Purity check methods for ionic liquids

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Introduction

Frequently, the purity of ionic liquids used for various studies is not specified. While not every impurity is crucial for every experiment, it is clear that the purity grade has to be assessed in some way or other in order to be able to evaluate the reliability of physical-chemical data, synthetic applications and biological tests. On this poster, we present an overview of the methods that have been applied in our groups facing this challenge.

Titration methods

WATER: Due to the influence of traces of water on the physical-chemical properties of ionic liquids, Karl-Fischer titration using coulometric detection of iodine decrease with specialised instruments is routinely applied. This quick method requires only a small sample size (approx. 0.05 – 0.1 mL), and 10 µg to 5 mg water content per sample, with a detection limit of 0.01 µg water can be determined.

HALIDES: Halide impurities, most frequently stemming from the alkylation of amines or phosphines with alkyl halides in the synthesis of ionic liquids, can be titrated by the Volhard method. However, only relatively high impurity levels of about 1 % wt. halide content can be determined thus. For water-immiscible ionic liquids, we have developed a method which allows for the use of acetone instead of water.

Halide levels in ppm concentrations are best determined using Nessler cylinders. In this semi-quantitative approach, a silver nitrate standard is added to a solution of ionic liquids. The opacity of the sample is then compared to the one obtained in standard halide solutions.

Ion-selective electrodes

HALIDES: The use of ion-selective electrodes, although successfully applied, requires a time-consuming calibration, since the slope and intercept of the calibration depend on the cationic part of the ionic liquid present in the solution. This technique features a reproducibility of the electrode of ± 2 %, if a calibration is carried out regularly. The upper detection limit of the electrode is 1 M of pure aqueous sodium chloride solutions. The lower detection limit is approximately 1.8 ppm, using the calibration technique with 4 standards. The error of measurement was determined to be 3 %.

ALKALI METALS: Alkali metal ions like Na^+ can be quantified by ion-selective electrodes in a similar manner. The lower detection limit in this case is 0.02 ppm for aqueous solutions.

Gas chromatography

Impurities that are volatile at temperatures up to the decomposition of the ionic liquids can be monitored by gas chromatography. In general, these are nonionic substances like the alkyl halides that are frequently used for quaternization of nitrogen or phosphorous, head groups for the cations like methyl imidazolium, quinoline or trialkyl phosphines or possible decomposition products (mainly of cations) like e.g. alkenes or the above head groups. In our quality check for volatile impurities, a combination of head space sampling and liquid injection has been chosen in order to cover an optimum range of possible impurities.

VOLATILES: With headspace-GC using an equilibration time of 30 min at 80 °C and a 50 m x 3 µm SE-54 column, a linear response can achieved for compounds up to the boiling point range of C_{10}-C_{12} alkanes (ca. 180 to 200 °C, cf. Figure 1). Volatile impurities down to 0.01 mg/g expressed as hexane equivalents (depending on FID response) can be detected by this method.

Figure 2 shows a typical chromatogram of such volatile impurities, in this case amounting to 0.6 mg/g hexane equivalents. Impurities detected in real ionic liquid samples with the headspace method ranged up to several mg/g.

SEMI-VOLATILES: In order to capture less volatile impurities, liquid injection on a standard injector (liner filled with quartz wool) can be used. After dosage of 1 µL of the sample solution (e.g. in MeOH/EtOH), the split of the injector is opened in order to remove any decomposition products that may form after volatiles have evaporated. The choice of column is less critical as in the above method, a DB-5 column with 0.25 µm film has proven adequate. By this method, semi-volatile substances up to the boiling point range of C_{24} alkanes can be detected.

Headspace GC

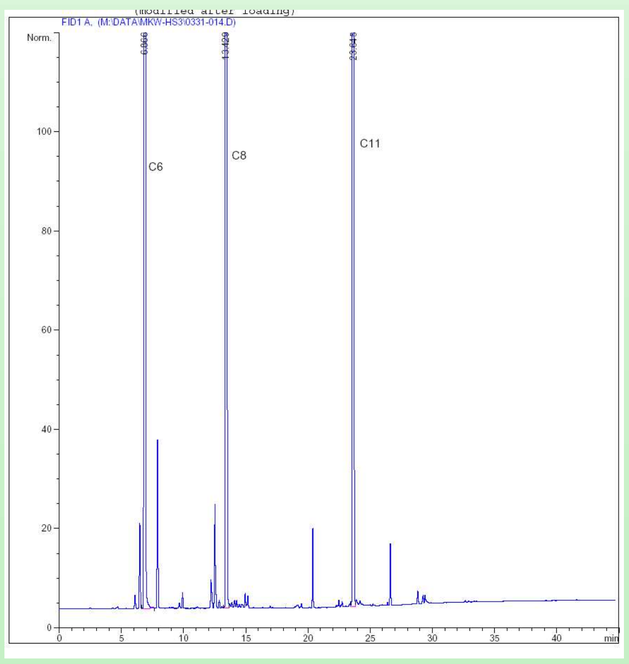

Figure 1: Alkane reference chromatogram

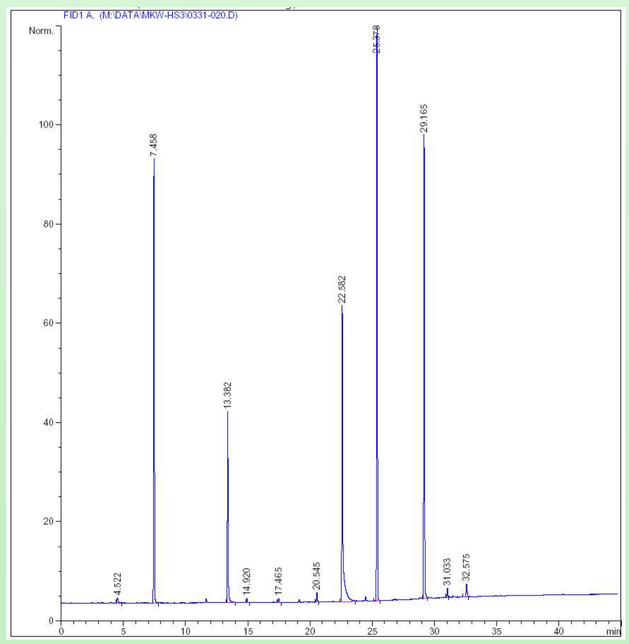

Figure 2: Volatile impurities

HPLC

Reversed-phase HPLC with UV detection was evaluated for the quantification of imidazole in ionic liquids. The isocratic method developed uses an eluent consisting of 30 % acetonitrile, and an aqueous phosphate buffer solution (pH %, 0.02 M). Best separation was obtained on a Hyperchrome 125-4, Prontosil 120-5-C8-SH 5.0 µm, at a flow rate of 1.2 mL / min. with detection at 207 nm. Calibration was carried out (linear range: 10 – 450 mg/L for both imidazoles dissolved in eluent) using either 1-methylimidazole or 1,2-dimethylimidazole, and giving a detection limit of 10 and 20 mg/L respectively. Further advantages include a short analysis time (< 7 min.) and a wide range of applicability as the method is suitable for ionic liquids with alkyl chains up to octyl.

HPLC

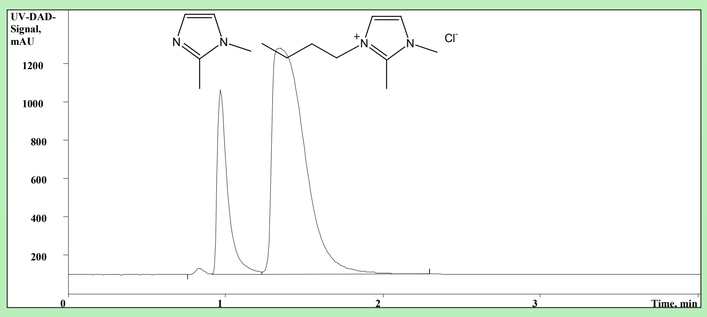

Figure 3: HPLC Chromatogram of a sample of [C_4dmim]Cl (6.092 g/L) with a DMIM content of 7.46 %

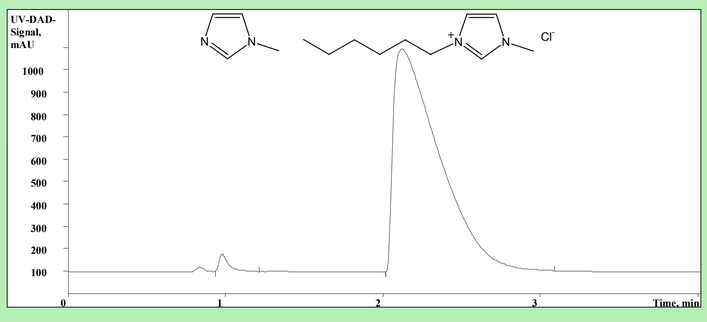

Figure 4:HPLC Chromatogram of a sample of [C_6mim]Cl (5.952 g/L) with a MIM content of 0.52 %.