

Ion chromatographic determination of structurally varied ionic liquid cations and anions—a reliable analytical methodology applicable to technical and natural matrices

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An ion chromatographic system with conductometric detection was used to analyse a broad structural variety of ionic liquid (IL) cations and anions. The selection of cationic entities covered the chemical space of IL cations as comprehensively as possible and contained the most common head groups substituted with different alkyl- and functionalized side chains. Also investigated was a set of commonly used IL anions showing a relatively wide polarity range, from comparatively hydrophilic species (*e.g.* dicyanamide and tetrafluoroethanesulfonic acid) to moderately hydrophobic entities (*e.g.* (CF₃SO₂)₂N[−] or B(CN)₄[−]) and to the strongly hydrophobic trifluorotris(pentafluoroethyl)phosphate anion (((C₂F₅)₃PF₃)[−]). The separation of these IL constituents from inorganic matrix-forming ions (Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺ or F[−], Cl[−], Br[−], SO₄^{2−}, HPO₄^{2−}) was achieved for all 30 tested IL structures, depending on the eluent used. Activated sludge samples from biodegradation experiments were chosen for a case study in order to illustrate the performance and the usefulness of the methods developed. The separation and quantification of traces of IL ions in the presence of large numbers of inorganic ions and high organic matrix loads were demonstrated. In general, the analytical system and its associated methods appear to be widely applicable to a broad range of IL structures as well as different technical and natural matrices.

Introduction

In recent years ionic liquids (ILs) have attracted considerable interest owing to their applicability in different fields of technology (summarized in ref. 1), which is based on their advantageous physico-chemical properties (*e.g.* high thermal and electrochemical stability, low vapour pressure and extraction behaviour) of certain compounds in this diverse substance class. This wide applicability of ILs demands reliable analytical techniques, which ideally are applicable to a broad spectrum of different anion and cation moieties. It must be possible to apply these methods not only to different technical or natural matrices but also to the very low concentrations of IL residues likely to be present not only in biological, environmental but also in some technological systems.²

Recently, a number of chromatographic methods for the analysis of cations and anions used in ILs were developed. Alkylimidazolium and alkylpyridinium IL cations were separated using RP-HPLC with ESI-MS and UV detection. The

mobile phases consisted of organic modifiers, aqueous solutions modified with ion pair reagents or different buffer systems, the compositions of which were optimized using the simplex algorithm.^{3–5} Additionally, various stationary phases, mainly those of increased polarity, were tested with the aim of improving the selectivity and specificity of the analytical methods.^{6–8} Furthermore, capillary electrophoresis for resolving selected imidazolium cations was reported as an additional method for analysing IL cations.^{9,10}

The anions were analysed using ion chromatography with conductometric detection¹¹ also with respect to determining the amount of halide impurities in ILs.¹² Moreover, IL cations and anions were determined simultaneously in one chromatographic run.^{13,14} Recently, isotachopheresis was also used to determine IL constituents in very complex matrices such as soil solutions.¹⁵

However, the applicability of the chromatographic systems mentioned is limited with respect to

(i) chromophore-free IL components, which excludes photometric detection;

(ii) IL cations exhibiting a wide range of polarity, and hydrophobic anions;

(iii) the simultaneous separation of IL cations or anions from inorganic ions like Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺ or F[−], Cl[−], Br[−], SO₄^{2−} and HPO₄^{2−} species;

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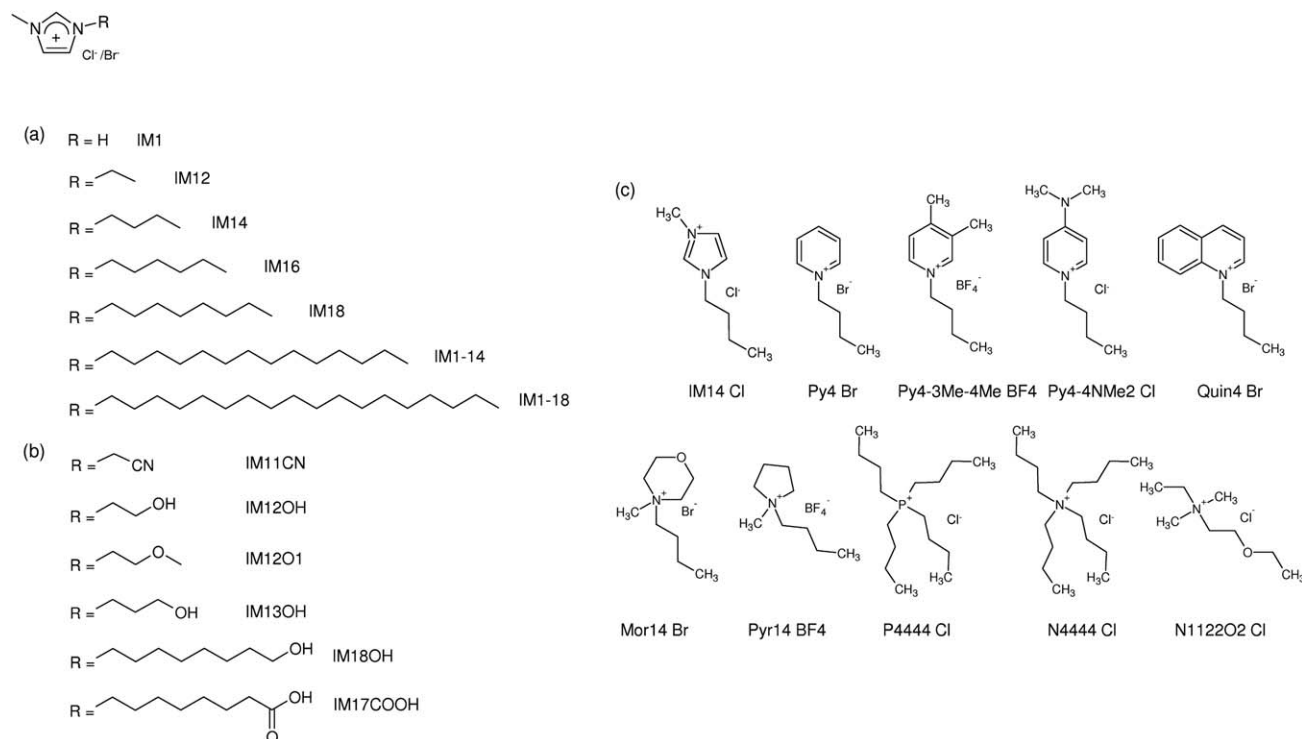


Fig. 1 Structures of the cationic analytes and their abbreviations (a) 1-methylimidazole (precursor) and imidazolium-based ILs with alkyl substituents of different length; (b) imidazolium-based ILs with functionalized side chains; (c) different cyclic (aromatic and aliphatic) and non-cyclic head groups.

(iv) the quantification of traces of IL ions in the presence of large amounts of inorganic ions and of a high organic matrix load of the sample.

Hence, the aim of this study was to develop a novel, fast, relatively simple and robust analytical methodology with low limits of detection that could be applied to a broad spectrum of different anion and cation moieties. Therefore it is not important to separate complex mixtures of different ILs, because this is of minor relevance in the light of environmental or technical questions; rather, the focus should be on the separation of single ILs from different organic/inorganic matrices, from their precursors or from biotic/abiotic degradation products likely to be present in environmental or technical matrices.

To circumvent the above limitations in the analysis of ILs we used an ion chromatographic system connected to a conductometric detector, capable of responding to all charged solutes in the samples. Two methods were developed, which were optimized with regard to the composition of the mobile phase using cation and anion exchange columns. The systematic selection of compounds also allowed us to analyse the influence of the analytes' structure on the separation process within the chromatographic systems used.

To demonstrate the performance of the methods, activated sludge samples from biodegradation experiments were chosen for this case study. Many laboratory test methodologies use activated sludge samples as a source of degrading microorganisms to simulate environmental biodegradation processes. This sludge represents some kind of "worst case" matrix for chromatographic techniques, because of its complex matrix consisting of biological flocs (bacteria, protozoa, rotifers, and higher forms of

invertebrates), biomolecules, simple and complex organic compounds and a broad variety of inorganic ions. Thus, if a method can provide reliable data under these difficult conditions, it is highly likely that it will also be applicable to other complex matrices.

According to recent studies of the biodegradability of ILs,¹⁶ classical biodegradation protocols—mainly applying non-specific sum parameters like dissolved organic carbon (DOC) or CO₂ to follow the course of biodegradation—have to be linked to detailed analytical biodegradation studies. This approach would allow for an evaluation of biodegradation pathways, their kinetics and for the identification of metabolites formed. This information is crucial for assessing the hazards posed by any chemicals under investigation.

Finally, other fields of application will be discussed for the methods developed within this study.

Selection of analytes

The cationic analytes were selected so as to cover the chemical space of IL cations as comprehensively as possible. Therefore, for the imidazolium cation, the most commonly used alkyl side chains from -ethyl to -octadecyl as well as functionalized chains containing -nitrile, -ether, -hydroxyl, and -carboxyl groups were included in the set of analytes (Fig. 1a and b). The most common aromatic (1-methylimidazolium, pyridinium, 4-(dimethylamino)pyridinium, and quinolinium), non-aromatic (4-methylmorpholinium, 1-methylpyrrolidinium) and non-cyclic (quaternary phosphonium and ammonium) cationic head groups were also chosen (Fig. 1c).

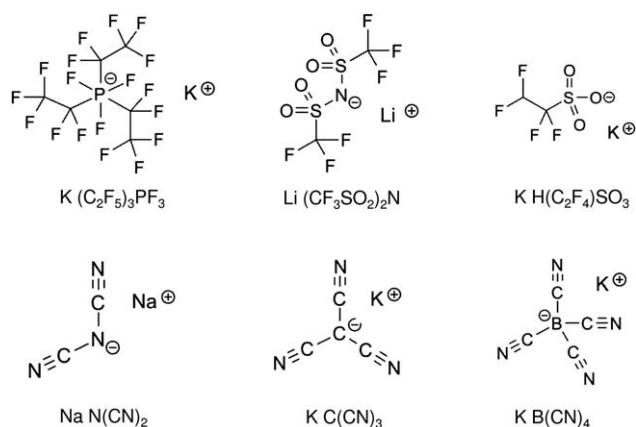


Fig. 2 Structures of the anionic analytes and their abbreviations.

The same strategy was applied to the selection of the anion species to be investigated in this study. We selected a set of commonly used IL anions (Fig. 2) of different polarities, ranging from comparatively hydrophilic anions (*e.g.* dicyanamide and tetrafluoroethanesulfonic acid) to moderately hydrophobic anions (*e.g.* $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ or $\text{B}(\text{CN})_4^-$) and the strongly hydrophobic trifluorotris(pentafluoroethyl)phosphate anion ($((\text{C}_2\text{F}_5)_3\text{PF}_3)^-$).

Materials and methods

Chemicals

The cations were obtained from the following halides and tetrafluoroborates (Merck KGaA, Darmstadt, Germany): 1-ethyl-3-methylimidazolium chloride (IM12 Cl), 1-butyl-3-methylimidazolium chloride (IM14 Cl), 1-hexyl-3-methylimidazolium chloride (IM16 Cl), 1-methyl-3-octylimidazolium chloride (IM18 Cl), 1-methyl-3-tetradecylimidazolium chloride (IM1-14 Cl), 1-methyl-3-octadecylimidazolium chloride (IM1-18 Cl), 1-(cyanomethyl)-3-methylimidazolium chloride (IM11CN Cl), 1-(2-methoxyethyl)-3-methylimidazolium chloride (IM12O1 Cl), 1-methylimidazolium (IM1), 1-(2-hydroxyethyl)-3-methylimidazolium chloride (IM12OH Cl), 1-(3-hydroxypropyl)-3-methylimidazolium chloride (IM13OH Cl), 1-(8-hydroxyoctyl)-3-methylimidazolium bromide (IM18OH Br), 1-(7-carboxyheptyl)-3-methylimidazolium bromide (IM17COOH Br), (2-ethoxyethyl)-*N*-ethyl-*N*,*N*-dimethylammonium chloride (N112O2 Cl), tetrabutylammonium bromide (N4444 Br), tetrabutylphosphonium chloride (P4444 Cl), 1-butyl-3-methylpyrrolidinium tetrafluoroborate (Pyr14 BF_4), 4-butyl-4-methylmorpholinium bromide (Mor14 Br), 1-butylquinolinium bromide (Quin4 Br), *N*-butylpyridinium bromide (Py4 Br), 1-butyl-3,4-dimethylpyridinium tetrafluoroborate (Py4-3Me-4Me BF_4), and 1-butyl-4-(dimethylamino)pyridinium chloride (Py4-4NMe2 Cl).

The anions were obtained from the following salts: lithium bis(trifluoromethylsulfonyl) imide ($\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$), sodium dicyanamide ($\text{Na N}(\text{CN})_2$), potassium tetracyanoborate ($\text{K B}(\text{CN})_4$), potassium trifluorotris(pentafluoroethyl)phosphate ($\text{K}(\text{C}_2\text{F}_5)_3\text{PF}_3$), potassium tricyanomethide ($\text{K C}(\text{CN})_3$), all purchased from Merck KGaA (Darmstadt, Germany).

Potassium 1,1,2,2-tetrafluoroethanesulfonic acid ($\text{K H}(\text{C}_2\text{F}_4)\text{SO}_3$) was obtained from Fluka (Buchs, Switzerland).

The inorganic cations were obtained from the following halides: lithium chloride (LiCl), potassium chloride (KCl), magnesium chloride (MgCl_2), calcium chloride (CaCl_2), all from Merck KGaA (Darmstadt, Germany) and sodium chloride from Fluka (Buchs, Switzerland).

Nitric acid(v) was purchased from Fluka (Buchs, Switzerland) and acetonitrile (HPLC grade) from VWR International (Darmstadt, Germany).

Anhydrous sodium carbonate and sodium bicarbonate and all salts of the inorganic activated sludge media (all pure p.a.) were purchased from the Sigma-Aldrich Corporation (Deisenhofen, Germany).

Ion chromatography

The chromatographic experiments were carried out using a Metrohm 881 Compact IC system (Metrohm, Herisau, Switzerland) equipped with an online eluent degasser, a 20 μL injection loop and a conductometric detector (maintained at $30 \pm 0.1^\circ\text{C}$). A self-regenerating Suppressor Module (MSM) and a CO_2 -suppressor (MCS) (both Metrohm, Herisau, Switzerland) were used to separate and determine the anions. All chromatographic data were recorded by Metrohm software (MagICNet version 1.1 compact). For the cation separations a silica-based (modified with carboxylic groups) Metrosep C4 ion exchange column (dimensions— 50×4.0 mm ID and 5 μm mean particle size) coupled with a Metrosep C4 Guard and a Metrosep RP Guard was used (all purchased from Metrohm, Herisau, Switzerland). A flow rate of 0.9 mL min^{-1} was applied. The mobile phase for cation analysis consisted of varying concentrations of aqueous nitric acid (1 to 4 mM) and different proportions of the organic modifier (acetonitrile). Anion chromatographic separations were performed with a Metrosep A supp ion exchange column (dimensions— 50×4.0 mm ID and 5 μm mean particle size) coupled with a Metrosep A Supp 4/5 Guard and a Metrosep RP Guard (all purchased from Metrohm, Herisau, Switzerland). The packing material consisted of polyvinyl alcohol and quaternary ammonium groups. A flow rate of 0.7 mL min^{-1} was used. The eluent was composed of varying proportions of acetonitrile and an aqueous solution containing 3.2 mM Na_2CO_3 and 1.0 mM NaHCO_3 . In general, all organic and inorganic ionic liquid ions were analysed at a concentration of 100 μM (representing the default concentration within our biodegradation experiments), and the retention factor (k) was calculated according to the expression $\log_{10}k = (R_t - R_0)/R_0$. Here, R_t represents the retention time and R_0 the hold-up time of the system (derived by the peak of the inorganic counter ion of the measured sample).

Activated sludge

Activated sludge was obtained from the wastewater treatment plant in Delmenhorst (northern Germany). The analytical samples consisted of 5 g L^{-1} activated sludge flocs (dry weight $5.05 \pm 0.01 \text{ g L}^{-1}$ containing a bacterial cell number of 10^4 to 10^5 cells), 100 μM of the analysed IL cation or anion, and a solution of an inorganic salt. The cell density was determined by using

paddle testers (Hach company, Loveland, USA). The freshly prepared inorganic media (pH = 7.2) was made up of 8.5 mg L⁻¹ KH₂PO₄, 21.75 mg L⁻¹ K₂HPO₄, 22.13 mg L⁻¹ Na₂HPO₄·2H₂O, 1.7 mg L⁻¹ NH₄Cl, 36.4 mg L⁻¹ CaCl₂·2H₂O, 22.5 mg L⁻¹ MgSO₄·7H₂O, 0.25 mg L⁻¹ FeCl₃. After centrifugation the solutions (5000 rpm, 15 min) were analysed directly in the chromatographic system. In both cation and anion exchange columns, a 2 μm inline filter (Metrohm, Herisau, Switzerland) preceded the guard column, precluding the separate filtration of each biodegradation sample before injection. The inline filter was changed at regular intervals (after about 25 measurements).

The inorganic salt media used, the amounts of activated sludge, and the test chemical concentrations were all chosen to simulate the conditions of biodegradation experiments. These conditions are in accordance with the OECD guideline 301 D (closed bottle test) for the screening of chemicals for ready biodegradability in an aerobic aqueous medium.¹⁷

Results and discussion

Analysis of cations

The influence of the mobile phase composition (concentration of nitric acid and organic modifier) on the separation behaviour of inorganic (Li⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺) and of IL cations (Fig. 1) on a short (50 mm) Metrosep C4 cation exchange column is presented and discussed in the following section.

Influence of HNO₃ concentration on separation

We examined the effect of different nitric acid concentrations (from 1 to 4 mM, constant acetonitrile content of 25%) on the retention factors. As expected, the retention factors increased with decreasing nitric acid concentrations in the case of both the IL cations (Fig. 3) and the inorganic cations (Fig. 4). Generally, for both cation classes the elution order was size-dependent, *i.e.* the larger the ion, the stronger the retardation and the greater the *k* factors. The resolution of IL cations is hardly altered by

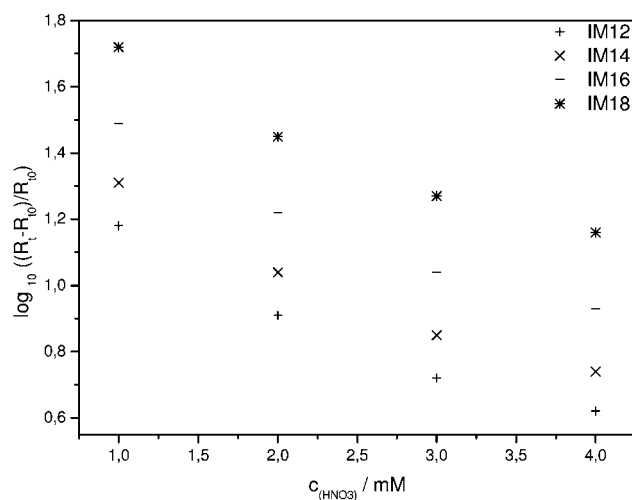


Fig. 3 Influence of HNO₃ concentration on the separation of IL cations. The retention factor of imidazolium-based ILs substituted with different side chains is plotted *versus* the concentration of HNO₃ (1 to 4 mM).

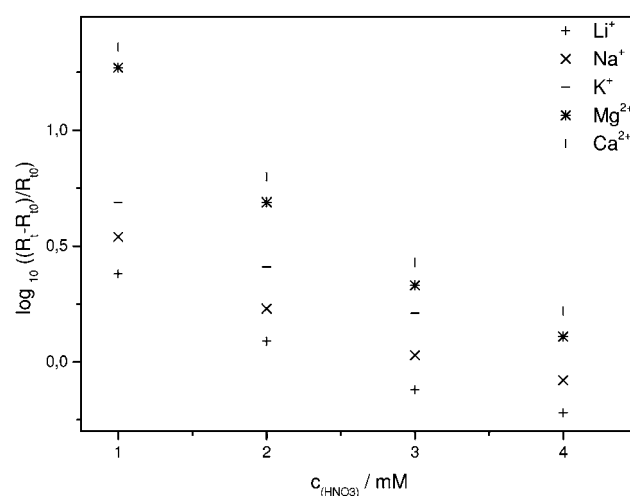


Fig. 4 Influence of HNO₃ concentration on the inorganic cation separation. The retention factor of inorganic cation is plotted *versus* the concentration of HNO₃ (1 to 4 mM).

changing the nitric acid concentration (all compounds of the relation run parallel to each other—see Fig. 3), whereas for inorganic compounds differences between monovalent and bivalent cations were observed. Here, a better resolution between monovalent and bivalent species was obtained with decreasing HNO₃ content (Fig. 4). With regard to the analysis time and separation quality, 2 mM nitric acid seems to represent the ideal eluent. For this mobile phase, baseline separation of a mixture composed of Li⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺ (in this elution order) was achieved within 12 min (data not shown).

Influence of acetonitrile content on separation

The influence of the organic modifier on the retention factors was examined in the range from 0 to 40% acetonitrile by volume and a constant HNO₃ concentration of 2 mM. For monovalent

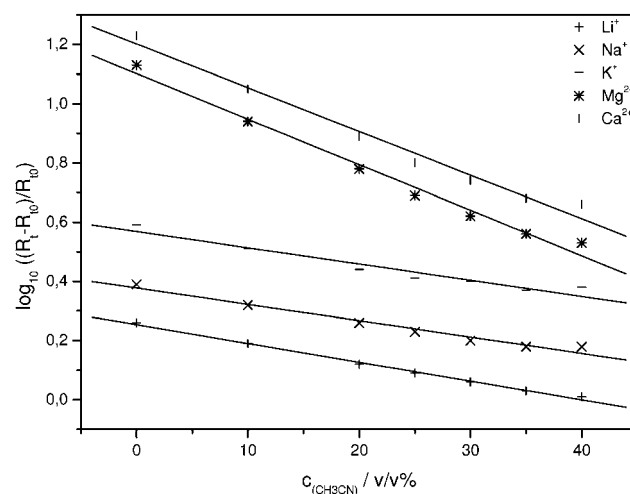


Fig. 5 Influence of acetonitrile on inorganic cation separation. The retention factor of the inorganic cations is plotted *versus* the volume percentage of acetonitrile (0 to 40%) using a constant HNO₃ concentration of 2 mM.

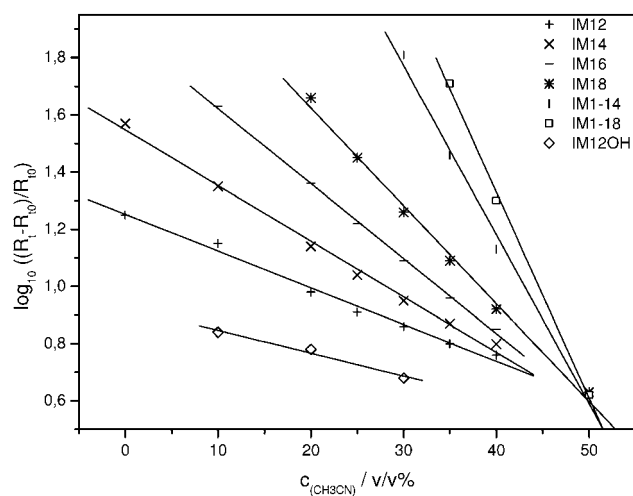


Fig. 6 Influence of acetonitrile on the separation of IL cations. The retention factor of imidazolium-based ILs substituted with different side chains is plotted *versus* the volume percentage of acetonitrile (0 to 50%) using a constant HNO_3 concentration of 2 mM.

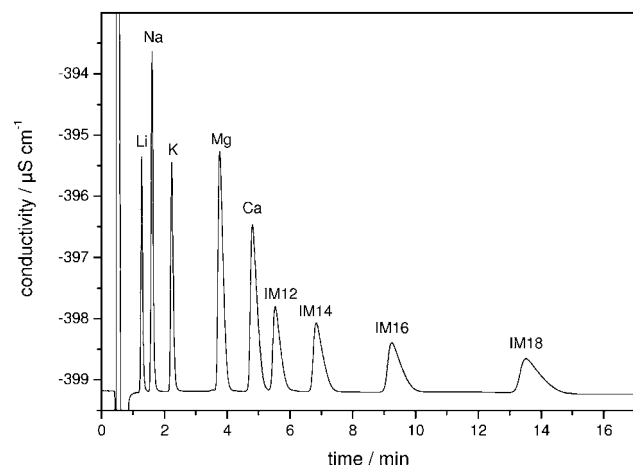


Fig. 7 Example chromatogram of a series of imidazolium-based ILs substituted with different alkyl side chains and inorganic cations.

inorganic cations, just a minor decrease in retention factors was found with increasing organic modifier content (a small slope of the corresponding regression lines; Fig. 5), whereas there was a more conspicuous reduction in the retention factors of the bivalent cations. In general, the resolution was lower with increasing acetonitrile content of the eluent owing to the peak broadening observed for the inorganic cations.

As expected, a smaller retention factor with increasing content of organic modifier was found for different imidazolium-based ILs with substituents of increasing side chain length (-ethyl to

-octadecyl) (see Fig. 6). Generally, the slopes of the regression lines were the larger, the greater the hydrophobicity of the corresponding cation. The strong influence of acetonitrile on markedly hydrophobic organic cations indicates that, apart from ion exchange mechanisms, reversed phase modes of elution—probably due to additional interactions with hydrophobic spacers between the silica-base and the linked carboxylic groups on the stationary phase—also contribute strongly to the separation.

A mixture of inorganic and several alkyl substituted imidazolium based cations (C2 to C8) can be baseline-separated by using, for example, a mobile phase composed of 2 mM nitric acid and 30% organic modifier (Fig. 7). However, with respect to analysis time and peak shape the separation can be easily improved when a less complex mixture is analysed and especially when baseline separation of the inorganic cation is not necessary.

To demonstrate the general applicability of this analytical technique to a broader structural variation, other cationic core structures (Table 1) and functionalized side chains (Table 2) were tested for two eluents. As regards the different head groups, the retention times were found to be size- and hydrophobicity-dependent and could be adjusted *via* the acetonitrile content of the eluent. Baseline separation of all the above-mentioned IL head groups from inorganic cations is achievable, whereas baseline separation of mixtures containing similar substituted IL head groups is possible only on a case by case basis.

Ca^{2+} and Mg^{2+} were co-eluted with different imidazolium-based ILs substituted with short, functionalized side chains and also with the synthetic precursor methylimidazole (Table 2). The influence of the acetonitrile content on retention times was low for different polar ILs such as the IM12OH cation (1-(2-hydroxyethyl)-3-methylimidazolium) (Fig. 6).

For these polar IL cations the use of an eluent composed of 1 mM HNO_3 and a small percentage of acetonitrile (0 to 10%) increased the retention times of Mg^{2+} and Ca^{2+} , whereas the elution times of both monovalent inorganic cations and polar (short-chain/functionalized) ILs were not affected. This made it possible to improve the separation process and to adjust the retention times of these IL cations (potentially overlapping bivalent inorganic cations) in the gap between monovalent and bivalent inorganic cations.

Analysis of anions

A Metrosep A supp anion exchange column was utilized to separate and quantify different commonly used IL anions exhibiting different polarities, ranging from comparatively hydrophilic anions (*e.g.* $\text{N}(\text{CN})_2^-$ and $\text{H}(\text{C}_2\text{F}_4\text{SO}_3)^-$) to moderately hydrophobic anions (*e.g.* $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ or $\text{B}(\text{CN})_4^-$) and to the strongly hydrophobic trifluorotris(pentafluoroethyl)-phosphate anion ($((\text{C}_2\text{F}_5)_3\text{PF}_3)^-$). Here, we focused on the

Table 1 Elution order with respect to acetonitrile for different head groups in comparison to inorganic cations (calcium shown as representative)

Eluent		Retention time of the cation/min									
HNO_3/mM	Acetonitrile (v/v%)	Ca^{2+}	Mor14	Py4	IM14	Pyr14	Py4-3Me-4Me	Py4-4NMe2	Quin4	N4444	P4444
2	20	6.34	7.64	8.84	8.87	9.60	13.21	18.22	19.63	25.98	32.75
2	30	4.90	5.46	6.07	5.94	6.47	7.91	9.58	10.45	11.20	12.85

Table 2 Elution order with respect to acetonitrile for different functionalized side chains in comparison to inorganic cations (calcium shown as representative)

Eluent		Retention time of the cation/min							
HNO ₃ /mM	Acetonitrile (v/v%)	Ca ²⁺	IM1	IM12OH	IM11CN	IM13OH	IM12OI	IM17COOH	IM18OH
2	20	6.34	3.71	4.21	4.62	4.88	6.23	8.34	12.26
2	30	4.90	3.06	3.45	3.71	3.87	4.73	4.87	7.01

separation of these IL anions from anions typically present in biological and technical matrices (Cl⁻, Br⁻, HPO₄²⁻, SO₄²⁻).

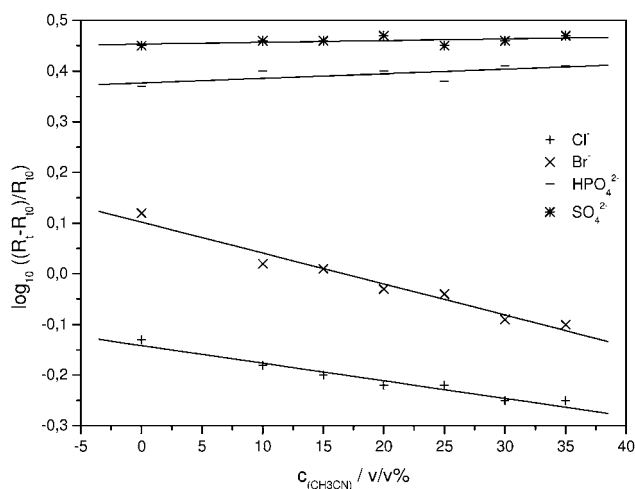
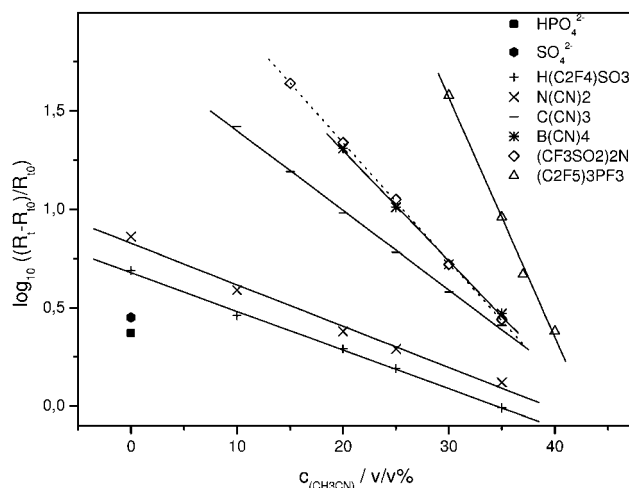
Influence of acetonitrile content on separation

Baseline separation of F⁻, Cl⁻, Br⁻, I⁻, HOPO₃²⁻ and SO₄²⁻ (100 μM each) was possible within 8 min when 100% buffer without additional organic modifier was used (data not shown). The influence of the acetonitrile content on the retention factors of inorganic anions was slight (Fig. 8).

The retention factor of hydrophobic anions (C(CN)₃⁻, B(CN)₄⁻, (CF₃SO₂)₂N⁻, (C₂F₅)₃PF₃⁻) can be almost freely adjusted with respect to the organic modifier (Fig. 9). In the case of the more polar anions (H(C₂F₄)SO₃⁻ and N(CN)₂⁻) the influence of the organic modifier is not so pronounced (Fig. 9). However, baseline separation of all the selected ILs anions from inorganic moieties (Cl⁻, Br⁻, HOPO₃²⁻, SO₄²⁻) and also of complex mixtures of different IL anions can be achieved; solely the B(CN)₄⁻ and the (CF₃SO₂)₂N⁻ anions are inseparable under these chromatographic conditions.

Case study: biodegradation sample

The applicability and validity of the analytical methods presented here have been demonstrated for biodegradation samples of selected imidazolium cations (IM12, IM14, IM16, IM18) and all the anions shown in Fig. 2. Activated sludge samples were

**Fig. 8** Influence of acetonitrile on the separation of inorganic anions. The retention factor of inorganic anions is plotted *versus* the volume percentage of acetonitrile. The eluent was composed of acetonitrile (0–35%) and an aqueous solution containing 3.2 mM Na₂CO₃ and 1.0 mM NaHCO₃.**Fig. 9** Influence of acetonitrile on the separation of IL anions. The retention factor is plotted *versus* the volume percentage of acetonitrile. The eluent was composed of acetonitrile (0–40%) and an aqueous solution containing 3.2 mM Na₂CO₃ and 1.0 mM NaHCO₃.

spiked with the respective IL and after centrifugation (as prepared in the Materials and methods section), each one was directly analysed in the chromatographic systems developed here for cations and anions. All the constituents were well separated from the matrix compounds, enabling easy identification and quantification of the spiked analytes. Table 3 presents the mean recovery rates of the analytes under investigation. In the case of alkylimidazolium cations, recovery rates decrease with increasing hydrophobicity of the compounds analysed; the recovery rate of the most polar IM12 cation was nearly 98%, whereas that of the least polar IM18 was only *ca* 76%. It is likely that the reduced recovery of compounds with longer alkyl chain moieties is due to their stronger sorption to the activated sludge particles, which were separated from the sample by centrifugation directly before the analysis. The trend whereby the tendency of IL cations to be sorbed onto soils, sediments or minerals is higher as their hydrophobicity increases has been observed elsewhere.^{18–20}

In the case of the anions the situation is not so obvious. High recoveries in the range from 100 to 107% were found for

Table 3 Recovery rates of investigated cations and anions

Cation	Recovery in %	Anion	Recovery in %
IM12	98	[(CF ₃ SO ₂) ₂ N] ⁻	100
IM14	93	[B(CN) ₄] ⁻	105
IM16	89	[C(CN) ₃] ⁻	107
IM18	76	[H(C ₂ F ₄)SO ₃] ⁻	89

Table 4 Basic validation parameters of the IL ions investigated

Ion	Repeatability/RSD%	Linearity (<i>R</i>)	LOD/ μ M	LOQ/ μ M
IM12	8.33	0.9999	<0.33	<1.00
IM14	5.34	0.9996	<0.33	<1.00
IM16	5.33	0.9998	<0.33	<1.00
IM18	9.07	0.9995	<0.33	<1.00
$[(F_3CSO_2)_2N]^-$	0.58	0.9999	<0.10	<0.30
$[B(CN)_4]^-$	3.16	0.9986	<0.10	<0.30
$[C(CN)_3]^-$	0.98	0.9993	<0.10	<0.30
$H(C_2F_4)SO_3^-$	1.35	0.9998	<0.10	<0.30
$[(C_2F_5)_3PF_3]^-$	1.69	0.9996	<0.10	<0.30
$[N(CN)_2]^-$	0.72	0.9987	<0.10	<0.30

$(C(CN)_3)^-$, $B(CN)_4^-$, and $(CF_3SO_2)_2N^-$ regardless of their differences in polarity. The lowest recovery, however, was measured for $H(C_2F_4)SO_3^-$ (89%), which may also be related to its potentially strong interaction with particles of activated sludge through dispersive (perfluoroethane fragment) and inter-ionic (sulfonate moiety) interactions.

The basic validation factors of the methods presented here, namely, repeatability, linearity, limits of detection (LOD) and quantification (LOQ), are summarized in Table 4. For both groups of analytes we obtained excellent linearities ($0.9986 < R < 0.9999$) in the concentration range (1 to 300 μ M). Repeatability expressed as relative standard deviation (%) was also satisfactory, ranging from 5.3 to 9.1 in the case of alkylimidazoliums and from 0.58 to 3.2 in the case of the anions. LOD and LOQ for all the cations under investigation were 0.33 and 1.0 μ M respectively, whereas for all the anions these values were 0.1 and 0.3 μ M respectively. Additionally, the long lifetime of both the cation and the anion exchange columns should be mentioned here with respect to the high organic matrix load from the activated sludge samples. So far several hundred activated sludge samples have been measured without a significant decrease in separation performance of the columns when the column regeneration protocol (according to the manufacturer's leaflet) is applied at regular intervals.

Experiential and further potential application

The methods presented in this paper are being used in different research projects of the Centre for Environmental Research and Sustainable Technology, investigating the environmental fate and technical applicability of ILs.

In the field of environmental research the ion chromatographic system was used to determine relevant physicochemical properties such as the solubility in water or the stability of ILs towards hydrolysis and photolysis. Moreover, complex matrices were investigated, including soil samples from sorption experiments as well as samples extracted from cells and organisms (bioaccumulation studies). Besides environmental samples, technical matrices such as process waters following biocatalytic transformations were also successfully analysed. Here, aqueous solutions containing traces of ILs were determined in the presence of cell extracts as well as large amounts of sugars and their metabolites. The details of the methods used and of the validation parameter will be reported in separate papers.

In general, the low LOD and LOQ values for typical levels of contamination by ILs (e.g. halides or synthetic precursors like

pyridine or 1-methylimidazole) provide an opportunity to use these methods for the purity control of ILs.

Conclusions

The analytical methods developed in the present work using an ion chromatographic system allow a broad spectrum of structurally very heterogeneous anions and cations to be analysed. The separation and quantification of traces of IL ions in the presence of large numbers of inorganic ions and high organic matrix loads (activated sludge samples) could be demonstrated. A fast, reliable and reproducible analysis of IL cations and anions with low limits of detection and quantification was achieved. This analytical system and the methods appear to be widely applicable to a broad range of IL structures and different technical and natural matrices.

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