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Chemical Physics Letters 415 (2005) 131–136
CHEMICAL PHYSICS LETTERS
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Purification of imidazolium ionic liquids for spectroscopic applications

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Received 14 July 2005
Available online 23 September 2005

Abstract

Ionic liquids are often contaminated by colored impurities. These impurities can be problematic for spectroscopic studies or for monitoring organic reactions by UV/Vis spectroscopy. The effect of different purification methods on the optical quality of colored ionic liquids was studied and compared. Yellowish ionic liquids can partially be decolorized by treatment with active charcoal or by recrystallization. Our experiments show column liquid chromatography is not always a good technique to prepare spectrograde imidazolium halide ionic liquids. Colorless and UV-transparent ionic liquids were synthesized by a method that can exclude the need for further purification steps.

1. Introduction

The research activity in the field of *ionic liquids* or *room temperature ionic liquids* (ILs or RTILs) has increased dramatically during the last years [1–4]. These compounds are a new class of solvents for organic reactions, both for catalyzed and uncatalyzed reactions. Their unique properties like a large liquidus range, a very low vapor pressure and high thermal, chemical and electrochemical stability promise a wide applicability [5–8]. The properties of ionic liquids can be adjusted by choosing specific combinations of cations and anions. For instance, they can be made either hygroscopic or hydrophobic. The number of already described and potential cation–anion combinations is very large, but most research has been devoted to the 1-alkyl-3-methylimidazolium salts [9].

Ionic liquids can be transparent in the near-ultraviolet and visible spectral regions. In contrast to many other polar organic solvents like DMF or DMSO, ionic liquids are non-coordinating ‘designer solvents’ which properties can be tuned. This makes that ionic liquids are very interesting solvents for spectroscopic measurements on dissolved metal salts and metal complexes. The visible and near-infrared emission of lanthanide salts and complexes dissolved in ionic liquids were reported recently [10–12]. Ionic liquids are also being used as a medium for photochemical reactions and for photophysical measurements [13,14]. Another potential application that requires a solvent with a good transparency in the ultraviolet and visible spectral region, is the monitoring of organic reactions by absorption spectroscopy [15–17].

One problem that limits the use of ionic liquids in optical applications is that many synthetic methodologies lead to ionic liquids with a yellowish or even a brown color. Especially, during the preparation of 1-alkyl-3-methylimidazolium halides that are frequently used as starting materials to synthesize other ionic liquids, a discoloration is difficult to avoid [9,18,19]. The impurities that cause this discoloration are reported to be below the detection limit of NMR spectroscopy and apparently these impurities do not affect organic or catalytic reactions which are carried out in ionic liquids [20]. Most commercially available ionic liquids also contain colored impurities.

The purification of ionic liquids was already the subject of several papers. Gordon reported most of the purification methods mentioned here, including the purification by charcoal, alumina columns and the precautions to be taken for the starting materials [20]. Samanta et al. [21,22] reported on the optical properties of ionic liquids and the preparation

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doi:10.1016/j.cplett.2005.08.128

of a spectrograde 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. Hilgers and Wasserscheid [23] reported on the quality aspects of the ionic liquid production and pointed to the difficulties in determining the chemical structure of the colored impurities. They also mention that the color is not the crucial parameter for most of the applications of ionic liquids. Cammarata et al. [24] report the use of infrared spectroscopy to investigate the state of water in RTILs based on the 1-alkyl-3-methylimidazolium cation. Holbrey et al. [25] reported a colorimetric method to detect traces of 1-methylimidazole by addition of a copper(II) solution.

In this Letter, we will discuss the effect of several purification methods on the transparency of ionic liquids. We show that UV/Vis spectrophotometry is an efficient method for the quality control of ionic liquids. Inspection of the optical quality by the naked eye is by no means a reliable method. Furthermore, we report a simple method for the preparation of pure and colorless spectrograde 1-alkyl-3-methylimidazolium halide and bis(trifluoromethanesulfonyl)imide (triflimide) ionic liquids. The synthetic procedure involves only slight modifications of commonly used synthetic routes, but results in colorless and transparent ionic liquids, which require no further purification. We compare the absorptivity of the ionic liquids synthesized by our method with that of ionic liquids synthesized by conventional methods.

2. Experimental

All products were characterized by ^1H NMR spectroscopy, CHN elemental analysis and mass spectrometry. ^1H NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer, operating at 300 MHz. CHN elemental analyses were performed on a CE Instruments EA-1110 elemental analyzer. Mass spectrometry was measured on a Thermo Finnigan LCQ mass spectrometer (ESI). The results of the analytical data were according to literature data [9]. All chemicals used in this work were purchased from Acros or Fluka. Absorption spectra were recorded on a Varian Cary 5000 spectrophotometer. The absorption measurements were made in quartz cuvettes with a path length of 2 mm or 1 cm. All ionic liquids were dried at 70 °C for 3 h on a rotary evaporator under reduced pressure before the spectroscopic measurements were made. The water contents of the ionic liquids were checked with a coulometric Karl Fischer titrator (Mettler-Toledo model DL-39).

2.1. 1-Hexyl-3-methylimidazolium bromide, $[HMIM][Br]_{colorless}$

1-Hexyl-3-methylimidazolium bromide was prepared under very mild conditions. 1-Methylimidazole (99%, purchased from Acros) was freshly distilled from potassium hydroxide under reduced pressure. 400 mL of 1-bromohexane (99%, purchased from Acros) was first distilled and extracted with four times 20 mL of concentrated sulfuric acid until no longer brownish discoloration of the acid phase appeared. Then, 1-bromohexane was washed with water, neutralized with a concentrated $NaHCO_3$-solution and washed with water again. Drying with $MgSO_4$ followed, and after filtration, the organic phase was distilled over P_2O_5 under reduced pressure.

Into a round-bottom flask equipped with a magnetic stirrer, a septum under argon atmosphere and cooled in an ice bath, were placed 0.25 mol (21.1 mL) of 1-methylimidazole and 60 mL of anhydrous toluene. This mixture was stirred for half-an-hour. An excess of 1-bromohexane (0.35 mol, 68 mL) was very slowly added drop wise by a syringe to the vigorously stirred mixture. The reaction mixture was protected from light by wrapping the flask in aluminum foil. After the reaction mixture had been stirred for 62 h, the mixture was allowed to warm to room temperature. The slightly viscous, colorless product was separated from the toluene phase and washed two times with 50 mL of toluene and then two times with 50 mL of ethyl acetate. The ionic liquid was thereafter dried for 5 h on a rotavap under reduced pressure at 70 °C. Yield: 82%. The product is an oily liquid at RT. Colorless products can also be obtained for other alkyl chain lengths (ethyl, butyl, octyl). The reagents should be purified prior to use, because otherwise ionic liquids with colored impurities are obtained. The reagents should be stored in the dark.

2.2. 1-Hexyl-3-methylimidazolium chloride, $[HMIM][Cl]_{colorless}$

The 1-hexyl-3-methylimidazolium chloride ([HMIM][Cl]) was synthesized in an analogous way as $[HMIM][Br]_{colorless}$ with the same quantities. Due to the lower reactivity of the 1-chlorohexane the reactants were also mixed under ice cooling, but after the temperature was risen to room temperature, no emulsion formation took place. The temperature was then carefully increased over a period of one day to a final reaction temperature of 48 °C. The reaction mixture was vigorously stirred for one week. Because higher temperatures are required, there is a higher chance to produce colored impurities. Yield: 76%. The product is an oil at room temperature.

2.3. 1-Hexyl-3-methylimidazolium bromide $[HMIM][Br]_{ref}$

As a 'reference' ionic liquid, 1-hexyl-3-methyl-imidazolium bromide ([HMIM][Br]), was synthesized according to the same procedures as described above using older reagents (two weeks after purification) and a slightly elevated temperature 35 °C. The quantities were the same as for the colorless ionic liquid. The color and transparency of this ionic liquid was compared with that of the samples prepared according to our synthetic procedure. The reactants were first purified in the same way as described above. The reaction was performed in a flask equipped with a condenser, an oil bath and a magnetic stirrer under argon atmosphere. The main difference in this synthetic method and the method we describe in this Letter, is the reaction temperature of 65 °C and the reaction time of 5 h. The workup of the products was similar to what was described above. The color of this ionic liquid can be described as pale yellow. Yield: 98%. The product is an oil at room temperature.

2.4. 1-Ethyl-3-methylimidazolium bromide, [EMIM][Br]$_{ref}$

1-Ethyl-3-methylimidazolium bromide ([EMIM][Br]) was synthesized in a similar way and with same quantities as the [HMIM][Br]$_{ref}$ ionic liquid. This compound is a slightly yellow solid at room temperature. Therefore, it was used for the study of the effect of recrystallization. Yield: 95%.

2.5. Purification of 1-hexyl-3-methylimidazolium bromide with charcoal, [HMIM][Br]$_{charcoal}$

Active charcoal (10 wt%, 3 g) was added to the ionic liquid (30 g) and the liquid was stirred for 24 h. After adding 20 mL of dichloromethane to reduce the viscosity of the ionic liquid, the mixture was filtrated over a filter paper. The solvent was removed under reduced pressure. The ionic liquid was thereafter dried for 5 h on a rotavap under reduced pressure at 70 °C.

2.6. Recrystallization of 1-ethyl-3-methylimidazolium bromide, [EMIM][Br]$_{recryst}$

The recrystallization was done by solving the compound in a small quantity of acetonitrile and by adding a small amount of toluene to the solution. This solution was cooled in a freezer (−18 °C), and white crystals of the ionic liquid were formed. After filtration, the crystals were washed with ice-cold toluene and the remaining solvent was removed by evaporation on a rotavap under reduced pressure.

2.7. 1-Hexyl-3-methylimidazolium bis(perfluoromethanesulfonyl)imide, [HMIM][NTf$_2$]

1-Hexyl-3-methylimidazolium bis(perfluoromethanesulfonyl)-imide, [HMIM][NTf$_2$], was synthesized by a metathesis reaction, following a procedure described by Bonhôte et al. [9]. An aqueous solution of lithium bis(trifluoromethanesulfonyl)imide was added to [HMIM][Br]. 35 g of the ionic liquid were washed several times with aliquots of water (20 mL) until no longer bromide residues were detected by the $AgNO_3$ test. Yield: 95%. The product is an oil at room temperature.

3. Results and discussion

The basic idea of our approach was to optimize the conditions for the synthesis of imidazolium ionic liquids in order to maximize the transparency in the visible and ultraviolet regions. The ultraviolet transparency depends on the type of counter ion. For instance, the ultraviolet spectral window of the halides is narrower than that of bis(trifluoromethanesulfonyl)imides, due to a charge transfer band in the halide ionic liquids.

Although the chemical nature of the colored impurities is not known yet, it is obvious that the quaternization step is the critical part in the synthetic procedure. Due to the low volatility of ionic liquids, only few purification methods are suitable, so that the formation of colored impurities should be prevented as far as possible during the preparation of the ionic liquid. It is evident that carefully purified reactants have to be used to obtain pure ionic liquids, but also the reaction conditions of the quaternization step have to be optimized (mild reaction conditions and low reaction temperatures).

The best results for the synthesis of the 1-alkyl-3-imidazolium bromides were obtained via a one-pot reaction with ice-cooled reactants, which were allowed to warm up very slowly to room temperature. As a result of the low reaction temperature, the reaction time had to be extended to about 4 days. The best quality of ionic liquids was obtained for rather small quantities of reactants up to about 0.3 mol of 1-methylimidazole. Larger quantities of the reaction mixture resulted in a decrease of the transparency of the ionic liquids, probably due to temporary higher local temperatures in the reaction mixture. This finding limits presently the up-scaling of the reaction under the given reaction conditions, but we are looking for methods to circumvent this inconvenience – e.g. by internal cooling of the reaction medium. The resulting ionic liquids are completely colorless and transparent. In order to compare our ionic liquids with those prepared following the standard synthetic procedures, we prepared a sample of the ionic liquid 1-hexyl-3-methylimidazolium bromide, [HMIM][Br]$_{ref}$, by a standard procedure. For this, the quaternization of 1-methylimidazole was performed at 65 °C, and the reaction was finished after 5 h of heating. A yellowish liquid was obtained.

In Fig. 1, the absorption spectra of different samples of the ionic liquid 1-hexyl-3-methylimidazolium bromide ([HMIM][Br]$_{colorless}$, [HMIM][Br]$_{ref}$) are shown. The spectra were recorded in a 1 cm quartz cell. For the yellowish ionic liquid [HMIM][Br]$_{ref}$, an absorbance of 0.5 is found at 410 nm, while in the colorless ionic liquid, [HMIM][Br]$_{colorless}$, the same absorbance value is measured below 300 nm. It should be noted that differences were found in the absorption spectra of colorless ionic liquids, depending on the method that was used for their purification. Therefore, the color (or the lack of color) of an ionic liquid is not the only criterion for the optical quality of an ionic liquid. It is evident that the optical absorption spectrum is a better tool to check the optical quality of an ionic liquid.

Because [HMIM][Br] is also miscible with water, we also recorded the absorption spectra of diluted samples of [HMIM][Br] and [HMIM][Cl] in water (Fig. 2). The

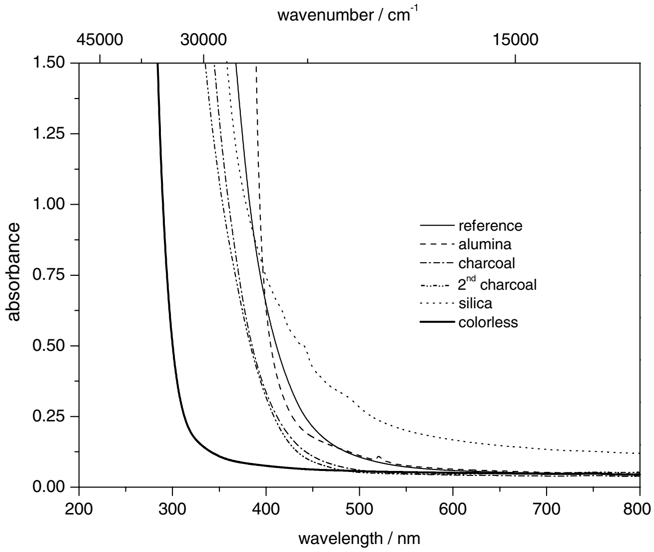

Fig. 1. Absorption spectrum of $[HMIM][Br]_{colorless}$ synthesized by low-temperature processing (thick solid line, 'colorless'), the ionic liquid $[HMIM][Br]_{ref}$ synthesized by standard procedures (thin solid line, 'yellowish') and this sample $[HMIM][Br]_{charcoal}$ treated with charcoal (dash/dot line), a sample with 2nd treatment by charcoal (dash/dot/dot line) silica gel (dotted line) and alumina (dashed line). All samples measured in a quartz cuvette with a path length of 1 cm.

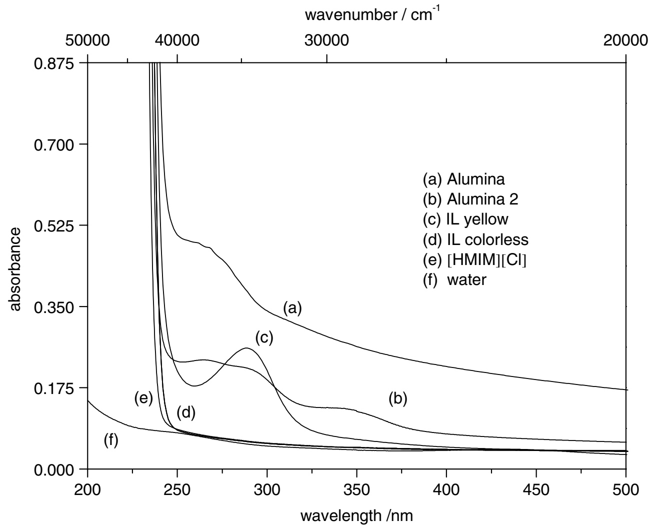

Fig. 2. Absorption spectrum of $[HMIM][Br]_{colorless}$ synthesized by low-temperature processing ((d) 'colorless'), the ionic liquid synthesized by standard procedures ((c) 'yellow'); this sample treated with alumina (a) and treated with already used alumina ((b) 'alumina 2'). (e) shows an absorption spectrum of [HMIM][Cl]; (f) deionized water. These samples were diluted with water to a concentration of 2 mmol/mL measured in a quartz cuvette with a path length of 2 mm.

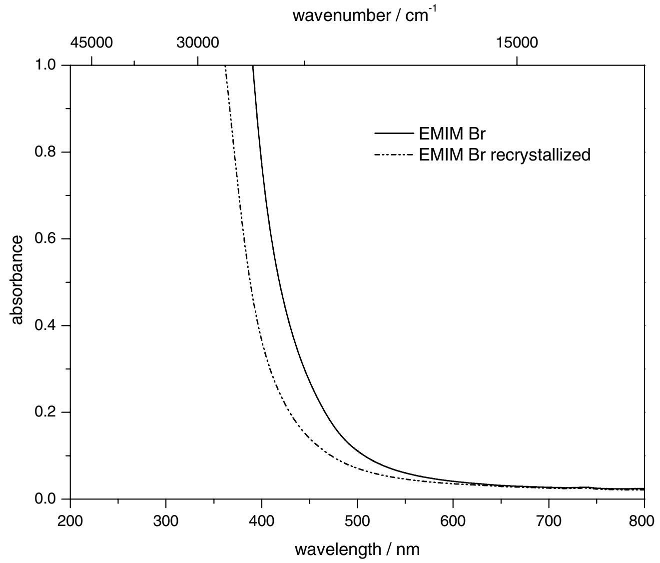

Fig. 3. Absorption spectrum of [EMIM][Br] synthesized by low-temperature processing (thick line) and after recrystallization (dotted line) in a quartz cuvette with a path length of 1 cm.

absorption spectrum of the yellowish ionic liquid shows an absorption maximum around 290 nm. The absorption spectrum points out the lower transparency of this batch. So only a few drops of the ionic liquid dissolved in water are enough to carry out an efficient quality control by absorption spectroscopy.

Addition of active charcoal is often recommended to decolorize ionic liquids after synthesis, because the colored impurities are adsorbed on the surface of active charcoal [26]. We tried to quantify the effect of charcoal on the transparency of the ionic liquid by measuring absorption spectra of the above mentioned yellowish 1-hexyl-3-methylimidazolium bromide, $[HMIM][Br]_{ref}$ before and after the treatment. The absorption spectra shown in Fig. 3 before and after the treatment indicate, that the 0.5 absorbance threshold was shifted from 410 (before treatment) to about 385 nm (after treatment). A second treatment with charcoal gave a shift of the 0.5 absorbance threshold from 385 to only 380 nm, so the effect diminished somewhat. These results show that treatment with active charcoal can help to enhance the transparency of the ionic liquid in the visible spectral region, but the method does not work well if one wants to obtain ionic liquids with a good transparency in the ultraviolet region. The treatment with charcoal had no significant effect on the ionic liquids that were obtained via the low-temperature synthesis method we describe in this Letter.

Ionic liquids can be regarded as molten salts, and salts can be purified by recrystallization. This method is hampered by the fact that many of the ionic liquids are oily liquids at room temperature or even at temperatures well below room temperature, and that they are quite difficult to crystallize. The ionic liquids that crystallize at room temperature, like 1-ethyl-3-methylimidazolium bromide, [EMIM][Br], are somewhat difficult to handle during spectroscopic measurements. In order to study the effect of recrystallization on the transparency of an ionic liquid, we measured the absorption spectrum of [EMIM][Br] using a supercooled melt at room temperature. The absorption spectrum of [EMIM][Br] (Fig. 3) shows that the position of the 0.5 absorbance value shifts from 420 nm ($[EMIM][Br]_{ref}$) to about 390 nm ($[EMIM][Br]_{recryst}$).

Column liquid chromatography with alumina (or sometimes silica) as the stationary phase is often recommended for the purification of ionic liquids [26]. The yellowish 'reference' ionic liquid 1-hexyl-3-methylimidazolium bromide ([HMIM][Br]$_{ref}$) was diluted with dichloromethane and the solution was passed through an alumina and a silica column, respectively. After evaporation of the solvent, both ionic liquid samples showed a slight Tyndall effect by looking through the sample (light scattering was observed). The spectra recorded in a 1 cm quartz cuvette showed a baseline that increases towards shorter wavelengths. This points to the presence of small particles in the liquid, probably colloidal particles of alumina or silica. Although the color of the sample treated with the silica column appears to brighten somewhat upon observation by the naked eye, the 0.5 absorbance threshold shifts for the [HMIM][Br] sample from 410 nm ([HMIM][Br]$_{ref}$) to about 440 nm. The absorption spectrum is shown in Fig. 1.

The ionic liquid sample treated with neutral alumina (Fluka Type 507C) also appears to contain some small particles. This was measured for a sample diluted with water in a 2 mm cell shown in Fig. 2. The effect of scattering by particles decreased by re-using an already used column, as shown for the spectrum in Figs. 1 and 2, so probably the small particles were partly removed from the alumina with the first batch of ionic liquid. Nevertheless, the purification by column chromatography remains a questionable procedure for this type of ionic liquid.

The 1-alkyl-3-methylimidazolium halides are often only used as precursors for other ionic liquids, because the halide anions (especially the bromides) can easily be exchanged by a metathesis reaction. An interesting class of ionic liquids for optical applications are the bis(trifluoromethanesulfonyl)imides, because they show a low melting point, low viscosity and a good transparency in the ultraviolet region, due to the absence of a charge transfer band that limits the ultraviolet transparency of the halide ionic liquids. The preparation of 'spectrograde' imidazolium hexafluorophosphate ionic liquids by methanthesis was already demonstrated [22,27]. The authors suggest purification with alumina after the preparation of [BMIM][PF$_6$]. The effect of column chromatography is not investigated and may depend on the used ionic liquid. We performed the metathesis reaction of 1-hexyl-3-methylimidazolium bromide following a literature procedure by adding an aqueous solution of lithium bis(trifluoromethanesulfonyl)imide to an aqueous solution of the bromide ionic liquid. This was done starting from the clean and colorless sample of [HMIM][Br]$_{colorless}$ and from the yellowish [HMIM][Br]$_{ref}$ sample. The resulting absorption spectra measured in a 1 cm quartz cell are shown in Fig. 4.

The sample synthesized from the yellowish [HMIM][Br]$_{ref}$ sample exhibits in the ultraviolet region between 250 and 300 nm absorption bands that were not present in the ionic liquid prepared from the colorless [HMIM][Br]$_{colorless}$ sample. This was probably due to some remaining colored impurities. This batch of [HMIM][NTf$_2$] was extracted again four times with small aliquots of water and the resulting absorption spectrum of the sample showed almost a complete removal of the colored impurities. However, this also resulted in a considerable loss of ionic liquid. Some traces of [HMIM][Br]$_{colorless}$ were added to this sample to check if the absorption bands could be attributed to some halide residues. The absorption spectrum is also shown in Fig. 4 and looks different.

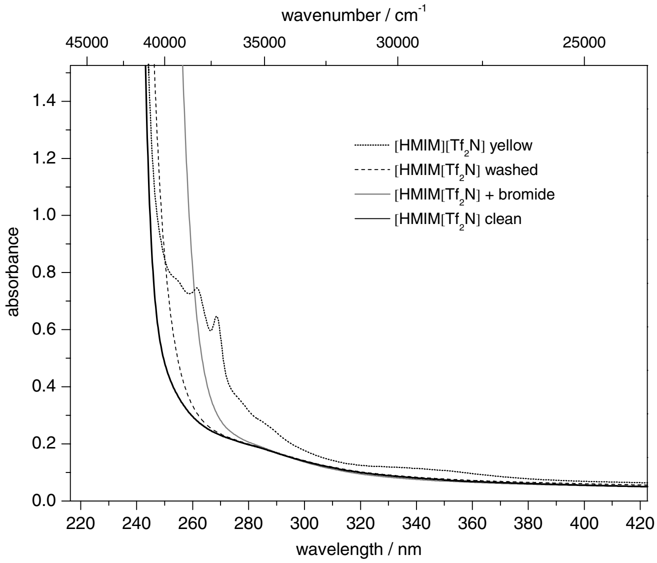

Fig. 4. Absorption spectrum of [HMIM][NTf$_2$] synthesized by a metathesis reaction from colorless [HMIM][Br]$_{colorless}$ (solid black line, 'clean'), from a yellowish [HMIM][Br]$_{ref}$ (dotted line, 'yellow') and this sample extracted with water (dashed line, 'washed') and after adding traces of [HMIM][Br]$_{colorless}$ (gray dotted line, '+ bromide'). All samples measured in a quartz cuvette with a path length of 1 cm.

So the metathesis reaction to transform [HMIM][Br] into [HMIM][NTf$_2$], only slightly depends on the quality of the starting imidazolium halide ionic liquid, provided that the ionic liquid is well purified after the metathesis reaction. There is of course always a loss due to the washing of the samples so that also here only the pure starting materials can be recommended.

4. Conclusion

The synthesis method using simple low-temperature processing of 1-methyl-3-alkylimidazolium halides has proven to yield colorless products suitable for spectroscopic requirements. Further, elaborate purification steps of the product synthesized by this route is not necessary. It was shown that it is difficult to remove traces of disturbing impurities by charcoal or by recrystallization, but a slight decolorization is possible – but not without a considerable loss of product. Purification by column liquid chromatography with alumina or silica as the stationary phase turned out to be problematical for this type of ionic liquids. For product of the metathesis reaction from the 1-methyl-3-alkylimidazolium halides to 1-methyl-3-alkylimidazolium bis(trifluoromethanesulfonyl)imides, the optical quality of the resulting ionic liquid was enhanced by the use of well purified starting materials.

Acknowledgements

K.D. and K.B. thank the F.W.O.-Flanders (Belgium) for a Postdoctoral Fellowship. P.N. is a Postdoctoral Fellow funded by the EU (GROWTH No: GRD2-2000-30346 OPAMD). Financial support by the F.W.O.-Flanders (G.0117.03), by the K.U.Leuven (GOA 03/03) and by the EU (GROWTH No: GRD2-2000-30346 OPAMD) is gratefully acknowledged.

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