Lipidic ionic liquid stationary phases for the separation of aliphatic hydrocarbons by comprehensive two-dimensional gas chromatography

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Abstract

Lipidic ionic liquids (ILs) possessing long alkyl chains as well as low melting points have the potential to provide unique selectivity as well as wide operating ranges when used as stationary phases in gas chromatography. In this study, a total of eleven lipidic ILs containing various structural features (i.e., double bonds, linear thioether chains, and cyclopropanyl groups) were examined as stationary phases in comprehensive two dimensional gas chromatography (GC $\times$ GC) for the separation of nonpolar analytes in kerosene. N-alkyl-N'-methyl-imidazolium-based ILs containing different alkyl side chains were used as model structures to investigate the effects of alkyl moieties with different structural features on the selectivities and operating temperature ranges of the IL-based stationary phases. Compared to a homologous series of ILs containing saturated side chains, lipidic ILs exhibit improved selectivity toward the aliphatic hydrocarbons in kerosene. The palmitoleyl IL provided the highest selectivity compared to all other lipidic ILs as well as the commercial SUPELCOWAX 10 column. The linoleyl IL containing two double bonds within the alkyl side chain showed the lowest chromatographic selectivity. The lipidic IL possessing a cyclopropanyl group within the alkyl moiety exhibited the highest thermal stability. The Abraham solvation parameter model was used to evaluate the solvation properties of the lipidic ILs. This study provides the first comprehensive examination into the relation between lipidic IL structure and the resulting solvation characteristics. Furthermore, these results establish a basis for applying lipidic ILs as stationary phases for solute specific separations in GC $\times$ GC.

1. Introduction

Comprehensive two-dimensional gas chromatography (GC $\times$ GC) is one of the most powerful tools available for the separation and identification of volatile and semi-volatile organic compounds in complex mixtures [1-3]. This technique involves connecting two columns possessing different selectivities (i.e., nonpolar $\times$ polar or polar $\times$ nonpolar column configuration) in order to maximize orthogonality [4, 5]. Compared to conventional gas chromatography (1D-GC), GC $\times$ GC provides increased peak capacity to resolve sample components from complex matrices. For example, the separation of complex petrochemicals can be improved by applying combinations of various polydimethyl(siloxane) (PDMS) and poly(ethyleneglycol) (PEG) derived stationary phases (i.e., DB-1 $\times$ BPX-50, DB-1 $\times$ DB-1701, and Solgel Wax $\times$ BPX-50 column sets) [6-9]. An essential requirement for maximizing peak capacity in GC $\times$ GC is to employ a combination of stationary phases possessing complementary selectivities. The PDMS and PEG-based stationary phases provide limited solvation capabilities and may not fully utilize the peak capacity of GC $\times$ GC [10]. Therefore, the development of new stationary phases possessing alternative selectivities is needed in order to fully exploit the separation power of GC $\times$ GC.

A number of ionic liquid (IL) based stationary phases have been commercialized and can offer unique selectivity when compared to PDMS or PEG-based GC stationary phases [11, 12]. ILs are typically composed of an organic cation paired with an inorganic or organic counter anion and have melting points less than 100 °C. ILs have enjoyed increasing popularity in GC due to their numerous advantages including negligible vapor pressure, wide liquid ranges, tunable viscosity, and high thermal stability [13-15]. Commercial IL-based columns have been

successfully utilized in GC $\times$ GC for the analysis of agricultural products, petrochemical samples, environmental samples, and pharmaceutical compounds [16-19]. Furthermore, IL and molten salt-based stationary phase can be structurally tailored to engage in multiple solvation interactions that can provide unique selectivities [20]. Recent studies from our group have demonstrated that the IL cation can be functionalized with long alkyl group substituents to improve the separation of nonpolar analytes in kerosene using GC $\times$ GC [21-23]. It was previously reported that imparting long alkyl side chains to the cationic moiety resulted in higher melting ILs due to the cumulative interchain dispersive forces [24]. For example, N-alkyl-N'-methyl-imidazolium tetrafluoroborate ILs with alkyl side chains of 6, 12, and 18 carbon atoms resulted in ILs with melting points of -82 °C, 19 °C, and 50 °C, respectively. The melting point is an important physical property of ILs when they are used as GC stationary phases as it largely determines the operating range of the IL stationary phase and is an important factor for the resulting retention mechanism. Typically, analytes can interact with IL-based stationary phases through either a partition or adsorption mechanism [25-27]. The partition-type retention mechanism generally provides greater separation efficiencies. When the melting point of the IL stationary phase is higher than the operating temperature, the retention mechanism is likely to be dominated by adsorption. Complex samples like kerosene usually contain a large number of different analytes possessing vastly different boiling points [28]. As a result, separation programs that range from lower temperatures and operate up to high temperatures are needed highlighting the requirement of stationary phases to possess unique selectivity as well as wide operating temperature ranges.

Recently, novel lipid-inspired ILs containing long alkyl side chains ($\geq C_8$) were reported [29-32]. By strategically incorporating various functional groups (i.e., double bonds, thioether

81 branched chains, and cyclopropanyl groups), the melting point of the resulting ILs can be
82 significantly reduced. Lipidic ILs with low melting points have the potential to provide wide
83 operating ranges when applied as GC stationary phases. In addition, the long alkyl side chain
84 appended to the IL cation can enhance the selectivity towards aliphatic hydrocarbons. Therefore,
85 lipidic ILs represent an intriguing class of materials that provide enhanced dispersive type
86 interactions while still being room temperature ionic liquids, an important requirement in high
87 efficiency GC $\times$ GC studies.

88 In this study, a total of eleven lipidic ILs were applied for the first time as stationary phases
89 in GC $\times$ GC separations. Compared to linear saturated IL stationary phases, superior resolution
90 of nonpolar hydrocarbons in kerosene at low separation temperatures was achieved by
91 employing a lipidic IL column in the second dimension. The palmitoleyl lipidic IL exhibited
92 excellent selectivity toward nonpolar analytes compared to the other lipidic ILs studied, as well
93 as the commercial SUPELCOWAX 10 column. Lipidic ILs with different structural features
94 including thioether branched chains and cyclopropanyl groups were investigated to study their
95 applicability under high separation temperatures. The solvation parameter model was employed
96 to examine the solvation properties of the lipidic IL-based stationary phases. This new class of
97 ILs provides improved separation of nonpolar analytes in complex samples and establishes an
98 additional basis for the structural design of IL-based stationary phases that has never been
99 explored.

101 **2. Material and methods**

102 *2.1. Materials*

103 Kerosene was purchased from a local distributor. Lithium

bis[(trifluoromethyl)sulfonyl]imide (LiNTf_2) was obtained from SynQuest Laboratories (Alachua, FL, USA). Bromoethane (98%) and propionic acid (99%) were purchased from Alfa Aesar (Ward Hill, MA, USA). Butyraldehyde (99%), ethyl acetate (99.9%), and 2-nitrophenol (99.8%) were purchased from Acros Organics (Morris Plains, NJ, USA). Toluene (99.5%), 1-butanol (99.9%), N,N-dimethylformamide (99.9%), and 2-propanol (99.6%) were purchased from Fisher Scientific (Fairlawn, NJ, USA). The compounds p-cresol (99%), m-xylene (99.5%), o-xylene (99.5%), and p-xylene (99.5%) were purchased from Fluka (Steinheim, Germany). Cyclohexanol (99%) was purchased from J.T. Baker (Phillipsburg, NJ, USA). Ethylbenzene (95%) was obtained from Eastman Kodak Company (Rochester, NJ, USA). Acetophenone (99%), aniline (99.5%), benzaldehyde (99%), benzene (99.8%), benzonitrile (99%), benzyl alcohol (99%), 1-bromohexane (98%), 1-bromooctane (99%), 1-chlorobutane (99%), 1-chlorohexane (99%), 1-chlorooctane (99%), 1,2-dichlorobenzene (99%), 1-iodobutane (99%), nitrobenzene (99%), 1-nitropropane (99%), 1-octanol (99%), octylaldehyde (99%), 2-pentanone (99%), phenetole (99%), phenol (99%), propionitrile (99%), pyridine (99.8%), pyrrole (98%), 1-decanol (99%), 1-methylimidazole (99%), 1-bromodecane (98%), cyclohexanone (99.8%), 2-chloroaniline (98%), 1-pentanol (99%), and dichloromethane (99.8%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All chemicals were used as received. Acetic acid (99.7%), methyl caproate (98%), naphthalene (98%), untreated fused silica capillary tubing (I.D. 0.25 mm) and a 30 m $\times$ 200 μm SUPELCOWAX 10 column ($d_f = 0.20 \mu\text{m}$) were purchased from Supelco (Bellefonte, PA, USA). A 30 m $\times$ 0.25 mm Rtx-5 capillary column ($d_f = 0.25 \mu\text{m}$) was purchased from Restek (Bellefonte, PA, USA).

2.2. Synthesis of ionic liquids

The chemical structures of all ILs examined in this study are shown in Figure 1. All of the ILs are [NTf₂⁻] salts in order to obtain the lowest possible melting points and highest thermal stabilities [33]. A detailed description of all synthetic methods used to prepare the new classes of lipidic ILs is provided in the supporting information. ILs **R1** (1-decyl-3-methylimidazolium NTf₂) and **R2** (1-hexadecyl-3-methylimidazolium NTf₂) were prepared according to previously reported procedures [34]. The detailed synthetic method and ¹H NMR data are provided in the supporting information. The synthetic procedures used for the lipidic ILs is described in previously published studies [29, 30]. As shown in Figure 1, IL **1** ((Z)-1-(9-hexadecenyl)-3-methylimidazolium NTf₂) (Palmitoleyl) contains a *cis*-double bond on 9th position of the C₁₆ side chain appended to the imidazolium cation. IL **2** ((Z)-1-methyl-3-(9-octadecenyl)-imidazolium NTf₂) (Oleyl) contains a *cis*-double bond on 9th position of the C₁₈ side chain. IL **3** ((Z)-1-methyl-3-(11-octadecenyl)-imidazolium NTf₂) (Vaccenyl) possesses a *cis*-double bond on 11th position of the C₁₈ side chain. IL **4** ((E)-1-methyl-3-(9-octadecenyl)-imidazolium NTf₂) (Elaidyl) contains a *trans*-double bond on 9th position of the C₁₈ side chain. IL **5** (1-methyl-3-((9Z,12Z)-octadecadienyl)-imidazolium NTf₂) (Linoleyl) has two double bonds on the 9th and 12th carbon position of the C₁₈ side chain. IL **6** is a mixture of the 1-(9-(ethylthio)octadecyl)-3-methylimidazolium and 1-(10-(ethylthio)octadecyl)-3-methylimidazolium NTf₂ salts. IL **7** is a mixture of 1-(9-(decylthio)octadecyl)-3-methylimidazolium NTf₂ and 1-(10-(decylthio)octadecyl)-3-methylimidazolium NTf₂. IL **8** is a mixture of 1-(9,12-bis(ethylthio)octadecyl)-3-methylimidazolium NTf₂, 1-(9,13-bis(ethylthio)octadecyl)-3-methylimidazolium NTf₂, 1-(10,12-bis(ethylthio)octadecyl)-3-methylimidazolium NTf₂, and 1-(10,13-bis(decylthio)octadecyl)-3-methylimidazolium NTf₂. IL **9** is a mixture of 1-(9,12-bis(decylthio)octadecyl)-3-methylimidazolium NTf₂, 1-(9,13-bis(decylthio)octadecyl)-3-

methylimidazolium NTf₂, 1-(10,12-bis(decylthio)octadecyl)-3-methylimidazolium NTf₂, and 1-(10,13-bis(decylthio)octadecyl)-3-methylimidazolium NTf₂. IL **10** (1-(3-(dodecylthio)propyl)-3-methylimidazolium NTf₂) possesses a thioether functional group within the alkyl side chain. IL **11** (1-(8-(2-heptylcyclopropyl)octyl)-3-methylimidazolium NTf₂) contains a cyclopropyl functional group within the side chain. All eleven lipidic ILs are liquids at room temperature.

2.3. Preparation and characterization of GC columns containing lipidic IL stationary phases

GC columns were prepared using the static coating method. Briefly, all ILs were dried in a vacuum oven overnight at 70 °C to remove residual water and organic solvent. A 0.25% or 0.45% (w/v) coating solution was prepared by dissolving the IL in dry dichloromethane. A five meter segment of untreated fused silica capillary (I.D. 0.25 mm) was coated by the static coating method at 40 °C. The coated columns were conditioned using a temperature program from 40 °C to 110 °C with a ramp of 1 °C min⁻¹ and held isothermally at 110 °C for 3 h. Helium was used as the carrier gas at a constant flow of 1 mL min⁻¹. The film thickness of the stationary phase was calculated using a previously reported method [35]. The column efficiency was determined using naphthalene at 100 °C; all columns possessed efficiencies of at least 2000 plates per meter (see Table 1). The solvation parameter model was used to characterize the solvation properties of the stationary phases. Table S1 lists the 46 probe molecules and their respective solute descriptors that were used for evaluating the IL columns in this study. All probe molecules were dissolved in dichloromethane and injected separately onto 5 m IL-based columns at three different temperatures (50, 80, 110 °C).

2.4. Instrumentation

The characterization of all IL-based columns was performed on an Agilent 7890B gas chromatography system with a flame ionization detector (GC-FID). Comprehensive two-dimensional separations were performed on a homebuilt GC $\times$ GC-FID system built from an Agilent 6890 GC-FID system with a two stage cryogenic loop modulator. A detailed illustration of the GC $\times$ GC FID system is described in previously published work [21].

2.5. GC $\times$ GC-FID analysis

A 30 m $\times$ 0.25 mm Rtx-5 capillary column (d_f = 0.25 μ m) was employed as the primary column and was connected to second dimension column containing the IL stationary phase (1.2 m $\times$ 0.25 mm, d_f = 0.15 μ m or 0.28 μ m). In total, all eleven lipidic IL-based stationary phases were investigated using the Rtx-5 $\times$ IL column set (see Table 1). For comparison purposes, a commercial SUPELCOWAX 10 column was evaluated as the secondary column for the analysis of aliphatic hydrocarbons in kerosene. The kerosene sample was diluted 20-fold (v/v) in dichloromethane. In all experiments, 0.5 μ L of the kerosene sample was injected using a 100:1 split ratio at 250 $^{\circ}$ C. The chromatographic oven was programmed from 40 to 120 $^{\circ}$ C at 2 $^{\circ}$ C min $^{-1}$, followed by a secondary ramp from 120 to 200 $^{\circ}$ C at 20 $^{\circ}$ C min $^{-1}$. Hydrogen was employed as the carrier gas at a constant flow of 1.2 mL min $^{-1}$. A modulation period of 7 s was utilized for all experiments.

3. Results and Discussion

3.1. Unique physical properties of lipidic IL-based stationary phases

The viscosity, surface tension, wetting ability on fused silica, thermal stability, and

melting point of ILs are all important for them to be successfully employed as GC stationary phases [20]. Among these properties, the melting point is critical since it determines the operating range of the stationary phase and influences the retention mechanism in GC analysis. In this study, N-alkyl-N'-methyl-imidazolium-based ILs containing different alkyl side chains were used as model structures to investigate the relationship between the structural features of alkyl moieties and the physicochemical properties of the ILs (see Figure 1). It was previously reported that the melting points of a homologous series of N-alkyl-N'-methylimidazolium salts sharply increases with the elongation of the side chain beyond seven carbon atoms [36]. The **R1** IL containing a saturated C₁₀ side chain is liquid at room temperature, whereas the **R2** IL containing a saturated C₁₆ side chain is solid at room temperature. The incorporation of double bonds, thioether linkages, and cyclopropyl groups as symmetry breaking moieties can significantly decrease the melting points of the lipidic ILs with a C₁₆ or C₁₈ side chain. All of the lipidic ILs are liquids at room temperature. As shown in Figure 2A, the melting point of **1** (-22.0 °C) is much lower than **R2** (46.9 °C) despite that both **1** and **R2** contain an alkyl side chain of the same length. This result indicates that lipidic ILs containing long alkyl chains provide much lower practical minimum operating temperatures compared to their saturated analogues when used as GC stationary phases. ~~This result indicates that lipidic ILs containing long alkyl side chains can provide a much wider operating temperature range when used as GC stationary phases.~~ Furthermore, this suggests that it is possible to design an IL with an alkyl side chain greater than C₁₈ while maintaining a room temperature liquid.

3.2. GC × GC separation of kerosene using lipidic IL based stationary phases

It has been previously reported that incorporating long alkyl chain substituents to the

cationic moiety of ILs can enhance the separation of nonpolar analytes in GC $\times$ GC [21]. To further evaluate this effect, two ILs containing long alkyl side chains appended to the imidazolium cations were studied. **R1** and **R2** were applied as secondary columns for the separation of kerosene by GC $\times$ GC. As shown in Figure 2B, **R1** provided good separation for the aliphatic hydrocarbons. **R2**, which possesses 6 more carbon atoms within the saturated alkyl chain, exhibited poorer selectivity in resolving the aliphatic hydrocarbons, as observed in Figure 2C. By comparing the melting points of these two ILs in Figure 2A, **R2** possesses a higher melting point (46.9 °C) compared to **R1** (-18.9 °C); therefore, the melting point of **R2** is higher than the employed starting temperature of the GC separation. As a result, very broad peaks were observed eluting from the secondary column (see Figure 2C). To further validate this assumption, IL **1** containing an unsaturated C₁₆ alkyl chain was employed as the second dimension column. It can be observed in Figure 2D that IL **1** exhibited significantly higher chromatographic efficiency compared to **R2**. Moreover, compared to **R1**, which possesses a shorter alkyl side chain substituent, IL **1** also exhibited a significant enhancement in the selectivity of nonpolar analytes, as observed in Figure 2D.

To further evaluate the resolving power of the lipidic IL-based stationary phase toward aliphatic hydrocarbons, the separation result for **1** was also compared with a PEG-based column (SUPELCOWAX 10) commonly employed as a second dimension column for the separation of nonpolar aliphatic hydrocarbons by GC $\times$ GC [7-9]. As shown in Figures 3A and 3B, a wider distribution of the analytes within the separation window was observed when employing the Rtx-5 $\times$ **1** column set. In order to better evaluate the selectivity of the second dimension column, a quantitative measurement was carried out by calculating the resolution values of selected pairs of analytes within the second dimension column. As shown in Figure S3 (Supporting Information),

three pairs of analytes were selected for comparison and their relative resolution values were calculated based on their retention times and peak widths within the secondary column. As shown in Table 1, IL **1** exhibited higher resolution values for all three pairs of analytes compared to the SUPELCOWAX 10 column. The resolution for the first two pairs of selected analytes increased from 1.96 and 1.29 to 2.69 and 1.98, respectively. For better comparison of the two dimensional chromatographic separations, 2D resolution values were calculated. As shown in Table S2, the improved separations of the selected analytes were observed employing the Rtx-5 $\times$ **1** column set. The 2D resolution values of selected analytes increased from 2.20, 2.05, and 7.23 to 2.81, 2.49, and 7.32, respectively. Moreover, as shown in the highlighted area of Figure 3, a few groups of analytes that could not be separated on the Rtx-5 $\times$ SUPELCOWAX 10 column set were fully resolved on the Rtx-5 $\times$ **1** column set. This result indicates that lipidic ILs containing long alkyl substituents on the imidazolium cation and possessing low melting points are promising candidates as GC stationary phases to provide further enhanced selectivity toward nonpolar analytes.

Lipidic ILs containing longer alkyl side chain substituents (i.e., C₁₈ chain) and double bonds in different positions of the side chain were also examined in this study (see Figures 1 and 4). ILs **2**, **3**, and **4** contains a *cis*-double bond on 9th position, a *cis*-double bond on 11th position, and a *trans*-double bond on 9th position within the C₁₈ side chain, respectively. In contrast, IL **5** contains two *cis*-double bonds on the 9th and 12th carbon position within the C₁₈ side chain. It can be observed in Figure 4 and Table 1 that the position and geometry of the double bond does not strongly influence the overall GC $\times$ GC separation. Very similar selectivities for the aliphatic hydrocarbons were obtained when applying ILs **2**, **3**, and **4** as stationary phases in secondary columns. Interestingly, when IL **5** was applied in the second dimension, the aliphatic

hydrocarbons exhibited much less retention compared to lipidic ILs containing only one double bond (see Figure 4D). The resolution of the selected pairs of analytes also decreased when comparing IL **2** (1.15, 0.68, and 2.42) and IL **5** (0.61, 0.42, and 1.84) despite the only structural difference being the additional double bond on the 12th position of the alkyl side chain. It was previously reported that the geometric change in the alkyl chain structure imposed by the *cis*-double bonds leads to a more cohesive IL and reduced capability for dispersive interactions [37, 38].

3.3. Thermal stability of lipidic IL stationary phases

Lipidic ILs with unsaturated side chains exhibit excellent selectivity toward nonpolar analytes in the GC × GC separation of kerosene. Since many petrochemicals contain analytes with large molecular weight and high boiling points, high separation temperatures are often required. Therefore, it is important to thoroughly evaluate the thermal stability of this new class of ILs. The robustness of the lipidic ILs was examined using a previously reported method [23]. The thermal stability of the columns was tested by evaluating the resolution of three pairs of selected analytes from kerosene after high temperature conditioning (i.e., 200 °C, 250 °C, 300 °C, and 350 °C). This approach is employed to detect any viscosity and/or morphology change of the stationary phases at elevated temperatures by examining the changes in the chromatographic efficiency and resolution. The best performing lipidic IL (IL **1**) was evaluated using this approach. The stationary phase was found to be thermally stable in the temperature range between 100 °C and 150 °C, as the resolution values for the selected analytes did not change appreciably. After the column was conditioned at 200 °C and the separation was performed, a significant decrease in resolution was observed (see supporting information, Figure S4). The

maximum allowable operating temperature (MAOT) for this IL was determined to be in the range between 150 °C and 200 °C. As previously reported, imidazolium-based ILs containing a double bond generally possess lower thermal stability compared to their saturated analogues [33]. At elevated temperatures, they can undergo slow oxidative decomposition at the site of the unit of unsaturation. Even though IL **1** exhibits excellent selectivity for aliphatic hydrocarbons at low operating temperature, it lacks the thermal stability needed for general use at higher separation temperatures.

Several approaches were employed to replace the double bond within the lipidic IL in an attempt to increase the thermal stability. One approach involves the addition of thiols to the double bond containing alkyl side chains to obtain ILs with branched chains. ILs **6-9** contain branched thioether chains and are all liquids at room temperature corresponding to previous reports that the addition of branched chains reduces the melting point of the ILs [29]. As shown in Figure 5 and Table 1, when used as stationary phase in second dimension columns, ILs possessing branched chains (i.e., IL **6-9**) exhibited better resolution for aliphatic hydrocarbons compared to ILs containing double bond (i.e., ILs **2** and **5**). It was also observed that the length of branched chain strongly influences the retention of the analytes. As shown in Figure 5, ILs **7** and **9** containing longer branched thioether side chains (C₁₀S) exhibited stronger retention of analytes in the second dimension, compared to ILs **6** and **8** (C₂S). IL **8**, which contains two C₂S branched thioether chains on the C₁₈ side chain, exhibited the best resolution of the selected analytes (Table 1). This result indicates that ILs with two short branched thioether side chains are beneficial for the separation of nonpolar analytes. IL **8** was found to be thermally stable in the temperature range between 100 °C and 150 °C. However, after the column was conditioned at 200 °C, a significant decrease in resolution was observed, indicating a MAOT between 150 °C

and 200 °C (see Figure S5).

Yet another approach for improving the thermal stability of the lipidic IL is to use the photoinitiated thiol-ene “click” reaction to insert a thioether functional group within the linear alkyl side chain. [29]. As shown in Figure 6, IL **10** exhibited good selectivity for aliphatic hydrocarbons. Compared to **R1** containing a C₁₀ side chain, the resolution of selected pairs of analytes in kerosene was enhanced from 0.96, 0.66, and 1.89 to 1.21, 0.89, and 2.54. After IL **10** was conditioned up to 200 °C, the resolution of selected analytes did not change appreciably. After high temperature conditioning to 250 °C, the resolution of the selected pairs of analytes decreased indicating that the MAOT for **10** was between 200 °C and 250 °C (see Figure S6). A final approach to improve the thermal stability of the lipidic IL involved the net addition of a methylene (CH₂) fragment to the double bond within the side chain to obtain an IL possessing a cyclopropanyl group in the side chain [32]. As shown in Figures S7 and S8, IL **11** exhibited a similar thermal stability to **R1**. After conditioning to 300 °C, IL **11** still exhibited good retention and selectivity for the nonpolar analytes in kerosene.

3.4. *Effect of stationary phase film thickness on GC × GC separations*

The stationary phase film thickness plays an important role in GC × GC separations. It is well-known that higher film thicknesses can reduce column over loading and offer improved selectivity in the second dimension. As shown in the previous sections, lipidic IL-based stationary phases possessing a film thickness of 0.28 µm provided good selectivity toward the aliphatic hydrocarbons in kerosene. However, thicker films in GC × GC can cause band broadening and wrap-around due to excessive retention (see Figures 2, 5, and 6). Therefore, these parameters need to be optimized to preserve selectivity and maximize the overall peak

capacity. As shown in Figure 7, stationary phases containing film thicknesses of 0.15 μm were prepared and applied as second dimension columns using ILs **1**, **7**, **10**, and **11**. Wrap-around was significantly reduced for these separations compared to those columns with the thicker films (see Figures 2D, 5B, 6A and 6B). However, the distribution of analytes within the separation window was reduced when employing a second dimension column with a film thickness of 0.15 μm (see Figures 2D, 5B, 6A and 6B). Columns containing a stationary phase film thickness of 0.28 μm exhibited higher selectivity for the selected analytes. These results show that the lipidic IL-based stationary phases with thicker films provide a higher resolution for the aliphatic hydrocarbons in the second dimension.

3.5. *Characterization of lipidic IL solvation interactions by the solvation parameter model*

The separations achieved in this study indicate that the lipidic ILs possess unique selectivity required to enhance the resolution of nonpolar analytes in kerosene. The numerous structural features within the lipidic ILs appear to play an important role in the selectivity of the lipidic IL-based stationary phases. To understand the solvation properties of this new class of ILs, the Abraham solvation parameter model was employed. This model is a linear free-energy relationship that describes the contribution of individual solvation interactions of a solvent (i.e., IL-based stationary phase) by evaluating the solute/solvent interactions [39-41].

$$\text{Log } k = c + eE + sS + aA + bB + lL \quad (1)$$

In Eq. (1), k is the retention factor of each probe molecule on the liquid stationary phase at a specific temperature. The solute descriptors (E , S , A , B , and L) have been previously determined and are shown in Table S1. The solute descriptors are defined as: E , the excess molar

refraction calculated from the solute's refractive index; S , the solute dipolarity/polarizability; A , the solute hydrogen bond acidity; B , the solute hydrogen bond basicity; and L , the solute gas hexadecane partition coefficient determined at 298 K. The system constants (e , s , a , b , and l) are used to characterize the strength of each solvation interaction and are defined as: e , the ability of the stationary phase to interact with analytes by electron lone pair interactions; s , a measure of the dipolarity/polarizability of the stationary phase; a and b , the IL hydrogen bond basicity and acidity of the stationary phase, respectively; and l describes the dispersion forces/cavity formation of the IL. The system constants of two reference ILs and four selected lipidic ILs at three different temperatures (50 °C, 80 °C, and 110 °C) are listed in Table 2. As expected, the interactions between the probe molecules and the stationary phases become weaker at higher temperature, resulting in a decreased values of the system constants.

To investigate the solvation properties of lipidic ILs, six ILs (**R1**, **R2**, **1**, **5**, **10**, and **11**) were examined in this study. The first comparison was made between **R1** and **R2**, where **R1** contains a C₁₀ side chain and **R2** possesses a longer C₁₆ side chain. As shown in Table 2, similar system constants were observed for the two ILs except for the e and l terms. The l term of **R2** ($l = 0.64$) is higher compared to that of **R1** ($l = 0.60$) at 80 °C. This result agrees with previous reports that have shown longer alkyl side chains within the cationic moiety result in less cohesive ILs [21-23].

To further explore the solvation properties, IL **1** was compared to **R1** where IL **1** contains a longer alkyl chain with a double bond. IL **1** has a higher l term ($l = 0.62$) than **R1** ($l = 0.60$) at 80 °C, indicating that **1** is less cohesive compared to **R1**. ILs **1** and **R2** are structural analogues with the only difference being a double bond within the alkyl side chain of the IL cationic moiety.

The *cis*-double bond incorporated in **1** appears to result in a lower l term relative to IL **R2**. The l term of **1** ($l = 0.62$) is lower than **R2** ($l = 0.64$) at 80 °C (see Table 2). This result supports the previous observations that alkanes generally have larger l terms than their alkene homologues [42]. IL **1** provided superior selectivity toward nonpolar analytes compared to **R1** as well as a wider separation range than **R2** (see Figure 2).

The system constants of IL **5** possessing two double bonds within the alkyl side chain are shown in Table 2. The l term of IL **5** ($l = 0.55$) decreased significantly compared to the lipidic IL **1** ($l = 0.62$) and **R1** ($l = 0.60$), despite the fact that IL **5** possesses two more carbon atoms within the side chain (C₁₈ side chain). This shows that IL **5** containing two double bonds within the alkyl side chain is less capable of nonspecific dispersive interaction, compared to the other lipidic ILs. The low l term for IL **5** may help explain the lower selectivity toward aliphatic hydrocarbons in the GC × GC separation of kerosene (see Figure 4).

The solvation properties of ILs **10** and **11** were examined in this study. IL **10** possesses a linear thioether side chain. As shown in Table 2, IL **10** has the same l term ($l = 0.62$) with IL **1** ($l = 0.62$), but higher a term ($a = 1.78$) than IL **1** ($a = 1.74$) at 80 °C. All other system constants are largely unchanged. IL **11** containing a cyclopropanyl group incorporated within a C₁₈ side chain is the most thermally stable IL among lipidic ILs. As shown in Table 2, IL **11** has a lower e term ($e = 1.41$) and a term ($a = 1.57$) compared to IL **1** ($e = 1.57$) ($a = 1.74$) or IL **10** ($e = 1.57$) ($a = 1.78$) at 80 °C, due to the lack of a double bond or thioether group. IL **11** possesses a high l term ($l = 0.66$), compared to IL **R1** ($l = 0.60$), IL **R2** ($l = 0.64$), and IL **1** ($l = 0.62$) at 80 °C. This result agrees with the previous observation that IL **11** exhibits strong retention of nonpolar analytes in the second dimension compared to IL **R1** or IL **R2** (Figures 1 and 6).

4. Conclusions

A total of eleven lipidic ILs were evaluated for the first time as GC stationary phases and were further examined by comprehensive two-dimensional gas chromatography. Lipidic ILs with unique physicochemical properties provided enhanced selectivity towards nonpolar analytes in kerosene compared to their saturated linear chain analogues. Although most of the lipidic ILs (ILs 2-11) exhibited lower selectivity compared to the commercial SUPELCOWAX 10 column, the structurally-tuned palmitoleyl lipidic IL (IL 1) provided the highest selectivity compared to all other lipidic ILs as well as the commercial SUPELCOWAX 10 column. The linoleyl IL (IL 5) with two double bonds exhibited the lowest selectivity since it is more cohesive and less capable of dispersive-type interactions. The lipidic IL containing a cyclopropanyl group within the alkyl side chain (IL 11) exhibited a MAOT of 300 °C and the highest thermal stability of all lipidic ILs studied. The best performing ILs were selected to prepare stationary phases with different film thicknesses. IL-based columns with thicker films provided improved selectivity for aliphatic hydrocarbons in kerosene. The solvation parameter model was used to evaluate the solvation properties of the lipidic ILs with the various symmetry breaking moieties in the alkyl side chain. Dispersive interactions were found to play a critical role in the separation of nonpolar analytes within the kerosene sample. Lipidic ILs can be designed to be less cohesive through the addition of symmetry breaking moieties to result in ILs with low melting points. This study demonstrates which structural features of lipidic ILs produce the highest thermal stabilities as well as solvation properties that provide the required selectivity to resolve analytes in complex samples.

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Figure captions:

Figure 1. Cation structures of two reference ILs and eleven lipidic ILs. ILs **R1** and **R2** possess saturated alkyl side chains. ILs **1-5** contain double bonds. ILs **6-9** are a mixture of ILs with branched thioether chains; the black dots indicate the positions of the branched side chains. IL **10** possesses a thioether linkage within the linear side chain. IL **11** contains a cyclopropanyl group within the alkyl side chain. All of the ILs investigated in this study are $[\text{NTf}_2^-]$ salts. The $\text{C}_n(\text{x}[\text{y}])$ represents the functional group and its position on the alkyl side chain.

Figure 2. Melting point comparison for reference ILs and lipidic IL-based stationary phases and their applications in the GC $\times$ GC separation of kerosene. (A) The melting points of ILs **R1**, **R2**, and **1**. GC $\times$ GC chromatograms of kerosene using lipidic ILs as ^2D columns: (B) Rtx-5 $\times$ **R1**, (C) Rtx-5 $\times$ **R2**, and (D) Rtx-5 $\times$ **1**. The melting points were obtained from reference [30].

Figure 3. Enlargement of selected parts of GC $\times$ GC chromatograms of kerosene employing (A) Rtx-5 $\times$ SUPELCOWAX 10 and (B) Rtx-5 $\times$ **1** column sets.

Figure 4. GC $\times$ GC contour plots of kerosene separation employing lipidic ILs as ^2D columns: (A) Rtx-5 $\times$ **2**, (B) Rtx-5 $\times$ **3**, (C) Rtx-5 $\times$ **4**, (D) Rtx-5 $\times$ **5**.

Figure 5. Use of lipidic ILs with branched thioether chains as ^2D column stationary phases in GC $\times$ GC separation of kerosene: (A) Rtx-5 $\times$ **6**, (B) Rtx-5 $\times$ **7**, (C) Rtx-5 $\times$ **8**, and (D) Rtx-5 $\times$ **9**.

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563
564 **Figure 6.** GC $\times$ GC separations of kerosene employing lipidic ILs with improved thermal
565 stabilities as 2 D column stationary phases: (A) Rtx-5 $\times$ **10** and (B) Rtx-5 $\times$ **11**.

566
567 **Figure 7.** Two-dimensional chromatograms showing the separation of kerosene using lipidic ILs
568 as 2 D column stationary phases with film thickness of 0.15 μm : (A) Rtx-5 $\times$ **1**, (B) Rtx-5 $\times$ **7**, (C)
569 Rtx-5 $\times$ **10**, (D) Rtx-5 $\times$ **11**.

570

571

Figure 1

IL	Abbreviation	Structure of IL Cation
R1	C ₁₀ (0)	
R2	C ₁₆ (0)	
1	C ₁₆ (1[9])	
2	C ₁₈ (1[9])	
3	C ₁₈ (1[11])	
4	C ₁₈ (1[9t])	
5	C ₁₈ (2[9,12])	
6	C ₁₈ (C ₂ S[9/10])	
7	C ₁₈ (C ₁₀ S[9/10])	
8	C ₁₈ (2C ₂ S[9/10, 12/13])	
9	C ₁₈ (2C ₁₀ S[9/10, 12/13])	
10	C ₁₆ (S[4])	
11	C ₁₈ (Cyclo[9])	

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Figure 2

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Figure 3

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Figure 4

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Figure 5

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Figure 6

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Figure 7

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Table 1

Table 1. Characteristics of lipidic ionic liquid based stationary phases examined in this study.							
IL No.	Specialized lipidic side chain feature	Abbreviation ^a	Film Thickness (μm)	Efficiency (Plates/Meter)	Resolution of selected analytes ^b		
					1 & 2	3 & 4	5 & 6
R1	None	C ₁₀ (0)	0.28	2400	0.96	0.66	1.89
R2	None	C ₁₆ (0)	0.28	2200	0.63	-	-
1	Double bond	C ₁₆ (1[9])	0.28	2300	2.69	1.98	6.88
2	Double bond	C ₁₈ (1[9])	0.28	2500	1.15	0.68	2.42
3	Double bond	C ₁₈ (1[11])	0.28	2500	1.04	0.67	1.95
4	Double bond	C ₁₈ (1[9t])	0.28	3600	1.18	0.77	3.41
5	Double bond	C ₁₈ (2[9,12])	0.28	2400	0.61	0.42	1.84
6	Branched thioether chain	C ₁₈ (C ₂ S[9/10])	0.28	2200	1.15	0.96	2.54
7	Branched thioether chain	C ₁₈ (C ₁₀ S[9/10])	0.28	3400	1.15	1.10	4.43
8	Branched thioether chain	C ₁₈ (2C ₂ S[9/10, 12/13])	0.28	4200	1.32	1.02	3.84
9	Branched thioether chain	C ₁₈ (2C ₁₀ S[9/10, 12/13])	0.28	3400	1.25	1.06	3.34
10	Linear thioether chain	C ₁₆ (S[4])	0.28	2700	1.21	0.89	2.54
11	Cyclopropanyl	C ₁₈ (Cyclo[9])	0.28	2400	0.97	0.47	1.94
SUPELCOWAX 10					1.96	1.29	6.81

^a The C_n(x[y]) represents the functional group and its position within the side chain.

^b Selected pairs of analytes are shown in representative GC × GC contour plot in Figure S3.

1 Table 2. System constants of the studied lipidic ionic liquids attained using the Solvation
 2 Parameter Model.

Stationary Phase	Temperature (°C)	System constants								
		<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>	<i>n</i> ^a	<i>R</i> ^{2 a}	<i>F</i> ^a
IL R1	50	-2.90 (0.09)	-0.21 (0.08)	1.71 (0.10)	1.97 (0.08)	0.26 (0.12)	0.72 (0.02)	39	0.99	549
	80	-2.91 (0.07)	-0.06 (0.06)	1.62 (0.08)	1.62 (0.06)	0.19 (0.10)	0.60 (0.01)	38	0.99	691
	110	-2.98 (0.06)	-0.07 (0.05)	1.56 (0.07)	1.36 (0.06)	0.11 (0.09)	0.52 (0.01)	36	0.99	632
IL R2	50	-2.97 (0.08)	-0.16 (0.07)	1.52 (0.08)	1.85 (0.08)	0.36 (0.11)	0.79 (0.02)	36	0.99	732
	80	-2.81 (0.07)	-0.12 (0.06)	1.44 (0.07)	1.56 (0.06)	0.15 (0.10)	0.64 (0.02)	35	0.99	684
	110	-2.81 (0.06)	-0.04 (0.06)	1.23 (0.07)	1.23 (0.06)	0.29 (0.09)	0.55 (0.01)	36	0.99	594
IL 1	50	-2.93 (0.07)	-0.13 (0.07)	1.69 (0.09)	2.01 (0.08)	0.29 (0.10)	0.73 (0.01)	36	0.99	899
	80	-2.91 (0.08)	-0.11 (0.07)	1.57 (0.08)	1.74 (0.08)	0.20 (0.11)	0.62 (0.02)	37	0.99	944
	110	-2.92 (0.07)	-0.05 (0.06)	1.42 (0.07)	1.44 (0.06)	0.24 (0.09)	0.53 (0.01)	35	0.99	550
IL 5	50	-2.96 (0.07)	-0.11 (0.07)	1.65 (0.08)	2.29 (0.06)	0.37 (0.10)	0.71 (0.01)	35	0.99	1010
	80	-2.53 (0.06)	-0.08 (0.05)	1.49 (0.06)	1.84 (0.06)	0.21 (0.09)	0.55 (0.01)	35	0.99	799
	110	-2.96 (0.07)	-0.02 (0.06)	1.45 (0.08)	1.58 (0.06)	0.26 (0.10)	0.50 (0.02)	37	0.99	463
IL 10	50	-2.91 (0.08)	-0.24 (0.07)	1.74 (0.08)	2.16 (0.07)	0.17 (0.10)	0.73 (0.02)	35	0.99	660
	80	-2.88 (0.06)	-0.15 (0.05)	1.57 (0.06)	1.78 (0.05)	0.16 (0.08)	0.62 (0.01)	40	0.99	1115
	110	-3.20 (0.07)	-0.09 (0.05)	1.52 (0.07)	1.57 (0.06)	0.24 (0.09)	0.56 (0.01)	35	0.99	682
IL 11	50	-2.93 (0.08)	-0.18 (0.07)	1.48 (0.08)	1.84 (0.07)	0.22 (0.11)	0.77 (0.02)	35	0.99	733
	80	-2.91 (0.06)	-0.19 (0.05)	1.41 (0.06)	1.57 (0.06)	0.09 (0.08)	0.66 (0.01)	36	0.99	872
	110	-2.93 (0.06)	-0.10 (0.05)	1.30 (0.06)	1.30 (0.05)	0.10 (0.08)	0.56 (0.01)	37	0.99	721

3 ^a Note: *n*, number of probe analytes subjected to multiple linear regression; *R*², correlation
 4 coefficient; *F*, Fisher coefficients.