



## Analysis of quaternary ammonium and phosphonium ionic liquids by reversed-phase high-performance liquid chromatography with charged aerosol detection and unified calibration

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### ARTICLE INFO

#### Article history:

Received 31 July 2008

Received in revised form 1 September 2008

Accepted 5 September 2008

Available online 11 September 2008

Dedicated to Prof. Franz L. Dickert, on the occasion of his 65th birthday.

#### Keywords:

Ionic liquids

Charged aerosol detection

Unified calibration

RP-HPLC

Tetraalkylammonium

Aliquat 336

Trihexyltetradecylphosphonium

Ion-pair HPLC

Thiol/disulfide analysis

### ABSTRACT

Several hydrophobic ionic liquids (ILs) based on long-chain aliphatic ammonium- and phosphonium cations and selected aromatic anions were analyzed by reversed-phase high-performance liquid chromatography (RP-HPLC) employing trifluoroacetic acid as ion-pairing additive to the acetonitrile-containing mobile phase and adopting a step-gradient elution mode. The coupling of charged aerosol detection (CAD) for the non-chromophoric aliphatic cations with diode array detection (DAD) for the aromatic anions allowed their simultaneous analysis in a set of new ILs derived from either tricaprylammonium chloride (Aliquat 336) and trihexyltetradecylphosphonium chloride as precursors. Aliquat 336 is a mix of ammonium cations with distinct aliphatic chain lengths. In the course of the studies it turned out that CAD generates an identical detection response for all the distinct aliphatic cations. Due to lack of single component standards of the individual Aliquat 336 cation species, a unified calibration function was established for the quantitative analysis of the quaternary ammonium cations of the ILs. The developed method was validated according to ICH guidelines, which confirmed the validity of the unified calibration. The application of the method revealed molar ratios of cation to anion close to 1 indicating a quantitative exchange of the chloride ions of the precursors by the various aromatic anions in the course of the synthesis of new ILs. Anomalies of CAD observed for the detection of some aromatic anions (thiosalicylate and benzoate) are discussed.

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### 1. Introduction

The interest in ionic liquids (ILs) regarding their synthesis, characterization and possible applications, is rapidly growing, as the properties of this class of organic salts with melting points below the boiling point of water have gained intensive attention in nearly all fields of chemistry [1–4]. Compared to classical salts with high melting points, low melting ILs generally consist of bulky, non-symmetrical organic cations such as imidazolium, pyrrolidinium, pyridinium, ammonium or phosphonium and numerous different inorganic or organic anions. Their unique properties such as a negligible vapour pressure, good thermal stability, a large liquidus range and tuneable miscibility with water or organic solvents, depending

on their ion combination, offer numerous advantages for a wide application field [1–4]. Their application in analytical chemistry has been demonstrated as stationary phase components for gas chromatography [5,6], running electrolytes for capillary electrophoresis [7–9] and mobile phase additives for high-performance liquid chromatography (HPLC) [10–12].

The by far best investigated group of ILs is based on the imidazolium cation. Consequently, the development of new analytical methods for characterization and purity determination has been concentrated on this type of ILs. Reversed-phase HPLC (RP-HPLC) has been widely used for the separation and analysis of various imidazolium cations employing UV detection and alkyl-bonded [13–18] or phenyl-bonded stationary phases [19] or silica packings with mixed polar and apolar functionalities [14,15]. Furthermore, ion chromatography (IC) [15,20] and capillary zone electrophoresis (CZE) [21–24] have been investigated as potential methods for the separation and purity determination of imidazolium- as well as pyridinium-based ILs.

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In recent years, several working groups investigated a new class of ILs based on the hydrophobic cation of tricaprilymethylammonium chloride (Aliquat 336). By a simple replacement of the chloride anion, several new hydrophobic Aliquat-derived ILs could be generated and tested, e.g. for their applicability as extracting agents for heavy metals or their absorption capacity for organic vapours [25–28]. Due to its ready availability in larger quantities Aliquat 336 represents a relatively cheap source as precursor for the production of new ILs with various anions. As a result of the promising properties of Aliquat-based ILs, more research and new applications are expected in the future. Hence, robust and accurate methods will be needed for the analytical characterization of these ILs such as their impurity determination and quantitative assays. However, several difficulties arise in the course of the analysis of Aliquat-based ILs. First of all, Aliquat 336 is a mixture of quaternary ammonium cations with different alkyl chain lengths rather than a well-defined pure compound. This property makes the quantification of the Aliquat cation, or more explicitly, the cation mix and hence all of its products more complicated. On the other hand, ILs based on quaternary phosphonium cations are already routinely produced by Cytec Industries and are widely used, e.g. as phase-transfer catalysts, solvents, lubricants and chemical sensors [29–33]. However, to our knowledge no applicable method for the liquid chromatographic characterization and/or purity determination of these two classes of ILs is mentioned in the literature. Only few studies addressed the composition analysis of Aliquat 336, e.g. by electrospray ionization mass spectrometry [34] and gas chromatography [35].

Herein, we present a RP-HPLC method with serially coupled diode array detection (DAD) and ESA Analytical Corona charged aerosol detection (CAD) for the analysis of several ILs based on the Aliquat cations and different aromatic anions, as well as for corresponding phosphonium-based ILs. Since the quaternary ammonium and phosphonium cations lack chromophoric groups, they cannot be detected with conventional UV-absorption detection, which is generally very attractive due to its wide linear range, relatively low cost and compatibility with most solvents used as mobile phase in both isocratic and gradient elution mode. This problem can be overcome by CAD, which is capable of detecting most non-volatile compounds irrespective of their spectral properties [36]. The principle of CAD is fairly simple. The effluent from the chromatographic system is nebulized with nitrogen and the volatile components are evaporated in a drying tube at ambient temperature minimizing the risk for analyte degradation. The non-volatile finely dispersed analyte particles are charged by charge transfer from ionized nitrogen, which is generated by flowing the gas over a corona discharge needle. The resultant current from the charged aerosol particles is finally measured by an electrometer [37]. CAD has been reported to be more sensitive than evaporative light scattering detection (ELSD) [38] showing a dynamic range up to 4 orders of magnitude. Unlike the concentration-dependent UV-absorption detection, CAD is a mass-dependent detection method. It generates a similar response for equal mass of analyte. This may provide the basis for the feasibility to perform a unified calibration with a single standard and use this calibration function for all other compounds or impurities for which no standards are available. The main drawback is that the CAD response may vary with the mobile phase composition, which is related to the nebulizing system [39]. An increase in the organic content of the mobile phase leads to a higher signal. An empirical solution for the compensation of this problem in gradient elution HPLC was recently proposed by Górecki et al. by postcolumn admixing an exactly inverse gradient so that a constant organic modifier content reached the CAD system [36].

Since the introduction of CAD by Dixon and Peterson [40], it has gained popularity in the pharmaceutical industry for the detec-

tion of compounds lacking UV-absorbing chromophores including carbohydrates, lipids and amino acids [41–43].

In this study, the combination of CAD with DAD allowed the simultaneous analysis of ILs with quaternary ammonium and phosphonium cations, lacking a chromophore group, and UV-absorbing aromatic anions. Such ILs composed of aromatic anions with functional groups have been shown to be suitable as extracting agents for heavy metals [26]. The application of CAD as add-on to UV detection enabled a sensitive quantitative analysis of analytes for which no standards were available, as in the case of Aliquat 336, employing a unified calibration function. In order to examine the applicability for quantitative analysis, a preliminary method validation was carried out and the developed method was finally applied to measure the molar ratios of the ionic constituents in the selected ILs.

## 2. Experimental

### 2.1. Materials

The structures of the ILs and their precursors (tricaprilymethylammonium chloride, tetradecyltriethylphosphonium chloride) used in this study are depicted in Fig. 1. 2-(Methylthio)benzoic acid (MTBAH) and ILs were synthesized according to the method reported in the literature [26,44]. All synthesized substances were characterized via one- and two-dimensional NMR spectroscopy. Additionally, the chloride content of each IL was determined and found to be always below 1% (w/w).

The standard substances Aliquat 336 (Aldrich, Vienna, Austria, purum >97%), thiosalicylic acid (TSH, Fluka, Buchs, Switzerland, purum >97%), benzoic acid (BAH; Riedel-de Haën, Seelze, Germany, purum >99%), (phenylthio)acetic acid (PTAH; Aldrich, purum 96%), hexadecyltrimethylammonium bromide ([HA][Br]; known as cetyltrimethylammonium bromide, CTAB; Fluka, puriss. analytical-reagent grade >99%) and trihexyltetradecylphosphonium chloride (PR<sub>4</sub>Cl; Fluka, purum >95%) were purchased from Sigma–Aldrich (Vienna, Austria), and used as received without further purification. Tris(2-carboxyethyl)phosphine hydrochloride (TCEP; from Fluka) was employed for reduction of thiosalicylic acid-containing samples. Acetonitrile (ACN) of HPLC grade (VWR, Vienna, Austria), trifluoroacetic acid (TFA; Fluka, for HPLC, ≥98.0%) as well as distilled water filtered through a Milli-Pore (Milli-Q) water-purification system to 18.2 MΩ quality were used for the preparation of the mobile phases.

### 2.2. Instrumentation and chromatographic conditions

HPLC experiments were carried out using the Agilent 1100 series LC system equipped with quaternary pump, autosampler, vacuum degasser, diode array detector, temperature-controlled column compartment (Agilent, Waldbronn, Germany) and Corona CAD (charged aerosol detector, ESA Analytical, Aylesbury, UK). The DAD and CAD systems were connected in series, attaching the outlet of the DAD system to the inlet of the CAD system. The nitrogen inlet pressure and flow rate for the CAD system were set to 35 psi (241.3 kPa) and 1.53 L/min. The DAD wavelength range was chosen from 200 to 400 nm, with a data acquisition rate at 2 Hz; the absorption signal at 250 nm was used for quantitation of the anions of all ILs. The data were processed with the Agilent ChemStation software (Rev. A. 10.01).

Unless otherwise stated all HPLC experiments were performed using 0.1% TFA in water as eluent A and HPLC grade acetonitrile with 0.1% TFA as eluent B. The final optimized method made use of the following step-gradient elution mode: 40% B from 0 to 10 min, then

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