



# Identifying important structural features of ionic liquid stationary phases for the selective separation of nonpolar analytes by comprehensive two-dimensional gas chromatography



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## ABSTRACT

A series of dicationic ionic liquid (IL)-based stationary phases were evaluated as secondary columns in comprehensive two-dimensional gas chromatography (GC × GC) for the separation of aliphatic hydrocarbons from kerosene. In order to understand the role that structural features of ILs play on the selectivity of nonpolar analytes, the solvation parameter model was used to probe the solvation properties of the IL-based stationary phases. It was observed that room temperature ILs containing long free alkyl side chain substituents and long linker chains between the two cations possess less cohesive forces and exhibited the highest resolution of aliphatic hydrocarbons. The anion component of the IL did not contribute significantly to the overall separation, as similar selectivities toward aliphatic hydrocarbons were observed when examining ILs with identical cations and different anions. In an attempt to further examine the separation capabilities of the IL-based GC stationary phases, columns of the best performing stationary phases were prepared with higher film thickness and resulted in enhanced selectivity of aliphatic hydrocarbons.

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## 1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) is a valuable tool for the separation and identification of volatile and semi-volatile constituents in many complex samples [1–7]. A typical GC × GC separation is generally achieved through the use of a modulation device situated between a long first column and a short secondary column, which results in increased peak capacities. In order to achieve a significant improvement in the resolving power, the stationary phases employed should possess complementary selectivities (i.e., distinct solvating capabilities). The most commonly employed columns in GC × GC separations are poly(siloxane)- or poly(ethylene glycol)-derived stationary phases in both nonpolar × polar and polar × nonpolar column configurations [8]. However, the solvation capabilities provided

by these stationary phases are still limited and may not provide complete separation of complex samples.

Ionic liquids (ILs) are organic salts with melting points below 100 °C. These compounds exhibit a number of unique characteristics such as high thermal stability, negligible vapor pressures, wide liquid ranges, and tunable viscosities [9]. More importantly, ILs can often be functionalized by the addition of substituents to the cations to provide a broad range of solvation interactions and unique selectivities toward different classes of analytes [10–12]. Many of these properties have made ILs an interesting new class of stationary phases in GC [13,14]. Currently, there are a number of commercial IL-based GC stationary phases available including SLB-IL 59, SLB-IL 60, SLB-IL 61, SLB-IL 76, SLB-IL 82, SLB-IL 100 and SLB-IL 111 [15]. These GC columns were successfully employed for the separation of mid- to high-polarity analytes, such as fatty acid methyl esters [16–18], polychlorinated dibenzo-*p*-dioxins and dibenzofurans [19], flavor and fragrance compounds [20], alkyl phosphates [21], benzothiazoles and benzotriazoles [22], and aromatic hydrocarbons [23] by conventional gas chromatography (1D-GC) and GC × GC [23–29]. However, it has been observed that due to the high polarity and cohesive forces of the commercial IL-based columns, nonpolar analytes such as aliphatic hydrocarbons are not well

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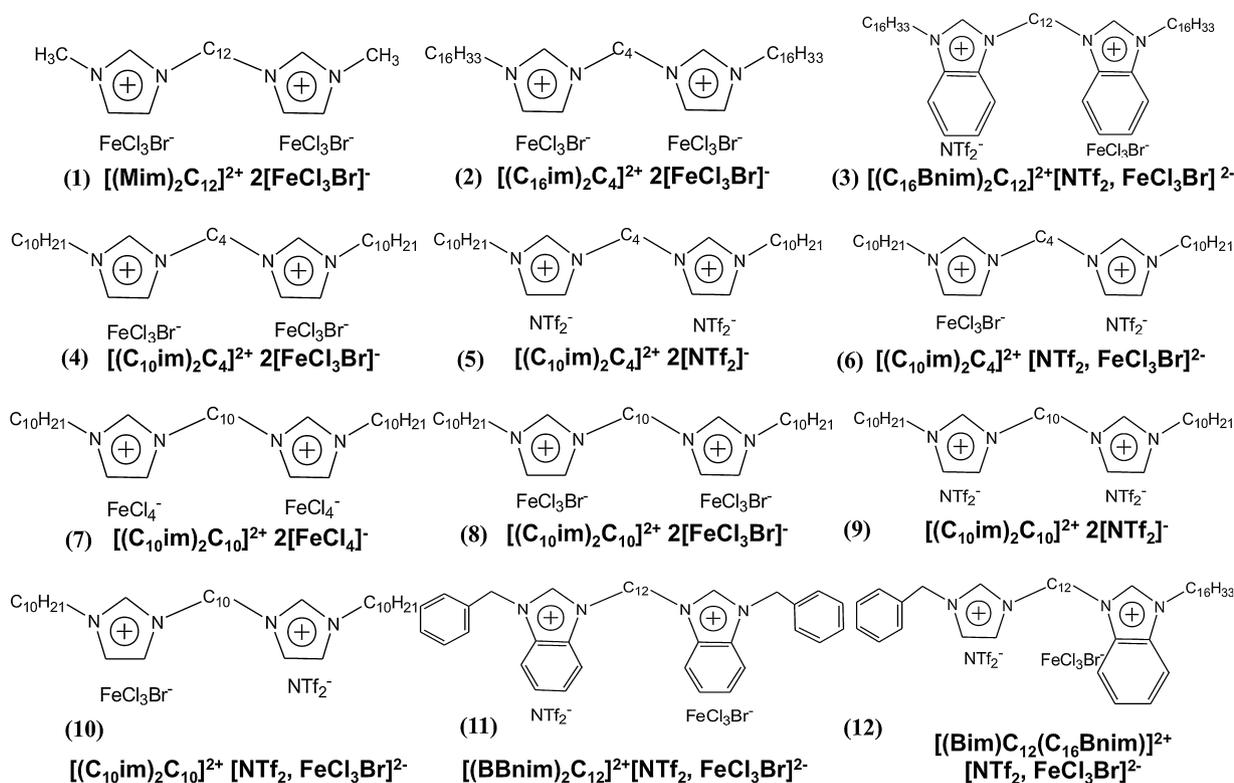


Fig. 1. Structure and abbreviations of ILs examined in this study.

resolved [20,23,29,30]. As a result, there is increasing interest in developing new IL-based stationary phases that are capable of exhibiting better separation performance compared to commercial IL-based columns.

Recently, a series of ILs were evaluated by our group as second dimension columns for the separation of aliphatic hydrocarbons in GC × GC [30]. The solvation parameter model was used to probe the solvation properties of the stationary phases to understand their role in providing the unique selectivity required to resolve nonpolar analytes. It was observed that ILs capable of strong dispersive interactions exhibited better separation of aliphatic hydrocarbons compared to the commercial SUPELCOWAX 10 column. However, the solvation properties of the ILs can be varied by combining different types of cations (e.g., imidazolium-based or phosphonium-based) and anions (e.g., bis[(trifluoromethyl)sulfonyl]imide ([NTf<sub>2</sub>]<sup>-</sup>) or tetrachloroferrate ([FeCl<sub>4</sub>]<sup>-</sup>)). Moreover, even with the same cation, slight modification of the functional groups (e.g., alkane or aromatic groups) appended to the cation can significantly vary their solvation properties [14].

Geminal dicationic ILs have been explored as commercial GC stationary phases due to their superior thermal stability [15]. In addition, their side chains and linker chains can be functionalized to impart different solvation properties to the resulting ILs [10]. Commercial IL-based columns such as SLB-IL82 and SLB-IL111 contain short alkyl side chains and possess high cohesive forces, which is not conducive for producing highly selective separation of nonpolar analytes such as aliphatic hydrocarbons [8,31]. Recently, our work revealed that imparting longer alkyl substituents into the cationic moiety can significantly decrease the cohesive forces of the IL and thus enhance the resolution of aliphatic hydrocarbons in GC × GC separations [30]. In order to further understand the role that structural features of ILs play on the enhanced selectivity of nonpolar analytes, a more comprehensive study is needed

to evaluate functionalized ILs with varied cation/anion composition. In this study, a total of twelve imidazolium-based dicationic ILs containing homoanions and heteroanions were examined as second dimension stationary phases in GC × GC separations. In order to better understand the physical properties of ILs, GC × GC was also applied to evaluate the lowest operation temperature of IL-based stationary phases. The solvation parameter model was employed to evaluate the solvation properties of the IL-based stationary phases. The best performing IL-based stationary phases were used to prepare highly selective GC columns for the separation of kerosene by GC × GC.

## 2. Experimental procedure

### 2.1. Materials

The reagents imidazole (99%), 1-methylimidazole (99%), acrylonitrile (99%), 1,4-dibromobutane (99%), 1,10-dibromodecane (97%), 1,12-dibromododecane (98%), 1-chlorodecane (98%), 1-bromodecane (98%), 1-bromohexadecane (97%) and iron (III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) (97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Lithium bis[(trifluoromethyl)sulfonyl]imide was purchased from SynQuest Labs (Alachua, FL, USA). Chloroform, methylene chloride, methanol, isopropanol, ethyl acetate, and hexane (HPLC grade) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Untreated fused silica capillary tubing (0.25-mm I.D.) was obtained from Supelco (Bellefonte, PA, USA). Kerosene was purchased from a local distributor. The forty-six probe molecules selected for the characterization of the IL stationary phases using the solvation parameter model have been described previously by our group [30]. A complete list of all probe molecules and their corresponding solute descriptors is shown in the Supplementary Information.

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