Supporting Information

Predictive screening of ionic liquids for dissolving cellulose and experimental verification

Yan-Rong Liu,[a,b,c] Kaj Thomsen,[b] Yi Nie,[c] Suo-Jiang Zhang,*[c] Anne S. Meyer*[a]

[a]*Center for Bioprocess Engineering, Department of Chemical and Biochemical Engineering, Technical University of Denmark, SøltoftsPlads 227, 2800, Lyngby, Denmark, E-mail: am@kt.dtu.dk*

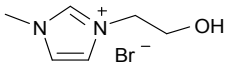
[b]*Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, SøltoftsPlads 229, 2800, Lyngby, Denmark, E-mail: kth@kt.dtu.dk*

[c]*Beijing Key Laboratory of Ionic Liquids Clean Process, Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, P.O. Box 353, Beijing, 100190, China, E-mail: sjzhang@ipe.ac.cn*

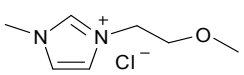
1. Synthesis and characterizations of ILs

1.1 Synthesis method

Synthesis of HOEtmimBr: In the experiment, 2-Bromoethanol (24.8997g, 0.20mol) was dropped slowly to 1-Methylimidazole (15.2200g, 0.19mol) in the ice-bath for 6h and stirred under the condition of nitrogen protection，then heated under reflux at 80℃ for 48 h. After cooling to room temperature, the mixture was washed with ethyl acetate (4×30 ml) and filtered the remaining solid. After drying at 80℃ under vacuum for 48 h, HOEtmimBr was obtained as white solid.

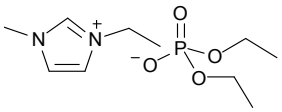


Synthesis of EtOMmimCl: 2-Chloroethyl Methyl ether (25.0000g, 0.26mol) was dropped slowly to 1-Methylimidazole (21.7100g, 0.26mol) in the ice-bath for 6h and stirred under the condition of nitrogen protection，then heated under reflux at 80℃ for 48 h. After cooling to room temperature, the mixture was washed with ethyl acetate (4×30 ml) and filtered the remaining solid. After drying at 80℃ under vacuum for 48 h, EtOMmimCl was obtained as white solid.

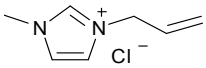


Synthesis of EmimDEP: 1-Methylimidazole (25.0000g, 0.30mol) and Triethyl phosphate (50.0000g, 0.30mol) was mixed and stirred under reflux at 80℃ for 8 h, and then the reaction mixture was stirred at 150℃ for 40h. After cooling to room temperature, the reaction mixture was washed withether (4×30ml).

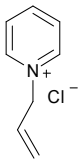
Then rotary vacuum evaporation of the product at 75℃ for 4h, and dried under vacuum at 80℃ for 48 h to abtain EmimDEP as pale yellow liquid.



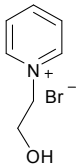
Synthesis of AmimCl: Allyl chloride (48.1278g, 0.63mol) was dropped slowly to 1-Methylimidazole (49.9880g, 0.61mol) in the ice-bath for 6h and stirred under the condition of nitrogen protection，then heated under reflux at 60℃ for 24h. After cooling to room temperature, the reaction mixture was washed with ethyl acetate (4×40ml). Then rotary vacuum evaporation of the product at 75℃ for 4h, and dried under vacuum at 80℃ for 48 h to obtain AmimCl as brown liquid.



Synthesis of ApyCl: Allyl chloride (35.5110g, 0.30mol) was dropped slowly to pyridine (23.2180g, 0.30mol) in the ice-bath for 6h and stirred under the condition of nitrogen protection，then heated under reflux at 60℃ for 24h. After cooling to room temperature, the mixture was washed with ethyl acetate (4×30 ml) and filtered the remaining solid. After drying at 80℃ under vacuum for 48 h, ApyCl was obtained as brown solid.



Synthesis of HOEtpyBr: 2-Bromoethanol (25.0000g, 0.20mol) was dropped slowly to pyridine (15.0300g, 0.19mol) in the ice-bath for 6h and stirred under the condition of nitrogen protection，then heated under reflux at 80℃ for 48 h. After cooling to room temperature, the mixture was washed with ethyl acetate (4×30 ml) and filtered the remaining solid. After drying at 80℃ under vacuum for 48 h, HOEtpyBr was obtained as brown solid.



1.2 NMR data of six ILs

The structures of these ILs were confirmed by ^{1}H and ^{13}C NMR spectroscopy with Bruker 600 spectrometer. The NMR data about these six kinds of ILs are as below.

HOEtmimBr: ^{1}H NMR (d6-DMSO): 9.17[s, 1H, (Im)], 7.77[t, J=1.7Hz, 1H, (Im)], 7.74[t, J=1.7Hz, 1H, (Im)], 5.17[s, 1H, OH], 4.24[m, 2H, N-CH_2], 3.88[s, 3H, N-CH_3], 3.73[m, 2H, O-CH_2]; ^{13}C NMR: 136.76, 122.96, 59.26, 51.55, 35.67.

EtOMmimCl: ^{1}H NMR (d6-DMSO): 9.42[s, 1H, (Im)], 7.84[t, J=1.7 Hz, 1H, (Im)], 7.79[t, J=1.7 Hz, 1H, (Im)], 4.40[m, 2H, CH_2-O-CH_3], 3.90[s, 3H, CH_3-O-CH_2], 3.7[m, 2H, N-CH_2], 3.27[s, 3H, N-CH_3]; ^{13}C NMR: 136.92, 123.39, 122.57, 69.57, 58.00, 48.49, 35.68.

EmimDEP: ^{1}H NMR (d6-DMSO): 9.56[s, 1H, (Im)], 7.85[t, J=1.7 Hz, 1H, (Im)], 7.76[t, J=1.6 Hz, 1H, (Im)], 4.22[q, J=7.3 Hz, 2H, CH_2-CH_3], 3.87[s, 3H, N-CH_3], 3.62[p, J=7.0 Hz, 4H, 2(O-CH_2)], 1.42[t, J=7.3 Hz, 3H, CH_2-CH_3], 1.07[t, J=7.1 Hz, 6H, 2(O-CH_2-CH_3)]; ^{13}C NMR: 136.86, 123.51, 121.94, 58.98, 43.98, 35.55, 16.68, 15.14.

AmimCl: ^{1}H NMR (d6-DMSO): 9.51[s, 1H, (Im)], 7.86[t, J=1.7 Hz, 1H, (Im)], 7.84[t, J=1.8 Hz, 1H, (Im)], 6.06[ddt, J=16.3, 10.3, 6.0 Hz, 1H, CH_2=CH], 5.33[m, 2H, CH_2=CH], 4.92[d, J=6.0 Hz, 2H, N-CH_2], 3.91[s, 3H, N-CH_3]; ^{13}C NMR: 136.77, 131.88, 123.72, 122.29, 120.05, 50.63, 35.76.

ApyCl: ^{1}H NMR (d6-DMSO): 9.27[d, J=5.5Hz, 2H, N=CH (Py)], 8.68[tt, J=7.8, 1.3 Hz, 1H, (Py)], 8.23[m, 2H, CH=CH (Py)], 6.19[ddt, J=16.6, 10.3, 6.3 Hz, 1H, CH_2-CH], 5.45[m, 2H, CH=CH_2], 3.44[m, 2H, CH_2-CH]; ^{13}C NMR: 145.83, 144.90, 131.89, 128.18, 121.81, 62.04.

HOEtpyBr: ^{1}H NMR (d6-DMSO): 9.08[d, J=5.5Hz, 2H, N=CH (Py)], 8.64[tt, J=7.8, 1.3 Hz, 1H, (Py)], 8.19[m, 2H, CH=CH (Py)], 5.26[s, 1H, -OH], 4.72[m, 2H, N-CH_2], 3.87[m, 2H, O-CH_2]; ^{13}C NMR: 145.53, 145.15, 127.66, 62.99, 59.98.

1.3 Purity of the seven ILs

The Nitrogen elements analysis and the water content results were shown in Table 1.

Table 1 Elemental analysis and water content of six analyzed ILs

Projects	HOEtmimBr Nitrogen (wt%)	EtOMmimCl Nitrogen (wt%)	EmimDEP Nitrogen (wt%)	AmimCl Nitrogen (wt%)	ApyCl Nitrogen (wt%)	HOEtpyBr Nitrogen (wt%)
original content	13.53	15.86	10.60	17.01	9.00	6.87
Experimental content	13.35	15.75	10.56	16.75	8.98	6.76
Purity (wt%)	98.67	99.31	99.62	98.53	99.78	98.33
Water content (ppm)	9331.86	4426.27	1941.37	2508.80	2198.20	9767.69

According to the report of R. P. Swatloski et al.,[1] when water concentration in ILs larger than 1 wt%, it will cause a significant problem in the cellulose dissolution process. Therefore, the water concentration in the six synthesized ILs was reduced to less than 1 wt%, suitable for dissolving the cellulose.

1.4 Melting point of four solid ILs

The melting points of four solid synthesized ILs exhibited in Fig. 1. From Fig. 1, the melting point of HOEtmimBr is 89.13 °C, EtOMmimCl is 81.13 °C, ApyCl is 87.13 °C and HOEtpyBr is 87.82 °C.

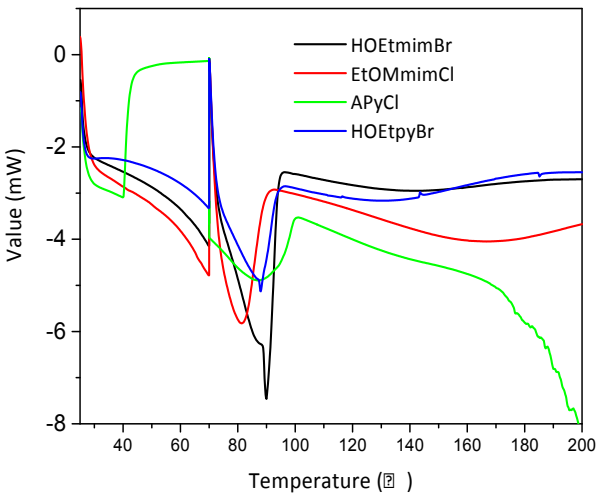


Fig. 1 Melting point of four solid ILs

The HOEtmimBr, EtOMmimCl, HOEtpyBr were heated from 25 °C to 200 °C, and kept the temperature at 70 °C for 10 min. The ApyCl was heated from 25 °C to 200 °C, and kept the temperature at 40 °C for 10 min. The ramp rate is 10 °C /min under nitrogen atmosphere.[2-3]

References

1 R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, 124, 4974–4975.

2 Q. Zhou, W. A. Henderson, G. B. Appetecchi and S. Passerini, *J. Phys. Chem. C*, 2010, 114, 6201–6204.

3 S. Agarwal, A. M. Hossain, Y. Choi, M. Cheong, H. G. Jang and J. S. Lee, *Bull. Korean Chem. Soc.*, 2013, 3771–3775.