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Original article

Hydrophilic interaction liquid chromatography with indirect ultraviolet detection for the separation and quantification of pyrrolidinium ionic liquid cations

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ABSTRACT

A method of hydrophilic interaction liquid chromatography with indirect ultraviolet detection was developed to determine three pyrrolidinium ionic liquid cations, *i.e. N*-methyl-*N*-ethyl pyrrolidinium cation ($[MEPy]^+$), *N*-methyl-*N*-propyl pyrrolidinium cation ($[MPPy]^+$) and *N*-methyl-*N*-butyl pyrrolidinium cation ($[MBPy]^+$). Chromatographic separation was achieved on a hydrophilic column using imidazolium ionic liquids and organic solvents as the mobile phase. The effects of the background ultraviolet absorption reagents, the imidazolium ionic liquids, detection wavelength, organic solvents, column temperature and the pH value of the mobile phase on the separation and determination of pyrrolidinium cations were investigated and the retention behaviors in hydrophilic interaction chromatography were discussed. The optimized chromatographic conditions were selected. Under the optimal conditions, the detection limits ($S/N = 3$) for $[MEPy]^+$, $[MPPy]^+$ and $[MBPy]^+$ were 0.59, 0.53 and 0.46 mg/L, respectively. The method has been successfully applied to the determination of the three ionic liquids synthesized in our chemistry laboratory. This research results may improve the analytical method of ionic liquid cations.

1. Introduction

Ionic liquids (ILs), resulting from the combination of organic cations and inorganic or organic anions, can be defined as organic salts that are liquid at or near room temperature. In order to meet the specific needs, the structure and types of ILs cations or anions should be modified. They possess non-volatile, extended liquid-state temperature range, strong dissolving ability and easily tunable properties. These unique physicochemical properties contributed to the creation of new applications [1,2]. With the expansion of the application scope of ILs, the method of detection and separation of ILs become very important [3]. Currently, the methods for the determination of ionic liquid cations mainly included reversed phase liquid chromatography (RPLC) [4], ion-pair chromatography (IPC) [5,6], ion chromatography (IC) [7] and hydrophilic interaction chromatography (HILIC) [8,9], *etc.* HILIC [10] is one of emerging areas in chromatography research in recent years. It is a chromatographic technique used to improve the poor retention behaviors of polar substances in RPLC. The determination of pyrrolidinium ionic liquid cations has been scarcely reported, and some experiments have been conducted using RPLC and IC [11,12]. The RPLC method was not recommended for analysis of pyrrolidinium cations whose alkyl side chains was shorter than 4 carbon atoms, since its retention and selectivity were poor, thus adding ion pair reagent was needed. IC with a conductivity detector used the specialized ion chromatography instruments. As a general application in laboratory, UV detector has been widely paired with liquid chromatography to detect compounds with UV group absorbance. For compounds with no UV absorbance groups, indirect ultraviolet (IUV) detection has been a suitable method [13]. The method was achieved by adding materials having UV absorption groups as background reagents to the mobile phase. Recently, research and applications of the HILIC-UV detection have been reported [8,9], but the research and applications of the relevant HILIC-IUV detection have not been reported.

The goal of this work was to develop a method to analyze pyrrolidinium ionic liquid cations that have side chains with carbon atoms fewer than 4 by HILIC with IUV detection. Results showed that the retention of strongly polar substances was improved compared to the RPLC method. The separation and IUV

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detection of pyrrolidinium cations were achieved on a hydrophilic column using imidazolium ILs and organic solvents as the mobile phase, and the method was simple and practical.

2. Experimental

The ILs (99% purity) were *N*-methyl-*N*-ethyl pyrrolidinium bromide ([MEPy][Br]), *N*-methyl-*N*-propyl pyrrolidinium bromide ([MPPy][Br]), *N*-methyl-*N*-butyl pyrrolidinium bromide ([MBPy][Br]), 1-ethyl-3-methyl imidazolium tetrafluoroborate ([EMIm][BF$_4$]), 1-propyl-3-methyl imidazolium tetrafluoroborate ([PMIm][BF$_4$]), 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIm][BF$_4$]), 1-amyl-3-methyl imidazolium tetrafluoroborate ([AMIm][BF$_4$]), 1-ethyl-3-methyl imidazolium trifluoroacetate ([EMIm][CF$_3$COO]), 1-ethyl-3-methyl imidazolium p-toluenesulfonate ([EMIm][C$_7$H$_7$SO$_3$]) and 1-ethyl-3-methyl imidazolium methanesulfonate ([EMIm][CH$_3$SO$_3$]) purchased from Shanghai Chengjie Chemical Ltd. (Shanghai, China). 4-Aminophenol hydrochloride, sulfosalicylic acid, nicotinamide and phthalic acid (analytical grade) were supplied by J&K Chemical Ltd. (Beijing, China). Methanol and acetonitrile (HPLC grade) were obtained from Dikma Technologies (Shanghai, China). Acetic acid and sodium hydroxide (analytical grade) were obtained from Shanghai reagent factory (Shanghai, China).

Standard solutions of ionic liquid cations at a concentration of 1 g/L were prepared in acetonitrile and deionized water (50/50, v/v), and then diluted to the concentration required for the experiment. They were then filtered through a 0.22 μm membrane.

A Millipore Milli-Q water purification system (Millipore, Bedford, MA, USA) was used to purify distilled water, and the deionized water produced at 18.2 MΩ cm was prepared for eluents and sample solutions. A model PHSF-3F pH meter (Shanghai Precision and Scientific Instrument, Shanghai, China) was used for pH measurement. Before use, mobile phases were filtered through a 0.22 μm filter, and then degassed for 15 min with a Model DOA-P504-BN pump (IDEX, USA).

All experiments were carried out on an Agilent 1200 HPLC system (Agilent, USA), which consisted of a quaternary pump (Model Quat pump-G1311A), a detector (Model DAD-G1315D), an autosample injector (Model ALSG1329A), a column oven (Model TCC-G1316A) and a degasser system (Model Degasser-G1322A). The chromatographic system control, data acquisition and data analysis were performed using the Agilent Rev.B.04.01 workstation (Agilent, USA).

All separations were performed on a 4.6 mm i.d. × 250 mm TSK-GEL Amide-80 HR column (TOSOH, Japan). The optimal mobile phase consisted of 0.8 mmol/L 1-ethyl-3-methyl imidazolium tetrafluoroborate aqueous solution/acetonitrile (40/60, v/v). The flow rate was set at 1.0 mL/min. The column temperature was 30 °C. The injection volume was 20 μL. IUV (210 nm) was employed.

3. Results and discussion

Pyrrolidinium cations have no UV absorption groups in their molecular structures, thus the addition of background UV absorbing reagents to the mobile phase is needed for the IUV detection method. The detection of pyrrolidinium cations was investigated using 4-Aminophenol hydrochloride, sulfosalicylic acid, nicotinamide and phthalic acid as background UV absorbing reagents at their respective maximum wavelength. The mobile phase used was a background UV absorbing reagent aqueous solution/acetonitrile (40/60, v/v). As a result, when sulfosalicylic acid, nicotinamide and phthalic acid were used as the mobile phase, there were no chromatographic peaks of pyrrolidinium cations appeared; when 4-Aminophenol hydrochloride was used as the mobile phase, although the peaks had appeared, the peak shape was poor and the separation of cations was not satisfactory. The imidazolium ionic liquid cations has a strong UV absorption. Using imidazolium ILs as the background UV absorbing reagents, with a 0.5 mmol/L 1-ethyl-3-methyl imidazolium tetrafluoroborate aqueous solution/acetonitrile (40/60, v/v) as the mobile phase, and under the maximum UV absorption wavelength of 210 nm, three pyrrolidinium cations were measured. From the chromatograms, it can clearly be seen that chromatographic peaks of the cations appeared. Based on this result, we used imidazolium ILs as the background UV absorbing reagent.

In order to investigate the effects of different imidazolium ILs with various alkyl groups on the determination of three pyrrolidinium cations, four imidazolium ILs [EMIm][BF$_4$], [PMIm][BF$_4$], [BMIm][BF$_4$] and [AMIm][BF$_4$] were examined as mobile phase components. The mobile phase used was imidazolium ionic liquid aqueous solution/acetonitrile (40/60, v/v). As shown in Fig. 1, in contrast to the RPLC, the HILIC had an elution order of which the less polar substances were eluted first and the more polar substances were eluted later. Alpert [10] confirmed that the reason was water in mobile phase adsorbed at the surface of the stationary phase, thus a dynamic "water-rich layer" is formed in which the polar substances were better retained, the retention of solutes was achieved by its partition between the water-rich layer and the organic phase. It was found that with the increase of the lengths of the alkyl substituent of imidazolium cation from ethyl to amyl led to shortened retention time of the cations. The longer alkyl chain length on the imidazole ring is, the less polar is the cation. Long alkyl chains attached on imidazolium cation weakened the polarity of the mobile phase, thus the analytes can be better retained in the stationary phase. When [BMIm][BF$_4$] and [AMIm][BF$_4$] were used as a mobile phase component, separately, the analytes' retention time was longer than the cases where [PMIm][BF$_4$] or [EMIm][BF$_4$] were used as a mobile phase, and the response of the analytes was low. Considering the factors of retention time and peak shape, [EMIm][BF$_4$] was selected as the mobile phase component.

The effect of [EMIm][BF$_4$] concentration on the determination of pyrrolidinium cations was investigated using [EMIm][BF$_4$] aqueous solution/acetonitrile (40/60, v/v) as the mobile phase. The concentrations of [EMIm][BF$_4$] were investigated at 0.3, 0.5, 0.8, 1.0 and 1.2 mmol/L and the results are shown in Table 1. The results showed that the retention times of pyrrolidinium cations

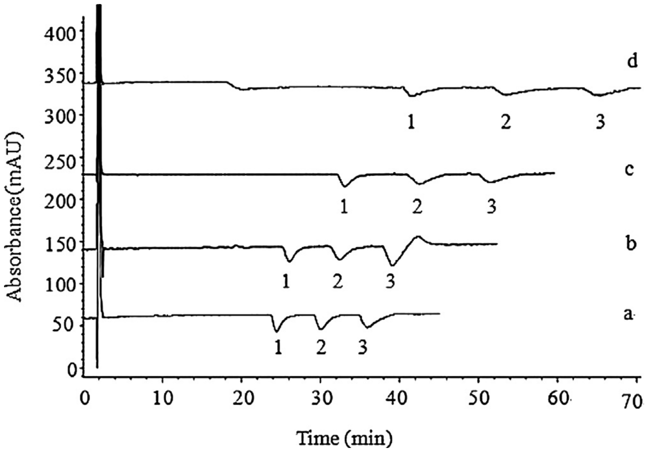

Fig. 1. Chromatograms obtained with mobile phases containing different imidazolium ILs. Chromatographic conditions: mobile phase, 0.5 mmol/L imidazolium ILs aqueous solution/acetonitrile (40/60, v/v); column, TSK-GEL Amide-80 HR (4.6 mm i.d. × 250 mm, 5 μm). Imidazolium ILs: a, [EMIm][BF$_4$]; b, [PMIm][BF$_4$]; c, [BMIm][BF$_4$]; d, [AMIm][BF$_4$]. Peaks (mg/L): 1, [MBPy]$^+$ (50); 2, [MPPy]$^+$ (50); 3, [MEPy]$^+$ (50).