

Quantification of Halide in Ionic Liquids using Ion Chromatography

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ABSTRACT

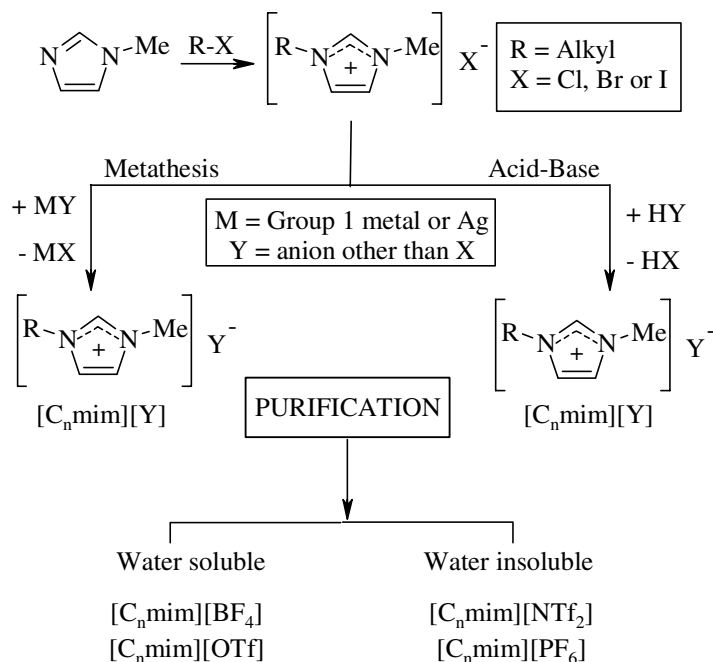
The determination of chloride impurities in ionic liquids using ion chromatography is described. A wide range of cation-anion combinations may be analysed using ion chromatography, including water immiscible ionic liquids. For all ionic liquids studied, the limit of quantification for chloride was found to be below 8 ppm.

INTRODUCTION

Ionic liquids (ILs) have been studied extensively as solvents for a wide range of chemical processes. The interest is a direct result of the diverse physical properties of these liquids and the way in which they may be systematically varied, *e.g.* the density, viscosity and water miscibility. Since they also have effectively zero vapor pressure, this makes them ideal engineering solvents for reactive chemistry allowing direct distillation of solutes from the solvent and simple solvent recycle without the production of VOC's.¹ However, due to their low vapor pressure these solvents cannot be purified by

simple distillation unlike conventional molecular liquids. Moreover, their synthesis inherently results in low levels of impurities, which influence both their physico-chemical properties as well as their performance as solvents, particularly for catalytic reactions.

Ionic liquids are generally prepared by one of two routes. For halide free ionic liquids, direct alkylation of a phosphine, amine, pyridine or azole can be performed using, for example, dialkylsulphates or alkyltriflates forming the corresponding alkylsulphate or triflate ionic liquid.² However, the range of ionic liquids which can be made *via* these routes are limited. Most ionic liquids are synthesized using a two-step process, whereby an organic halide salt is formed *via* alkylation using a haloalkane. The quaternisation reaction is followed then by a metathesis reaction using an alkali metal salt, *e.g.* NaBF₄ to produce the tetrafluoroborate ionic liquid, or by anion exchange using acid addition, *e.g.* trifluoromethanesulphonic acid, forming the corresponding triflate ionic liquid. This procedure is shown schematically in Scheme 1 for imidazolium-based ionic liquids. Although the alkylation step can result in organic impurities, usually unreacted starting materials, it is the metathesis step which is most problematic. Metathesis produces a molar amount of halide waste some of which gets trapped in the ionic liquid product. Although quantitative ion exchange can occur in theory, the extent of extraction of the halide from the ionic liquid using water is strongly dependent on the ionic liquid being used, *e.g.* its miscibility with water, as well as the number of extractions used. In essence it is virtually impossible to get a truly halide free ionic liquid *via* this route.



Scheme 1. General preparation of imidazolium-based ionic liquids.

Ionic liquids containing halide contaminants are problematic since the halide content can seriously affect the usefulness of the IL as a solvent for a given chemical reaction. Seddon *et. al* showed that some physico-chemical properties are highly dependent on the presence of halide impurities.⁴ In general, the presence of chloride ions increases the viscosity and decreases the density of ionic liquids. Halide impurities can also affect the potential limits and the corresponding electrochemical window of an ionic liquid; chloride, bromide and iodide are more easily oxidized than perfluorinated anions used in many common air and water stable ionic liquids, and may thus significantly decrease the anodic potential limit observed.⁵ Halides can also have a detrimental effect on transition-metal catalyzed reactions^{6,7} and poison heterogeneous catalysts suspended in ionic liquids.⁸

To date, research using ionic liquids has focused mainly on reactions and physical characterization; however, in most of these studies, only limited information concerning the purity of the ionic liquid has been reported and this has concentrated on water content. Despite the negative impact of halide content of ionic liquids being generally known, few analytical methods have been reported for its quantification in ionic liquids. These include Volhard and chloride-selective electrodes,⁴

spectrophotometric method with fluorescent indicators,⁹ ion chromatography (IC)^{10,11} and electrochemistry.¹² Seddon *et al.*⁴ measured the chloride contents of ionic liquids containing the [C₄mim]⁺ cation using a chloride-selective electrode. It was found that the intercept and the slope of the calibration curve for chloride were strongly dependent on the type of cation. They attributed this effect to the different polarities of the various ionic liquids studied and also on the cation-dependent degree of hydrogen bonding. Chloride-selective electrodes are also relatively expensive, need special maintenance and their performance decays with use. Furthermore, the chloride-selective electrode method is usually validated against the Volhard method. Although the Volhard procedure can detect all halides, the method is only applicable to water miscible ionic liquids and it requires the use of toxic reagents (potassium thiocyanate and AgNO₃), thereby producing hazardous waste. Anthony *et al.*⁹ investigated the effect of chloride contamination on the water vapor solubility in different ionic liquids. Using quinoline derivatives as fluorescent indicators, the chloride content was reported with an associated uncertainty of *ca.* 10 % for values of chloride of approximately 1000 ppm. Xiao and Johnson¹² determined the chloride content of [C₄mim][BF₄] ionic liquid by cyclic voltammetry and square wave voltammetry using the method of standard additions, reporting a detection limit of 2.8 mM (99 ppm) of chloride.

Although ion chromatography is used routinely for determination of chloride in aqueous media,¹³ there have only been two reports using ion chromatography to quantify chloride in ionic liquids.^{10,11} However, to the best of our knowledge, a validation of its use in ionic liquid analysis has not yet been reported. The current investigation reports a methodology for the determination of chloride in both water miscible and water immiscible ionic liquids. The parameters investigated include sample preparation, solvent effect, and sample stability. Results presented include sample quantification, peak-area repeatability, limit of detection (LOD), and limit of quantification (LOQ).

EXPERIMENTAL

All chromatographic analysis were performed at room temperature using a Metrohm Model 761 Compact IC (Metrohm, Herisau, Switzerland) with suppressor module, equipped with an ICsep AN2TM analytical column (250 x 4.6 mm) and an ICsep AN2TM guard column (50 x 4.6 mm). The substrate of the AN columns is a highly cross-linked, modified styrene divinylbenzene resin, derivatized with alkyl-ethanol ammonium functionalities. The anions were detected using a suppressed conductivity detector, with a full scale of 250 $\mu\text{S cm}^{-1}$, optimized with respect to the maximum signal-to-noise ratio for the anions being analyzed. The injection volume was 20 μL . Data were collected using a Metrohm 761 data acquisition system interfaced to a computer running IC 1.1 SR2 software (Metrohm)

Millipore (Bedford, MA, USA) Milli-Q 18 M Ω water was used for all eluent, sample and standard preparation. HPLC grade methanol and acetonitrile were used as solvents to dilute the ionic liquids. Analytical grade sodium carbonate (Aldrich) and sodium hydrogen carbonate (J.T. Baker) were used to prepare the eluent.

1-Butyl-3-methylimidazolium chloride ([C₄mim]Cl) , *N*-butylpyridinium chloride ([C₄py]Cl) , 1-butyl-2,3-dimethylimidazolium chloride ([C₄dmim]Cl), 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([C₄mim][OTf]), 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]), 1-ethyl-3-methylimidazolium ethylsulfate ([C₂mim][EtSO₄]) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C₂mim][NTf₂]) were prepared following standard preparative procedures, the details may be found elsewhere.^{2,314,15} 2-Hydroxyethyl-trimethylammonium chloride (choline chloride) 99 % was obtained from Lancaster and used as received. The eluent used was a 3.2 mM Na₂CO₃ + 1.0 mM NaHCO₃ mixture and the suppressor regenerating solution was 0.1 M H₂SO₄. The eluent was prepared daily, degassed by bubbling nitrogen and filtered through a 2 μm filter. The chloride standard (0.0994 N) and fluoride standard (200 ppm) were obtained from Aldrich and TelLab, respectively. Working standards and spiked samples were prepared daily by further diluting the previous standards to the range expected for the anion of interest. All calibration standards and

samples were prepared in containers that had been thoroughly cleaned and presoaked in deionized water for at least 24 h.

IC samples were prepared by dissolving 0.11 g of IL in either 10 mL of deionised water or in 2 mL of acetonitrile before being diluted to 10 mL with deionised water.

RESULTS AND DISCUSSION

Cation Effect

To investigate the effect of the cation on chloride content determinations using ion chromatography, four aqueous solutions of choline chloride, [C₄dmim]Cl, [C₄Py]Cl, and [C₄mim]Cl, containing 5.1 ± 0.4 ppm of chloride were measured and compared with an aqueous solution containing 5.1 ppm NaCl. This selection of cations was chosen in order to examine whether IC is versatile over the wide range of cation types which are available. For example, choline chloride is acyclic and saturated with a hydroxyl-funtionalised side chain, [C₄dmim]Cl and [C₄mim]Cl are unsaturated five-membered heteroaromatic rings, with the former deprotonated at the C(2) position and replaced with a methyl group, and [C₄Py]Cl is a six-membered unsaturated ring which is more basic than the imidazolium cations.

The ion chromatograms of these four ionic liquids and NaCl show that the retention times and peak area of chloride are essentially independent of the sample matrices with the relative standard deviations (RSD) of the retention times and peak area determined as 0.3 % and 5.3 %, respectively (Table 1). In general, for an analyte concentration below 10 ppm, a relative standard deviation of ≤ 10 % is an acceptable value for the concentration (peak area),¹⁶ and ≤ 2 % is an acceptable value for the retention time.¹⁷

Table 1. Peak area and retention time of solutions containing 5.1 ppm of chloride (data shown in supplementary data figure S1).

Chloride salt	Peak area (arb. units)	Retention time (min)
NaCl	43.822	5.96
[C ₄ mim]Cl	42.658	5.92
[C ₄ Py]Cl	43.880	5.92
[C ₄ dmim]Cl	39.546	5.93
choline chloride	45.781	5.94
Mean	43.137	5.93

Effect of IC sample diluent type

The solubility of the ionic liquids in water is strongly dependent on both the length of the alkyl chains attached to the cation and the anion used. For example, whilst [C₂mim][BF₄] is totally soluble in water, [C₆mim][BF₄] has very limited solubility in water at room temperature and [C₄mim][BF₄] only has good solubility with water at room temperature; on cooling to close 0 °C the solubility decreases significantly.¹⁵ The equivalent hexafluorophosphate ionic liquids are significantly less soluble in water in comparison. For fluorinated anions there is also a complication that hydrolysis to fluoride may occur and therefore different solvents were tested in order to find an appropriate solvent which can prevent the formation of a high concentration of fluoride ions and solubilize the water miscible and immiscible ionic liquids.

Figure 1 shows the formation of fluoride ions with time determined by ion chromatography using a sample of 9.7 g L⁻¹ of [C₄mim][BF₄] dissolved in four different solvents, *i.e.* water, eluent, 20 vol% acetonitrile in water and 20 vol% methanol in water. Clearly the rate of hydrolysis is strongly dependent on the protic nature of the diluent used. Acetonitrile solubilizes most ionic liquids and also limits the hydrolysis of hydrolytically unstable anions and therefore the acetonitrile-water diluent was used for all subsequent analyses. It should be noted; however, that despite the lower rate of

hydrolysis, for very low concentration of chloride (<0.1 ppm), the fluoride generated does interfere with the detection of chloride. Measuring the same sample every 30 minutes showed that above a threshold level of 0.6 ppm fluoride, a decrease in the measured chloride area was observed. To limit this problem samples were measured immediately after dilution and, in these experiments, the chloride peak area was reproducible if measured within 60 mins of preparation.

Compared with $[\text{BF}_4]^-$ based ionic liquids, ionic liquids containing $[\text{PF}_6]^-$ showed little hydrolysis at room temperature when dissolved in 20 vol% acetonitrile in water. Figure 2 shows ion chromatograms for a sample of 11.2 g L^{-1} of $[\text{C}_4\text{mim}][\text{PF}_6]$ spiked with 0.10 ppm of chloride over 19 hours. It is clear that, over this time period, the fluoride peak does not significantly change. It is interesting to note that, although several papers have reported on the hydrolysis problems of hexafluorophosphate,^{18,19} there has been much less attention on the problems associated with tetrafluoroborate even though it is clear that significant decomposition still occurs and may even be more problematic than for hexafluorophosphate.

Chromatographic system

Since the chloride is an impurity in a medium containing only ions which includes a high concentration of, in general, bulky and polarizable anions with corresponding long retention times, the development of a method for the detection of trace amounts of chloride has to balance the separation efficiency of the analyte of interest with the retention time of elution of the main anion from the ionic liquid. An eluent concentration mixture of $3.2 \text{ mM Na}_2\text{CO}_3 + 1.0 \text{ mM NaHCO}_3$ was found to be the optimum concentration to enable good separation of chloride peak from the other features observed in the traces, *e.g.* interference from the water dip, carbonate dip and fluoride. In order to have good separation efficiency at the retention time corresponding to the chloride peak, the samples were run at 1 mL min^{-1} during the first 10 min, and thereafter the flow rate was raised up to 1.6 mL min^{-1} to speed up the elution of the main anion from the ionic liquid. Representative chromatograms are shown in Figures 3 and 4 for $[\text{C}_4\text{mim}][\text{BF}_4]$, and $[\text{C}_4\text{mim}][\text{OTf}]$, respectively.

The addition of organics to the eluent can be used to change the retention time of anions. However, the addition of 10 vol% of acetone to the eluent did not improve the elution of the main anion significantly and reduced the separation of the fluoride and chloride peaks. The retention time for the different anions depends of the charge, size and polarizability of the anion and were found to follow the order $[\text{BF}_4]^- \sim [\text{EtSO}_4]^- < [\text{OTf}]^- \ll [\text{PF}_6]^- \ll [\text{NTf}_2]^-$. The hexafluorophosphate took 2 hours to begin to elute while no elution of the bis(trifluoromethanesulfonyl)imide was observed after 5 hours. Preliminary data using a gradient elution system and a hydroxide column has shown that this limitation may be overcome; however, this work is still ongoing.²⁰ A range of cation-anion combinations were studied and, in each case, the chromatograms were found to be independent of the cation, in agreement with the chloride samples described above. Further examples of the chromatograms observed are given as supplementary data.

The problems associated with measurement of trace chloride in medium containing high concentrations of other anions is analogous to the measurement of trace anions in seawater. There have been a number of solutions reported including the use of preconcentration columns whereby the trace anion is retained on the column and then eluted, removal of major anion from the sample prior to analysis, *e.g.* using columns based on Ag^+ for removal of chloride, and using column switching.²¹ Similarly in the ionic liquids, for the large anions in particular, *i.e.* $[\text{PF}_6]^-$ and $[\text{NTf}_2]^-$, the strong adsorption on the column packing does allow the major anion to be removed efficiently prior to analysis by a secondary column and this is currently being investigated.

Matrix effect

Due to the complexity of the matrix and the presence of large amount of ions, the possible effect of the matrix on the detection of chloride was investigated using a chloride free ionic liquid, $[\text{C}_2\text{mim}][\text{EtSO}_4]$. This ionic liquid is prepared by direct alkylation of 1-methylimidazole with diethyl sulphate and, as described above, therefore eliminates any halide contamination. Table 2 summarises the results of standard addition recoveries of chloride from samples of 11.3 g L^{-1} of $[\text{C}_2\text{mim}][\text{EtSO}_4]$

ionic liquid with a known added concentration of sodium chloride and samples of water with equivalent concentrations of sodium chloride..

Table 2. Recoveries of chloride in two different matrices.

Chloride added (mg L ⁻¹)	Water sample (mg L ⁻¹)	Recovery (%)	[C ₂ mim][EtSO ₄] sample (mg L ⁻¹)	Recovery (%)
0.030	0.028	93	0.030	100
0.050	0.048	96	0.048	97
0.075	0.073	98	0.068	91
0.100	0.103	103	0.105	105
0.200	0.203	101	0.188	94
0.350	0.347	99	0.345	99

All the recoveries were found to be within the acceptable limit, *i.e.* for analyte concentrations $\leq 0.5 \text{ mg L}^{-1}$, the recovery percentage expected is between 60-115 %.¹⁶

Limit of detection (LOD) and Limit of quantification (LOQ)

The standard definition of the LOD is the analyte concentration giving a signal equal to the blank signal, plus three standard deviations of the blank²² whereas the LOQ is the analyte concentration that produces a signal sufficiently greater than the blank such that it can be detected within specified level of precision, typically a signal 10 standard deviations above the blank signal. For the system used in the present experiments the LOD gave a value 10 ppb for chloride. Both these definitions do not take into account the matrix. However, in practice LOQ values depend on the analyte and the matrix.²³ As described above, due to the preparation method, ionic liquids cannot, in general, be completely halide free. To estimate the LOQ for the method described herein, the method of known additions was used to determine the LOQ for the different ionic liquids. In this case, the limit of quantification of the

method is given by the onset of the deviation from linearity at low concentrations in the area *vs.* concentration of the chloride curve. This is an effect caused by the matrix. To illustrate the method, the area *vs.* concentration of chloride curve corresponding to 11.3 g L⁻¹ of [C₄mim][OTf] ionic liquid compared with the calibration curve at low chloride concentration is shown in Figure 6. The LOQ in this case is the lowest concentration at which the area difference between the calibration and the sample remains constant. The results of standard addition recoveries of chloride in [C₄mim][OTf] are summarized in Table 3.

Table 3. Standard addition of chloride in [C₄mim][OTf] ionic liquid. \bar{X} and RSD refer to the mean and standard deviation found for the difference values.

Entries	Chloride added (mg L ⁻¹)	Chloride Determined (mg L ⁻¹)	Difference in Chloride (mg L ⁻¹) ^a
1	0	0.042	0.042
2	0.030	0.079	0.049
3	0.040	0.114	0.074
4	0.050	0.123	0.073
5	0.075	0.157	0.082
6	0.100	0.183	0.083
7	0.200	0.276	0.076

^a $\bar{X} = 0.078$ mg L⁻¹, RSD = 6.0% calculated for the entries 3-7

Unlike for [C₄mim][OTf], no deviation from linearity was observed above the chloride impurity level found in either [C₄mim][BF₄] or [C₄mim][PF₆] ionic liquids. In these cases, the LOQ was estimated as the lowest chloride concentration measured in the ionic liquid, *i.e.* without any addition of chloride. This is obviously an upper limit to the LOQ. The standard addition curves for each case are given as supplementary data.

The LOQ values obtained for the different ionic liquids are shown in Table 4 and compared with NaCl. These values show the LOQ in the ion chromatography sample, *i.e.* the diluted ionic liquid sample (LOQ[sample]), and the value in the ionic liquid (LOQ[IL]). Clearly the LOQ [IL] is dependant on the dilution factor and lower values may be obtained if larger volumes of ionic liquid are used. However, there is a compromise between the elution time of the main anion of the ionic liquid, and hence sample turnaround, and the detection limit for a particular ionic liquid.

Table 4. LOQ of different ionic liquids compared with aqueous NaCl.

Ionic liquid	LOQ[sample] (mg L ⁻¹)	LOQ[IL] (ppm)
[C ₄ mim][OTf]	0.078	6.9
[C ₄ mim][BF ₄]	0.051	4.5
[C ₄ mim][PF ₆]	0.075	7.1
[C ₂ mim][EtSO ₄]	0.030	2.7
NaCl	0.030	-

Similar detection limits have been found for halide found in aqueous ammonium hydroxide solutions. Wang *et al* reported a detection limit of 1.7 ppm for chloride and 5.7 ppm for bromide in a 29% (w/w) ammonium hydroxide solution with recoveries of 93% and 89%, respectively.²⁴ In this case the ammonium hydroxide was neutralised prior to analysis and directly injected into the IC.

Commonly a “silver nitrate” test has been used to determine whether ionic liquids are halide free.²⁵ This test is performed on the water layer during the extraction of halide from the ionic liquid after the metathesis step. Comparing the silver nitrate test on the washings with IC measurements on both the water and ionic liquid layers shows that a negative result is observed below ~10 ppm chloride within the ionic liquid. It should be noted; however, that this is dependent on the ionic liquid being prepared since for water miscible ionic liquids, such as [C₄mim][BF₄], significant concentrations of the ionic

liquid are washed into the water layer and this changes the ionic strength of the media and, therefore, the point at which precipitation occurs.

Reproducibility and precision.

The reproducibility of the method for each ionic liquid was determined by analysing the results obtained from seven runs of a sample containing the chloride concentration close to the concentration defined as the limit of quantification. Table 5 shows the RSD of the chloride concentration and retention time. For all three ionic liquids the RSD of the chloride concentration was below 10%, while the RSD of the retention time were less than 1%, *i.e.* within the accepted RSD values for retention time and peak area reproducibility.^{16,17} Therefore, the method for the different ionic liquids is considered reproducible

Table 5. Reproducibility of chloride in different ionic liquids.

Ionic liquid	Concentration Cl		Retention time	
	Mean of seven samples (mg L ⁻¹)	RSD	Mean of seven samples (min)	RSD
[C ₄ mim][OTf]	0.104	9.6	5.65	0.2
[C ₄ mim][BF ₄]	0.101 ^a	0.6	5.68 ^a	0.3
[C ₄ mim][PF ₆]	0.085	6.3	5.64	< 0.1

^aDue to [BF₄]⁻ decomposition, three different samples of [C₄mim][BF₄] were run.

Accuracy

In routine measurements, single, rather than duplicate, chloride spikes of different samples are preferred instead of duplicate spikes of the same sample.²⁶ Chloride content in different ionic liquids was determined and compared with the expected value of a spiked sample. Table 6 shows that for all samples investigated the %recoveries obtained range from 90 to 110 %.

Table 6. Recoveries of chloride in different matrices.

Ionic liquid	Chloride in non-spiked IL (ppm)	Chloride in spiked IL (ppm)	Chloride spiked (ppm)	Recovered Chloride (ppm)	Recovery (%)
[C ₄ mim][OTf]	9.4	49.8	45.0	40.4	90
[C ₄ mim][BF ₄]	46.1	87.4	45.0	42.4	94
[C ₄ mim][PF ₆]	15.9	61.3	45.0	45.4	101

CONCLUSIONS

The results of this study show that IC with suppressed conductivity detection is a reliable technique to determine chloride for a range of water miscible and immiscible ionic liquids. In terms of precision and accuracy, ion chromatography is well suited to serve as a quality control method in the production of ionic liquids.

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SUPPORTING INFORMATION

Further exemplar chromatograms and standard addition data used to determine the LOQ values. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

REFERENCES

- ¹ Freemantle, M. *Chem. Eng. News* **1998**, 76, 32 March 30; Holbrey, J. D.; Seddon, K. R. *Clean products and processes* **1999**, 1, 223-236.
- ² Holbrey, J.D.; Reichert, W.; Swatloski, R.P.; Broker, G.A.; Pitner, W.R.; Seddon, K. R.; Rogers, R.D. *Green Chemistry* **2002**, 4, 407-413.
- ³ Bonhôte, P.; Dias, A.P.; Armand, M.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, 35, 1168-1178.
- ⁴ Seddon, K.R.; Stark, A.; Torres, M.J. *Pure Appl. Chem.* **2000**, 72, 2275-2287.
- ⁵ Trulove, P.C.; Mantz, R.A. *Ionic Liquids in Synthesis*, Wasserscheid, P.; Welton T. Eds., Wiley-VCH Verlag, Weinheim, 2003.
- ⁶ Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, 39, 3772-3790.
- ⁷ Owens, G.S.; Mahdi, M.A. In *Ionic Liquids - Industrial Applications to Green Chemistry*; Rogers, R.D.; Seddon, K.R., Eds; ACS Symposium Series 818; American Chemical Society: Washington, DC, pp. 321-333, 2002.
- ⁸ Anderson, K.; Goodrich, P.; Hardacre, C.; Rooney, D.W. *Green Chemistry* **2003**, 5, 448-453.
- ⁹ Anthony, J.L.; Maginn, E.J.; Brennecke, J.F. *J. Phys. Chem. B* **2001**, 105, 10942-10949.
- ¹⁰ Billard, I.; Moutiers, G.; Labet, A.; El Azzi, A.; Gaillard, C.; Mariet, C.; Lutzenkirchen, K. *Inorg. Chem.* **2003**, 42, 1726-1733.
- ¹¹ Anderson, J.L.; Ding, J.; Welton, T.; Amstrong, D.W. *J. Am. Chem. Soc.* **2002**, 124, 14247-14254.
- ¹² Xiao, L.; Johnson K.E. *J. Electrochem. Soc.* **2003**, 150, E307-E311.
- ¹³ European Standards EN ISO 10304-1: 1995; EN ISO 10304-1: 1997; 1999 EN ISO 10304-4:1999.
- ¹⁴ Suarez, P.A.Z.; Einlof, S.; Dullius, J.E.L.; de Souza, R.F.; Dupont, J. *J. Chim. Phys.* **1998**, 95, 1626-1639.
- ¹⁵ Holbrey, J.D.; Seddon, K.R. *J. Chem. Soc. Dalton Trans.* **1999**, 2133-2139.
- ¹⁶ Fajgelj, A.; Ambrus, A. Eds, *Principles and Practices of Method Validation*, The Royal Society of Chemistry, 2000.
- ¹⁷ *Validation of Metrohm Ion Chromatography Systems by using Standard Operation Procedures (SOP)*, Application Bulletin 277/1 e, Metrohm.
- ¹⁸ Visser, A.E; Swatloski, R.P.; Reichert, W.M; Griffin, S.T.; Rogers, R.D. *Ind. Eng. Chem. Res.* **2000**, 39, 3596-3604.

- ¹⁹ Swatloski, R.P.; Holbrey, J.D.; Rogers, R.D. *Green Chemistry* **2003**, 5, 361-363.
- ²⁰ Villagrán, C; Banks, C.E.; Deetlefs, M, Driver, G., Pitner, W.R.; Compton, R.G.; Hardacre, C. *submitted to ACS symposium series Ionic Liquids: Progress and Prospects*.
- ²¹ For example Ito, K. *Anal. Chem.* **1997**, 69, 3628-3632; Stratford, M.R.L.; Dennis, M.F.; Cochrane, R.; Parkins, C.S. *J. Chromatog. A* **1997**, 770, 151-155; Villasenor, S.R. *Anal. Chem.* **1991**, 63, 1362-1366
- ²² *Statistics for Analytical Chemistry*, Miller J.C., and Miller J.N., 3th Edition, Ellis Horwood PTR Prentice Hall, England, 1993.
- ²³ *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, APHA-AWWA-WEF, 1998.
- ²⁴ Wang, K.; Lei, Y.; Eitel, M.; Tan, S. *J. Chromatography A* **2002**, 956, 109–120.
- ²⁵ Hilgers, C.; Wasserscheid, P. *Ionic Liquids in Synthesis*, Wasserscheid, P.; Welton T. Eds., Wiley-VCH Verlag, Weinheim, 2003.
- ²⁶ Parkany, M. Ed, *The Use of Recovery Factors in Trace Analysis*, The Royal Society of Chemistry, 1996.

Figure 1. Time variation of the formation of fluoride ions during $[\text{C}_4\text{mim}][\text{BF}_4]$ hydrolysis in water (■), 20 vol% methanol in water (●), 3.2 mM Na_2CO_3 + 1.0 mM NaHCO_3 eluent (▲) and 20 vol% acetonitrile in water (◆).

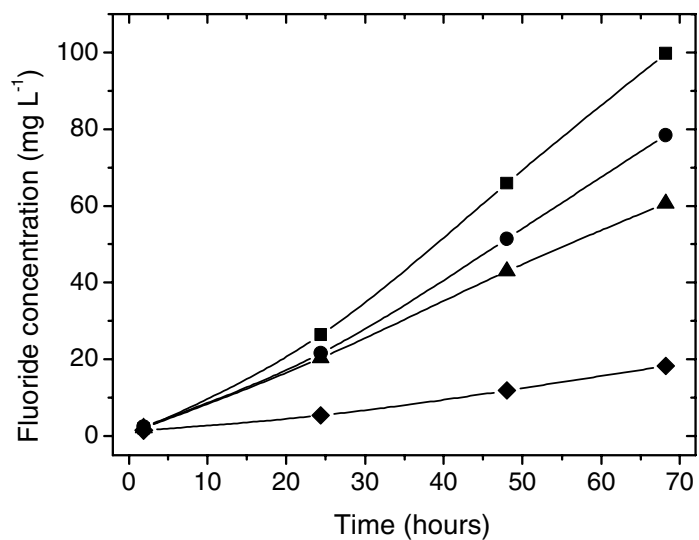


Figure 2. Ion chromatograms of 11.2 g L^{-1} $[\text{C}_4\text{mim}][\text{PF}_6]$ dissolved in 20 vol% acetonitrile in water following (a) 1 hr. of preparation, (b) 10 hrs. of preparation and (c) 19 hrs. of preparation.

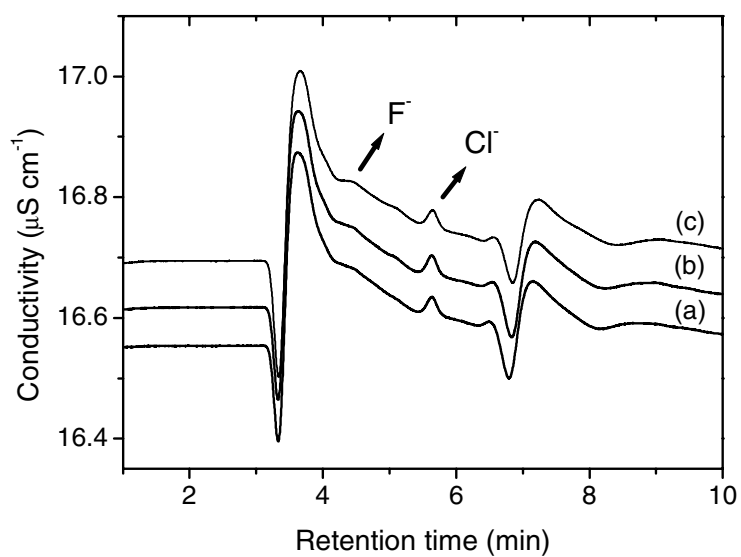


Figure 3. Ion chromatogram of $[\text{C}_4\text{mim}][\text{BF}_4]$ using an eluent containing 3.2 mM Na_2CO_3 + 1.0 mM NaHCO_3 and a flow rate of 1 mL min^{-1} during the first 10 min and thereafter 1.6 mL min^{-1} . The peaks highlighted are due to (1) $[\text{BF}_4]$ anion, (2) displacement of eluent anions in equilibrium with the column into the mobile phase due to the injection of large amount of anions, (3) fluoride, (4) chloride, and (5) the carbonate dip. The insert shows an expanded view of the trace highlighted by the dashed box.

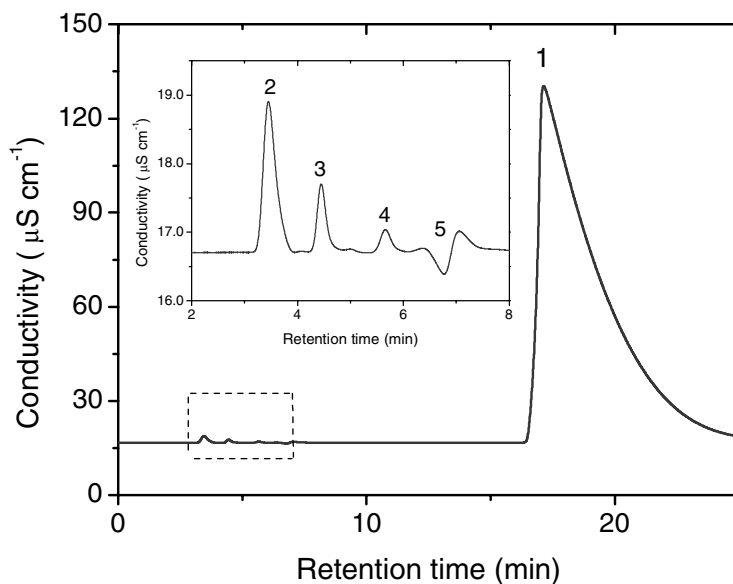


Figure 4. Ion chromatogram of $[\text{C}_4\text{mim}][\text{OTf}]$ using an eluent containing 3.2 mM Na_2CO_3 + 1.0 mM NaHCO_3 and a flow rate of 1 mL min^{-1} during the first 10 min and thereafter 1.6 mL min^{-1} . The peaks highlighted are due to (1) $[\text{OTf}]$ anion, (2) displacement of eluent anions in equilibrium with the column into the mobile phase due to the injection of large amount of anions and (3) chloride. The insert shows an expanded view of the trace highlighted by the dashed box.

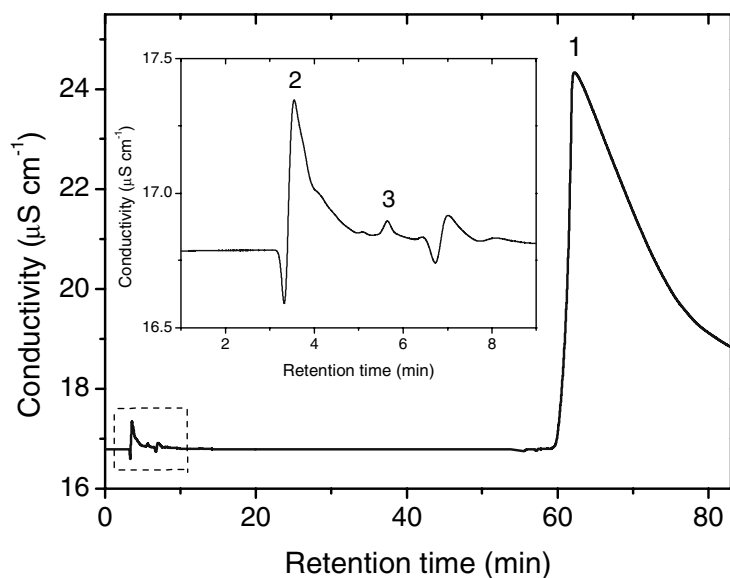


Figure 6. Comparison of the standard addition of chloride variation in water(▲) and 11.3 g L⁻¹ [C₄mim][OTf](■), and the corresponding difference in area between the two plots (○).

