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# Tuning the Selectivity of Ionic Liquid Stationary Phases for Enhanced Separation of Nonpolar Analytes in Kerosene Using Multidimensional Gas Chromatography

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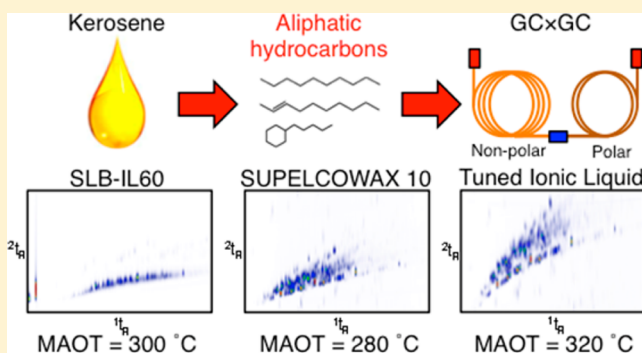
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## S Supporting Information

**ABSTRACT:** In this study, a series of ionic liquids (ILs) are evaluated as stationary phases in comprehensive two-dimensional gas chromatography (GC × GC) for the separation of aliphatic hydrocarbons from kerosene. IL-based stationary phases were carefully designed to evaluate the role of cavity formation/dispersive interaction on the chromatographic retention of nonpolar analytes by GC × GC. The maximum allowable operating temperature (MAOT) of the IL-based columns was compared to that of commercial IL-based columns. Evaluation of the solvation characteristics of GC columns guided the selection of the best performing IL-based stationary phases for the resolution of aliphatic hydrocarbons, namely, trihexyl(tetradecyl)phosphonium tetrachloroferrate ([P<sub>66614</sub>][FeCl<sub>4</sub>]) and trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate ([P<sub>66614</sub>][FAP]) ILs. The best performing [P<sub>66614</sub>][FeCl<sub>4</sub>] IL-based column exhibited a MAOT of 320 °C, higher than the commercial SUPELCOWAX 10 (MAOT of 280 °C) and commercial IL-based columns (MAOT up to 300 °C). The structurally tuned [P<sub>66614</sub>][FeCl<sub>4</sub>] IL stationary phase exhibited improved separation of aliphatic hydrocarbons by GC × GC compared to the commercial columns examined (e.g., OV-1701, SUPELCOWAX 10, SLB-IL60, SLB-IL100, and SLB-IL111).



Multidimensional gas chromatography (MDGC) is an extremely valuable tool for the separation, detection, and identification of volatile and semivolatile constituents in many complex samples.<sup>1–4</sup> As in any MDGC technique, two or more gas chromatographic separations are employed in a sequential fashion.<sup>1</sup> The paramount requirement to effectively enhance peak capacity in the composite system is to employ a combination of GC stationary phases possessing different selectivities. Until recently, most chromatographic separations employed the contemporary poly(siloxane)- and poly(ethylene glycol)-based stationary phases.<sup>5</sup> Their combination and use in MDGC offered separations with higher peak capacities compared to conventional gas chromatography (1D-GC). However, the solvation capabilities offered by commercial stationary phases is limited and can oftentimes be redundant.<sup>5</sup>

Ionic liquids (ILs) are organic salts that possess melting points at or below 100 °C. They are typically composed of an organic cation paired with an inorganic or organic counteranion. Unlike contemporary stationary phases, ILs are capable of undergoing a multitude of different solvation interactions that can provide unique chromatographic selectivities.<sup>6–8</sup> In addition, ILs can be structurally tailored to possess high viscosities and thermal stabilities permitting the production of

GC columns that exhibit high separation efficiency and broader maximum allowable operating temperatures (MAOT).<sup>9,10</sup> Today's commercial IL stationary phases reportedly consist of various cations paired with the bis[(trifluoromethyl)sulfonyl]imide ([NTf<sub>2</sub>]) anion and possess MAOTs up to 300 °C.<sup>11</sup>

Commercial IL stationary phases have been employed in the separation of mid- to high-polarity analytes, such as fatty acid methyl esters,<sup>12,13</sup> flavor and fragrance compounds,<sup>14,15</sup> aromatic hydrocarbons,<sup>16</sup> alkylphosphonates,<sup>17</sup> alkyl halides,<sup>18</sup> and other polar analytes (oxygen-, nitrogen-, and sulfur-containing compounds) by 1D-GC and comprehensive two-dimensional gas chromatography (GC × GC).<sup>18–20</sup> However, in both the nonpolar × polar and polar × nonpolar column sets, it was observed that nonpolar analytes, such as aliphatic hydrocarbons and monoterpene hydrocarbons, were not significantly retained by the IL-based columns including SLB-IL59, SLB-IL61, SLB-IL100, and SLB-IL111.<sup>12,14,16–20</sup> These results seem to indicate that less polar IL stationary phases may be interesting alternatives for the separation of nonpolar

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analytes in complex samples. Recently, commercial IL-based columns, namely, SLB-IL59, SLB-IL76, SLB-IL82, and SLB-IL100, were characterized as being very polar and highly cohesive with similar solvation capabilities.<sup>21</sup> Thus, rational structural design of IL stationary phases may impart the required solvation capabilities needed to separate nonpolar analytes in complex samples. Also, IL-based columns should possess high MAOTs to allow highly efficient separation of high boiling point analytes. These features are of utmost importance on the separation of nonpolar analytes with a broad range of vapor pressures, such as those found in the fields of petroleomics, fuel analysis, and flavor and fragrance analysis.<sup>14,22</sup>

Recently, our group has shown that the solvation capabilities of IL-based stationary phases can be tailored through careful structural design of the IL.<sup>23,24</sup> It was observed that imparting longer alkyl substituents into the cationic moiety had a significant effect on the cohesive forces of the IL and could also be regulated by the anionic component. In an effort to overcome the shortcomings of commercial IL stationary phases, new IL stationary phases capable of expanding the range of analytes that can be efficiently separated by GC  $\times$  GC employing IL-based columns have been developed. In this study, two groups of IL stationary phases are carefully examined in the separation of aliphatic hydrocarbons from kerosene. The first group consists of more cohesive imidazolium-based IL stationary phases, while the second group consists of less cohesive phosphonium-based IL stationary phases capable of nonspecific dispersive interactions. From these experiments, the role of dispersive interactions on the chromatographic retention of nonpolar analytes was evaluated. The assessment of the solvation characteristics of GC columns guided the selection of the best performing IL-based stationary phases for the resolution of aliphatic hydrocarbons. The analytical performance and MAOT of the IL-based columns derived in this study were compared to that of commercial columns (i.e., OV-1701, SUPELCOWAX 10, SLB-IL60, SLB-IL100, and SLB-IL111). This study demonstrates that oriented structural design of IL-based stationary phases can provide greater selectivities for classes of analytes that current IL-based columns separate poorly. These new IL-based stationary phases provide improved separation of nonpolar analytes in complex samples as well as the ability to perform separations at high temperatures. This is very important in the fields of petroleomics, fuel analysis, and flavor and fragrance analysis where highly selective and low bleed stationary phases are essential.

## MATERIALS AND METHODS

**Chemicals and Materials.** Kerosene was purchased from a local distributor. The reagents 1-methylimidazole, 1-chlorobutane, iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), and a  $\text{C}_8$ – $\text{C}_{20}$  *n*-alkane standard mixture were purchased from Sigma-Aldrich (St. Louis, MO, USA). The OV-1701 silicone oil (poly(cyanopropylphenyldimethylsiloxane) with 14% cyanopropylphenylsiloxane monomer incorporation) and a 30 m  $\times$  200  $\mu\text{m}$  SUPELCOWAX 10 (PEG) column ( $d_f = 0.20 \mu\text{m}$ ) were purchased from Supelco (Bellefonte, PA, USA). The 15 m  $\times$  100  $\mu\text{m}$  SLB-IL60 (1,12-di(tripropylphosphonium)dodecane  $[\text{NTf}_2]$ ) ( $d_f = 0.08 \mu\text{m}$ ), 20 m  $\times$  180  $\mu\text{m}$  SLB-IL100 (poly(1,9-di(3-vinylimidazolium)nonane)  $[\text{NTf}_2]$ ) ( $d_f = 0.14 \mu\text{m}$ ), and 30 m  $\times$  250  $\mu\text{m}$  SLB-IL111 (1,5-di(2,3-dimethylimidazolium)-pentane  $[\text{NTf}_2]$ ) ( $d_f = 0.20 \mu\text{m}$ ) columns were provided as a

gift by Supelco. The trihexyl(tetradecyl)phosphonium chloride ( $[\text{P}_{66614}][\text{Cl}]$ ) IL was purchased from Strem Chemicals (Newburyport, MA, USA) and the trihexyl(tetradecyl)-phosphonium tris(pentafluoroethyl)trifluorophosphate ( $[\text{P}_{66614}][\text{FAP}]$ ) IL was provided as a gift by Merck KGaA (Darmstadt, Germany). Forty-six probe molecules were selected for the characterization of the IL stationary phases using the solvation parameter model (see Supporting Information).

**Instrumentation.** All gas chromatography measurements used to characterize the stationary phases and determine the MAOT (i.e., bleed profile) of the IL-based columns were performed on an Agilent 6890 GC-FID. Two-dimensional separations were performed on a GC  $\times$  GC-FID prototype assembled on an Agilent 6890 GC-FID equipped with a two-stage cryogenic loop modulator. A full description and illustration of the GC  $\times$  GC prototype are included in the Supporting Information.

**Ionic Liquid Synthesis and Preparation of IL-Based GC Columns.** The detailed synthesis procedures of 1-butyl-3-methylimidazolium tetrachloroferrate ( $[\text{C}_4\text{MIM}][\text{FeCl}_4]$ ),  $[\text{C}_4\text{MIM}][\text{NTf}_2]$ , trihexyl(tetradecyl)phosphonium tetrachloroferrate ( $[\text{P}_{66614}][\text{FeCl}_4]$ ), and  $[\text{P}_{66614}][\text{NTf}_2]$  are included as Supporting Information. Prior to coating the IL-based columns, all ILs were placed under vacuum at 60  $^\circ\text{C}$  overnight to remove residual water. A 0.25% (w/v) coating solution was prepared by dissolving the neat IL in dry methylene chloride. During preparation of the IL coating solutions, no wetting agents were employed as they may alter the selectivity of the stationary phase.<sup>5</sup> Five-meter untreated capillary columns were coated by the static method at 40  $^\circ\text{C}$ . The solvation parameter model was used to characterize the IL-based columns. Detailed descriptions of the column preparation and characterization are included as Supporting Information.

**GC  $\times$  GC-FID Analysis.** While evaluating the selectivities of the IL-based columns, the primary column consisted of a Rtx-5 capillary column (poly(diphenyldimethylsiloxane) with 5% diphenylsiloxane monomer incorporation;  $d_f = 0.25 \mu\text{m}$ ) (Restek, Bellefonte, PA, USA) connected to the secondary capillary column consisting of an IL-based stationary phase. A total of eight IL stationary phases, listed in Table S7, Supporting Information, were used to investigate the Rtx-5  $\times$  IL column set. The following five IL-based columns were examined:  $[\text{C}_4\text{MIM}][\text{NTf}_2]$ ,  $[\text{C}_4\text{MIM}][\text{FeCl}_4]$ ,  $[\text{P}_{66614}][\text{NTf}_2]$ ,  $[\text{P}_{66614}][\text{FAP}]$ , and  $[\text{P}_{66614}][\text{FeCl}_4]$ . For comparison, three commercially available IL-based columns were also evaluated, namely, SLB-IL60, SLB-IL100, and SLB-IL111. In addition, SUPELCOWAX 10 and OV-1701 were used as reference stationary phases for the analysis of aliphatic hydrocarbons.

In all experiments, 1  $\mu\text{L}$  of the kerosene sample was injected using a 300:1 split ratio at 250  $^\circ\text{C}$ . The chromatographic oven was programmed from 40 to 120  $^\circ\text{C}$  at 2  $^\circ\text{C min}^{-1}$ , followed by a secondary ramp from 120 to 200  $^\circ\text{C}$  at 20  $^\circ\text{C min}^{-1}$ . Hydrogen was employed as carrier gas at a constant flow of 1.2 mL  $\text{min}^{-1}$ , except for the SLB-IL60 column, which employed 0.6 mL  $\text{min}^{-1}$ . The modulation period was 7 s for all experiments. All experiments were performed in duplicate.

## RESULTS AND DISCUSSION

**Solvation Parameter Model.** The solvation parameter model, developed by Abraham and co-workers,<sup>25</sup> is a linear free-energy relationship that describes and estimates the strength of individual solvation interactions of the stationary

phase. The model, as described by eq 1, uses  $k$  as the retention factor for each probe molecule and the parameters  $E$ ,  $S$ ,  $A$ ,  $B$ ,  $L$  as the solute descriptors. The model measures the contribution of specific intermolecular interactions during the solvation process, namely, the ability of the liquid stationary phase to interact with analytes by electron lone pair interactions ( $e$ ), dipole-type and dispersive interactions ( $s$  and  $l$ , respectively), and the hydrogen bond basicity and acidity of the stationary phase ( $a$  and  $b$ , respectively).<sup>25</sup>

$$\log k = c + eE + sS + aA + bB + lL \quad (1)$$

The system constants are estimated by multiple linear regression analysis of the retention factor for a number of solutes with known solute descriptors. The choice of solute and the corresponding solute descriptors is of fundamental importance in order to provide accurate estimate of the solvation capabilities of the stationary phase. The selected solutes must have a broad coverage of the solute descriptor space and be sufficient in number to allow statistical and chemical validity of the model.<sup>26</sup>

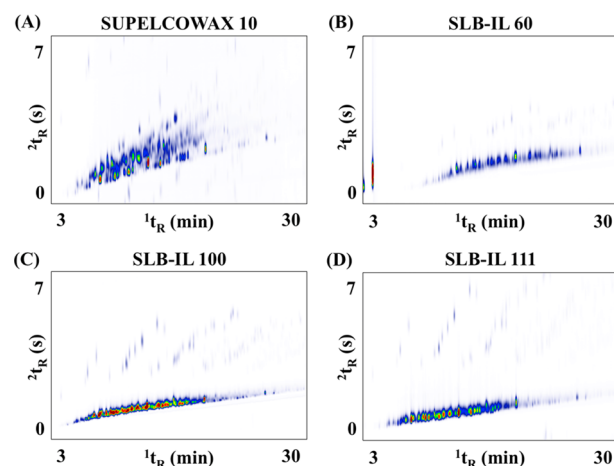
**Characterization of Ionic Liquid Stationary Phases.** A significant advantage of IL-based stationary phases is their ability to have moderate to high thermal stability while also exhibiting a broad multitude of solvation capabilities, characteristic of their unique selectivities. For the past several years, the use of commercial IL-based stationary phases in the analysis of complex samples has revealed comparable and even superior chromatographic performance compared to contemporary polar stationary phases (e.g., OV-1701 and SUPELLOWAX 10 columns). However, these results seem to be limited to the separation of mid- to high-polarity analytes.<sup>12–20</sup> Despite their success, commercial IL-based stationary phases lack the resolving power of nonpolar analytes, particularly cycloalkanes and saturated and unsaturated hydrocarbons (i.e., aliphatic hydrocarbons). This lack of selectivity has dampened enthusiasm among some separation scientists who may downplay the feature of structural tuning (in terms of cation/anion pairing and structural features of each component) when developing ILs to exhibit high selectivity and strong resolving power.

To address the limitations of commercial IL-based stationary phases, kerosene was selected as the model complex sample because it is composed of numerous aliphatic hydrocarbons and its group-type separation by GC  $\times$  GC is already known and well-described in previous literature reports (see Supporting Information). Five IL-based stationary phases were carefully designed and evaluated as the <sup>2</sup>D column in GC  $\times$  GC separations by employing the common nonpolar  $\times$  polar setup.<sup>1</sup> In addition, three commercial IL-based stationary phases and two traditional polar stationary phases were evaluated for comparison purposes. A total of ten column sets, as listed in Table S7, Supporting Information, were examined in this study.

This study began by examining the Rtx-5  $\times$  IL column sets. As in any MDGC separation, the column set must combine stationary phases with different selectivities (i.e., solvation capabilities).<sup>27</sup> The Rtx-5 stationary phase is characterized by low cohesion with governing contribution to retention being the favorable cavity formation/dispersion interactions.<sup>5</sup> This stationary phase is also weakly dipolar/polarizable and hydrogen bond basic, as shown in Table S8, Supporting Information. Hence, an appropriate <sup>2</sup>D column should possess complementary solvation interactions (i.e., capable of dipole-

type, electron lone pair, hydrogen bond basic, or hydrogen bond acidic interactions).

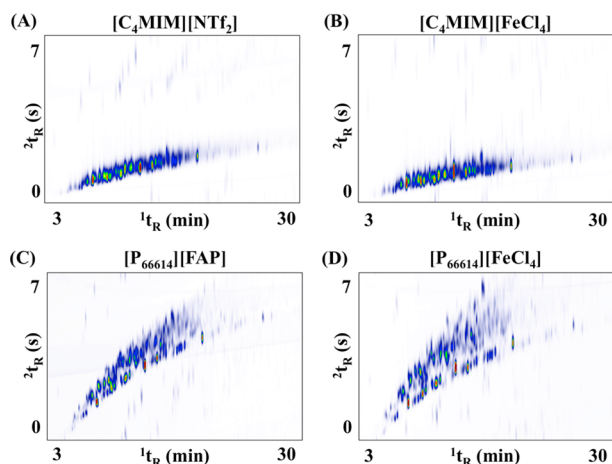
Typically, the use of more polar secondary columns, such as OV-1701 (MAOT of 250 °C) and SUPELLOWAX 10 (MAOT of 280 °C), generates increased resolution of nonpolar analytes in GC  $\times$  GC separations. Poly-(cyanopropylphenyldimethylsiloxane) stationary phases (e.g., OV-1701) are more cohesive and strongly dipolar/polarizable and hydrogen bond basic, while PEG stationary phases (e.g., SUPELLOWAX 10) are also more hydrogen bond basic and strongly dipolar/polarizable but are generally less cohesive.<sup>5</sup> Figure S6A, Supporting Information, and Figure 1A show the



**Figure 1.** GC  $\times$  GC-FID chromatograms of kerosene employing several Rtx-5  $\times$  polar column sets: (A) SUPELLOWAX 10, (B) SLB-IL60, (C) SLB-IL100, and (D) SLB-IL111.

GC  $\times$  GC-FID chromatograms for the separation of aliphatic hydrocarbons in kerosene employing the Rtx-5  $\times$  OV-1701 and Rtx-5  $\times$  SUPELLOWAX 10 column sets, respectively. It can be observed that the separation of aliphatic hydrocarbons was significantly enhanced when using SUPELLOWAX 10 compared to OV-1701. Recently, some commercial IL-based columns were characterized as being highly cohesive phases with governing contribution to retention being dipole-type and hydrogen bond basic interactions.<sup>21</sup> Figure 1B–D shows the separation of aliphatic hydrocarbons in kerosene by GC  $\times$  GC-FID employing commercial IL-based <sup>2</sup>D columns, namely, SLB-IL60 (MAOT of 300 °C), SLB-IL100 (MAOT of 230 °C), and SLB-IL111 (MAOT of 270 °C). It can be observed that aliphatic hydrocarbons are not resolved by any of the commercial IL-based columns. Hence, the structural design of IL-based stationary phases to provide greater selectivity for classes of analytes that commercial IL-based columns separate poorly is desperately needed.

The [C<sub>4</sub>MIM][NTf<sub>2</sub>] and [C<sub>4</sub>MIM][FeCl<sub>4</sub>] ILs were evaluated as <sup>2</sup>D stationary phases in GC  $\times$  GC separations employing the Rtx-5  $\times$  IL column sets. Figure 2A shows a GC  $\times$  GC-FID chromatogram of kerosene using the Rtx-5  $\times$  [C<sub>4</sub>MIM][NTf<sub>2</sub>] column set. The [C<sub>4</sub>MIM][NTf<sub>2</sub>] IL stationary phase (MAOT of 185 °C) is more cohesive and exhibits no hydrogen bond acidic behavior and no electron lone pair interactions, but it is hydrogen bond basic and can accommodate strong dipole-type interactions (see Table S8, Supporting Information). However, the [C<sub>4</sub>MIM][NTf<sub>2</sub>] IL stationary phase did not resolve the aliphatic hydrocarbons in kerosene. The [C<sub>4</sub>MIM][FeCl<sub>4</sub>] IL stationary phase (MAOT



**Figure 2.** GC  $\times$  GC-FID chromatograms of kerosene employing several Rtx-5  $\times$  IL column sets: (A)  $[\text{C}_4\text{MIM}][\text{NTf}_2]$  IL, (B)  $[\text{C}_4\text{MIM}][\text{FeCl}_4]$  IL, (C)  $[\text{P}_{66614}][\text{FAP}]$  IL, and (D)  $[\text{P}_{66614}][\text{FeCl}_4]$  IL.

of 230  $^{\circ}\text{C}$ ) is cohesive, more hydrogen bond basic, and is capable of stronger dipole-type interactions than the  $[\text{C}_4\text{MIM}][\text{NTf}_2]$  IL. Figure 2B shows a GC  $\times$  GC-FID chromatogram of kerosene using the Rtx-5  $\times$   $[\text{C}_4\text{MIM}][\text{FeCl}_4]$  column set. By visual inspection, it can be observed that this IL stationary phase also did not resolve the nonpolar aliphatic hydrocarbons. In the light of these results, it seems that more cohesive IL stationary phases cannot provide the selectivity required for the separation of aliphatic hydrocarbons.

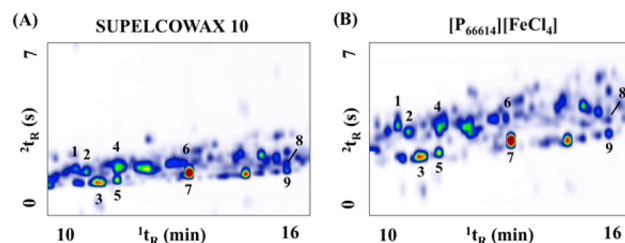
#### Structural Tuning of Ionic Liquid Stationary Phases.

Heavily alkylated phosphonium ILs, such as  $[\text{P}_{66614}][\text{NTf}_2]$  and  $[\text{P}_{66614}][\text{FAP}]$ , have been previously characterized by the solvation parameter model.<sup>23,28</sup> The data in these studies indicated that imparting long alkyl chains to the cationic moiety generates less cohesive IL stationary phases capable of nonspecific dispersive interactions. Figure S6B, Supporting Information, illustrates a GC  $\times$  GC-FID chromatogram of kerosene using the Rtx-5  $\times$   $[\text{P}_{66614}][\text{NTf}_2]$  column set. The resulting separation indicates that less cohesive IL stationary phases might possess the selectivity needed to enhance the resolution of aliphatic hydrocarbons. It has been shown previously that solvation capabilities of IL stationary phases are largely determined by the nature of the counteranion.<sup>23,24</sup> Recently, it was demonstrated that replacing the  $[\text{NTf}_2]$  anion by the  $[\text{FAP}]$  anion, while maintaining the same cation, reduced significantly the cohesion of the IL stationary phase.<sup>23</sup> To explore the selectivity of the  $[\text{P}_{66614}][\text{FAP}]$  IL, the Rtx-5  $\times$   $[\text{P}_{66614}][\text{FAP}]$  column set was evaluated. Figure 2C shows a GC  $\times$  GC-FID chromatogram of kerosene exploring this column set. It can be readily observed that enhanced resolution of the aliphatic hydrocarbons was attained with the less cohesive  $[\text{P}_{66614}][\text{FAP}]$  IL stationary phase when compared to the commercial IL-based stationary phases, shown in Figure 1. Also, symmetric chromatographic peaks were observed for aliphatic hydrocarbons indicating no significant column reactivity toward these nonpolar compounds (see Table S9, Supporting Information). In addition, the  $[\text{P}_{66614}][\text{FAP}]$  IL (MAOT of 290  $^{\circ}\text{C}$ ) can be operated at higher operating temperatures than the OV-1701, SUPELCOWAX 10, SLB-IL100, and SLB-IL111 commercial columns.

**Evaluation of Multiple Solvation Capabilities.** In an attempt to outperform the SUPELCOWAX 10 PEG stationary

phase, an IL stationary phase capable of stronger dipole-type interactions while maintaining low cohesion forces was sought. Inspection of the  $[\text{C}_4\text{MIM}][\text{NTf}_2]$  and  $[\text{C}_4\text{MIM}][\text{FeCl}_4]$  IL system constants indicated that the  $[\text{FeCl}_4]$  anion may impart the required solvation capabilities, while also providing high thermal stability to the resulting IL. IL-based stationary phases exhibiting high thermal stability are necessary to provide efficient separation of high boiling point analytes while minimizing baseline signal drift due to stationary phase volatilization/degradation during high temperature GC analysis.

The  $[\text{P}_{66614}][\text{FeCl}_4]$  IL stationary phase possesses comparable cohesion forces to the  $[\text{P}_{66614}][\text{FAP}]$  IL but is more hydrogen bond basic and can engage in stronger dipole-type interactions, as shown in Table S8, Supporting Information. Figure 2D shows a GC  $\times$  GC-FID chromatogram of kerosene using the Rtx-5  $\times$   $[\text{P}_{66614}][\text{FeCl}_4]$  column set. It can be readily observed that increased resolution of the aliphatic hydrocarbons was achieved as compared to the commercial IL-based phases and the more cohesive imidazolium ILs, namely,  $[\text{C}_4\text{MIM}][\text{NTf}_2]$  and  $[\text{C}_4\text{MIM}][\text{FeCl}_4]$ . Figure 3 shows a



**Figure 3.** Expanded GC  $\times$  GC-FID chromatograms of kerosene employing (A) Rtx-5  $\times$  SUPELCOWAX 10 and (B) Rtx-5  $\times$   $[\text{P}_{66614}][\text{FeCl}_4]$  column set. The separation performance metrics for selected pairs of analytes are shown in Tables S9 and S10, Supporting Information.

side-by-side comparison of an expanded region of the GC  $\times$  GC-FID chromatogram of kerosene exploring the Rtx-5  $\times$  SUPELCOWAX 10 and Rtx-5  $\times$   $[\text{P}_{66614}][\text{FeCl}_4]$  column sets. Visual inspection of these chromatograms show that the  $[\text{P}_{66614}][\text{FeCl}_4]$  IL exhibits increased resolution of the aliphatic hydrocarbons when used as the  $^2\text{D}$  stationary phase compared to SUPELCOWAX 10. For validation, comparison of the separation performance metric for the selected analytes, shown in Figure 3, indicated that larger values of  $^2\text{D}$  separation capacity were attained when the structurally tuned  $[\text{P}_{66614}][\text{FeCl}_4]$  IL was examined as the  $^2\text{D}$  stationary phase (Table S9, Supporting Information). This IL-based column provided greater selectivity, symmetrical peaks, and an absence of column reactivity toward nonpolar analytes (see Tables S10 and S11, Supporting Information) that commercial columns separate poorly. In addition, the  $[\text{P}_{66614}][\text{FeCl}_4]$  IL can operate at a MAOT of 320  $^{\circ}\text{C}$ , which is higher than those exhibited by all of the commercial GC columns examined in this study. The analytical performance of the  $[\text{P}_{66614}][\text{FeCl}_4]$  IL-based column was not affected by continuous exposure to the temperature program employed in the analysis of kerosene. Finally, the outstanding thermal stability of this stationary phase is 40  $^{\circ}\text{C}$  higher than that of the SUPELCOWAX 10 stationary phase.

## CONCLUSIONS

ILs have drawn considerable attention as GC stationary phases because of their tunable physical and chemical properties. However, commercial IL-based GC columns have not explored all of the solvation properties that can be offered by ILs. In this study, cavity formation/dispersive interaction was demonstrated as an important solvation interaction on the chromatographic retention of nonpolar analytes in GC  $\times$  GC separations. Evaluation of the solvation characteristics of GC columns successfully guided the selection of the best performing IL-based stationary phases for the resolution of aliphatic hydrocarbons, namely, the  $[P_{66614}][FeCl_4]$  and  $[P_{66614}][FAP]$  ILs. Careful structural design of the  $[P_{66614}][FeCl_4]$  IL produced a stationary phase capable of strong dipole-type and dispersive interactions and thereby improved the resolution of aliphatic hydrocarbons from kerosene compared to the commercial columns examined. The  $[P_{66614}][FeCl_4]$  IL-based GC column exhibited a MAOT of 320 °C, significantly higher than that of other commercial IL-based and SUPELCOWAX 10 columns. This study demonstrates that oriented structural design of IL-based stationary phases can provide greater selectivities for the classes of analytes that current commercial IL-based stationary phases separate poorly.

## ASSOCIATED CONTENT

### Supporting Information

Additional information as noted in text. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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### Notes

The authors declare no competing financial interest.

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