

Ultra Purification of Ionic Liquids by Melt Crystallization

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Abstract

Ionic liquids (ILs) have received a great increase in attention in the fields of engineering during last decade due to their unique properties. ILs are a very important class of non volatile environmentally friendly solvents ($T_m < 100^\circ\text{C}$) in (bio)catalysis -applicable to many ionic, polar and non polar structure groups- and as efficient electrolytes [1]. The applications range from electrochemistry, sensors, analysis, separation techniques to catalysis and reaction engineering. Furthermore it is most important to realize low production cost including efficiently 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 in lab scale [2] und layer crystallization for static and dynamic crystallization conditions in pilot scale. Results are used for basic engineering of large scale plants. In the case of EMIM-Chloride segregation coefficients are in the range of $0,05 < k_{\text{seg}} < 0,6$ depending on crystallization rate, yield, feed impurity concentration and techniques used. The crystallization behavior of purified Ionic Liquids will be discussed in detail in respect those of organic substances with similar melting points. Purification potential of EMIM-Chloride will be discussed in respect to different crystallization techniques and different scales used for crystallization.

The excellent purification results of EMIM-Chloride offer a high purification potential of melt crystallization techniques for Ionic Liquids as a new innovative class of solvents and reactants. Melt crystallization is a very efficient method to produce in different scales from 0.5 g up to 1000 kg ultra pure Ionic liquids $w_{\text{IL}} > 99,99\%$.

Keywords: Ionic Liquids, ultra purification, crystallization, green engineering, emim chloride

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. Their catalytic activity and their 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 [3], membrane technologies [4] as well as crystallisation [5] discussed in literature for purification of ionic liquids widely. BASF company is claiming all kinds of industrial and laboratory crystallization techniques for purification of ionic liquids [6].

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-ethyl-3-methyl-imidazolium) by melt crystallization. Feed stock of all experiments is EMIM-Chloride from FLUKA company in BASF Quality with purity $w > 93\%$ for lab scale experiments and from MERCK company with purity $> 98\%$ for large scale experiments.

EMIM-Bromide $w \sim 95\%$ was synthesised by the group of Prof. Wasserscheid.

Impurity content larger than $w_{\text{im}} > 3\%$ was measured by ion chromatographic system ICS-3000 from DIONEX Corp., CA, USA [8, 11]. 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 $\lambda = 320 \text{ nm}$. The content of Imidazolium MIM as an educt was

Ultrapurification of Ionic Liquids

measured by HPLC system ULTIMATE-3000 from DIONEX Corp., CA, USA using UV/VIS Detection.

The calorimetric measurements are performed with NETSCH DSC 200 F3.

Purification at lab scale was done by different techniques. 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 $0.01 \text{ mm/h} < dL/dt < 40 \text{ mm/h}$. The experiments in larger scale are operated as falling film technique in a double jacketed glass heat exchange tube with inner diameter $d_i=60 \text{ mm}$ and length of 400 mm. Purification by dry sweating was operated in a heated filter centrifuge at acceleration of $z=1000 \cdot g$.

The experiments on industrial scale were carried out with a falling film crystallizer that contains vertical tubes in which the crystal layers grow as cylindrical shells. The collecting vessel beneath the tubes is built integrally with the crystallizer. Figure 4 shows the simplified flow diagram with a single-tube crystallizer that was used for the experiments. At the start of a stage this vessel is filled with a batch of material. The circulating pump then is started to irrigate the tubes, while coolant temperature ramping is begun on the shell side of the crystallizer. The melt circulation rate is high compared to the rate of crystal deposition so that conditions of temperature and composition are approximately uniform down the length of the tubes. The shell-side temperature is ramped down at a constant rate until the collecting vessel level drops to a preset value, indicating the desired amount of product is suspended in the tubes. At the end of crystallization phase the thickness of the crystalline layer is approximately 5 to 20 mm. Following draining, the shell side temperature is gently ramped up to a value just below the product's melting point to sweat out included impurities and assist further draining.

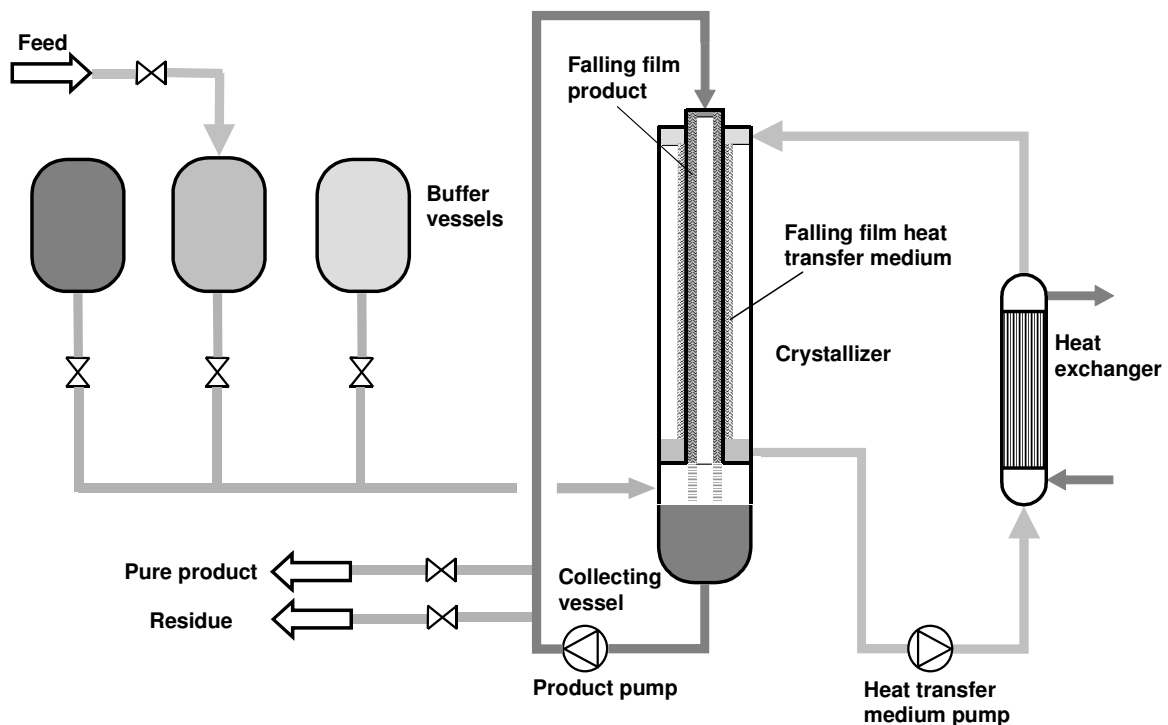


Figure 4: Flow diagram of industrial falling film Crystallization

The cooling medium also flows as a falling film. A large pump-around rate and uniform distribution at the top of each tube allows precise control of temperature ramping, particularly important for sweating. Shell-side cross-flow is also prevented. Because each crystallizer tube undergoes exactly the same hydraulic and thermal conditions on both sides of the tube wall, the scale-up is trivial and reliable. Pilot plant tests on a single full size tube are used to design plants with several thousand tubes.

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 [9]

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.

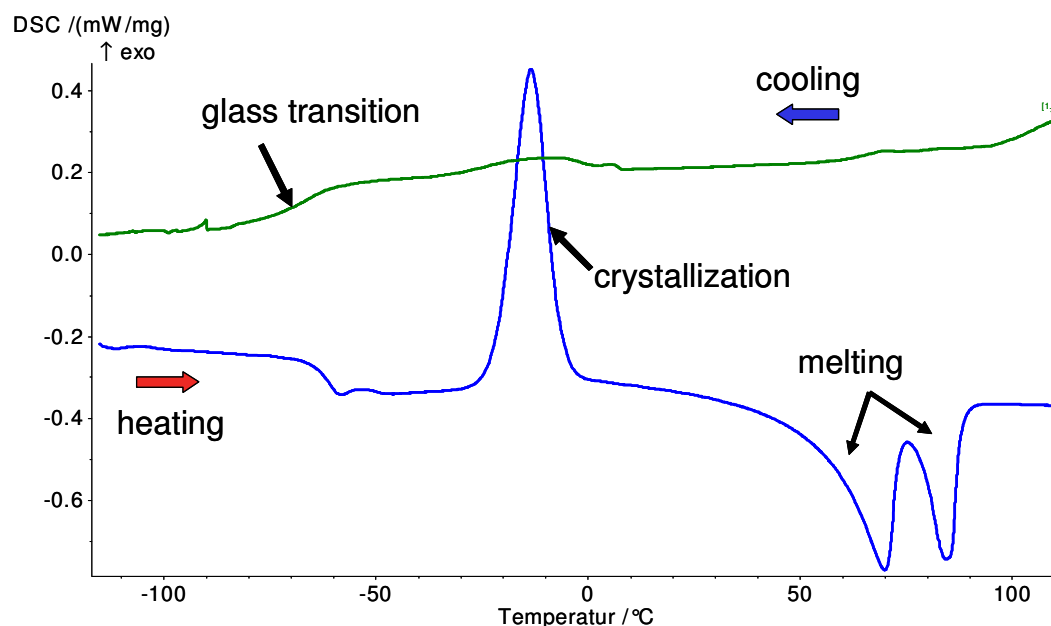


Figure 1: DSC melting and crystallization experiment of EMIM-Chloride, $dT/dt = 10K/min$

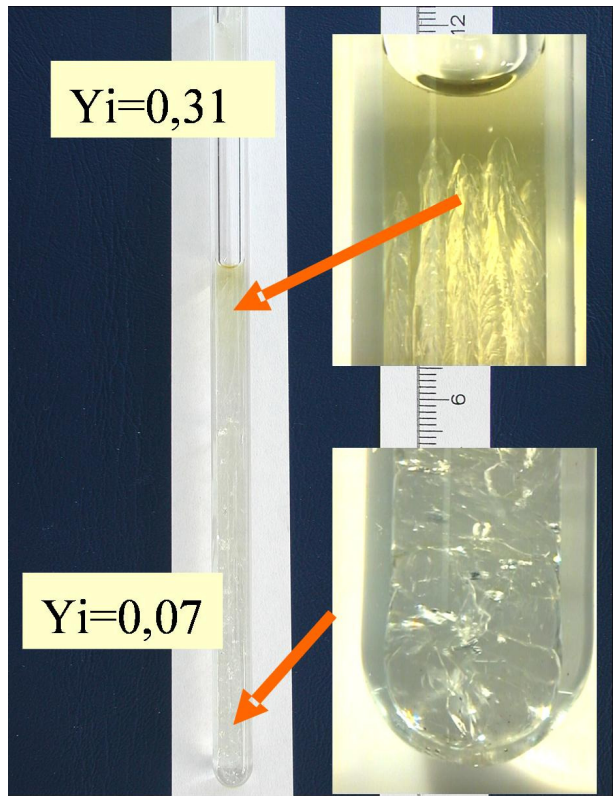


Figure 2: Zone melting of EMIM-Cl, 2nd passages, $dL/dt=1,4$ mm/h



Figure 3: Static layer crystallization of EMIM-Cl, $m_{\text{Feed}} = 50$ g

Smooth crystallization operates in presents of seed crystals using zone melting and static layer technique. Using zone melting at small travelling rates ($dL/dt < 4$ mm/h) well shaped crystals built up. It can be seen at the solid liquid inter-phase in Fig. 1. The load of impurities Y (extinction at $\lambda=320$ 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 $w_{\text{imp}} < 1,5\%$ starting with feed impurity content of $w_{\text{imp}}=5\%$ 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 $m \sim 1$ g and $m \sim 50$ g tested with the crystallization techniques zone melting and static layer crystallization motivates to purify EMIM-Chloride in larger scale up to $m \sim 1000$ 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.

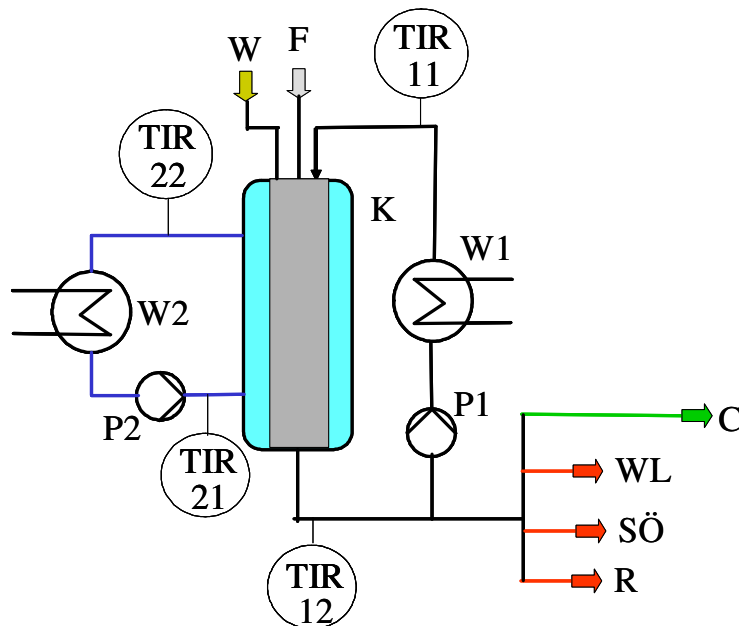


Figure 4: Mini plant for dynamic and static melt crystallization [10]

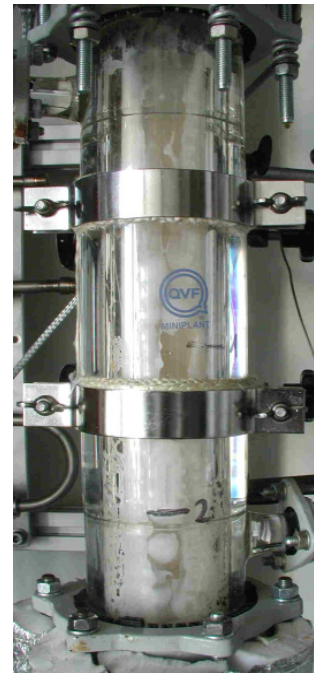


Figure 5: Dynamic layer crystallization of EMIM-Cl

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 $4 \text{ kg/h}\cdot\text{m}^2$ at run V3 down to $1,3 \text{ kg/h}\cdot\text{m}^2$ 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 $\text{GR}_{\text{spec}}=4,4 \text{ kg/h}\cdot\text{m}^2$ means a travelling rate of $dL/dt=4 \text{ mm/h}$. Results of the relationship between purification and travelling rate can be used for forecasting of process parameters at dynamic layer crystallization directly.

Table 2: Lab scale dynamic layer crystallization of EMIM-Chloride

		V3	V4	V5	V6
feed	g	570	540	540	410
$Y_{\text{imp,feed}}$	%	3,4	5,7	4,1	1,1
yield crystallization	%	63	63	59	63
yield after sweating	%	44	33	38	38
growth rate spec.	$\text{kg/h}\cdot\text{m}^2$	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.

The results of large scale experiments are shown in Table 3 and Table 4 for static and falling film melt crystallization. Static layer results give good purification for specific growth rates $GR_{spec} < 3 \text{ kg/h}\cdot\text{m}^2$. It is seen that sweating improves purification significantly and indicates the importance of the post crystallization treatment for industrial application.

Table 3: Pilot scale static layer crystallization of EMIM-Chloride

		2-1	3-1	6-1
feed	kg	0,984	5,126	6,343
yield crystallization	%	85,26	85,80	93,65
yield after sweating	%	66,77	60,75	79,93
growth rate spec.	kg/h*m ²	2,4	4,6	6,4
PP crys	-	0,648	0,908	1,027
PP crys&swaet	-	0,387	0,303	0,600

The top view of a crystal layer of the static layer crystallization of run 2-1 after solid liquid separation by draining the liquid is shown in Figure 6. Well shape crystals can be seen. At the outside wall the crystals looking yellow. In the direction of the midsection the colour of the crystals get browner. This is the results that the impurities accumulate in the liquid phase.

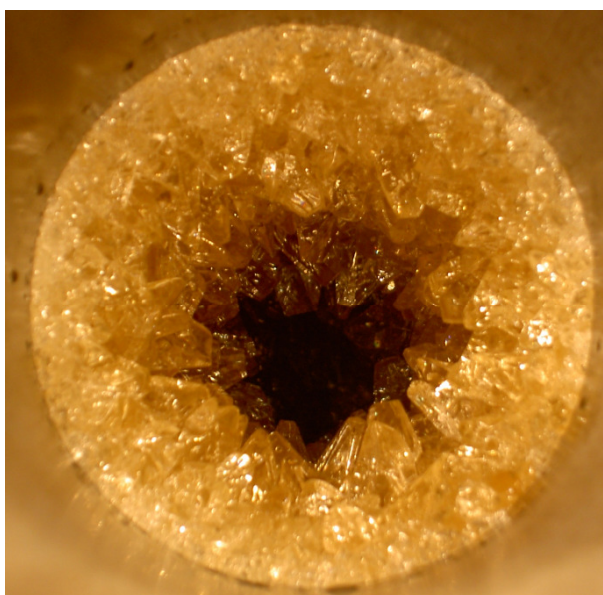


Figure 6: Top view of the crystal layer of the run 2-1 after liquid draining

Falling film crystallization produces high efficient purification results, see Table 4. In comparison with the static crystallization technique higher specific growth rates can be operated at the same level of purification as estimated in respect to other applications done before. Sweating improves purification significantly too.

Table 4: Pilot scale dynamic layer crystallization of EMIM-Chloride

		4-1	4-2	5-1	5-2
feed	kg	8,113	5,700	8,730	6,050
yield crystallization	%	75,08	72,54	76,88	75,07
yield after sweating	%	70,75	59,40	71,03	64,86
growth rate spec.	kg/h*m ²	5,7	9,2	5,5	8,0
PP crys	-	0,410	0,761	0,405	0,832
PP crys&swaet	-	0,322	0,496	0,234	0,590

As discussed before Ionic Liquids can contain a lot of impurities for many reasons. Up to now purification was discussed using the brown color of EMIM Chloride. Figure 7 shows the HPLC plot of the feed and the product of falling film experiment 5-1. The impurity 1 (Imp1) with the retention time of $t_R=4,46$ min could be identified as Methylimidazolium MIM. MIM is an educt using direct synthesis route of EMIM Chloride and indicates conversion rate $R<100\%$ during synthesis of the batch. After crystallization the product contains traces of MIM only. The PP value of $PP<0.01$ is very good and indicates high purification selectivity of crystallization in respect to Methylimidazolium.

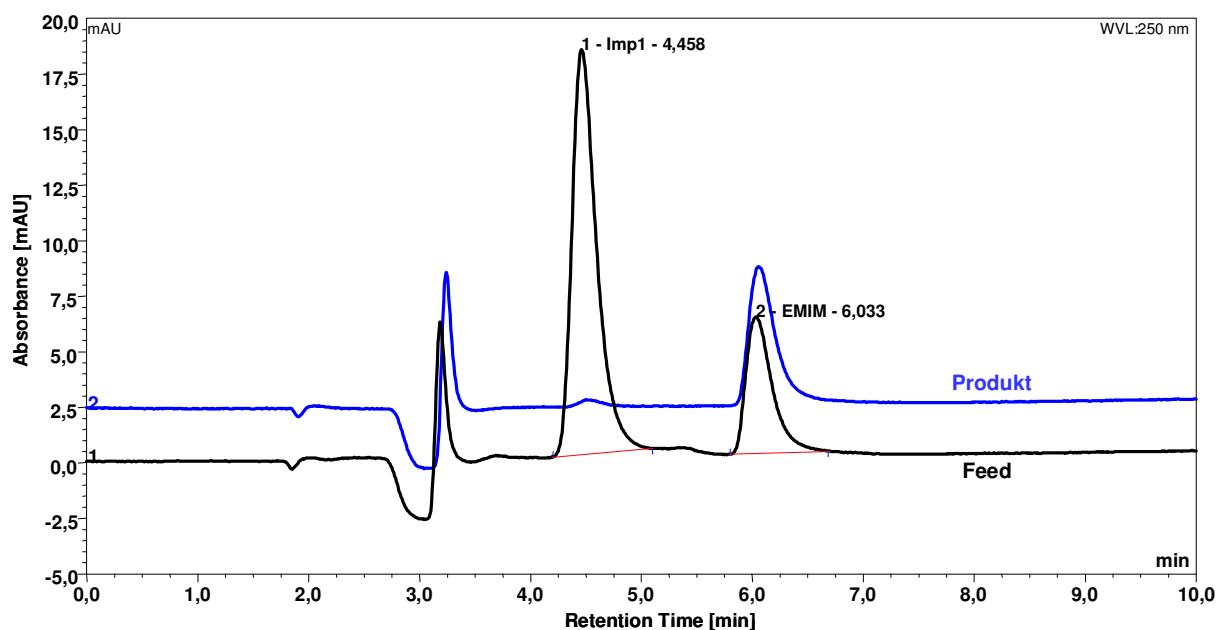


Figure 7: HPLC plot of feed and product of falling film experiment 5-1 [8]

Progress of purification for Naphthalene crystallization from Naphthalene/Biphenyl mixture has similar values operated in the same equipment und conditions. For Naphthalene progress of purification yields $PP=0.4$ at Biphenyl content of 20% and at growth rate of $4 \text{ kg/h}\cdot\text{m}^2$ in respect to $PP=0,36$ at run V4, 4-1 or 5-1 for EMIM-Chloride.

The results received during this work motivate to further investigations in respect to purification by crystallization of ionic liquids. Analysis and trace analysis of impurities in

ionic liquids is still a field of 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 ($T_m < 100^\circ\text{C}$). 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 0,5 g, 50 g, and 1000g are prepared in lab scale using for scientific investigations. It offers the possibility supporting research teams in purifying their ionic liquids. Samples of capacity > 100 kg are produced in pilot (industrial) scale supporting manufactures and end users of industrial applications of Ionic Liquids.

Furthermore melt crystallization is an efficient technique for purification and ultra purification in respect to realize low production costs. Melt crystallization is a proven technology to make ILs at any desired purity at reasonable cost and without limitation for capacity.

Ionic liquids have similar crystallization behavior like classical organic melts. EMIM-Chloride crystallization and purification by melt crystallization is in principle comparable with e.g. that of Naphthalene or Biphenyl.

6. References

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