Anal. Chem. **2007,** *79,* 758−764

Technical Notes

Decolorization of Ionic Liquids for Spectroscopy

Martyn J. Earle,[†] Charles M. Gordon,[‡,§] Natalia V. Plechkova,[†] Kenneth R. Seddon,[*,†] and Thomas Welton[||]

QUILL, The Queen's University of Belfast, Stranmillis Road, Belfast, BT9 5AG, Northern Ireland, UK, Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, UK, and Department of Chemistry, Imperial College London, London SW7 2AZ, UK

It has been widely recognized that although ionic liquids should be colorless, they are frequently not. Colored samples appear to be pure by most analytical techniques (e.g., NMR spectroscopy, mass spectrometry, HPLC, and ion chromatography), and there have been many attempts to identify the source of color in our own laboratories and others—after 20 years the best that can be said is that the impurities are at a very low level (probably parts per billion) with very high molar extinction coefficients. In this paper, we do not identify these impurities but describe a practical method for removing them for spectrochemical applications. We clearly note that the method is not "green", but we anticipate that it will only be applied to the small volumes of ionic liquids required for fundamental spectroscopic studies in academia but not in industrial processes.

Since the earliest days of ionic liquids, they have been analytically pure to NMR spectroscopy and mass spectrometric microanalysis, but have frequently been yellow, brown or in the worst cases black in color (Figure 1). (The ionic liquids marketed as Basionics (BASF) are visibly colored, many being black and opaque (http://www.basionics.com, BASF (2006), Merck KGaA, Ionic Liquids.)

Overheating when making ionic liquids can cause the color, but this is not the only source of color (vide infra): color can be generated in isothermal reactions at room temperature.

Ionic liquids may contain water, halides, and chromophores (the word "chromophore" is applied here for any sort of impurity that imparts color to ionic liquids). Both high water and halide content generally make ionic liquids unsuccessful candidates for catalytic processes.[1] It is possible to minimize the halide content in ionic liquids by washing them with water and then subsequent drying in vacuo at 65 °C for 24 h. However, there is a problem for certain types of ionic liquids, such as those that contain the hexafluorophosphate ($[PF_6]^-$) anion, prepared from halide ionic liquids. Hexafluorophosphate ionic liquids are immiscible with water (hydrophobic ionic liquids) in general and are frequently purified by aqueous extraction.[2,3] As the halide is removed (halide concentration can be determined by ion chromatography[4,5]) water is introduced concomitantly into the ionic liquid, which then itself has to be removed. If these ionic liquids containing water from the washings are heated under vacuum at 65 °C, they undergo partial hydrolytic decomposition to liberate HF and form complex oxo- and hydroxophosphates. Additionally, if ionic liquids are hydrophilic, every time a water wash is carried out, a considerable amount of ionic liquid is lost in the aqueous layer.

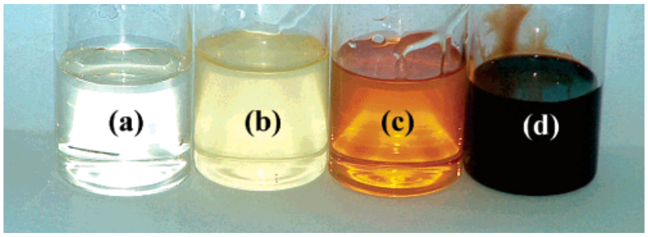

Figure 1. Typical examples of ionic liquids: (a) 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide (bistriflamide) ($[C_4mim][NTf_2]$); (b) 1-octyl-3-methylimidazolium chloride ($[C_8mim]Cl$); (c) 1-hexyl-3-methylimidazolium chloride ($[C_6mim]Cl$); (d) 1-propyl-2,3,5-trimethylpyrazolium methanesulfonate ($[C_3tmpyr][OMs]$).

With regard to the chromophoric impurities in ionic liquids, there have been attempts to decolorize (or remove the chromophores) for the last two decades. It is still not known which chromophores they contain, except that they must be present at the ppb level. However, some sources say that the chromophores are the products of side reactions occurring at high temperatures (higher than 75 °C de bene esse) in the alkylation reactions when ionic liquid halides are made.[6]

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[*] To whom correspondence should be addressed. E-mail: k.seddon@qub.ac.uk.

[†] The Queen's University of Belfast.

[‡] University of Strathclyde.

[§] Current address: Pfizer Global Research and Development, Ramsgate Rd., Sandwich, Kent CT 13 9NJ, UK; e-mail: charles.gordon@pfizer.com.

[||] Imperial College London.

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10.1021/ac061481t CCC: $37.00

According to Gordon and co-workers,[7] the possibilities to get "spectroscopic grade" ionic liquids can be represented in four ways, notably (i) purification of starting materials, (ii) control of conditions for quaternisation reactions, (iii) anion exchange, and (iv) cleaning of the ionic liquid. Some of these procedures have been taken from the paper by Welton et al.[8]

The first two methods focus on the purification of the starting materials and control of the quaternization process temperature. The last two methods deal with creating the right conditions for the synthesis of the final product and its cleaning. Most approaches in the literature center upon making the ionic liquids pure in the first place.[9] In this paper, the problem of how to remove colored impurities once generated is tackled, so the proposed method deals with the cleaning of an ionic liquid. The halide ionic liquid precursors used in this paper were as follows: 1-butyl-3-ethylimidazolium chloride ($[C_4mim]Cl$), 1-butyl-2,3-dimethylimidazolium chloride ($[C_4dmim]Cl$), 1-decyl-3-methylimidazolium bromide ($[C_{10}mim]Br$), 1-butylpyridinium chloride ($[C_4py]Cl$), 1-decyl-3-methylimidazolium chloride ($[C_{10}mim]Cl$). The final ionic liquids include the following: 1-butyl-3-methylimidazolium bistriflamide ($[C_4mim][NTf_2]$), 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$), 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$), 1-butylpyridinium bistriflamide ($[C_4py][NTf_2]$), 1-butyl-2,3-dimethylimidazolium bistriflamide ($[C_4dmim][NTf_2]$), 1-decyl-3-methylimidazolium triflate ($[C_{10}mim][OTf]$), 1-butyl-3-methylimidazolium triflate ($[C_4mim][OTf]$), and trihexyl(tetradecyl)phosphonium diisobutylphosphate ($[P_{6\,6\,6\,14}][{}^{i}Bu_2PO_2]$).

EXPERIMENTAL SECTION

The ionic liquids used in this paper were prepared at QUILL, except for trihexyl(tetradecyl)phosphonium diisobutylphosphate, which was donated by Cytec.

$Li[NTf_2]$ was purchased from 3M. 1-Methylimidazole, chloroalkanes, bromooctane, pyridine, $Na[BF_4]$, $Na[PF_6]$, $Na[OTf]$, dichloromethane, ethyl ethanoate, and 1,2-dimethylimidazole were purchased from Aldrich. 1-Methylimidazole, 1,2-dimethylimidazole, and pyridine were distilled before the quaternization step. For the decolorization of ionic liquids, decolorizing charcoal was purchased from Acros Organics, silica gel for flash chromatography from Fluorochem, and Celite from Aldrich. Deuteriated solvents were obtained from Aldrich.

Because many of the ionic liquids are either hygroscopic or deliquescent, the reactions to produce them or use them have to be carried out under a dry dinitrogen atmosphere. Every ionic liquid made in this paper was stored in a sealed, dark glass bottle having been dried in vacuo (5−10 mbar) at 70 °C for 24 h prior to use.

Differential scanning calorimetry (DSC) traces were recorded with two different systems from Perkin-Elmer. For measurements below room temperature down to −100 °C, a Pyris 1 instrument with dinitrogen cooling was used. For temperature ranges from room temperature to 300 °C, a DSC 7 was employed. The heating and cooling rates for both were 10 °C min^{-1}. The melting point and glass transitions were defined as peak maxima. Calibration of the DSC machines was carried out with iridium samples. Ultraviolet−visible (UV−vis) spectra were recorded on a Perkin-Elmer Lambda 800 instrument. The samples were contained in 1-mm quartz cuvettes. Distilled dichloromethane was used as a reference, and ionic liquid was used as a sample. The water content of ionic liquids was measured with an Aquapal III Karl Fischer titrator. The compartment solutions were obtained from Riedel deHaën (Hydranal-Coulomat AG and Hydranal-Coulomat CG). All NMR spectra were recorded at room temperature on a Bruker Avance spectrometer DPX 300.

When sodium sulfate was used to eliminate water from ionic liquids, both metal and sulfur analyses were performed (after insoluble sodium sulfate was separated from the ionic liquid by filtration): no traces of either sodium or sulfur were detected.

All ionic liquids studied in this work were routinely monitored by NMR spectroscopy, mass spectrometry, and ion chromatography: there was no example where these methods could distinguish between a colored and a decolorized ionic liquid. Moreover, Karl Fischer analyses were performed before and after the decolorization, and in no case did the water content increase after treatment.

Quaternization. *1-Butyl-3-methylimidazolium Chloride.* 1-Methylimidazole (123 g, 1.50 mol) and 1-chlorobutane (157 g, 1.70 mol) were placed in a 2-L round-bottomed flask. A slight excess of the haloalkane was used to guarantee the consumption of 1-methylimidazole. Ethanenitrile (100 cm^3) was added to reduce the viscosity of the mixture, which was left to stir under reflux at 70 °C for 96 h. The halide salt separated as a second phase from the ethanenitrile. The excess of ethanenitrile was removed by decantation.

The halide salt was then recrystallized from ethyl ethanoate. The volume of ethyl ethanoate used for the recrystallization was approximately half that of the halide salt. The ethyl ethanoate was decanted, followed by the addition of fresh ethyl ethanoate, and this step was repeated twice. After the third cycle, the remaining ethyl ethanoate (bp 77 °C) and 1-chlorobutane (bp 77 °C) were removed under reduced pressure at 70 °C and the chloride salt was finally dried in vacuo at 70 °C. The product was obtained as a very pale yellow solid (251 g, 1.44 mol, 96.0% yield; mp (DSC), 69 °C; lit. mp (DSC), 69 °C).[10]

1-Decyl-3-methylimidazolium Chloride. 1-Methylimidazole (123 g, 1.50 mol) and 1-chlorodecane (300 g, 1.70 mol) were placed in a 2-L round-bottomed flask. A slight excess of the haloalkane was used to guarantee the consumption of 1-methylimidazole. Ethanenitrile (100 cm^3) was added to reduce the viscosity of the mixture, which was left to stir under reflux at 70 °C for 168 h. The halide salt separated as a second phase from the ethanenitrile. The excess of ethanenitrile was removed by decantation. The excess of 1-chlorodecane was removed during recrystallization.

The halide salt was then recrystallized from ethyl ethanoate. The volume of ethyl ethanoate used for the recrystallization was approximately half that of the ionic liquid phase. The ethyl ethanoate was decanted, followed by the addition of fresh ethyl ethanoate, and this step was repeated twice. After the third cycle, the remaining ethyl ethanoate (bp 77 °C) was removed under reduced pressure at 70 °C and the chloride salt was finally dried

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in vacuo at 70 °C. The product was obtained as a yellow solid (375 g, 1.45 mol, 97% yield).

1-Butyl-2,3-dimethylimidazolium Chloride. 1,2-Dimethylimidazole (13.0 g, 135 mmol) and 1-chlorobutane (13.165 g, 142.17 mmol) were placed in a 2-L round-bottomed flask. A slight excess of the haloalkane was used to guarantee the consumption of 1,2-dimethylimidazole. Ethanenitrile (100 cm^3) was added to reduce the viscosity of the mixture, which was left to stir under reflux at 70 °C for 288 h. The halide salt separated as a second phase from the ethanenitrile. The excess of ethanenitrile was removed by decantation.

The halide salt was then recrystallized from ethyl ethanoate. The volume of ethyl ethanoate used for the recrystallization was approximately half that of the ionic liquid phase. The ethyl ethanoate was decanted, followed by the addition of fresh ethyl ethanoate, and this step was repeated twice. After the third cycle, the remaining ethyl ethanoate (bp 77 °C) and chlorobutane (bp 77 °C) were removed under reduced pressure at 70 °C and the chloride salt was finally dried in vacuo at 70 °C. The product was obtained as a yellow solid (21.6 g, 125 mmol, 92% yield).

1-Butylpyridinium Chloride. Pyridine (126 g, 1.50 mol) and 1-chlorobutane (157 g, 1.70 mol) were placed in a 2-L round-bottomed flask. A slight excess of the haloalkane was used to guarantee the consumption of pyridine. Ethanenitrile (100 cm^3) was added to reduce the viscosity, and the mixture was left to stir under reflux at 70 °C for 288 h. The halide salt separated as a second phase from the ethanenitrile. The excess of ethanenitrile was removed by decantation.

The halide salt was then recrystallized from ethyl ethanoate. The volume of ethyl ethanoate used for the recrystallization was approximately half that of the ionic liquid phase. The ethyl ethanoate was decanted, followed by the addition of fresh ethyl ethanoate, and this step was repeated twice. After the third cycle, the remaining ethyl ethanoate (bp 77 °C) and chlorobutane (bp 77 °C) were removed under reduced pressure at 70 °C and the chloride salt was finally dried in vacuo at 70 °C. The product was obtained as a yellow solid (224 g, 1.31 mol, 87% yield).

1-Octyl-3-methylimidazolium Bromide.[11] 1-Methylimidazole (275 g, 3.30 mol) was poured into a 2-L three-necked round-bottomed flask and placed in an oil bath at 70 °C. Distilled bromooctane (714 g, 3.70 mol) was added dropwise at a rate to maintain the reaction temperature below 90 °C. The mixture was left to stir for 24 h under reflux at 70 °C. The reaction flask was covered with foil to avoid photolytic side reactions. Ethanenitrile (50 cm^3) was then added to reduce the viscosity, and the halide salt was then recrystallized by addition of ethyl ethanoate. The volume of ethyl ethanoate used for the recrystallization was approximately half that of the ionic liquid phase. The ethyl ethanoate was decanted, followed by the addition of fresh ethyl ethanoate, and this step was repeated twice. After the third decanting, the remaining ethyl ethanoate (bp 77 °C) was removed under reduced pressure at 70 °C and the bromide salt was finally dried in vacuo at 73 °C. The product was obtained as a yellow liquid (817 g, 2.97 mol, 90% yield).

Metathesis. *1-Butyl-2,3-dimethylimidazolium Bistriflamide.* [C$_4$dmim]Cl (66.12 g, 350.4 mmol) and Li[NTf$_2$] (108.3 g, 377.2 mmol) were dissolved in a mixture of dichloromethane (200 cm^3) and water (20 cm^3) and stirred for 6 h. The lower dichloromethane layer containing the ionic liquid was washed with water (6 × 20 cm^3) and then dried with anhydrous sodium sulfate (20 g), which was removed by filtration. The filtrate was heated in vacuo at 40 °C to remove the excess solvent. The product was obtained as a pale yellow liquid (147 g, 340 mmol, 97% yield).

1-Butylpyridinium Bistriflamide. [C$_4$py]Cl (60.15 g, 350.4 mmol) and Li[NTf$_2$] (108.3 g, 377.2 mmol) were dissolved in a mixture of dichloromethane (200 cm^3) and water (20 cm^3) and stirred for 6 h. The lower dichloromethane layer containing the ionic liquid was washed with water (6 × 20 cm^3) and then dried with anhydrous sodium sulfate (20 g), which was removed by filtration. The filtrate was heated in vacuo at 40 °C to remove the excess solvent. The product was obtained as a yellow liquid (136 g, 326 mmol, 93% yield).

1-Butyl-3-methylimidazolium Tetrafluoroborate.[12] [C$_4$mim]Cl (125 g, 716 mmol) was dissolved in 200 cm^3 of water, an aqueous solution (100 cm^3) containing Na[BF$_4$] (82.56 g, 751.8 mmol) was added, and the resulting mixture was left to stir overnight. The resulting homogeneous mixture ([C$_4$mim][BF$_4$] is hydrophilic at ambient temperature), was extracted 5 times with dichloromethane (400 cm^3 each time), and then dried with anhydrous sodium sulfate (30 g), which was removed by filtration. The dichloromethane (bp 40 °C) was then removed by heating at 40 °C under reduced pressure and finally by heating at 60 °C in vacuo for 24 h. The product was obtained as a yellow liquid (150 g, 665 mmol, 93% yield).

1-Butyl-3-methylimidazolium Hexafluorophosphate. Since the hydrolysis of hexafluorophosphate is known to be acid catalyzed,[13] the synthesis of [C$_4$mim][PF$_6$] was performed by metathesis from Na[PF$_6$] rather than the acid.

Hexafluorophosphoric acid (250 g, 60 wt % aqueous solution, 1.03 mol) was slowly added to water (250 cm^3) in an ice−water bath. This solution was then added dropwise from a polyethylene dropping funnel to an equimolar aqueous solution of NaOH (41 g dissolved in 160 cm^3 of water), placed in an ice−water bath, to generate aqueous Na[PF$_6$]. All steps described above are exothermic, and they should be performed with care. Periodically the pH of the solution was checked with universal pH paper to ensure that the pH of the final solution was ~7.

[C$_4$mim]Cl (179 g, 948 mmol) was added to the Na[PF$_6$] (167 g, 996 mmol) solution in water, and the resulting mixture was left to stir overnight. The upper, aqueous phase was removed by decantation and the product, which appeared as a yellow oily liquid at the bottom of the round-bottom flask, was dissolved in dichloromethane (50 cm^3) and extracted 7 times with water cooled to 4 °C (7 × 30 cm^3). The dichloromethane was then removed by heating at 40 °C under reduced pressure and finally by heating at 60 °C in vacuo. The product was obtained as a yellow liquid (251 g, 882 mmol, 93% yield).

1-Decyl-3-methylimidazolium Triflate. [C$_{10}$mim]Cl (90.69 g, 350.4 mmol) and Na[OTf] (64.90 g, 377.2 mmol) were dissolved in water (200 cm^3) and stirred for 6 h. Then the aqueous solution was extracted with dichloromethane (6 × 100 cm^3). The dichloromethane layer was dried with sodium sulfate (20 g), filtered, and the solvent evaporated under reduced pressure and finally by heating at 60 °C in vacuo. The product was obtained as a yellow

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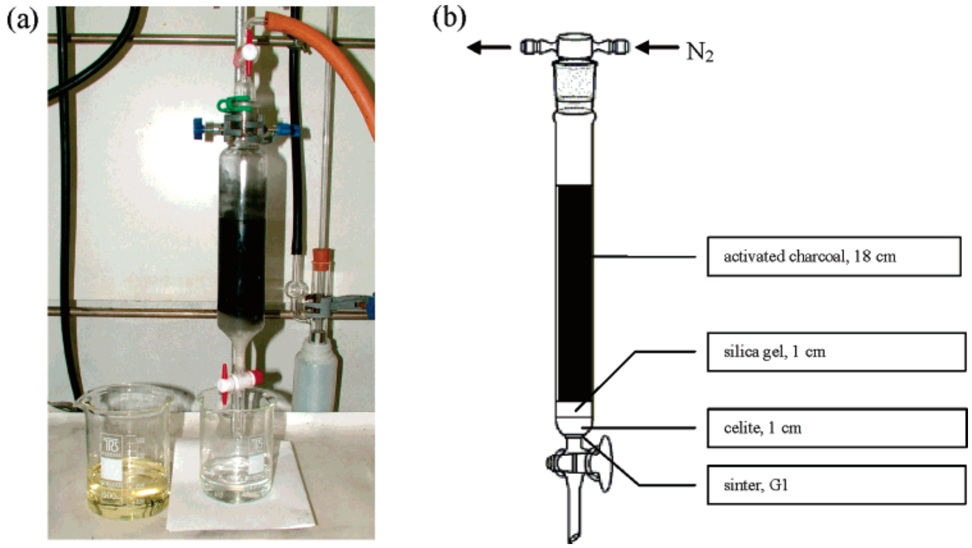


Figure 2. Experimental apparatus for decolorizing of ionic liquids.

liquid (121 g, 326 mmol, 93% yield).

1-Butyl-3-methylimidazolium Triflate. [C_4mim]Cl (61.20 g, 350.4 mmol) and Na[OTf] (64.90 g, 377.2 mmol) were dissolved in water (200 cm^3) and stirred for 6 h. Then the aqueous solution was extracted with dichloromethane (6 × 100 cm^3). The dichloromethane layer was dried with sodium sulfate (20 g), filtered, and the solvent evaporated under reduced pressure and finally by heating at 60 °C in vacuo. The product was obtained as a yellow liquid (90.91 g, 315.4 mmol, 90% yield).

1-Butyl-3-methylimidazolium Bistriflamide.[2] [C_4mim]Cl (61.20 g, 350.4 mmol) and Li[NTf_2] (108.3 g, 377.2 mmol) were dissolved in a mixture of dichloromethane (200 cm^3) and water (20 cm^3), and the resultant mixture was stirred for 6 h. The lower dichloromethane layer containing the ionic liquid was washed with water (6 × 20 cm^3) and then dried with anhydrous sodium sulfate (20 g), which was then removed by filtration. The filtrate was heated in vacuo at 40 °C to remove the excess solvent. The product was obtained as a pale yellow liquid (139 g, 331 mmol, 95% yield).

Decolorization of Halide Precursors and Ionic Liquids. A special column was designed for the decolorization. The column was packed with the following compounds: Celite on the bottom to trap charcoal particles, flash chromatographic silica gel in the middle for decolorizing/removal of polar and inorganic impurities, and charcoal on the top for decolorizing (Figure 2). The dimensions of the column are illustrated in the Figure 2b.

The column was similar to the one used in conventional chromatography. The size of the column was 50 cm long, 42-mm outer diameter, and 36-mm inner diameter.

An ionic liquid (200 cm^3) was mixed with dichloromethane (600 cm^3) (v/v 1:3). In the case of halide salts that were more viscous, the volume ratio between a halide salt and dichloromethane was 1:6; the dichloromethane was added in order to decrease the viscosity of the ionic liquid. If an ionic liquid was only slowly miscible with dichloromethane, it could be heated to less than the boiling point of dichloromethane (40 °C), to speed up the dissolution.

The column was pretreated with dichloromethane (200 cm^3) prior to its use with ionic liquids. Then the dichloromethane solution of the ionic liquid was passed through the column, and finally, dichloromethane (200 cm^3) was passed in order to elute the remainder of the ionic liquid. In order to purge ionic liquid through the column, dinitrogen was passed over the column.

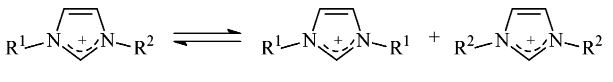
Once eluted, the eluate was dried under reduced pressure and finally by heating at 60 °C in vacuo.

RESULTS

Synthesis and Characterization. Generally the synthesis of most ionic liquids consists of a quaternization step followed by a metathesis step—anion exchange.[14] All the procedures used were standard literature ones with slight modifications.

The ionic liquids were analytically pure. ^{1}H NMR spectra were recorded for all compounds.[15,16] There were no detectable signs of organic impurities, which was true whether or not the compounds were colored. The water content, as measured by Karl Fischer titration for all ionic liquids, was below 20 ppm.[17]

Quaternization Step. A slight molar excess (1.05−1.1 equiv) of alkylating agent, usually a 1-haloalkane, must be used. The removal of unreacted 1-methylimidazole from 1-alkyl-3-methylimidazolium chloride, and 1,2-dimethylimidazole from an 1-butyl-2,3-dimethylimidazolium chloride, is extremely difficult due to their high boiling points correspondingly (198 and 202 °C). The reaction is usually carried out in ethanenitrile. The solvent helps to reduce the viscosity of the reaction mixture. It was found that it is best to perform the quaternization step at ~80−90 °C (conventional heating) for several days, rather than at higher temperatures for a shorter period, to avoid charring and alkyl chain scrambling (eq 1).[9,18]



Equation 1 shows the scrambling of the 1-R^1-3-R^2-imidazolium cation.

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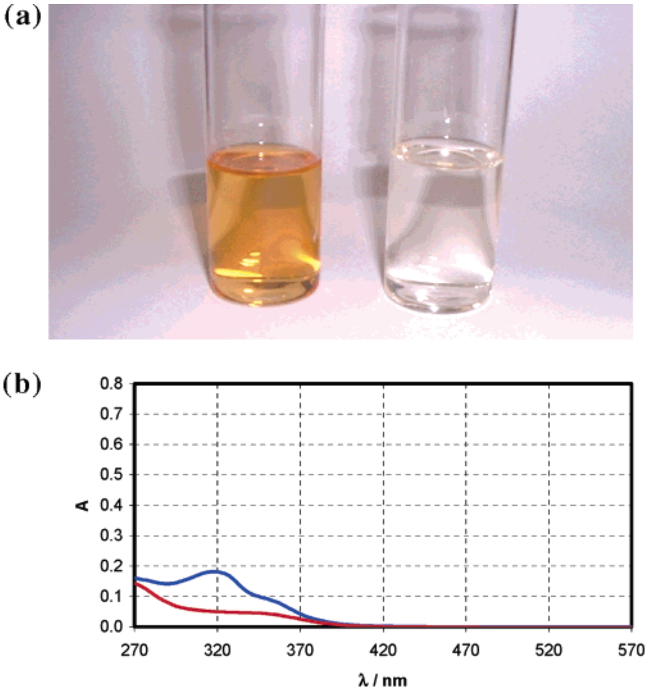

Figure 3. (a) [C_4py][NTf_2] before (left) and after (right) passing through the column. (b) Electronic absorption spectra of [C_4py][NTf_2] before (blue) and after (red) passing through the column.

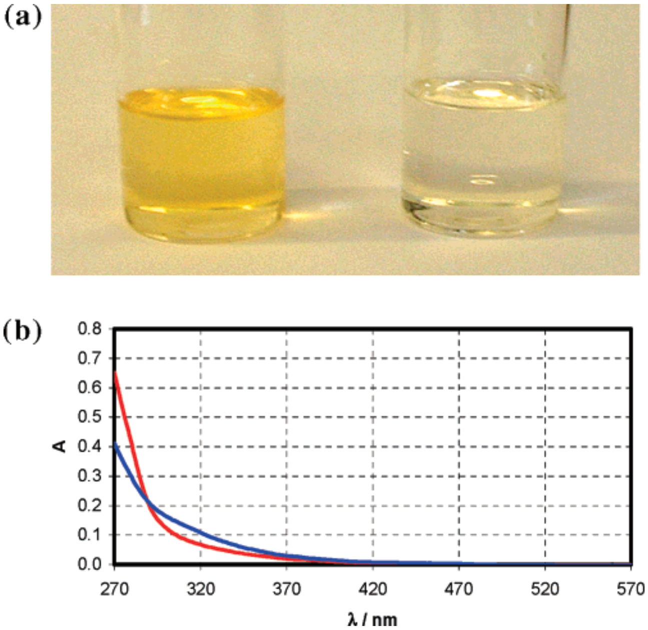

Figure 4. (a) [C_4dmim][NTf_2] before (left) and after (right) passing through the column. (b) Electronic absorption spectra of [C_4dmim][NTf_2] before (blue) and after (red) passing through the column.

The removal of the haloalkanes and reaction solvents is generally not a problem, especially for the relatively volatile shorter chain haloalkanes. In the case of longer chain haloalkanes, their boiling points are higher than shorter ones, and they are removed in the washing (recrystallization) cycles.

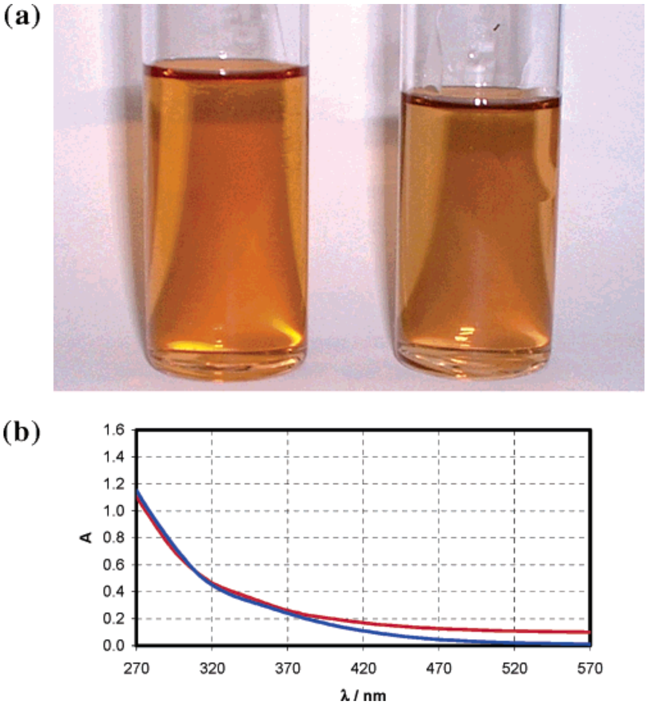

Figure 5. (a) Trihexyl(tetradecyl)phosphonium diisobutylphosphate before (left) and after (right) passing through the column. (b) Electronic absorption spectra of trihexyl(tetradecyl)phosphonium diisobutylphosphate before (blue) and after (red) passing through the column.

Metathesis Step. Most of the ionic liquids studied were water immiscible; they are mainly [NTf_2]$^-$, [PF_6]$^-$, and [BF_4]$^-$ salts, which simplifies the metathesis step because the removal of halide ion can be carried out by washing with water.

The halide salt [Q]X and the respective metal salts MY (M = Li^+, Na^+, K^+, or [NH_4]$^+$; Y = [NTf_2]$^-$, [PF_6]$^-$, [BF_4]$^-$, or [OTf]$^-$) dissolved in dichloromethane (~300 cm^3/mol of ionic liquid) were repeatedly extracted with small amounts of water (20−50 cm^3). After removing the organic solvent, the ionic liquid was dried ready for use. Drying is usually carried out under high vacuum at elevated temperatures. However, when working with tetrafluoroborates or hexafluorophosphates, temperatures of 50−60 °C should not be exceeded (to avoid excessive hydrolytic decomposition).

Decolorization Step. Although the colored impurities might be aesthetically displeasing, there is no evidence that the chromophoric impurities affect either the chemistry or the physical properties of ionic liquids. However, they have a major effect upon measurements involving light absorption or emission; thus, they interfere with studies involving electronic absorption, luminescence, or Raman spectroscopy.

A number of methods in the literature for specific ionic liquids have been reported. We are attempting to create a methodology for generic ionic liquid decolorization. Thus, after many trial-and-error experiments, the column reported here, which combines learning from previous attempts of decolorization,[7−9] seems the most effective.

Decolorization by the column was attempted for both halide salts and ionic liquids. Pictures of several ionic liquids before and after decolorization by the column were taken (Figures 3a−5a and Figures Ia−IVa, Supporting Information), and their electronic

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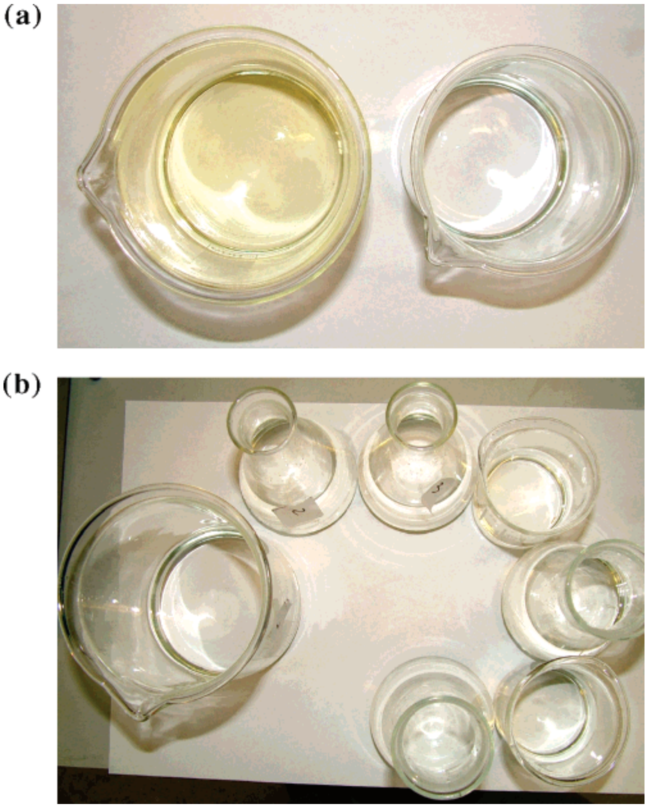

Figure 6. (a) [C_4mim][NTf_2] before (left) and after (right) decolorization. (b) Several fractions of [C_4mim][NTf_2] collected.

absorption spectra were recorded (Figures 3b−5b and Figures Ib−IVb, Supporting Information). The spectra of purified ionic liquids are generally featureless in the region of absorption 270−600 nm but show an increase to shorter wavelengths, as the tail of the cation charge-transfer band is approached.

During the first attempt to decolorize the [C_4mim][NTf_2] ionic liquid (200 cm^3 of the ionic liquid in 600 cm^3 of dichloromethane), several fractions of ~100 cm^3 were collected and UV−vis spectra recorded on each of them. There was no significant difference between spectra, so the decolorization process did not lose its efficiency (Figure 6).

Relationship between the Chromophore and Fluorescence. Since the early days of ionic liquids, it has been observed that there is often a background fluorescence stimulated by UV irradiation, which can cause problems when attempting to measure Raman spectra.[19] One means of removing these has been brief exposure to lithium "peas", which become rapidly coated with a black deposit, with concomitant elimination of the fluorescent impurities. We report here that these fluorescent impurities are disconnected with the colored impurities, as the fluorescence of the samples studied here is reduced but not eliminated by the decolorization procedure.

CONCLUSION

The results presented here demonstrate that, for most ionic liquids, it was possible to remove the chromophoric impurities.

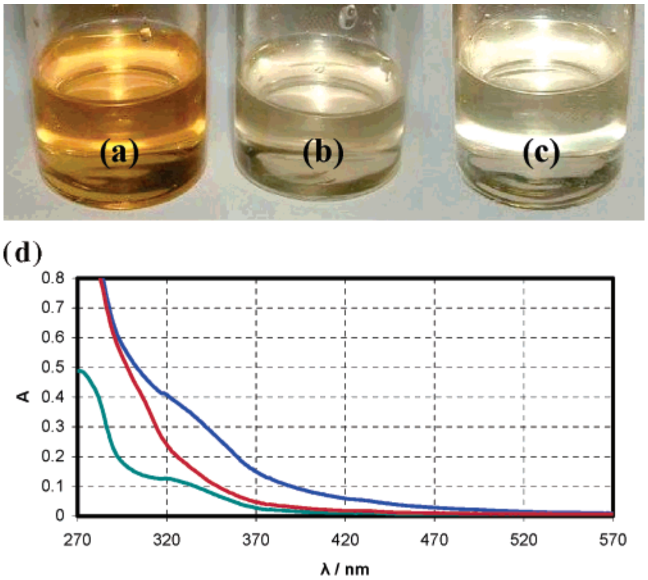

Figure 7. (a) [C_4mim][OTf] before decolorization; (b) after the first decolorization using the column described above; (c) after the second attempt of decolorization using the second column. (d) [C_4mim][OTf] before decolorization (blue); after the first attempt of decolorization (red); after the second attempt of decolorization (green).

In particular, excellent results were obtained for ionic liquids containing [NTf_2]$^-$, [BF_4]$^-$, and [PF_6]$^-$ anions, irrespective of the cation.

Decolorization for trihexyl(tetradecyl)phosphonium diisobutylphosphate is not effective, due to the fact this ionic liquid appears to interact with the charcoal and dissolves some colored material. Another possibility is that the diisobutylphosphate anion forms colored complex ions with traces of metals.

Some ionic liquids are not decolorized effectively by this method. These tend to be ionic liquids with anions that undergo strong hydrogen-bonding interactions, for example, halides or phosphinates. In addition, ionic liquids based upon the triflate anion are not so efficiently decolorized with this system (see Figure III, Supporting Information).

Our results suggest that the best strategy is to decolorize the final ionic liquid rather than the halide salt. Using this methodology, it is possible to decolorize ~200 cm^3 of an ionic liquid in 4−5 h. While we have optimized the column for use with ionic liquids including the [NTf_2]$^-$, [BF_4]$^-$, and [PF_6]$^-$ anions, different configurations of the column might be better for other anions.

A second equivalent column could be used if further decolorization is required. [C_4mim][OTf] was chosen as an example, as it could not be decolorized completely during the first attempt. It can be seen in Figure 7 that the second attempt of decolorization using the second parallel column improves the results of decolorization compared to the first attempt.

We recommend this methodology for ionic liquids where extremely low levels of chromophores are needed. We have optimized the methodology for the specific ionic liquids described here, but we believe the approach is versatile enough to be adapted for other ionic liquids, providing they do not contain strongly hydrogen-bonding anion, or cations that interact significantly with carbon.

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ACKNOWLEDGMENT

The authors gratefully acknowledge QUILL and its Industrial Advisory Board, as well as the EPSRC (Portfolio Partnership Scheme, grant EP/D029538/1) for funding. We are also extremely grateful to Dr. Al Robertson (Cytec) for supplying the phosphonium ionic liquids used.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

Received for review August 9, 2006. Accepted November 4, 2006.

AC061481T