



Review article

Recent development of ionic liquid stationary phases for liquid chromatography



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ARTICLE INFO

Article history:

Received 29 July 2015

Received in revised form

28 September 2015

Accepted 29 September 2015

Available online 9 October 2015

Keywords:

Ionic liquid

Stationary phase

Liquid chromatography

HILIC

ABSTRACT

Based on their particular physicochemical characteristics, ionic liquids have been widely applied in many fields of analytical chemistry. Many types of ionic liquids were immobilized on a support like silica or monolith as stationary phases for liquid chromatography. Moreover, different approaches were developed to bond covalently ionic liquids onto the supporting materials. The obtained ionic liquid stationary phases show multi-mode mechanism including hydrophobic, hydrophilic, hydrogen bond, anion exchange, π - π , and dipole-dipole interactions. Therefore, they could be used in different chromatographic modes including ion-exchange, RPLC, NPLC and HILIC to separate various classes of compounds. This review mainly summarizes the immobilized patterns and types of ionic liquid stationary phases, their retention mechanisms and applications in the recent five years.

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1. Introduction

As a kind of non-molecular solvents, ionic liquids (ILs) remain in liquid state at a temperature below 100 °C and usually consisted of cationic and anionic parts [1]. As shown in Fig. 1, the common cationic part includes imidazolium, pyridinium, glucaminium, quinolinium, etc. The anionic part includes chloride, bromide, iodide, bis(trifluoromethylsulfonyl)imide, methyl orange, etc. ILs

possess many unique physicochemical properties such as variable viscosity, high thermal stability and negligible vapor pressure [2–4]. Therefore, ILs have been applied in many fields of analytical chemistry including gas chromatography (GC), capillary electrophoresis (CE), liquid chromatography (LC) and sample preparation in recent years, as seen from a number of review articles [5–18].

In LC field, ILs were initially used as additives of mobile phase in order to improve the separation of polar compounds on the reversed-phase (RP) column [19–22]. Later, ILs were immobilized on a support like silica and monolith as stationary phases for LC [23]. Different approaches were used to bond covalently the cations or

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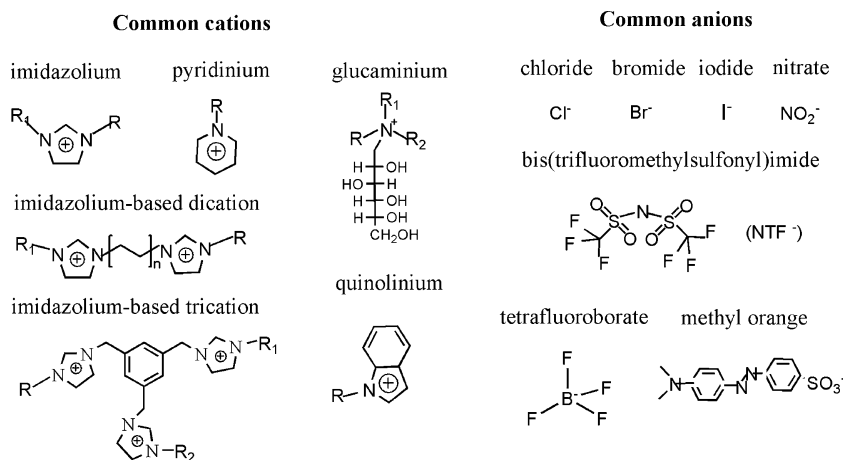


Fig. 1. Chemical structure of common cations and anions of ionic liquid used in stationary phases for liquid chromatography.

anions of ILs onto the support materials. Until now, many ionic liquid stationary phases (ILSPs) have been developed based on their designability and tuneability [24–27].

The previous reviews mainly focus on the preparation, chromatographic behavior, and analytical performance of ILSPs in ionic exchange chromatography (IE), normal phase liquid chromatography (NPLC) and RP liquid chromatography (RPLC). Recently, some novel ILSPs were prepared and studied with the emergence of new ionic liquids and supporting substrates, especially for hydrophilic interaction chromatography (HILIC). This review mainly summarizes the immobilized patterns and types of ILSPs as well as their retention mechanisms and applications in the recent five years.

2. Immobilized pattern of ionic liquid stationary phases

Generally, ILs are immobilized on the surface of supports by the covalent bonding or polymerization of their cations or anions [25]. Therefore, theoretically there are about five patterns for the immobilization of ILs onto the supports as shown in Fig. 2 [28]. In Fig. 2(a) and (b) only the cations or anions of ILs are immobilized on the supports and the counterions are free. When the cations are attached on the supports and the anions are free, this case is relative easily prepared and the free anions can be easily exchanged by other anions, thus the surface properties of ILSPs could be modified slightly by the conversion of various anions. Whereas, the anions of ILs are rarely immobilized on the supports and the cations are free except for the individual case. Qiu et al. prepared sulfonic azobenzene-grafted silica and 1-octadecyl-3-methylimidazolium was regarded as the counterions through

electrostatic interactions [29]. However, the counterions in this pattern of stationary phases are easily exchanged by the ionic species of mobile phases during use. The zwitterionic ILs can avoid this issue owing to their cations and anions linking through covalent bonds (Fig. 2(c) and (d)). Qiao et al. prepared a zwitterionic IL of 1-vinyl-3-(butyl-4-sulfonate) imidazolium and then bonded it to the surface of 3-mercaptopropyl modified silica as a novel stationary phase for HILIC [30]. In the other patterns, the cations and anions of ILs are co-immobilized on the supports, which can enhance similarly the stability of ILSPs during the use of buffer in mobile phase (Fig. 2(e)). For example, a stable ILSP was developed by the copolymerization of alkylimidazolium and p-styrenesulfonate monomer pairs on silica, which could be used in RPLC and HILIC modes with high selectivity and stability [31].

Several chemically bonding reactions were usually used to prepare the ILSPs, including “thiol-ene” click chemistry [30], surface radical chain-transfer reaction [32] or nucleophilic substitution reaction [33]. Recently, the “thiol-ene” click reaction has already been paid much attention to the preparation of stationary phases owing to its many merits of exceptional versatility and high conversion under mild conditions [34–37]. Moreover, this click strategy can avoid the metal ion residues in the stationary phases unlike the classical alkyne-azide Huisgen reaction using Cu as the catalyst [38]. This approach has been used in the preparation of ILSPs [27,30,39]. Recently, Qiu et al. developed a facile method for IL immobilization based on the reaction between isocyanate and amine through the quaternization of urea-functionalized imidazolyl silane. The new preparation strategy consists of multiple steps. The urea-functionalized imidazolyl silane was firstly synthesized by a nucleophilic addition reaction [40,41]. This method avoids the preparation of alkenyl imidazolium salts. Moreover, it provides high bonding amount, flexible designability and tunable hydrophobicity. As a result, a series of ILSPs with different length of aliphatic chains or a large aromatic group were prepared based on the method.

3. Type of ionic liquid stationary phases

Based on the designability of ionic liquids, various types of ionic liquids were expanded for use as stationary phase in LC including single-cation and multi-cation ionic liquids, polymeric ionic liquids as well as chiral ionic liquids as listed in Table 1. These new ILSPs can provide unique properties compared to the classic stationary phases.

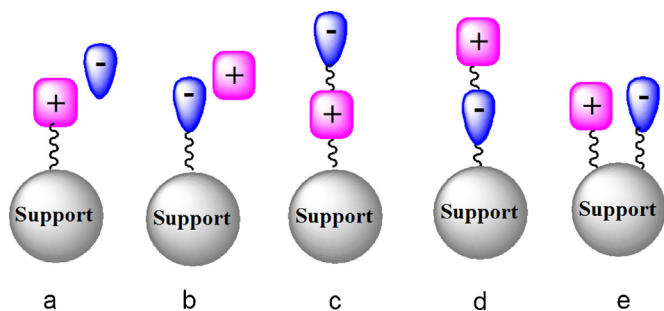


Fig. 2. Schematic illustrations of immobilized pattern of ILSPs. (a) and (b) ionic liquids immobilized via their cations or anions; (c) and (d) zwitterionic ILs immobilized via their cations or anions; (e) co-immobilized via anions and cations.

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