CHINESE JOURNAL OF ANALYTICAL CHEMISTRY
Volume 38, Issue 7, July 2010
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com

Cite this article as: Chin J Anal Chem, 2010, 38(7), 1003–1006.

RESEARCH PAPER

Phosphonium Ionic Liquids as Stationary Phases in Gas Chromatography

ZHU Hai-Yan, LU Xian-Bo, TIAN Yu-Zeng, CHEN Ji-Ping*
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Abstract: As a relatively new material, ionic liquids (ILs) have attracted increasing attention in recent years because of their unique properties and potential applications in many fields. In this study, a phosphonium-based IL (tetra-butyl phosphonium methanesulfonate), which possessed high thermal stability and large viscosity, was systematically investigated as a stationary phase for gas chromatography. The IL column was prepared by the static coating method and the chromatographic properties, polarity, and retention character of the column were studied. The column efficiency was tested using tetradecane at 120 ºC. The column provided an efficiency of 1381 plates per meter and an average polarity of 559.6 that was comparable to the polarity of the commercial PEG20M and FFAP (polyethylene glycol treated with nitro-terephthalic acid). Experimental results showed that the IL column demonstrated strong interaction with the molecules with strong proton donor groups. Both the retention factor and the selectivity for the meta and para isomers of many aromatic compounds were larger on the IL column than on the PEG20M. In addition, symmetrical peak shapes and unique separation selectivities were obtained when the IL column was used to separate the mixtures of a series of alkanes, polycyclic aromatic hydrocarbons, chlorinated benzenes, alcohols, etc.

Key Words: Ionic liquid; Stationary phase; Gas chromatography; Chromatographic properties

1 Introduction

Ionic liquids (ILs) are a class of organic molten salts that have melting points below 100 ºC. These salts are usually composed of asymmetrical nitrogen or phosphorus-containing organic cations and inorganic anions. Because of the special combination between their cations and anions, ILs possesses unique physico-chemical properties such as low volatility, broad liquid range, high thermal stability, and strong polarity. Given these properties, ILs can be extensively used in electrochemistry, organic synthesis, biocatalysis, and separation sciences[1–3]. One important milestone is the use of ILs as gas chromatography (GC) stationary phase in separation sciences[4]. Recently, 1-butyl-3-methylimidazolium hexafluorophosphate and analogous chloride IL were first used as GC stationary phase by Armstrong and co-workers[5]. These two IL stationary phases have been used to separate the mixtures of a series of alkanes, alcohols, phenols, etc. The results demonstrated the dual nature selectivity of the two IL stationary phases. Subsequently, the research of IL as GC stationary phase received increased attention by many chemists. Thus far, most of the research has been focused on the nitrogen-based ILs, especially on the imidazolium-based ILs[6–10]. Whereas there are only a few research on the phosphonium-based ILs[11–12]. Pomaville and coworkers pointed out that the tetra-n-butylphosphonium salts with strong nucleophilic anions were more stable than the analogous tetra-*n*-butylammonium salts[13]. In addition, the advantages of phosphonium-based ILs with better thermal stability and stronger viscosity than the imidazolium-based ILs made them more suitable for GC stationary phase[12]. In this work, a new phosphonium-based IL (tetra-butyl phosphonium methanesulfonate, illustrated in Fig.1) was used as GC stationary phase. The chromatographic properties and

---

Received 25 December 2009; accepted 18 January 2010

* Corresponding author. Email: chenjp@dicp.ac.cn

This work was supported by the National Program on Key Basic Research Project of China (No. 2009CB421602), and the National High-tech R&D Program of China (No. 2007AA061601).

DOI: 10.1016/S1872-2040(09)60056-6

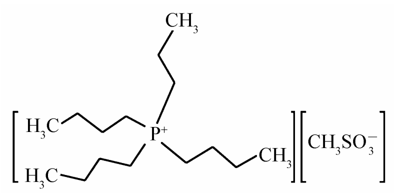

Fig.1 Structure of tetra-butyl phosphonium methanesulfonate ionic liquid

analytical applications of the IL stationary phase were systematically studied. The phosphonium-based IL stationary phases demonstrated promising applications for the separation of the mixtures of a series of alkanes, polycyclic aromatic hydrocarbons, chlorinated benzenes, alcohols, etc.

2 Experimental

2.1 Instruments and reagents

The untreated fused silica capillary columns (0.25 mm i.d.) were provided by Hebei Yongnian Reafine Chromatography Ltd., China. Tetra-butyl phosphonium methanesulfonate (> 98%) was purchased from Sigma-Aldrich and nano-SiO_2 (99.9%, 80 nm) was purchased from Alfa (Shanghai, China). Other reagents (analytical grade) were obtained from Tianjin Kermel Chemical Reagents Co., Ltd., China. A Hewlett Packard model 5890 series gas chromatography was used for all separations. Split injection and flame ionization detection were used. The injector and detector were held at 250 and 260 ºC, respectively, and N_2 (0.4 mL min^{-1}) was used as carrier gas.

2.2 Preparation of IL column

The untreated capillary column (15.8 m × 0.25 mm) was heated at 200 ºC for 2 h under nitrogen stream. The IL GC column was obtained using the static coating method at 35 ºC with a 0.25% (*w/V*) solution of the studied IL in dichloromethane. Before the static coating was performed, the capillary was pretreated with the suspension of nano-SiO_2[14]. Afterwards, the column was conditioned from 60 to 220 ºC at 1 ºC min^{-1} and held at 220 ºC for 6 h.

3 Results and discussion

3.1 Efficiency and thermal stability of IL column

The IL column has an efficiency of 1381 plates per m, which was obtained using tetra-decane at 120 ºC. The IL column demonstrated a tailor factor of 1.05 when *n*-octanol was used as test reagent. From the above results, it can be concluded that the IL column provided excellent symmetrical peak shapes and high efficiency.

The bleeding profile of the column is illustrated in Fig.2. It was observed that the IL stationary phase had obvious bleeding when the temperature was over 220 ºC, resulting in a noticeable rising baseline. The viscosity of ILs dramatically declined with the increase of temperature may be the most important reason for column bleed. Thus, following the decrease of the viscosity, the original uniformity of the film might be changed. Therefore, its maximum column operating temperature is likely ameliorated by changing coating method.

3.2 Polarity of IL column

The McReynolds phase constants are used to evaluate the polarity and selectivity of the IL column. The McReynolds constants of the five probe solutes on three different kinds of columns were listed in Table 1. The data for the first stationary phase (i.e. IL) were obtained at 120 ºC, while others were taken from the literature for the purpose of comparison[15]. The single-phase constants are thought to represent: dispersive interactions (X′), proton donor and acceptor capabilities plus dipolar interactions (Y′), dipolar interactions plus weak proton acceptor, but not proton donor capabilities (Z′), dipolar interactions (U′), and strong proton acceptor (but not donor) capabilities (S′)[5]. By way of contrast, it is observed that the average polarity of the IL column is larger than the two commercial polarity columns. The result demonstrates that the IL stationary phase also belongs to strong polarity stationary phase. The contribution of individual phase constants to retention is also considered. Unlike the two commercial stationary phases that have smaller variations in these phase constants, the IL stationary phase exhibits significant variations (Table 1). Particularly,

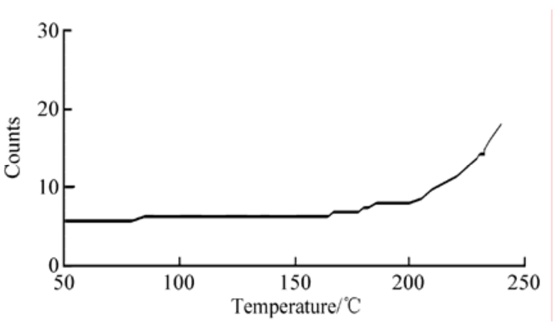

Fig.2 Bleeding profile of tetra-butyl phosphonium methanesulfonate ionic liquid column

Table 1 McReynolds constants and average polarity of IL and other kinds of columns (120 °C)

Column	Benzene (X′)	Butanol (Y′)	Pentanone-2 (Z′)	Nitropropane (U′)	Pyridine (S′)	Average polarity
IL	298	862	412	667	559	560
Carbowax 20M[a]	322	536	368	572	510	462
FFAP[b]	340	580	397	602	627	509

a: a strong polar stationary phase named polyethylene glycol; b: polyethylene glycol treated with nitro-terephthalic acid, which also belong to polar stationary phase[15].