



Review

Preparation and applications of surface-confined ionic-liquid stationary phases for liquid chromatography

Mingliang Zhang^{a,b}, Xiaojing Liang^a, Shengxiang Jiang^a, Hongdeng Qiu^{a,*}^aKey Laboratory of Chemistry of Northwestern Plant Resources, Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China^bUniversity of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Keywords:

HPLC
Liquid chromatography
Ionic liquid
Room-temperature ionic liquid
RTIL
SCIL
Solid-phase microextraction
Stationary phase
Surface-confined ionic liquid
Synthesis

ABSTRACT

Ionic liquids (ILs) are a class of substances completely comprised of ions. Due to their unique properties (e.g., electric conductivity, low volatility, thermostability and tenability), their use has attracted considerable interest, including an increasing number of publications on their use in preparing stationary phases (SPs) of high-performance liquid chromatography. We highlight the existing pathways for making IL-based SPs, and we propose potential strategies for synthesis. We also give up-to-date information on their applications in different chromatographic modes.

© 2013 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	60
2. Preparations of surface-confined ionic-liquid stationary phases	61
2.1. Monomeric route	61
2.2. Polymeric route	65
2.3. Practicable new routes	66
3. Applications of surface-confined ionic-liquid stationary phases	69
4. Other applications	70
5. Conclusions	70
Acknowledgements	71
References	71

1. Introduction

Ionic liquids (ILs), namely room-temperature ILs (RTILs), can be defined as a class of ionic, non-molecular solvents. Usually, the cationic component of an IL is organic, such as imidazolium, pyridinium, alkylammonium and phosphonium, while the anionic part could be inorganic and organic, such as halide, nitrate, acetate, hexafluorophosphate, tetrafluoroborate and trifluoromethanesulfo-

nimide, as shown in Fig. 1. It is not until the first introduction of a stable imidazole-based RTIL in 1992 that research on the preparations, properties and applications of ILs gained momentum in the chemistry community [1].

As solvents, ILs are capable of dissolving a wide range of substances, from inorganic minerals to organic polymeric materials. They are seen as green solvents due to their stability, thermoconductivity, mobility, non-combustibility and non-volatility. The big family of ILs is still expanding. Amongst ILs, the alkyl-substituted imidazolium has attracted more attention, because of its availability and convenient tunability [2–4].

* Corresponding author. Tel.: +86 931 4968877; Fax: +86 931 8277088.
E-mail address: hdqiu@licp.cas.cn (H. Qiu).

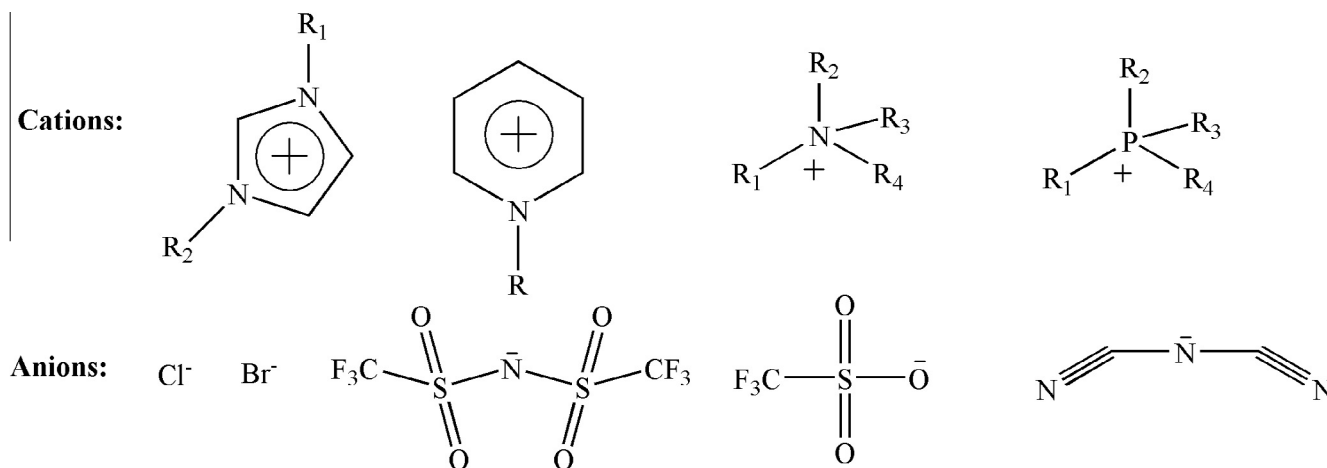


Fig. 1. Structural diagrams of selected cations and anions of common ionic liquids (ILs).

The physicochemical properties of an IL are simultaneously influenced by both its cation and anion. For example, the density of IL with a given anion would decrease with increasing length of the alkyl chain, whereas the viscosity would increase. Also, water solubility depends on both cation and anion. For example, highly water-soluble 1-butyl-3-methylimidazolium chloride would become slightly soluble or insoluble on replacing the butyl group with an octyl one or the chloride with hexafluorophosphate. In view of the remarkable differences resulting from combinations of diverse cations and anions, ILs are deemed “tunable” materials, which could be purposefully designed and modified to satisfy various needs.

The essential applied value of ILs is universally acknowledged. Undeniably, there is much room for the development of ILs for specific tasks. With the advance of research, the utilization of ILs has extended from its cradle (i.e. synthesis chemistry) to many fields, such as material chemistry, catalytic chemistry and spectroscopy, as highlighted in the literature [5–8]. Applications of ILs in analytical chemistry have been a research hotspot because of their excellent properties and convenient tunability. [9–12]

ILs also play an exceptionally important role in high-performance liquid chromatography (HPLC), where they have been used as additives to the mobile phase (MP) in place of conventional aliphatic amines. This approach is found to be convenient and effective when separating polar analytes on a C18 column, as selectivity, retentivity and efficiency towards originally poorly separated analytes tend to be greatly improved [13–16], so the ILs are believed to surpass organic amines due to their capability of performing multiple interactions with the analytes, plus shielding the residual silanol groups on the silica surface. However, the addition of ILs to the mobile phase can cause interference during detection. In particular, when using an evaporative light-scattering detector (ELSD) or a mass spectrometry (MS) detector, ILs are inapplicable as additives due to their non-volatility. Also, the ultraviolet absorption of ILs used in the mobile phase usually causes fluctuations of the baseline.

In order to bypass these disadvantages, an approach involving confinement of ILs to the surface of the stationary phase (SP) seemed a practical choice. The imidazolium-bonded silica SP was first prepared in 2004 [17]. Undoubtedly, this generation of surface-confined IL (SCIL) packing material ushered in a brand new methodology for preparation of SPs and enlarged the scope for utilization of HPLC SPs [18–40]. It should be borne in mind that, once bound to a solid support, the cation/anion pair no longer constitutes a true IL. However, the ability to modify the properties of the silica-based SP by changing easily the structural make-up of

the cation/anion pair draws obvious correlations to the tunability of classic ILs [19]. Although the morphology of ILs varies upon immobilization, the intrinsic characteristics, which depend on the structure of cation cores, substituents and anions, can be preserved, guaranteeing the participation of multiple interactions, such as hydrophobic (hydrophilic), dipole-dipole, π - π and electrostatic interactions, plus hydrogen bonding, in LC separation. Also, the tunability of ILs leaves much leeway for intentional modification of the SPs.

In this review, we summarize the development of SCIL SPs. We illustrate the existing routes concerning the preparations of SCIL SPs, and propose viable new procedures. We wish to integrate the techniques of synthesis and hopefully offer useful concepts for more task-specific SPs.

2. Preparations of surface-confined ionic-liquid stationary phases

The diversity and the multi-functionality of heteroatomic ILs have given HPLC desirable chromatographic performance. Irrefutably, the foundation of all chromatographic evaluations is the successful preparation of the SP, so it is necessary to adopt an effective scheme for synthesis. A handling procedure using obtainable reagents operated in non-harsh conditions is advisable. Another factor to be taken into consideration is that such a procedure must achieve relatively high bonding, as bonding has a direct, decisive impact on the chromatographic behavior of the SP.

The preparation of SCIL SPs usually involves using silane-coupling agents, which bridge the silica substrate and the IL ligands. As displayed in Fig. 2, the agents frequently employed are terminally functionalized propyltrimethoxysilane (PTMS), such as γ -chloro-PTMS (CPTMS) and γ -mercapto-PTMS (MPS), with CPTMS being preferred in the synthesis of monomerically IL-bonded SPs, and MPS for IL-polymerized SPs. Accordingly, the following description is divided into two parts, viz monomeric and polymeric. The primary structures of reported SCIL SPs are exhibited in Tables 1 and 2. The abbreviation for each SP is used corresponding to the original paper, except for post-fixing the anion.

2.1. Monomeric route

As the term suggests, ligands are bonded to SPs in the form of monomer via the monomeric route. To achieve successful immobilization, the silica must be pre-modified so as to carry active

Download English Version:

<https://daneshyari.com/en/article/1248447>

Download Persian Version:

<https://daneshyari.com/article/1248447>

[Daneshyari.com](https://daneshyari.com)