Ultra purification of Ionic Liquids by Melt Crystallisation

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Abstract

Ionic liquids (ILs) have received a great increase in attention in the fields of engineering during the last decade due to their unique properties. ILs are a very important new class of non-volatile environmentally friendly solvents (T_m< 100°C). The applications range from electrochemistry, sensors, analysis, separation techniques to catalysis and reaction engineering. Furthermore it is very important to realize low production costs including efficient techniques for purification and ultra purification.
The paper will present results of purification and ultra purification of EMIM-Chloride and EMIM-Bromide (EMIM: 1-ethyl-3-methyl-imidazolium) by melt crystallization. Different techniques for purification are discussed: zone melting, layer crystallization and dry sweating. The crystallization behaviours of purified Ionic Liquids will be discussed in detail in respect to those of organic substances with similar melting points like Biphenyl and Naphthalene.

1. Introduction

Ionic liquids are non-volatile, not-flammable and thermally stable solvents that are very promising as a replacement for the traditional volatile organic solvents used in chemical industry and chemistry research laboratories. Alkyl-Imidazolium and Alkyl-Pyridinium salts as Chlorides or Ethylsulfates are common ionic liquids [1].
Many ionic liquids display a liquid phase at room temperature, and are easy and inexpensive to manufacture. For incorporation this new kind of solvents into industrial applications a deep knowledge of their physical and chemical properties is needed. The physical and chemical properties of ionic liquids can be influenced significantly by small amounts of impurities. There catalytic activity and there electrochemical behaviour highly depend on the purity level of the ionic liquid. The quality of ionic liquids became an important consideration. Ionic liquid synthesis in a commercial context is in many respects quite different from academic ionic liquid preparation. In commercial scenario laboratory intensive steps add significantly to the price of the product. Commercial producers try to make ionic liquids in the highest quality that can be achieved at reasonable cost. Usually grades of purity are greater than 95% "for synthesis", greater than 99% "high pure" and greater than 99,9% "ultra pure". Typical impurities are colours, organic starting materials and other volatiles, halide impurities, protic impurities, other ionic impurities from incomplete metathesis reactions and water. Analysis and trace analysis of impurities in ionic liquids is still a field of ongoing fundamental research.
Ionic liquid is still a quite different product from traditional organic solvents, simply because it cannot be purified by distillation directly, due to its non-volatile character. The counterpoint to this is that any volatile impurity can, in principle, be separated from ionic liquid by distillation. Other unit operations are e.g. extraction [2], membrane technologies [3] as well as crystallisation [4] discussed in literature for purification of ionic liquids widely. BASF

Proceedings of the 13th International Workshop on Industrial Crystallization BIWIC 2006,
September 13-15, 2006, Delft, The Netherlands, 79-84

company is claiming all kinds of industrial and laboratory crystallization techniques for purification of ionic liquids [5].
Melt crystallization is a technique suited for purification of organic chemicals as well as for ionic liquids. The principle of the technique is to cool a melt in a controlled way in order to crystallize a fraction of the melt. Crystallisation rate and the yield are important parameters operating the technology properly. The formed crystalline state will be in general more pure than the feed. The high purity of the crystalline state is the result of strong spatial ordering of the molecules in the crystal lattice. Molecules with deviating shape and/or size often do not fit into this crystal lattice. For this reason, the selectivity of melt crystallization considering the purification of ionic liquids usually is higher than for other separation processes like distillation and extraction. The actual purity of the crystalline state depends on kinds and concentrations of all impurities and on how the purification is carried out. It was recently observed [6] that ionic liquids are often good glassformers, i. e. that they can be cooled from the liquid state, down to very low temperatures, without crystallizing.
In this context, it is of great importance to understand of the phase and the crystallization behaviour of this new class of materials.

2. Experimental

The present work studied purification and ultra purification of EMIM-Chloride and EMIM-Bromide (EMIM: 1-*e*thyl-3-*m*ethyl-*im*idazolium) by melt crystallization. Feed stock of all experiments is EMIM-Chloride from FLUKA company in BASF Quality with purity w>93%. EMIM-Bromide w~95% was synthesised by the group of Prof. Wasserscheid.
Impurity content larger than $w_{im}>3\%$ was measured by ion chromatographic system ICS-3000 from DIONEX Corp., CA, USA [7]. The ionic liquids EMIM-Cl and EMIM-Br show a slightly brown colour. Low impurity contents were measured by the intensity of brown colour using photometric method at $\lambda=320$ nm. The calorimetric measurements are performed with NETSCH DSC 200 F3.
Zone melting experiments were carried out in glass tube of 4 mm and 8 mm inner diameter and length of 100 mm. The width of heating section is 5 mm. Growth was adjusted by the travelling rate of the glass tube in the range of 0.01 mm/h < dL/dt < 40 mm/h. The experiments in larger scale are operated as falling film technique in a double jacketed glass heat exchange tube with inner diameter $d_i=60$ mm and length of 400 mm. Purification by dry sweating was operated in a heated filter centrifuge at acceleration of z=1000*g.

3. Results and Discussion

Rough comparison of physical data of EMIM-Chloride with that of Biphenyl and Naphthalene show (see Tab. 1) similarity of typical ionic liquid and classical organics which can be purified by melt crystallization. Heat of fusion is slightly smaller and viscosity is a little bit higher at EMIM-Chloride.

Table 1: Comparison of thermo physical data

		EMIM-Chloride	Biphenyl	Naphthalene
melting point	°C	80 87[1)]	69,5	80
molar mass	kg/kmole	146	154	128
heat of fusion	kJ/mole	5,1 7,3[1)]	18,6	18,9
viscosity	mPas	47	1,4	1

1) Data from literature [8]

DSC melting and crystallization experiments (see Fig. 1) show a strong super cooling behaviour for EMIM-Chloride. During cooling from 100°C down to -120°C glass transition takes place at -70°C. During heating of the sub-cooled system anti glass transition occurs at -70°C and real crystallization starts at -20°C. Afterwards the crystallized product melts in terms of two melting peaks. In opposite Naphthalene crystallizes very well during cooling.

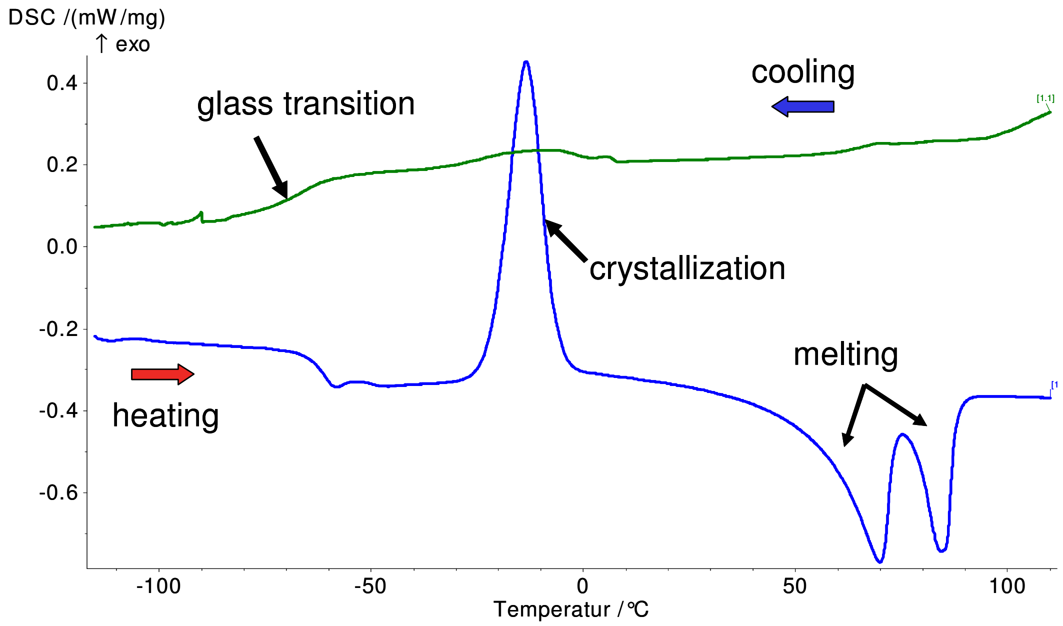

Figure 1: DSC melting and crystallization experiment of EMIM-Chloride , dT/dt = 10K/min

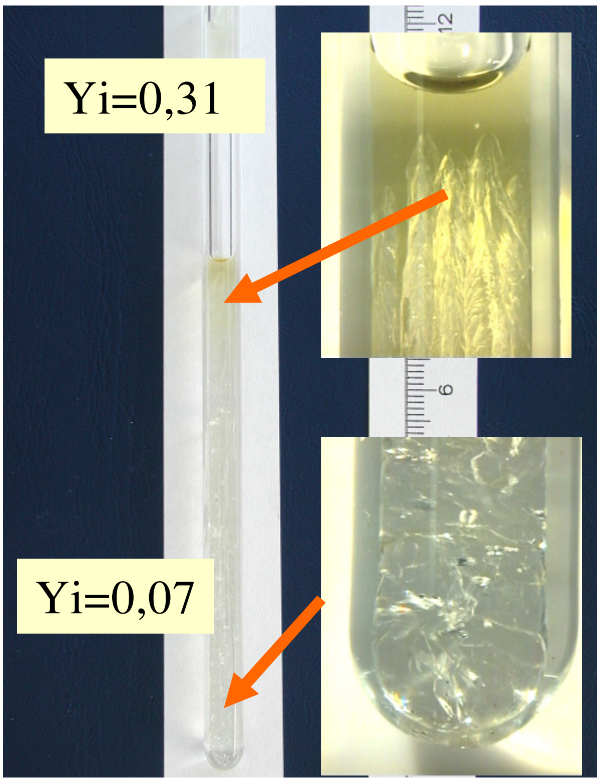

Figure 2: Zone melting of EMIM-Cl,

Fig. 3: Static layer crystallization

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2nd passages, dL/dt=1,4 mm/h of EMIM-Cl, m_{Feed} = 50 g

Smooth crystallization operates in presents of seed crystals using zone melting and static layer technique. Using zone melting at small travelling rates (dL/dt<4mm/h) well shaped crystals built up. It can be seen at the solid liquid interphase in Fig. 1. The load of impurities *Y* (extinction at λ=320 nm / mass of EMIM-Cl) increases from bottom to top. The feed impurity load was Y_i=0,17. After 2nd passage the final purity is Y_i=0,07 and crystal structure becomes more developed.

Static crystallization (see Fig. 2) operates well too. In combination with solid liquid separation in the centrifuge high pure EMIM-Chloride was produced. Final impurity content reduced to w_{imp}<1,5% starting with feed impurity content of w_{imp}=5% in one stage. The residue has intensive brown colour and is liquid at room temperature indicating the collection of impurities in the liquid phase.

Good purification results from small scale m~1 g and m~50 g tested with the crystallization techniques zone melting and static layer crystallization motivates to purify EMIM-Chloride in larger scale up to m~1000 g with our lab scale layer crystallization unit, which is shown in Fig. 4 in principle. All experiments are done as dynamic layer crystallization in falling film technique at the product side. Figure 5 shows the crystallization section with a white crystal layer of EMIM-Chloride. The aim of the experiments was to produce larger amounts of ultra pure EMIM-Chloride for further investigations with rigid requirements in respect to purity. Table 2 summarizes selected results of the test series.

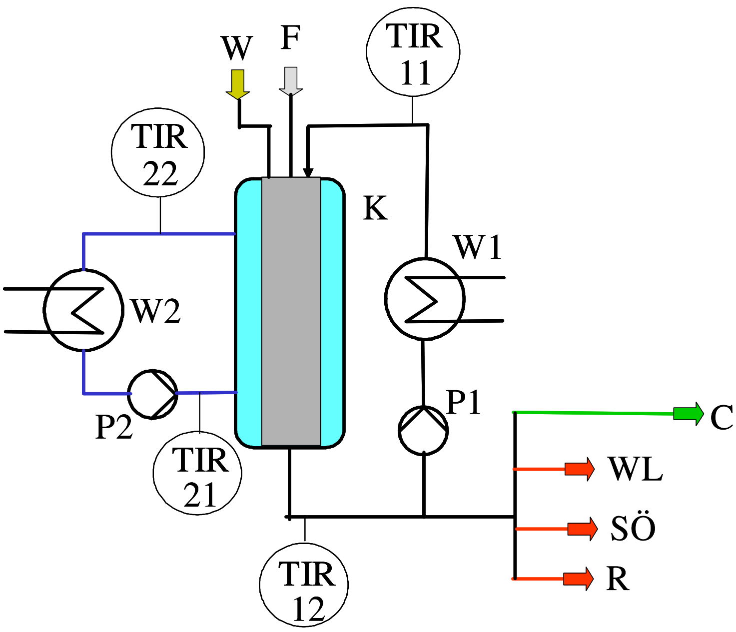

Figure 4: Mini plant for dynamic and static melt crystallization [9]

Fig. 5: Dynamic layer crystallization of EMIM-Cl

Run V3 and V4 are done with original EMIM-Chloride from FLUKA. In one stage the final purity was better than 99%. At run V4 the feed impurity level was higher than at run V3. The better result in purification depends on lower crystallization rate and on higher sweating rate. Reducing the crystallization rate from 4 kg/h*m^2 at run V3 down to 1,3 kg/h*m^2 at run V5 the purity of the ionic liquids improves too. The best results obtained from run V6. The low impurity content of feed in combination with the low crystallization rate is reason for good result in purification. This batch reaches the quality level of “ultra pure” ionic liquid. The

feed of run V6 was collected from the crystalline product of run V3 and V4. The residue from V3 and V4 including the sweating oil fractions was crystallized by dry sweating technique in the filter centrifuge. The crystal fraction from this stripping stage procedure was used as feed for run V5. It demonstrates that dry sweating technique operates very well for ionic liquids too. The impurity content of the crystal fraction is similar to that of the original EMIM-Chloride from FLUKA . For impurity contents higher than 5% and moderate viscosities this technique has some advantages in respect to layer crystallisation techniques.
Comparison of zone melting and falling film layer crystallisation shows similar purification efficiency. The specific growth rate used are similar each other since specific growth rate of GR_{spec}=4,4 kg/h*m^2 means a travelling rate of dL/dt=4 mm/h. Results of the relationship between purification and travelling rate can be used for forecasting of process parameters at dynamic layer crystallization directly.

Table 1: Dynamic layer crystallization of EMIM-Chloride

		V3	***V4***	***V5***	***V6***
feed	g	570	540	540	410
$Y_{imp,feed}$	%	3,4	5,7	4,1	1,1
yield crystallization	%	63	63	59	63
yield after sweating	%	44	33	38	38
growth rate spec.	kg/h*m^2	4,4	3	1,3	1,3
PP cryst.	-	0,20	0,36	0,19	0,28
PP crys&sweat	-	0,11	0,08	0,06	0,05
Y_{IL}	%	>99	>99	>99,5	>99,9

Experiments of purification of EMIM-Bromide show very similar results like EMIM-Chloride. EMIM-Bromide was operated by a combination of dry sweating and static crystallization within 2 stages. In the first stage 100 g of feed *F* w=87% was purified to 47 g of crystals *C1* w=97%. In second stage crystal *C1* was purified once again to 17 g of crystals *C2* at "high pure" quality with w>99%.

Progress of purification *PP*, which is defined as ratio of the impurity content of the solid phase in respect to that of the feed material, shows that the sweating procedure is an important process step. The solid phase after crystallization includes a lot of mother liqueur. On the other hand it indicates that the purification potential of the crystallization step is rather high. Progress of purification for Naphthalene crystallization from Naphthalene/Biphenyl mixture has similar values operated in the same equipment. For Naphthalene progress of purification yields PP=0.4 at Biphenyl content of 20% and at growth rate of 4 kg/h*m^2 in respect to PP=0,36 at run V4 for EMIM-Chloride. The results of purification obtained with ionic liquids fit in principle very well the results obtained with classical organic melts investigated with used crystallization techniques.

The results received during this work motivate to further investigations in respect to crystallization of ionic liquids. Analysis and trace analysis of impurities in ionic liquids is still a field further research. Individual distribution coefficients in the matrix of impurities are not available for ionic liquids up to now.
Investigations in respect to phase and crystallization behaviour of ionic liquids are a main topic of our actual and further research activities.

4. Conclusions

Ionic liquids (ILs) are a very important new class of non-volatile environmentally friendly solvents (T_m< 100°C). For many applications ionic liquids are required as “ultra pure” substances. EMIM-Chloride and –Bromide were purified by melt crystallization up to “ultra pure” grade with purity of w>99,9%.
Different crystallization techniques zone melting, static and dynamic layer crystallization, dry sweating and suspensions crystallization are tested successfully in respect to purification. Samples of 1g, 50 g and 500g are prepared using for scientific investigations. It offers the possibility supporting research teams in purifying their ionic liquids.
Furthermore melt crystallization is an efficient technique for purification and ultra purification in respect to realize low production costs.
Ionic liquids have similar crystallization behaviour like classical organic melts. EMIM-Chloride crystallization and purification by melt crystallization is in principle comparable with e.g. that of Naphthalene or Biphenyl.

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