

Ion Chromatography – A Valuable Method for the Quality Control of Ionic Liquids



Tom Beyersdorff, Marcin Gonsior and T.J.S. Schubert
IOLITEC GmbH & Co. KG, Denzlingen, Germany.

Introduction: What are Ionic Liquids?

Ionic Liquids are a new class of salt-like materials, consisting entirely of ions, which are liquid at unusual low temperatures. For the most common definition of Ionic Liquids (probably for emotional reasons) the boiling point of water was chosen as reference value:

„Ionic Liquids is the generic term for materials consisting entirely of ions, which are in the liquid state below 100°C.“

Ionic Liquids build large, but still mobile molecular clusters. As a consequence, they exist in the liquid phase over a large temperature-range, in some cases even up to 300°C. Furthermore, the strong ionic (Coulomb-) interactions causing a negligible low, in some cases not measurable vapour-pressure.

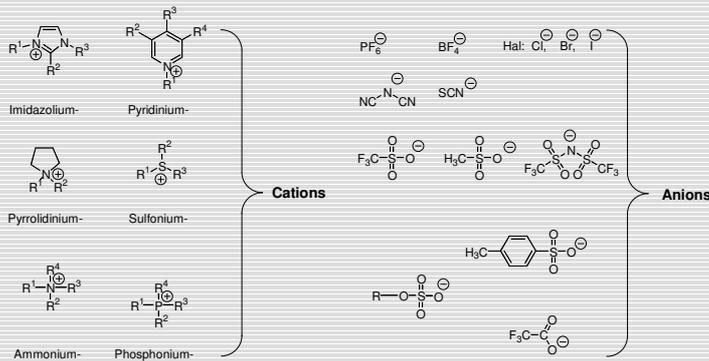


Fig. 1. Structures of common ionic liquids.

Typical structural motifs combine organic cations with inorganic, or, still more rarely, organic anions. If ionic liquids are compared with pure inorganic salts, e.g. with kitchen salt (NaCl, m.p. 801°C), a lower symmetry and a distribution of the charge over larger parts of the molecule by resonance are mainly responsible for the low melting points of ionic liquids.

The combination of a broad variety of already known and theoretically possible cations and anions leads to the number of 10¹⁸ theoretically possible ionic liquids. The actual number of compounds to fall under the above definition, is presumably some magnitudes smaller, but still amazingly high. Today more than 1500 materials are described in literature, more than 300 are commercially available. The physical and chemical properties are only characterized for a few ionic liquids in a sufficient way. So one of the major challenges in ionic liquids research will surely be the determination of physical and chemical data.

Today, ionic liquids are not just used as solvents, but also for physico- and electrochemical applications. In this context, there's a strong need for materials with a defined, reproducible quality. At the beginning of ionic liquids research, exactly this was a crucial point: How can large organic cations and large complex anions be detected next to molecular components as amines or alkyl halides? How is it possible to detect as well impurities like chloride or bromide? The answer is simple: ion chromatography!

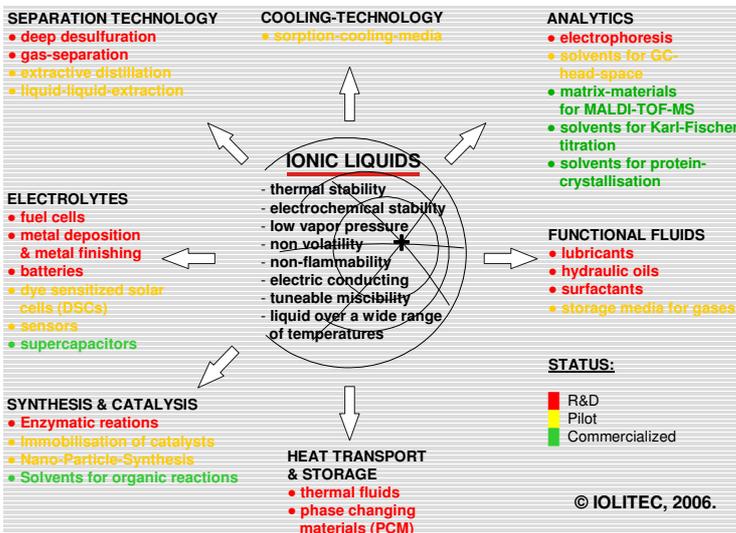


Fig. 2. Status of Realisation of ionic liquids applications.

In co-operation with Deutsche Metrohm (Filderstadt, Germany), IOLITEC established ion chromatography and ion-pair chromatography as the method of choice for the quality control of ionic liquids. With this method it became possible to detect inorganic cations (Na⁺, K⁺) and inorganic anions (Cl⁻, Br⁻) as well as typical organic cations (imidazolium, phosphonium, ammonium) or large and/or complex anions (e.g. tosylate, hexafluorophosphate).

The detection of metal-cations and of chloride and bromide-anions in particular is quite important, since a number of ionic liquids are produced by an exchange of the anions (anion metathesis, Fig. 3).

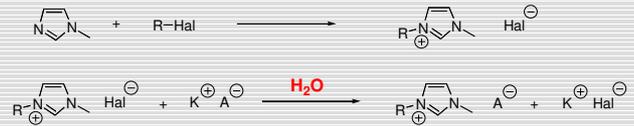


Fig. 3. A typical synthesis pathway: alkylation of 1-methyl-imidazole followed by anion-metathesis.

In this context, an effect that is worth to be noted, is the strong tendency of ionic liquids to form ion pairs: If we go to cation-detection and take e.g. the 1-butyl-3-methyl-imidazolium-cation, this cation is eluted after 17.0 min, if it is combined with a hexafluorophosphate-anion (BMIM PF₆, Fig. 4), but after 22.5 min, if it is combined with a NTf₂-anion (BMIM NTf₂, Fig. 5). Fig. 4 shows as well a sodium-impurity (it was of course the analysis of a competitive product!).



Fig. 4. [BMIM] PF₆.
Eluent: 8.00 mM Tartaric Acid, 0.75 mM 2,6-Pyridindicarboxylic acid in 750 ml water and 250 ml Acetone. PFA: HighFluorophosphate-anion.
Column: Metrohm Metrosep C2 150.

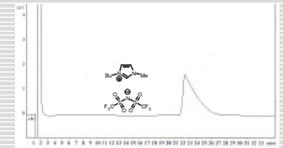


Fig. 5. [BMIM] NTf₂.
Eluent: 8.00 mM Tartaric Acid, 0.75 mM 2,6-Pyridindicarboxylic acid in 750 ml water and 250 ml Acetone. NTf₂ (with BF₄): Bis(trifluoromethyl)ammonium.
Column: Metrohm Metrosep C2 150.

Similar effects are obtained, if we switch to anion chromatography: the thiocyanate-anion from potassium thiocyanate has a retention time of 14.8 min, instead 1-ethyl-3-methyl-imidazolium thiocyanate has a retention time of 23.5 min. Using the same eluent the effect is a bit weaker for dicyanamide: Sodium dicyanamide elutes after 19.9 min, 1-ethyl-3-methyl-imidazolium dicyanamide after 20.6 min. In Fig. 8 and 9, the chloride content of the starting material and the corresponding ionic liquid (at approx. 5 min) is quite evident.

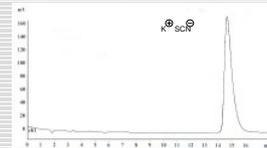


Fig. 6. Potassium thiocyanate.
Eluent: 2.00 mM NaHCO₃, 2.40 mM Na₂CO₃ in 950 ml water vs. 50 ml Acetone.
Column: Metrohm Metrosep A, Supp. 4, with chem. Suppression.



Fig. 7. [EMIM] SCN.
Eluent: 2.00 mM NaHCO₃, 2.40 mM Na₂CO₃ in 950 ml water vs. 50 ml Acetone.
Column: Metrohm Metrosep A, Supp. 4, with chem. Suppression.

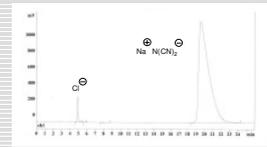


Fig. 8. Sodium dicyanamide.
Eluent: 2.00 mM NaHCO₃, 2.40 mM Na₂CO₃ in 950 ml water vs. 50 ml Acetone.
Column: Metrohm Metrosep A, Supp. 4, with chem. Suppression.

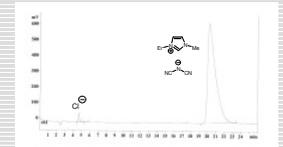


Fig. 9. [EMIM] N(CN)₂.
Eluent: 2.00 mM NaHCO₃, 2.40 mM Na₂CO₃ in 950 ml water vs. 50 ml Acetone.
Column: Metrohm Metrosep A, Supp. 4, with chem. Suppression.

Finally, another interesting fact is that even amines can be detected with ion chromatography: Since the cation eluent is typically acidic, amines such as 1-methylimidazole are protonated – and become detectable cations (Fig. 10).

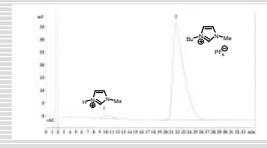


Fig. 10. [BMIM] PF₆ and Protonated MIM.
Eluent: 2.00 mM NaHCO₃, 2.40 mM Na₂CO₃ in 950 ml water vs. 50 ml Acetone.
Column: Metrohm Metrosep A, Supp. 4, with chem. Suppression.

Summary

In conclusion, ion (pair-)chromatography is a powerful method for the detection of impurities and thus for the quality control of ionic liquids.

Contact:

IOLITEC -Ionic Liquids Technologies GmbH & Co. KG
Ferdinand-Porsche-Str. 5/1
D-79221 Denzlingen, Germany
Phone: +49 (0) 7666 - 913929
Fax: +49 (0) 7666 - 9129345
www.iolitec.de, info@iolitec.de

Acknowledgement:

Deutsche Metrohm, Filderstadt (co-operation partner)
Silvia Geng and Yvonne Kiefer (IOLITEC, experiments)