.45 ppm; that of DA: 6.17, 6.18, 6.09, 5.57, 2.99, 2.13, 1.45 ppm).

*E-mail: shanyongkui@sina.com

Scheme 1 Reaction equation



(X = Ac, TF, BF, PF, SO, Cl)

Table 1 The properties of the ionic liquids

Salts	Con. μs/cm (°C)	m.p°C	η cp (°C)	solubility	Ecw V
DAAc	2.9×10^2(20)	-12	27.2(20)	At.(s) Wa.(i) Al.(s) To.(i) ch.(i) be.(i)	2.38
DATF	5.4×10^3(20)	-9	6.1(20)	At.(s) Wa.(i) Al.(s) To.(s) ch.(s) be.(s)	2.07
DABF	7.5×10^3(100)	64	25.5(100)	At.(s) Wa.(s) Al.(s) To.(i) ch.(i) be.(i)	1.25
DAPF	1.3×10^3(90)	88	>100(90)	At.(s) Wa.(s) Al.(s) To.(i) ch.(i) be.(i)	2.33
DASO	2.5×10^3(110)	56	>100(110)	At.(s) Wa.(s) Al.(s) To.(i) ch.(i) be.(i)	
DACl	2.8×10^3(85)	72	18.5(85)	At.(s) Wa.(s) Al.(s) To.(i) ch.(i) be.(i)	2.60

Ecw-electrochemical window, At.-acetone, Wa.-water, Al.-alcohol, To.-toluene, ch.-chloroform, Be.-benzene; s-soluble, i- insoluble; con – conductivity, η - viscosity

The properties of ILs such as melting point, conductivity, viscosity *etc*. were listed in **Table 1**. The conductivity of DAAc is 2.9×10^2 μs/cm, and that of the others is in the range from 1.3×10^3 to 7.5×10^3 μs/cm at different temperatures. Melting points of DAAc and DATF determined by DSC are -12°C and -9°C respectively, which are room temperature ILs, and that of the others are less than 100°C. It was seen from **Table 1** that the viscosities of DAAc, DATF, DABF and DACl are 27.2, 6.1, 25.5 and 18.5 cp respectively, while that of DAPF and DASO are more than 100 cp so that the cyclovoltammetry determination of DASO is very difficult. The solubility of DABF, DAPF, DASO and DACl is identical, which are all soluble in acetone, water, alcohol and insoluble in toluene, chloroform and benzene, however DAAc is soluble in acetone, alcohol and insoluble in water, toluene, chloroform and benzene, DATF is only insoluble in water and soluble in the other five solvents. The electrochemical windows of DAAc, DATF, DABF, DAPF and DACl obtained by cyclovoltammetry are 2.38, 2.07, 1.25, 2.33 and 2.60 V(SCE) respectively.

Acknowledgment

We thank the financial Support of Shanghai Sci. and Tech. Development Foundation(01JC14002).

References

1. H. O. Bourbigou, L. Magna, *Journal of Molecular Catalysis A: Chemical,* **2002**,*182-183,* 419.
2. B. L. Ann, *Diss. Abstr. Int.*, **2001**, *61* (9), 4846.
3. D. A. Costa, W. H. Smith, J. H. Dewey, *Proc. Electrochem. Soc.*, **2000**, *99-41*, 80.
4. D.R. Macfarlane, J.Golding, S.Forsyth, M.Forsyth, G.B.Deacon, *Chem. Commun.*, **2001**, 1430.
5. H.L.Ngo, K.L.LeCompte, L.Hargens, A. B. EcEwen, *Thermochimica Acta*, **2000**, *357-358*, 97.
6. D. B. Zhao, M. Wu, Y. Kou, E. Z. Min, *Catalysis Today*, **2002**, *74* (1-2), 157.
7. M.S.Zheng, X.N.Sheng, J.G.Xuan, *Hua Xue Shi Jie*(*Chem. World,* in Chinese), **1985**, *10*, 371.

Received 22 July, 2002