

Anion Analysis of Ionic Liquids and Ionic Liquid Purity Assessment by Ion Chromatography

Christina Rutz,^[a] Laura Schmolke,^[a] Vasily Gvilava,^[a] and Christoph Janiak^{*[a]}

Dedicated to Professor Walter Frank on the Occasion of his 60th Birthday

Abstract. The simultaneous determination of halide impurities (fluoride, chloride, bromide, and iodide) and ionic liquid (IL) anions (tetrafluoroborate, hexafluorophosphate, and triflimide) using ion chromatography was developed with a basic, non-gradient ion chromatography system. The non-gradient method uses the eluent $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ in water/acetonitrile (70:30 v:v) on the AS 22 column to enable a rapid and simultaneous analysis of different IL and halide anions within an acceptable run-time (22 min) and with good resolution R of larger than 2.4, a capacity k' between 0.4 and 5.1, selectivities α between 1.3 and 2.1, and peak asymmetries A_s of less than 1.5. Halide impurities below 1 ppm ($1 \text{ mg}\cdot\text{L}^{-1}$ of prepared sample solution) could be quantified. A range of ionic liquids with tetrafluoroborate $[\text{BF}_4]^-$, hexafluorophosphate $[\text{PF}_6]^-$, and bis(trifluoromethylsulfonyl)imide (triflimide) $[\text{NTf}_2]^-$ anions combined with cations based on imidazole, pyridine, and tetrahydrothiophene could be analyzed for their anion purity. The IL-cations do not influence the chro-

matographic results. With the analysis of 18 ILs differing in their cation-anion combination we could prove the general applicability of the described method for the anion purity analysis of ionic liquids with respect to halide ions. The IL-anion purity of most ILs was above 98 wt%. The highest IL-anion purity was 99.8 wt%, implying anion impurities of only 0.2 wt%. The used halide anion from the synthesis route was the major anion impurity, yet with chloride also bromide and fluoride (potentially from hydrolysis of $[\text{BF}_4]^-$) were often detected. When iodide was used, at least chloride but sometimes also bromide and fluoride was present. However, even if the IL-anion content is above 99 wt%, it does not necessarily indicate an ionic liquid devoid of other impurities. From the IC analysis, one can also deduce a possible cation impurity if one takes into account the expected (calculated) IL-anion content. A matching experimental and theoretical IL-anion content excludes, a higher experimental content indicates the presence of residual KBF_4 , NH_4PF_6 , or LiNTf_2 salt from the halide to IL-anion exchange.

Introduction

Ionic liquids (ILs) are saline substances containing weakly coordinating anions and cations.^[1,2] By definition the melting point of these salts should be below 100 °C preferably even a below room temperature. ILs are alternatives to aqueous or organic solvents,^[3,4] and are regarded as a new liquid medium^[5,6] for the preparation of inorganic materials.^[7–14] Ionic liquids are stable at high temperatures, have no vapor pressure and a high ionic conductivity.^[15–17] Contrary to common organic solvents they are not flammable.^[18,19] The density, viscosity, and hydrophilic properties of ILs can be systematically varied through the choice of cation, anion, or cation-anion combination.^[20] The miscibility of ionic liquids with water or organic solvents varies with the side-chain lengths in the cation and with the character of the anion. Because of their physical properties ionic liquids are regarded as designer solvents with a potential wide range of applications in science and technology.^[21–24] A wide range of applications for ionic liquids has

been reported. They are used in organic chemistry, catalysis or electrochemistry.^[25–30]

There are generally two different routes to synthesize ionic liquids. The common way is to use a two-step process. The first step is the formation of an organic halide salt via alkylation using a haloalkane. After that a metathesis reaction introduces the weakly coordinating anion to form the ionic liquid. An alkali metal salt like KBF_4 or acids like HBF_4 can be used to give, e. g., a tetrafluoroborate ionic liquid in the anion exchange reaction (Scheme 1).^[31–33] For halide free ionic liquids, direct alkylation of imidazole, pyridine or amine can be done using esters or anhydrides.^[34–36]

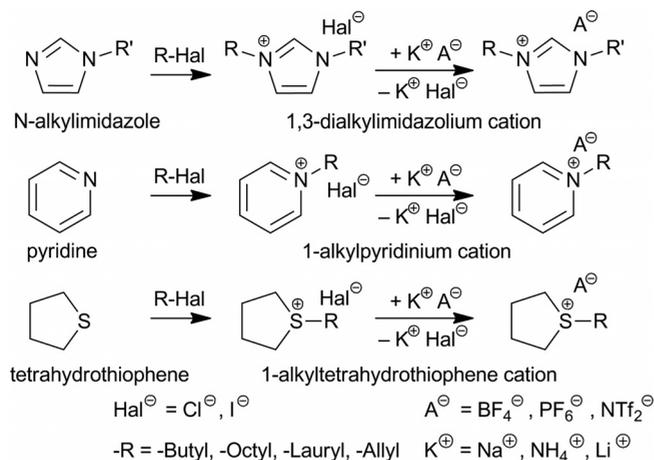
The problems about halide containing ionic liquids are well known.^[37] Halides reduce the thermal stability and stability of the inter-ionic network.^[38] The viscosity and the density also depend on the purity of the ionic liquids. Furthermore, halide impurities decrease the electrochemical window, i.e. oxidation and reduction potential limits.^[21] It requires a more positive potential to oxidize perfluorinated anions than chloride, bromide, and iodide. A significant decrease of the anodic potential can be observed with halide impurities.^[21]

Although these problems are known, just a few analytical methods have been reported for the quantification of halide impurities in ILs. Common methods are reversed-phase liquid chromatography,^[39–43] ion pair chromatography,^[44–46] hydrophilic interaction chromatography,^[47,48] capillary electrophoresis,^[49,50] and ion chromatography.^[49,51]

* Prof. Dr. C. Janiak
E-Mail: janiak@uni-duesseldorf.de

[a] Institut für Anorganische Chemie und Strukturchemie
Universität Düsseldorf
Universitätsstr. 1
40225 Düsseldorf, Germany

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.201600437> or from the author.



Scheme 1. Synthesis scheme of 1,3-dialkylimidazolium, 1-alkylpyridinium, and 1-alkylthiophenium ionic liquids via *N*-alkylation and anion exchange.

Ion chromatography (IC) is a relatively easy, fast, and standard method for the simultaneous analysis of anions. IC is used routinely for the determination of halides in aqueous media.^[52] IC should also be applicable for the analysis of anions of ionic liquids and anion impurities like halides but the utilization of IC for the analysis of ionic liquids is rarely reported. The main challenge here is to achieve a good peak resolution. *Hardacre* et al. published a method about the determination of chloride impurities in tetrafluoroborate ionic liquids.^[53] A good resolution for the halide impurities in an adequate time was reached, but the tetrafluoroborate peak exhibited a strong tailing and its symmetry should be improved. A good peak symmetry could be obtained by using an eluent gradient system, which allows variation of the eluent concentration during the measurement.^[54,55] *Nesterenko* et al. reported a method for the determination of the hydrolysis products from alkali metal hexafluorophosphate salts by using a reagent-free eluent generator in 2012. The separation of the hydrolysis products fluoride (F^-), hydrogenmonofluorophosphate (HPO_3F^-), hydrogenphosphate (HPO_4^{2-}), and difluorophosphate (PO_2F_2^-) anions could be achieved with a good resolution.^[56] With a gradient system a simultaneous analysis of different IL anions in combination with halide impurities has been reported^[54,55] but a gradient system is more expensive and may not be readily available with every IC device. Herein we describe a method for the simultaneous determination of halide anions in ionic liquids with the anions tetrafluoroborate, hexafluorophosphate, or triflimide using a basic, standard ion chromatography system without a gradient pump or a reagent-free eluent generator.

Experimental Section

All ion chromatographic measurements were carried out with a Dionex ICS 1100 instrument with suppressed conductivity detection. The suppressor (AERS 500, Dionex) was regenerated with an external water module. The system was equipped with the analytical column IonPac AS 14 or IonPac AS 22 from Dionex (4×250 mm) with the corresponding guard column AG 14 or AG 22 (4×50 mm), respec-

tively. The instrument was controlled by Chromeleon® software (version 7.1.0.898). The injection volume was 25 μL . Milli-Q 18 M Ω water was used for all eluent, sample, and standards preparation. Analytical grade sodium carbonate and sodium hydrogen carbonate (both Applichem) were used to prepare the eluent. HPLC grade acetonitrile (VWR) was added to the eluent. The standard eluent used was a 4.5 $\text{mmol}\cdot\text{L}^{-1}$ Na_2CO_3 and 1.0 $\text{mmol}\cdot\text{L}^{-1}$ NaHCO_3 mixture with an addition of 30 vol % acetonitrile. For the method development we used different eluent mixtures. The eluent was prepared daily and degassed by bubbling nitrogen through the solution for 20 min.

The calibration standards were prepared from sodium fluoride (Applichem), sodium chloride (Fisher Chemical), potassium bromide (Grüssing), potassium iodide (Applichem), potassium tetrafluoroborate (Acros Organics), ammonium hexafluorophosphate (Alfa Aesar), and bis(trifluoromethane)sulfonimide lithium salt (lithium triflimide, TCI) by dissolving a defined amount in water with further dilution to different precise concentrations (halides: 0.1–5 $\text{mg}\cdot\text{L}^{-1}$, ionic liquid anions: 5–100 $\text{mg}\cdot\text{L}^{-1}$). Exact masses and volumes for the standard solutions can be found in the Supporting Information (Tables S1–S9, Supporting Information). A calibration curve was established by measuring seven samples of each anion as an external standard at different concentrations. The concentration range of fluoride, bromide and iodide was 0.1 to 5.0 $\text{mg}\cdot\text{L}^{-1}$, chloride 0.1 to 20.0 $\text{mg}\cdot\text{L}^{-1}$, and the IL anions were calibrated from 5.0 to 100.0 $\text{mg}\cdot\text{L}^{-1}$ (Table S13, Supporting Information). Every determination was done threefold and the averaged results including standard deviation were used. The estimated errors were calculated and added to the standard deviation. The calibration was checked by analyzing control samples with known concentrations regularly.

All ionic liquids were prepared following standard preparative procedures.^[21] Details can be found in the Supporting Information. Six different tetrafluoroborate-based ILs were analyzed. These ILs were 1-allyl-tetrahydro-1*H*-thiophenium-tetrafluoroborate ([ATH][BF₄]), 1-butyl-3-methyl-imidazolium-tetrafluoroborate ([BMIm][BF₄]), 1-butyl-pyridinium-tetrafluoroborate ([BPy][BF₄]), 4-butyronitrile-pyridinium-tetrafluoroborate ([NCC₃Py][BF₄]), 1-lauryl-pyridinium-tetrafluoroborate ([LPy][BF₄]), and 1-octyl-tetrahydro-1*H*-thiophenium-tetrafluoroborate ([OTh][BF₄]). For [BMIm][BF₄] three different samples were analyzed, one obtained from anion exchange with KBF₄, and two different batches from anion exchange with HBF₄. The two hexafluorophosphate-based ILs were 1-allyl-3-methyl-imidazolium-hexafluorophosphate ([AMIm][PF₆]) and 4-butyronitrile-pyridinium-hexafluorophosphate ([NCC₃Py][PF₆]). Eight triflimide-based ILs 1-allyl-3-methyl-imidazolium-triflimide ([AMIm][NTf₂]), 1-allyl-tetrahydro-1*H*-thiophenium-triflimide ([ATH][NTf₂]), 1-butyl-3-methyl-imidazolium-triflimide ([BMIm][NTf₂]), 1-butyl-pyridinium-triflimide ([BPy][NTf₂]), 1-butyl-tetrahydro-1*H*-thiophenium-triflimide ([BTh][NTf₂]), 1-lauryl-pyridinium-triflimide ([LPy][NTf₂]), 1-octyl-3-methyl-imidazolium-triflimide ([OMIm][NTf₂]), and 1-octyl-pyridinium-triflimide ([OPy][NTf₂]) were analyzed.

IC samples were prepared by dissolving a defined mass of IL in a defined volume of either deionized water (if soluble) or in the prepared eluent solution to achieve an IL-anion concentration between 50–100 $\text{mg}\cdot\text{L}^{-1}$. Exact masses and volumes for the IL sample solutions can be found in the Supporting Information.

Supporting Information (see footnote on the first page of this article): Synthesis equations for ILs, concentrations of solutions for calibration, concentrations for sample solutions, chromatograms from column AS 14, chromatograms without column, chromatograms with column AS 22 for method development, chromatograms with AS 22 of IL sam-

ples, cake diagrams of anion fractions in ILs, data tables, formulae for data analysis.

Results and Discussion

Method Development and Optimization of IC Separation

The selection of the ion-exchange column for the separation of ILs and halides is not trivial. Fluoride can react with silica, so silica-based anion-exchange columns are not applicable.^[56] Our initial separation studies were done with an AS 14 column. The substrates of the AS 14 column are highly cross-linked macroporous resin pellets with a diameter of 9 μm . They consist of styrene, which is cross-linked with divinylbenzene and is functionalized with quaternary alkyl ammonium groups. As the AS 14 column is routinely used for the analysis of halide anions in aqueous solutions, we tried to develop a method for the analysis of the IL anions together with the halide anions. This application for the AS 14 column is, so far, unknown in literature. We investigated the use of different eluent solutions of sodium carbonate/sodium hydrogen carbonate mixture, sodium borate or sodium carbonate at different concentrations to try to reach a good peak resolution. Details for these eluent mixtures can be found in the figure captions of the chromatograms in Figures S4–S9 (Supporting Information). Test measurements were carried out with potassium tetrafluoroborate, ammonium hexafluorophosphate, and lithium bis(trifluoromethylsulfonyl)imide (triflimide). Only the $[\text{BF}_4]^-$ peak but neither hexafluorophosphate nor triflimide could be detected with the AS 14 column (Figures S4–S9, Supporting Information). Detection of $[\text{BF}_4]^-$ with the AS 14 column suffered from its asymmetric peak (Figure 1) which failed to become symmetrical in the tested eluents.

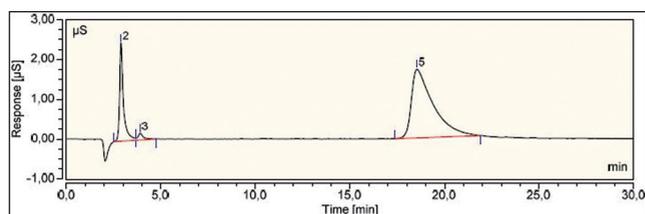


Figure 1. Example chromatogram of potassium tetrafluoroborate showing the typical asymmetric $[\text{BF}_4]^-$ peak on the AS 14 column; peak assignment: 2 F^- , 3 Cl^- , 5 $[\text{BF}_4]^-$. Flowrate: $1.20 \text{ mL}\cdot\text{min}^{-1}$; eluent: $2.5 \text{ mmol}\cdot\text{L}^{-1}$ sodium carbonate and $2.5 \text{ mmol}\cdot\text{L}^{-1}$ sodium hydrogen carbonate; run-time: max. 60 min.

The retention time of the tetrafluoroborate peak correlates with the elution potency of the eluent. With a higher concentrated eluent, the retention time could be shortened (Figure S6, Supporting Information).

Hydrophobic ions, such as hexafluorophosphate or triflimide may be strongly retained by styrenedivinylbenzene polymeric anion-exchangers and this will affect both the runtime and reproducibility of separations. Due to the hydrophobic nature of ions like hexafluorophosphate or triflimide, it is necessary to minimize the non-specific adsorption of the analytes by using a hydrophilic anion exchange.^[56] To prove the unsuitability of

the AS 14 column material for the separation of the IL anions and to exclude other instrumental artefacts, measurements without column were performed. These measurements showed the suitability of the ICS 1100 system for the analysis of ionic liquid and halide anions. Without an analytical column sharp peaks of tetrafluoroborate, hexafluorophosphate, and triflimide were detected after a few seconds using eluents at different concentrations containing sodium carbonate/sodium hydrogen carbonate mixture or sodium hydroxide (Figures S10–S21, Supporting Information). With these results the detection failure of $[\text{PF}_6]^-$ and $[\text{NTf}_2]^-$ could be traced to the AS 14 column.

Hence, for subsequent successful measurements we used the analytical column AS 22 from Dionex. The substrate of the AS 22 column is a highly cross-linked modified styrene divinylbenzene resin derivatized with alkyl-ethanol ammonium functionalities. Its capacity is $210 \mu\text{eq}$ with a low hydrophobicity. Using the analytical column AS 22 and a $4.5 \text{ mmol}\cdot\text{L}^{-1}$ sodium carbonate and $1.4 \text{ mmol}\cdot\text{L}^{-1}$ sodium hydrogen carbonate eluent, the analysis of tetrafluoroborate was achieved within a retention time of 15 min with an acceptable baseline separation and peak shape (Figure 2). A small peak tailing of the tetrafluoroborate peak could be observed, but due to an asymmetry factor of 1.7 (that is larger than 1.5) the shape should still be improved (Figure 2).

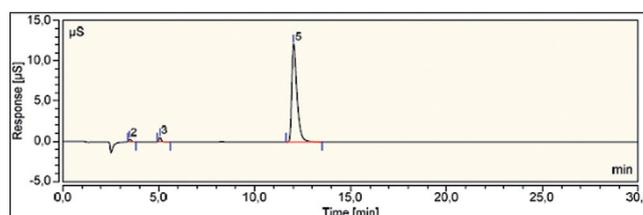


Figure 2. Chromatogram of potassium tetrafluoroborate; peak assignment: 2 F^- , 3 Cl^- , 5 $[\text{BF}_4]^-$. Column: AS 22; flowrate: $1.00 \text{ mL}\cdot\text{min}^{-1}$; eluent: $4.5 \text{ mmol}\cdot\text{L}^{-1}$ sodium carbonate and $1.4 \text{ mmol}\cdot\text{L}^{-1}$ sodium hydrogen carbonate; run-time: max. 60 min.

Still, the simple aqueous sodium carbonate/sodium hydrogen carbonate eluent was not applicable for the analysis of hexafluorophosphate and triflimide salts or ILs. Hexafluorophosphate was only detected at a long retention time of 55 min showing a distinctive tailing (asymmetry factor of 2.2) (Figure S28, Supporting Information), whereas triflimide could not be detected at all (Figure S29, Supporting Information).

The retention time for anions depends of the charge, size, and polarizability of the anion. The addition of organic solvents to the eluent can be used to change the retention time of anions. Hu et al. could show a simultaneous analysis of hexafluorophosphate with halide ions like fluoride, chloride, and bromide with acceptable peak shape and baseline separation within 25 min using an AS 22 column.^[57] Consequently, in our runs a separation of fluoride, chloride, bromide, iodide, and the IL anions tetrafluoroborate, hexafluorophosphate, and triflimide was achieved within an acceptable run-time of 22 min using an eluent mixture of $4.5 \text{ mmol}\cdot\text{L}^{-1}$ sodium carbonate and $1.4 \text{ mmol}\cdot\text{L}^{-1}$ sodium hydrogen carbonate with 30 vol % acetonitrile added. All peaks show a baseline separation and a good resolution (Figure 3).

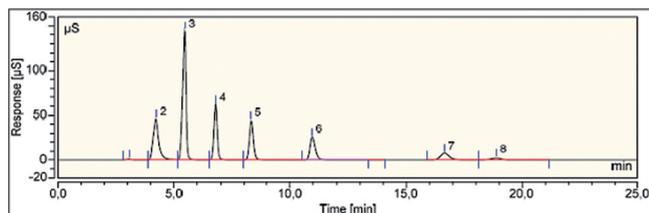


Figure 3. Chromatogram of sodium fluoride ($0.30 \text{ mg}\cdot\text{L}^{-1}$), sodium chloride ($0.50 \text{ mg}\cdot\text{L}^{-1}$), potassium bromide ($0.20 \text{ mg}\cdot\text{L}^{-1}$), potassium tetrafluoroborate ($10.00 \text{ mg}\cdot\text{L}^{-1}$), sodium iodide ($0.50 \text{ mg}\cdot\text{L}^{-1}$), ammonium hexafluorophosphate ($10.00 \text{ mg}\cdot\text{L}^{-1}$), and lithium triflimide ($10.00 \text{ mg}\cdot\text{L}^{-1}$); peak assignment: 2 F^- , 3 Cl^- , 4 Br^- , 5 $[\text{BF}_4]^-$, 6 I^- , 7 $[\text{PF}_6]^-$, 8 $[\text{NTf}_2]^-$. Column: AS 22; flowrate: $0.90 \text{ mL}\cdot\text{min}^{-1}$; eluent: $4.5 \text{ mmol}\cdot\text{L}^{-1}$ sodium carbonate, $1.4 \text{ mmol}\cdot\text{L}^{-1}$ sodium hydrogen carbonate and 30% acetonitrile; run-time: set to max. 22 min. For chromatograms of the actual investigated ILs with column AS 22 see Figures S30–S43 (Supporting Information).

In order to judge the quality of the chromatographic separation we calculated the factors for resolution R , capacity k' , selectivity α , and asymmetry A_S for every adjacent peak (Table 1) (formulae are given in Supporting Information).

The quality parameter resolution R should be larger than 0.8, the capacity k' should give a value between 1 and 5, the selectivity α values lie between 1.05 and 3, and the asymmetry A_S

should be between 0.9 to 1.1, but values up to 1.5 for A_S are accepted as well.^[58–63] The determined quality parameters confirm a successful simultaneous chromatographic separation of the IL-anion and halide impurities.

With the aforementioned method for the AS 22 column we measured a series of synthesized ionic liquids (see Supporting Information for chromatograms, Figures S30–S43). All chromatograms showed the same good peak resolution, which we could achieve in the above test measurements (cf. Figure 3 and Table 1). The anion purity of most of the ILs was above 98 wt%. Detailed values are given in the Supporting Information. We were able to determine the halide impurities of the ILs below 1 ppm (below $1 \text{ mg}\cdot\text{L}^{-1}$ in the prepared sample solution) (Tables S14–S16, Supporting Information).

It is not trivial, however, to judge the overall purity of an IL. Even if the IL-anion content is above 99 wt%, it does not necessarily indicate an ionic liquid devoid of impurities. The examples of $[\text{BMIm}][\text{BF}_4]$ and $[\text{BPy}][\text{NTf}_2]$ illustrate how the IC anion analysis can give additional information on the IL purity and, hence, for a possible optimization of the anion exchange and washing step in the IL synthesis. With more than 99 wt% IL-anion fraction the ILs $[\text{BMIm}][\text{BF}_4]$ (from KBF_4 or from HBF_4), $[\text{BMIm}][\text{NTf}_2]$ and $[\text{BPy}][\text{NTf}_2]$ (from LiNTf_2) seem to be quite pure (Table 2 and Figure 4). Yet,

Table 1. Quality parameters for the chromatographic separation of halide and IL anions.^{a)}

Peak	$t_R^{(c)}$ /min	$w_b^{(c)}$ /min	$h^{(c)}$ / μS	$R^{(c)}$	$k'^{(c)}$ /	$\alpha^{(c)}$	$A_S^{(c)}$
H_2O	3.05	0.29	0.73	3.46	0.00	n.a.	1.55
Fluoride ^{b)}	4.14	0.34	0.15	4.18	0.35	2.11	1.45
Chloride ^{b)}	5.31	0.22	0.70	6.78	0.74	1.62	1.40
Bromide ^{b)}	6.70	0.19	0.07	5.96	1.20	1.42	1.21
$[\text{BF}_4]^-$ ^{b)}	8.25	0.33	2.76	6.28	1.70	1.53	1.31
Iodide ^{b)}	10.98	0.54	0.07	8.55	2.60	1.49	1.51
$[\text{PF}_6]^-$ ^{b)}	16.62	0.78	0.65	2.39	3.88	1.30	1.44
$[\text{NTf}_2]^-$ ^{b)}	18.49	0.87	0.27	n.a.	5.06	n.a.	1.13

a) Based on chromatogram in Figure 3; column: AS 22; flowrate: $0.90 \text{ mL}\cdot\text{min}^{-1}$; eluent: $4.5 \text{ mmol}\cdot\text{L}^{-1}$ sodium carbonate, $1.4 \text{ mmol}\cdot\text{L}^{-1}$ sodium hydrogen carbonate and 30% acetonitrile; run-time: 22 min. b) Anion source: sodium fluoride, sodium chloride, potassium bromide, potassium tetrafluoroborate, sodium iodide, ammonium hexafluorophosphate, and lithium triflimide. c) Retention time t_R , peak width w_b , peak height h , resolution R , capacity factor k' , selectivity α , and asymmetry A_S ; see Supporting Information for details of formulae.

Table 2. Mean value \bar{X} and measurement uncertainty σ_g of halide and IL anions, and the calculated theoretical content of IL anion.

Ionic liquid	Sample conc. ^{a)} / $\text{mg}\cdot\text{L}^{-1}$	Mean value \bar{X} and measurement uncertainty $\sigma_g^{(b)}$ of anion concentrations / $\text{mg}\cdot\text{L}^{-1}$ (wt%)					$[\text{IL-anion}]_{\text{theo}}^{(c)}$ / $\text{mg}\cdot\text{L}^{-1}$	Deviation from $[\text{IL-anion}]_{\text{theo}}^{(c)}$ /%
		F^-	Cl^-	Br^-	$[\text{BF}_4]^-$	$[\text{NTf}_2]^-$		
$[\text{BMIm}][\text{BF}_4]$ (from KBF_4)	636.0	0.5 ± 0.1 (0.2)	0.4 ± 0.2 (0.15)	0.0	258 ± 7 (99.7)	–	245 ± 1	+5
$[\text{BMIm}][\text{BF}_4]_1$ (from HBF_4)	294.0	0.1 ± 0.1 (0.1)	0.1 ± 0.1 (0.1)	0.0	112 ± 2 (99.8)	–	113 ± 1	within exp. error
$[\text{BMIm}][\text{BF}_4]_2$ (from HBF_4)	136.0	0.2 ± 0.2 (0.4)	0.4 ± 0.4 (0.8)	0.2 ± 0.1 (0.4)	52 ± 1 (98.5)	–	52 ± 1	none
$[\text{BMIm}][\text{NTf}_2]$ (from LiNTf_2)	138.6	0.0	0.2 ± 0.2 (0.2)	0.0	–	97 ± 1 (99.8)	93 ± 1	+4
$[\text{BPy}][\text{NTf}_2]$ (from LiNTf_2)	170.0	0.1 ± 0.1 (<0.1)	0.2 ± 0.1 (0.15)	0.1 ± 0.1 (<0.1)	–	125 ± 3 (99.7)	118 ± 1	+6

a) IC samples were prepared by dissolving a defined mass of IL in a defined volume of either deionized water (if soluble) or in the prepared eluent solution to achieve an IL-anion concentration between $50\text{--}100 \text{ mg}\cdot\text{L}^{-1}$. Exact masses and volumes for the IL sample solutions can be found in the Supporting Information. b) Every determination was done in triplicate and the averaged results including standard deviations were used. The estimated errors were calculated and added to the standard deviation to give the measurement uncertainty σ_g . c) The standard deviation for the expected theoretical $[\text{IL-anion}]_{\text{theo}}^{(c)}$ value stems from the weighing and volume measurement uncertainty when preparing the solution from the neat IL.

when comparing the expected theoretical $[\text{BF}_4]^-$ or $[\text{NTf}_2]^-$ content with the experimentally found amount it can become apparent that the overall IL-purity can be less due to remaining alkali metal salt of the IL-anion from the exchange process (Table 2). Thus, it can be problematic when determining and ascertaining IL purity only by halide and IL-anion analysis.

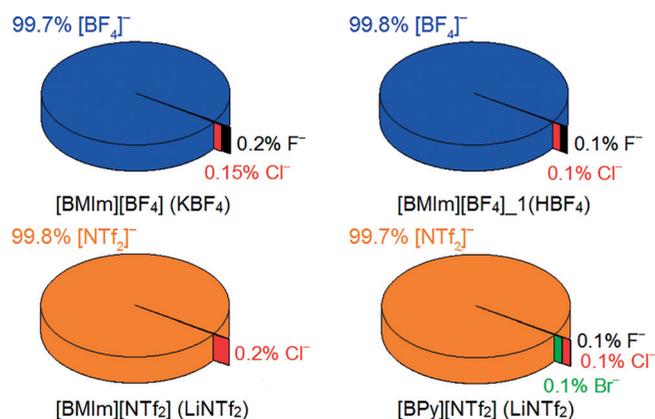


Figure 4. Weight percentage of anions in different ILs. Blue: $[\text{BF}_4]^-$, black: F^- , red: Cl^- , green: Br^- , orange: $[\text{NTf}_2]^-$. The compound for the halide to IL-anion exchange is given in parentheses. For more graphical presentations of the determined anion weight percentages see Figures S44–S50 (Supporting Information).

The ionic liquid $[\text{BMIm}][\text{BF}_4]$ was synthesized in two different ways. Following the alkylation of imidazole the anion exchange was carried out using either KBF_4 or HBF_4 . The triflimide-based ionic liquids were synthesized with lithium triflimide salt for the anion exchange. We were able to trace the different anion exchange in the ion chromatographic analysis of the product by comparing the measured concentration to the expected concentration of the IL anion, here tetrafluoroborate and triflimide, which is calculated from the sample mass and volume of solvent (Table 2).

The sample of $[\text{BMIm}][\text{BF}_4]$, which was synthesized using KBF_4 for the anion exchange contained a higher amount of tetrafluoroborate in comparison to the expected (theoretical) content. Similar for $[\text{BMIm}][\text{NTf}_2]$ (LiNTf_2) and $[\text{BPy}][\text{NTf}_2]$ (LiNTf_2) a higher than expected anion content was found. Whereas, the experimental $[\text{BF}_4]^-$ content of two charges of the $[\text{BMIm}][\text{BF}_4]$ IL synthesized by anion exchange with HBF_4 was almost identical to the expected concentration. The main reason for a higher than theoretical anion content seems to be the solubility of the KBF_4 , NH_4PF_6 , or LiNTf_2 salt used for anion exchange. The purification consisted of washing with water to remove the alkali halide (here potassium or lithium chloride) as well as the excess KBF_4 , NH_4PF_6 , or LiNTf_2 salt from the anion exchange reaction (see Supporting Information for details). Due to the low water solubility of KBF_4 and LiNTf_2 , an excess of this salt may not have been fully removed. The positive deviation from the expected theoretical content confirmed this for $[\text{BMIm}][\text{BF}_4]$ (KBF_4), $[\text{BMIm}][\text{NTf}_2]$ (LiNTf_2), and $[\text{BPy}][\text{NTf}_2]$ (LiNTf_2) and showed a leftover of KBF_4 and LiNTf_2 exchange salt in the IL. In contrast, HBF_4 is readily soluble in water, so it could be easily removed during the washing process. After the washing

procedure, the IL was dried in vacuo to remove residual water and other solvents like dichloromethane. Any remains of HBF_4 would be removed further within this step due to the HBF_4 volatility.

Therefore, we were not only able to analyze the IL for its halide content; we could also draw conclusions about the quality of the anion exchange and purification process. Even when the IL-anion percentage is above 99 wt% (Figure 4), it does not necessarily indicate an ionic liquid devoid of impurities. When judging the anion purity of an IL it is not only necessary to quantify possible halide impurities but also to compare the experimental and expected (theoretical) IL-anion content from the examined sample mass (for more examples see Tables S14–S16, Supporting Information).

Conclusions

A new method for anion purity analysis of ionic liquids by ion chromatography is described using a simple, non-gradient chromatographic system. The method is based on the AS 22 column with the eluent $4.5 \text{ mmol}\cdot\text{L}^{-1}$ sodium carbonate, $1.4 \text{ mmol}\cdot\text{L}^{-1}$ sodium hydrogen carbonate, and 30 vol% acetonitrile. The method allowed the simultaneous determination of the IL anions tetrafluoroborate, hexafluorophosphate, and triflimide and the halide anions fluoride, chloride, bromide, and iodide with resolutions R larger than 2.4, a capacity k' between 0.4 and 5.1, selectivities α between 1.3 and 2.1 and peaks asymmetries A_S of less than 1.5. Halide impurities below 1 ppm (below $1 \text{ mg}\cdot\text{L}^{-1}$ of the prepared sample solution) could be quantified. With the analysis of 18 ILs differing in their cation-anion combination, the general applicability of the described method for the IL-anion purity was demonstrated. The IL cations were based on imidazole, pyridine and tetrahydrothiophene. The cations do not appear to affect the chromatographic process. Further, we show that caution has to be exerted to base the IL purity on the weight fraction of the IL anion and the halide impurities only. An IL-anion content above 99 wt% does not necessarily indicate an ionic liquid devoid of other impurities. The experimentally found IL-anion concentration must also be compared to the calculated expected IL-anion content from the sample concentration. A matching experimental and calculated IL-anion content excludes, a higher experimental content indicates the presence of residual KBF_4 , NH_4PF_6 , or LiNTf_2 salt from the halide to IL-anion exchange.

Acknowledgements

We thank Mrs. Susann Wegner for the synthesis of the ionic liquids. Our work was supported by the Deutsche Forschungsgemeinschaft (DFG) through grant Ja466/31–1 within the priority program “Materials synthesis at room temperature” (SPP 1708).

Keywords: Ion chromatography; Ionic liquids; Halides; Purity

References

- [1] P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926–3945; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789.
- [2] H. Weingärtner, *Angew. Chem.* **2008**, *120*, 664–682; *Angew. Chem. Int. Ed.* **2008**, *47*, 654–670.
- [3] T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2084.
- [4] A. Kuchenbach, R. Giernoth, *ChemistryOpen* **2015**, *4*, 677–681; C. Feldmann, *Z. Naturforsch.* **2013**, *68b*, 1057. Introduction to special issue on ionic liquids in chemical synthesis.
- [5] J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508–3576.
- [6] T. Torimoto, T. Tsuda, K. Okazaki, S. Kuwabata, *Adv. Mater.* **2010**, *22*, 1196–1221.
- [7] C. Janiak, *Z. Naturforsch.* **2013**, *68b*, 1059–1089; C. Janiak, *AIMS Mater. Sci.* **2014**, *1*, 41–45.
- [8] P. S. Campbell, M. H. G. Precht, C. C. Santini, P.-H. Haumesser, *Curr. Org. Chem.* **2013**, *17*, 414–429.
- [9] D. Freudenmann, S. Wolf, M. Wolff, C. Feldmann, *Angew. Chem. Int. Ed.* **2011**, *50*, 11050–11060.
- [10] E. Ahmed, J. Breternitz, M. F. Groh, M. Ruck, *CrystEngComm* **2012**, *14*, 4874–4885; E. Ahmed, M. Ruck, *Dalton Trans.* **2011**, *40*, 9347–9357; M. F. Groh, U. Müller, E. Ahmed, A. Rothenberger, M. Ruck, *Z. Naturforsch.* **2013**, *68b*, 1108–1122.
- [11] E. R. Parnham, R. E. Morris, *Acc. Chem. Res.* **2007**, *40*, 1005–1013.
- [12] E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, *Nature* **2004**, *430*, 1012–1016.
- [13] J. Dupont, J. D. Scholten, *Chem. Soc. Rev.* **2010**, *39*, 1780–1804.
- [14] K. Klauke, B. Hahn, K. Schütte, J. Barthel, C. Janiak, *Nano-Struct. Nano-Objects* **2015**, *1*, 24–31; R. Marcos Esteban, K. Schütte, D. Marquardt, J. Barthel, F. Beckert, R. Mülhaupt, C. Janiak, *Nano-Struct. Nano-Objects* **2015**, *2*, 28–34; R. Marcos Esteban, K. Schütte, P. Brandt, D. Marquardt, H. Meyer, F. Beckert, R. Mülhaupt, H. Kölling, C. Janiak, *Nano-Struct. Nano-Objects* **2015**, *2*, 11–18.
- [15] Y. Lin, S. Dehnen, *Inorg. Chem.* **2011**, *50*, 7913–7915.
- [16] T. Lodge, *Science* **2008**, *321*, 50–51.
- [17] R. E. Morris, *Chem. Commun.* **2009**, *21*, 2990–2998.
- [18] J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667–3692.
- [19] C. E. Song, *Chem. Commun.* **2004**, *9*, 1033–1043.
- [20] A. E. Visser, R. P. Swatloski, W. M. Reichert, J. H. Davis Jr., R. D. Rogers, R. Mayton, S. Sheff, A. Wierzbicki, *Chem. Commun.* **2001**, *1*, 135–136.
- [21] P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, 1st ed. Wiley-VCH, Weinheim, **2003**.
- [22] W. Sundermeyer, *Angew. Chem.* **1965**, *77*, 241–258; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 222–238.
- [23] W. Sundermeyer, *Chem. Unserer Zeit* **1967**, *1*, 150–157.
- [24] S. V. Volkov, *Chem. Soc. Rev.* **1990**, *19*, 21–28.
- [25] S. A. Siddiqui, U. C. Narkhede, S. S. Palimkar, T. Daniel, R. J. Lahoti, K. V. Srinivasan, *Tetrahedron* **2005**, *61*, 3539–3546.
- [26] S. S. Shinde, B. S. Lee, D. Y. Chi, *Org. Lett.* **2008**, *10*, 733–735.
- [27] M. C. Buzzeo, R. G. Evans, R. G. Compton, *ChemPhysChem* **2004**, *5*, 1106–1120.
- [28] J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, R. D. Rogers, *Chem. Commun.* **1998**, 1765–1766.
- [29] J. L. Anderson, D. W. Armstrong, *Anal. Chem.* **2003**, *75*, 4851–4858.
- [30] H. Qiu, S. Jiang, X. Liu, L. Zhao, *J. Chromatogr. A* **2006**, *1116*, 46–50.
- [31] A. Aupoix, B. Pégot, G. Vo-Thanh, *Tetrahedron* **2010**, *66*, 1352–1356.
- [32] P. D. Vu, A. J. Boydston, C. W. Bielawski, *Green Chem.* **2007**, *9*, 1158–1159.
- [33] D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti, P. J. Dyson, *J. Am. Chem. Soc.* **2004**, *126*, 15876–15882.
- [34] D. J. Kim, K. H. Oh, J. K. Park, *Green Chem.* **2014**, *16*, 4098–4101.
- [35] R. Arvai, F. Toulgoat, B. R. Langlois, J.-Y. Sanchez, M. Médebielle, *Tetrahedron* **2009**, *65*, 5361–5368.
- [36] M. Javaherian, F. Kazemi, M. Ghaemi, *Chin. Chem. Lett.* **2014**, *25*, 1643–1647.
- [37] K. R. Seddon, A. Stark, M. J. Torres, *Pure Appl. Chem.* **2000**, *72*, 2275–2287.
- [38] S. Watanabe, H. Seguchi, K. Yoshida, K. Kifune, T. Tadaki, H. Shiozaki, *Tetrahedron Lett.* **2005**, *46*, 8827–8829.
- [39] P. Stepnowski, A. Muller, P. Behrend, J. Ranke, J. Hoffmann, B. Jastorff, *J. Chromatogr. A* **2003**, *993*, 173–178.
- [40] P. Stepnowski, W. Mroziak, *J. Sep. Sci.* **2005**, *28*, 149–154.
- [41] L. M. Meng, H. Yu, X. Huang, Y. J. Ma, *Chin. J. Anal. Chem.* **2012**, *40*, 409–414.
- [42] E. Dagher-Wojtkowiak, S. Studzinska, B. Buszewski, R. Kaliszczak, M. J. Markuszewski, *Anal. Methods* **2014**, *6*, 1189–1196.
- [43] H. Yu, Y. M. Sun, C. M. Zou, *Chin. Chem. Lett.* **2014**, *25*, 1371–1374.
- [44] M. Y. Wang, H. Yu, P. Li, J. Li, Y. F. Gao, *Chin. J. Chromatogr.* **2014**, *32*, 773–787.
- [45] C. M. Zou, H. Yu, M. Y. Wang, *Chin. Chem. Lett.* **2014**, *25*, 201–204.
- [46] Y. J. Ma, Y. F. Gao, H. Yu, M. Li, *J. Liq. Chromatogr. Relat. Technol.* **2014**, *37*, 73–87.
- [47] G. Le Rouzo, C. Lamouroux, C. Bresson, A. Guichard, P. Moisy, G. Moutiers, *J. Chromatogr. A* **2007**, *1164*, 139–144.
- [48] C. Lamouroux, G. Foglia, G. Le Rouzo, *J. Chromatogr. A* **2011**, *1218*, 3022–3028.
- [49] A. Markowska, P. Stepnowski, *Anal. Sci.* **2008**, *24*, 1359–1361.
- [50] M. Shi, Q. Gao, J. Feng, *J. Chromatogr. Sci.* **2012**, *50*, 547–552.
- [51] R. Q. Zhang, H. Yu, Y. Z. Liu, *Chin. J. Chromatogr.* **2012**, *30*, 728–732.
- [52] European Standards EN ISO 10304–1: 1995; EN ISO 10304–1: 1997; 1999 EN ISO 10304–4:1999.
- [53] C. Villagrán, M. Deetlefs, W. R. Pitner, C. Hardacre, *Anal. Chem.* **2004**, *76*, 2118–2123.
- [54] Dionex Corporation, “IC-MS Determination of Anionic Ionic Liquids, Counterions, and Impurities”, **2009**.
- [55] Dionex Corporation, “Determination of Tetrafluoroborate, Perchlorate, and Hexafluorophosphate in a Simulated Electrolyte Sample from Lithium Ion Battery Production”, **2010**.
- [56] L. Terborg, S. Nowak, S. Passerini, M. Winter, U. Karst, P. R. Haddad, P. N. Nesterenko, *Anal. Chim. Acta* **2012**, *714*, 121–126.
- [57] Z. Hu, G. Pan, M. Ye, *Chin. J. Chromatogr.* **2009**, *3*, 337–340.
- [58] M. H. Gey, *Instrumentelle Analytik und Bioanalytik*, 2. Aufl., Springer, Heidelberg, **2008**.
- [59] K. Camman, *Instrumentelle Analytische Chemie*, 1. Aufl., Spektrum-Akademischer Verlag, Heidelberg, **2001**.
- [60] V. R. Meyer, *Praxis der Hochleistungs-Flüssigchromatographie*, 10. Aufl., Wiley-VCH, Weinheim, **2009**.
- [61] S. Petrozzi, *Instrumentelle Analytik*, 1. Aufl., Wiley-VCH, Weinheim, **2010**.
- [62] *Chromatogramme richtig integrieren und bewerten. Ein Praxis-handbuch für die HPLC und GC*, (Eds.: S. Kromidas, H.-J. Kuss), Wiley-VCH, Weinheim, **2008**.
- [63] J. W. Dolan, *LC-GC Europe* **2002**, *15*, 334–337.

Received: November 23, 2016

Published Online: January 12, 2017