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Original article

Imidazolium ionic liquid as the background ultraviolet absorption reagent for determination of morpholinium cations by high performance liquid chromatography-indirect ultraviolet detection

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ABSTRACT

A novel analytical method was developed for determining morpholinium cations lacking ultraviolet absorption groups. This determination was carried out by high performance liquid chromatography-indirect ultraviolet (HPLC-IUV) detection using imidazolium ionic liquid as background absorption reagents, and imidazolium ionic liquid aq. soln.–organic solvent as mobile phase by a reversed-phase C18 column. The background ultraviolet absorption reagents, imidazolium ionic liquids and organic solvents were investigated. The imidazolium ionic liquid in the mobile phase is not only the background ultraviolet absorption reagent for IUV, but also an active component to improve the separation of morpholinium cations. It was found that morpholinium cations could be adequately determined when 0.5 mmol/L 1-ethyl-3-methylimidazolium tetrafluoroborate aq. soln./methanol (80:20, v/v) was used as mobile phase with an IUV detection wavelength of 210 nm. In this study, the baseline separation of *N*-methyl, ethylmorpholinium cations (MEMo) and *N*-methyl, propylmorpholinium cations (MPMo) was successfully achieved in 8.5 min. The detection limits (S/N = 3) for MEMo and MPMo were 0.15 and 0.29 mg/L, respectively. This simple and practical method has been successfully applied to the determination of two morpholinium ionic liquids synthesized by the chemistry laboratory.

1. Introduction

Ionic liquids (ILs) are a broad class of salts that are composed of organic cations (*e.g.*, alkylimidazolium, alkylpyridinium, alkylmorpholinium) and inorganic or organic anions. The ILs with the unique properties of low vapor pressure, incombustibility, good thermal stability, strong dissolving ability and electrolytic conductivity could be widely applied in the fields of catalytic chemistry, organic synthesis, electrochemistry and analytical chemistry [1–4]. In recent years, various methods were developed for the separation and detection of ILs [5], such as reversed-phase liquid chromatography (RPLC) [6–9], ion chromatography (IC) [10], ion-pair chromatography (IPC) [11], hydrophilic interaction chromatography (HIC) [12,13] and capillary electrophoresis (CE) [14]. Among them, RPLC has received much attention. In previous reports, the determinations of ILs principally focus on imidazolium and pyridinium cations [6–13], since one of the most important advantages of these cations was strong ultraviolet (UV) absorption, which makes the detection easier. However, the determinations of cations lacking UV absorption groups (morpholinium cations) have not been reported thus far.

Detection by UV is the common detection technique in high performance liquid chromatography (HPLC) to determine the materials with a UV absorption group. To be useful, two other effective methods could be used to deal with the analytes without UV absorption in HPLC-UV. One way is derivatization. We can attach, *via* chemical reaction, strong UV absorption groups to the structures of the measured molecule, so as to directly detect the samples, but it is a complex method. The other method is by indirect ultraviolet (IUV) detection. The HPLC-IUV technique entails adding materials with UV absorption as background UV absorption reagents to the mobile phase to permit detection of analytes lacking UV absorption. So far, there are only a few reports focusing on HPLC-IUV [14–16], and the main objects of analysis are hydrocarbons and inorganic ions.

The aim of this work was to determine morpholinium cations without UV absorption by HPLC-IUV utilizing imidazolium ionic liquid as the background UV absorption reagent. Chromatographic

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separation was performed on a reversed phase C18 column using imidazolium ionic liquids–organic solvents as mobile phase. The effects of the background UV absorption reagents, imidazolium ionic liquids and organic solvents on the determination of morpholinium cations were investigated. A simple and practical HPLC-IUV method was developed for the determination of morpholinium cations.

2. Experimental

The ILs (≥99% purity) were *N*-methyl, ethylmorpholinium bromide ([MEMo]Br), *N*-methyl, propylmorpholinium bromide ([MPMo]Br), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm]BF_4), 1-propyl-3-methylimidazolium tetrafluoroborate ([PMIm]BF_4), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF_4), 1-amyl-3-methylimidazolium tetrafluoroborate ([AMIm]BF_4), respectively. These ILs were purchased from Shanghai Chengjie Chemical Ltd. (Shanghai, China). 4-Aminophenol hydrochloride, 5-sulfosalicylic acid, nicotinamide and phthalic acid (analytical grade) were purchased from J&K Chemical Ltd. (Beijing, China). Methanol and acetonitrile (HPLC grade) were obtained from Dikma Technologies (Shanghai, China).

Standard solutions of all morpholinium cations were prepared in 18.2 MΩ cm deionized distilled water from a Millipore Milli-Q water purification system (Millipore, Bedford, MA, USA). Stock standard solutions were prepared monthly. Working standard solutions were prepared daily, as needed, from the respective stock solutions. The working solutions were filtered using a 0.22 μm membrane filter before injection.

Milli-Q water was also used to prepare the mobile phases. Aqueous solutions of imidazolium ionic liquids were prepared at appropriate concentrations. The mobile phases were filtered through a 0.22 μm filter, and then degassed for 10 min using DOA-P504-BN pump (IDEX, CHI, USA).

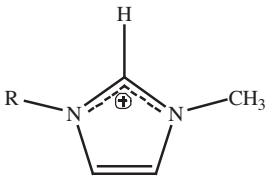
The entire chromatographic experimentation was carried out on an Agilent 1200 HPLC system (Agilent, USA), which consisted of a quaternary pump (Model Quat pump-G1311A), a detector (Model DAD-G1315D), an autosampler injector (Model ALS-G1329A), a column oven (Model TCC-G1316A) and a degasser system (Model Degasser-G1322A). The chromatographic system control and data analysis were performed using the Agilent Rev.B.04.01 workstation.

All separations were performed on a ZORBAX Eclipse XDB-C18 column (150 mm × 4.6 mm, i.d., 5 μm, Agilent, USA). The suitable mobile phase was 0.5 mmol/L [EMIm]BF_4 aq. soln./methanol (80:20, v/v). The flow rate was set at 1.0 mL/min. Column temperature was 30 °C. The injection volume was 20 μL. Indirect UV detection (210 nm) was employed.

3. Results and discussion

Since there were no UV absorption groups in the molecular structure of the morpholinium cations, so in order to detect these cations by UV detection, the background UV absorbing reagents were added to the mobile phase. As previous reported, 4-aminophenol hydrochloride [16], 5-sulfosalicylic acid [17], nicotinamide [17] and phthalic acid [17] were used as common background UV absorbing reagents. In this study, 0.5 mmol/L 4-aminophenol hydrochloride/methanol (80:20, v/v), 0.5 mmol/L 5-sulfosalicylic acid/methanol (80:20, v/v), 0.5 mmol/L nicotinamide/methanol (80:20, v/v), and 0.5 mmol/L phthalic acid/methanol (80:20, v/v) were chosen as the mobile phases for detecting *N*-methyl, ethylmorpholinium cation (MEMo) and *N*-methyl, propylmorpholinium cation (MPMo) when the detection wavelengths were 240 nm, 297 nm, 268 nm and 255 nm, respectively. All the results show that the chromatographic peaks, *i.e.*, detector responses, of these two morpholinium cations do not appear.

Table 1
The structures of imidazolium ionic liquid cations.

Imidazolium ionic liquid cations	R	Structure
EMIm	CH_3CH_2	
PMIm	$CH_3CH_2CH_2$	
BMIm	$CH_3CH_2CH_2CH_2$	
AMIm	$CH_3CH_2CH_2CH_2CH_2$	

Ionic liquids are "green solvents", and some ionic liquids, such as imidazolium ionic liquids, have UV absorption groups in their molecular structures, so we considered using imidazolium ILs as the background UV absorbing reagents. With regard to imidazolium ILs, [EMIm]BF_4 is commonly used, and therefore it was initially chosen as the background UV absorbing reagent since [EMIm]BF_4 has strong UV absorption at 210 nm. When the determination of MEMo and MPMo was performed using [EMIm]BF_4 aq. soln./methanol as mobile phase at 210 nm, we can clearly see the chromatographic peaks (responses) of the cations in the chromatogram. Therefore, in the following investigations, we use imidazolium ILs ([EMIm]BF_4) as the background UV absorbing reagent.

Although the maximum absorption wavelength of [EMIm]BF_4 is 200 nm, the organic solvents (methanol) also have strong absorption at this wavelength. In order to avoid interferences, the detection wavelength at 210 nm was chosen since it was found that the chromatographic baseline was stable under this condition.

In order to investigate the influence of different imidazolium ILs with various alkyl groups on the determination of morpholinium cations MEMo and MPMo, four imidazolium ILs [EMIm]BF_4, [PMIm]BF_4, [BMIm]BF_4 and [AMIm]BF_4 were examined as mobile phase components, respectively. The structures of imidazolium ionic liquid cations are shown in Table 1. The mobile phases used were imidazolium ionic liquid aq. soln./methanol (80:20, v/v). As shown in Fig. 1, the retention times of MEMo and MPMo were clearly decreases as the lengths of the alkyl substituent of the imidazolium cation increases from ethyl to amyl. With growing alkyl chain lengths on the imidazole ring, the polarity of the cation

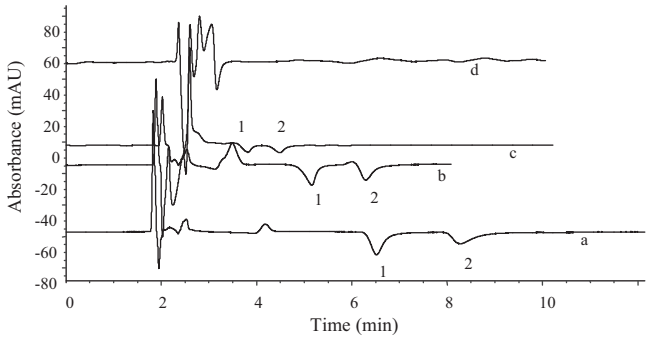


Fig. 1. Chromatograms obtained with mobile phases containing different imidazolium ionic liquids. (a) Mobile phase, 0.5 mmol/L [EMIm]BF_4 aq. soln./methanol (80:20, v/v); (b) mobile phase, 0.5 mmol/L [PMIm]BF_4 aq. soln./methanol (80:20, v/v); (c) mobile phase, 0.5 mmol/L [BMIm]BF_4 aq. soln./methanol (80:20, v/v); (d) mobile phase, 0.5 mmol/L [AMIm]BF_4 aq. soln./methanol (80:20, v/v). Chromatographic conditions: column, ZORBAX Eclipse XDB-C18 column (150 mm × 4.6 mm, i.d., 5 μm); flow rate, 1.0 mL/min; column temperature, 30 °C; indirect UV detection, 210 nm; inject volume, 20 μL. Peaks (mg/L): 1, MEMo (31.0); 2, MPMo (32.2).