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Characterizing Olefin Selectivity and Stability of Silver Salts in Ionic Liquids Using Inverse Gas Chromatography

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Abstract
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Characterizing Olefin Selectivity and Stability of Silver Salts in Ionic Liquids Using Inverse Gas Chromatography

Philip Eor, Donghyun Ryoo, He Nan, and Jared L. Anderson*

ABSTRACT: Separation systems utilizing silver(I) ion-olefin complexion have limitations since silver(I) ions can be poisoned or reduced to metallic silver. Ionic liquids (ILs) are used as solvents for silver(I) ions to facilitate separations since their physico-chemical properties can be easily tuned. To develop separation systems with sustainable olefin selectivity, factors that affect silver(I) ion stability need to be understood. In this study, a total of 13 silver salt/IL mixtures were examined by inverse gas chromatography to identify the effects of silver salt anion and IL cation/anion combination on silver(I) ion stability. The effects of temperature and three different exposure gases on silver(I) ion stability were systematically studied. Exposing silver salt/IL mixtures to hydrogen at high temperatures had a greater effect on decreasing silver(I) ion-olefin complexion. Silver(I) ions from the silver bis[(trifluoromethyl)sulfonyl]imide ([NTf2−]) salt were more stable in [NTf2−]-containing ILs than in [BF4−]-containing ILs. Optimum mixtures exhibited high olefin selectivity and were stable beyond 90 h when exposed to hydrogen gas.

1. INTRODUCTION

Silver(I) ion has been applied as a component in various separation techniques because of its capability of undergoing reversible complexation with unsaturated compounds, such as alkenes, alkynes, and ketones.1−3 It has been widely used as a carrier in facilitated transport membranes (FTMs),4−7 as an adsorbent for ethylene/ethane separation4 and fatty acid methyl ester separation,5 and as a stationary phase additive for the separation of alkene isomers.6,10−11 To effectively utilize silver(I) ions in separation systems, an understanding of its stability under the operating conditions of the separation method is vital. It is well-known that silver(I) ion stability can be affected by a number of factors, including light and exposure to various elements/chemicals such as hydrogen, hydrogen sulfide, and acetylenic compounds.10,11 For example, hydrogen gas can facilitate the reduction of silver(I) ion to metallic silver resulting in a loss of selective complexation with olefins.12 To improve silver(I) ion stability, several approaches have been utilized such as the addition of stabilizing reagents, regenerating silver(I) ion using peroxide/acid treatment, and dissolving silver salts into various protective media such as task-specific solvents and polymers.13,16−22

A number of studies have utilized ionic liquids (ILs) as solvents to dissolve silver salts to improve separation performance.23−27 ILs are a class of nonmolecular solvents with melting points lower than 100 °C.28 ILs possess a number of desirable properties such as negligible vapor pressure that precludes their loss due to evaporation at elevated temperature, excellent thermal stability that extends the temperature range of the separation technique, and structural tunability that provides the capability of imparting desired selectivity toward target compounds.29−33 Fallanza and co-workers have evaluated the solubilities of propane and propylene in membrane separations using different combinations of imidazolium, pyridinium, and ammonium-based ILs and silver salts such as silver tetrafluoroborate, silver nitrate, and silver bis[(trifluoromethyl)sulfonyl]imide ([NTf2−]).23 It was found that anions of the silver salt and structural features of IL solvents strongly affect the olefin capacity and selectivity. Huang and co-workers applied silver-IL complexes, in which the silver(I) ion was a component of the cation, to separate olefin/paraffin mixtures using FTMs.24 [Ag(olefin)][NTf2−] and [Ag(PrNH2)+][NTf2−] silver-IL complexes exhibited excellent separation performance due to fast molecular diffusion as well as efficient transport of the olefin ligands via shifting between silver(I) ion centers. Agel and co-workers reported that the [Ag(propene)3+][NTf2−] silver-IL complex possessing a high silver(I) ion concentration exhibited...
increased olefin capacity and selectivity in the FTM separation of light olefin/paraffin mixtures.\textsuperscript{43} Silver-containing ILs have also been applied as stationary phases for the separation of saturated and unsaturated analytes by one-dimensional and comprehensive two-dimensional gas chromatography.\textsuperscript{26,27} Compared to widely used polar stationary phases composed of poly(ethylene glycol) (PEG), the silver-containing IL stationary phases exhibited improved separation of olefins, esters, and unsaturated fatty acids. Moreover, both studies indicated that ILs contribute to the stabilization of silver(I) ion and play an important role in developing sustainable separation systems that exploit the complexation capability of the silver(I) ion.

Separation systems are often exposed to many different environmental conditions that can affect temporal stability. An evaluation of silver(I) ion stability in separation systems under these conditions is critical toward understanding factors that lead to degradation and reduced selectivity of the separation media. Previous studies have compared the initial and final performances of FTMs impregnated with silver(I) compounds after hydrogen gas exposure and thermal cycling.\textsuperscript{26,24,34} Until now, no study has systematically evaluated the role of silver salt anion, the nature of dissolving solvent, as well as the effect of temperature and exposure to inert/reactive gases on the stability of silver(I) ions. To achieve this, a sensitive approach capable of monitoring the degradation of silver(I) ions over time is necessary to guide the design of more stable and sustainable materials. Inverse gas chromatography (IGC) is a technique in which solvation characteristics of the stationary phase (solvent) are measured based on the chromatographic retention of probe molecules.\textsuperscript{35,36} IGC has been applied to measure the surface energy of materials\textsuperscript{37,38} and absorption/adsorption properties,\textsuperscript{39} determine the solubility/diffusion coefficients\textsuperscript{40} and phase transitions,\textsuperscript{44} and obtain the thermodynamic information for a diverse array of materials.\textsuperscript{42} As a versatile and powerful technique to characterize advanced materials, IGC is ideal to examine silver(I) ion stability, particularly, since important conditions, such as temperature and gas exposure, can be carefully controlled.

In this study, IGC is used to investigate the effects of temperature and gas streams (e.g., helium, nitrogen, and hydrogen) on the temporal stability of silver(I) ions in various mixtures of silver salts and ILs with different cation and anion compositions. The results from this study are important in delineating the role of silver salt and IL in designing separation systems that can sustain high olefin selectivity under various conditions.

2. RESULTS AND DISCUSSION
To study the temporal stability of silver(I) ion under different conditions, it is important that the silver salt be completely soluble in the IL solvent.\textsuperscript{44} Solubilities of four silver salts in PEG and four ILs with different chemical structures and compositions were examined, as described in the Supporting Information. Based on the results in Figures S4–S6, only silver salts that were soluble in the solvents were studied by IGC.

2.1. Silver(I) Ion-Olefin Complexation in IL Solvents.

The complexation of silver(I) ion and olefinic compounds was monitored by studying the retention behavior of probe molecules using IGC. Figure 1 describes the role of IGC in studying silver(I) ion-olefin complexation. The probe molecules hexane, 1-hexene, 2-hexyne, and methyl tiglate (see Table S3 of the Supporting Information) were injected in the carrier gas and allowed to partition to a thin layer of silver salt/IL mixture (stationary phase). The probes are retained according to the strength of their interaction with the silver salt/IL mixture. The probe molecules were selected because of their structural similarities and the fact that they possess different π-bonding character. The retention factor (k), calculated by k = (tR – t0)/t0, where tR is the retention time of the probe molecule and t0 is the dead time measured with propane, is used to compare the strength of silver(I) ion-olefin complexation.\textsuperscript{45} Larger retention factors indicate stronger interaction (i.e., stronger complexation) of the probe to the silver salt/IL mixture.

As shown in Table 1, columns of PEG or neat IL solvents without silver salts (columns 17–22) did not exhibit a discernible difference in the retention of hexane, 1-hexene, and 2-hexyne. Since methyl tiglate is a more polar molecule, its retention varies depending on the polarity/solvation properties of the solvent. However, upon addition of silver salt to the IL solvents, the retention factors of 1-hexene and 2-hexyne increased, and the extent to which the retention factor increased was observed to depend largely on the composition of silver salt/IL mixture. For example, addition of [Ag⁺][NTf₂⁻] to each corresponding IL resulted in increased retention factors for 1-hexene and 2-hexyne. Table S4 shows the ratio between the initial retention factor of olefin probes on neat IL columns and [Ag⁺][NTf₂⁻]/IL-based columns. The [Ag⁺][NTf₂⁻]/[BMIM⁺][NTf₂⁻] (column 1) and [Ag⁺][NTf₂⁻]/[BMIM⁺][BF₄⁻] (column 3) mixtures exhibited a remarkable increase in olefin retention compared to their corresponding neat ILs (columns 17 and 19 in Table 1, respectively). All silver salt/PEG mixtures exhibited low retention of these probes, for which all retention factors were lower than 1.0 (see Table 1). IL-based mixtures such as [Ag⁺][NTf₂⁻]/[BMIM⁺][BF₄⁻] (column 3), [Ag⁺][BF₄⁻]/[BMIM⁺][BF₄⁻] (column 8), [Ag⁺][NTf₂⁻]/[DMIM⁺][NTf₂⁻] (column 14), and [Ag⁺][NTf₂⁻]/[DMIM⁺][BF₄⁻] (column 16) exhibited considerably high olefin retention, with
2.2. Environmental Conditions Affecting Silver (I) Ion Stability. To simulate the effect of environmental factors on the interaction of probe molecules with silver salt/IL mixtures, the IGC system was configured to expose the system to pure varying gas streams and temperatures.

2.2.1. Effect of Silver Salt Counter Anion. The variations of 1-hexene retention in the [Ag⁺][NTf₂]⁻/[BMIM⁺][NO₃⁻] (column 14) and [Ag⁺][TfO⁻]/[DMIM⁺][NTf₂]⁻ (column 15) mixtures are shown in Figure 2a. The initial retention factor of 1-hexene in columns 14 and 15 was 4.61 and 5.42, respectively. The retention factor of 1-hexene in column 14 was stable until 110 °C under helium exposure. However, after exposure to nitrogen at 110 °C, the retention factor began to decrease. For column 15, the retention factor under nitrogen exposure did not change until approximately at 80 °C, and a notable decrease was observed after hydrogen exposure at 80 °C. The retention factor decreased much more dramatically with increased temperature compared to column 14. As shown in Figure S8a, the variation of retention factor for 2-hexyne in columns 14 and 15 was analogous to that for 1-hexene.

Table 1. Composition of Silver Salt and Dissolving Solvent (PEG or IL) for Chromatographic Columns Examined in this Study. Initial Retention Factors of Hexane, 1-Hexene, 2-Hexyne, and Methyl Tiglate were Determined with Each Column

<table>
<thead>
<tr>
<th>Column no.</th>
<th>silver salt (cation/anion)</th>
<th>dissolving solvent</th>
<th>column length (m)</th>
<th>initial k_hexane</th>
<th>initial k₁-hexene</th>
<th>initial k₂-hexyne</th>
<th>initial k_methyl tiglate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>[BMIM⁺][NTf₂⁻]</td>
<td>4.6</td>
<td>0.05</td>
<td>2.78</td>
<td>7.55</td>
<td>16.53</td>
</tr>
<tr>
<td>2</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>[BMIM⁺][NO₃⁻]</td>
<td>5.0</td>
<td>0.02</td>
<td>0.04</td>
<td>0.22</td>
<td>5.23</td>
</tr>
<tr>
<td>3</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>[BMIM⁺][BF₄⁻]</td>
<td>5.0</td>
<td>0.02</td>
<td>22.83</td>
<td>66.43</td>
<td>20.38</td>
</tr>
<tr>
<td>4</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>[BMIM⁺][TfO⁻]</td>
<td>5.3</td>
<td>0.05</td>
<td>1.00</td>
<td>2.70</td>
<td>12.27</td>
</tr>
<tr>
<td>5</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>PEG</td>
<td>5.4</td>
<td>0.08</td>
<td>0.13</td>
<td>0.75</td>
<td>12.33</td>
</tr>
<tr>
<td>6</td>
<td>[Ag⁺][NO₃⁻]</td>
<td>[BMIM⁺][NO₃⁻]</td>
<td>5.0</td>
<td>0.03</td>
<td>0.05</td>
<td>0.25</td>
<td>5.57</td>
</tr>
<tr>
<td>7</td>
<td>[Ag⁺][BF₄⁻]</td>
<td>[BMIM⁺][NO₃⁻]</td>
<td>5.0</td>
<td>0.02</td>
<td>0.05</td>
<td>0.30</td>
<td>6.93</td>
</tr>
<tr>
<td>8</td>
<td>[Ag⁺][BF₄⁻]</td>
<td>[BMIM⁺][BF₄⁻]</td>
<td>5.4</td>
<td>0.30</td>
<td>18.18</td>
<td>54.79</td>
<td>16.97</td>
</tr>
<tr>
<td>9</td>
<td>[Ag⁺][BF₄⁻]</td>
<td>PEG</td>
<td>4.5</td>
<td>0.06</td>
<td>0.10</td>
<td>0.61</td>
<td>9.98</td>
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<tr>
<td>10</td>
<td>[Ag⁺][TfO⁻]</td>
<td>[BMIM⁺][NTf₂⁻]</td>
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<td>0.04</td>
<td>2.02</td>
<td>5.52</td>
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<tr>
<td>11</td>
<td>[Ag⁺][TfO⁻]</td>
<td>[BMIM⁺][NO₃⁻]</td>
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<td>0.02</td>
<td>0.04</td>
<td>0.27</td>
<td>6.29</td>
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<tr>
<td>12</td>
<td>[Ag⁺][TfO⁻]</td>
<td>[BMIM⁺][TfO⁻]</td>
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<td>0.31</td>
<td>0.95</td>
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<td>10.04</td>
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<td>[Ag⁺][TfO⁻]</td>
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<td>0.04</td>
<td>0.08</td>
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<td>6.35</td>
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<td>14</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>[DMIM⁺][NTf₂⁻]</td>
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<td>0.18</td>
<td>4.61</td>
<td>11.16</td>
<td>28.77</td>
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<tr>
<td>15</td>
<td>[Ag⁺][TfO⁻]</td>
<td>[DMIM⁺][NTf₂⁻]</td>
<td>5.0</td>
<td>0.14</td>
<td>5.42</td>
<td>12.85</td>
<td>22.21</td>
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<tr>
<td>16</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>[DMIM⁺][BF₄⁻]</td>
<td>5.2</td>
<td>0.19</td>
<td>15.90</td>
<td>33.03</td>
<td>21.65</td>
</tr>
<tr>
<td>17</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>[BMIM⁺][NTf₂⁻]</td>
<td>4.6</td>
<td>0.06</td>
<td>0.10</td>
<td>0.41</td>
<td>15.08</td>
</tr>
<tr>
<td>18</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>[BMIM⁺][NO₃⁻]</td>
<td>5.0</td>
<td>0.03</td>
<td>0.04</td>
<td>0.27</td>
<td>6.37</td>
</tr>
<tr>
<td>19</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>[BMIM⁺][BF₄⁻]</td>
<td>5.0</td>
<td>0.02</td>
<td>0.03</td>
<td>0.20</td>
<td>6.08</td>
</tr>
<tr>
<td>20</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>[BMIM⁺][TfO⁻]</td>
<td>5.0</td>
<td>0.04</td>
<td>0.07</td>
<td>0.34</td>
<td>10.72</td>
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<tr>
<td>21</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>[DMIM⁺][NTf₂⁻]</td>
<td>4.8</td>
<td>0.18</td>
<td>0.22</td>
<td>0.76</td>
<td>23.17</td>
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<tr>
<td>22</td>
<td>[Ag⁺][NTf₂⁻]</td>
<td>PEG</td>
<td>4.8</td>
<td>0.07</td>
<td>0.11</td>
<td>0.77</td>
<td>12.79</td>
</tr>
</tbody>
</table>

"Initial values are the first retention factors measured immediately after column preparation/conditioning and prior to high temperature exposure.

Silver salt was not added. The internal diameter (0.25 mm) of the capillary columns and the film thickness (0.28 µm) of stationary phases were identical for all prepared columns. Retention measurement conditions: helium flow rate, 1 mL min⁻¹; inlet temperature, 150 °C; oven temperature, 35 °C; FID temperature, 160 °C.

near zero. For every exposure event, the type of gas applied and the temperature setpoint are labeled at the top of each plot. Because of the difference in the magnitude of measured retention factors, plots (a) and (b) in Figure 2 have different scales in their y-axes. Analogous plots for 2-hexyne and methyl tiglate are shown in Figures S8 and S9, respectively. The stability of silver(I) ion in the IL solvent can be evaluated by monitoring the change in the retention factor upon exposure to varying gas streams and temperatures.
Figure 2 shows the retention factor change of 1-hexene in the structure on silver(I) ion-olefin complexation was investigated. Figure 2a shows the retention factor change of 1-hexene in the [Ag⁺][NTf₂−]/[BMIM⁺][NTf₂−] (column 1) and [Ag⁺][NTf₂−]/[DMIM⁺][NTf₂−] (column 14) mixtures, where the initial retention factor of 1-hexene in column 14 was approximately 65.8% larger than that in column 1. The stability of silver(I) ion in both ILs was similar since the retention factors of 1-hexene and 2-hexyne in both columns were stable under helium exposure until 110 °C, followed by a dramatic decrease from 110 °C under hydrogen exposure and finally dropping to lower than 0.3 at 170 °C. The retention behavior of methyl tiglate in columns 1 and 14 was notably different from those of 1-hexene and 2-hexyne, as shown in Figure S9a, and did not change from the beginning to end of the evaluation.

The retention behavior of 1-hexene in the [Ag⁺][TfO−]/[BMIM⁺][NTf₂−] (column 10) and [Ag⁺][TfO−]/[DMIM⁺][NTf₂−] (column 15) mixtures was also similar. The initial retention factor of 1-hexene in column 10 (2.02) was approximately 37.2% that of column 15 (5.42). In column 10, the retention factor of 1-hexene did not change under nitrogen until 95 °C, decreased under hydrogen at 110 and 125 °C, and fell below 0.2 at 140 °C. In both columns 10 and 15, a significant decrease was observed after exposing the mixtures to hydrogen at 95 and 110 °C. The retention change of 2-hexyne was nearly analogous to that of 1-hexene in both columns (Figure S8a), and the retention factor of methyl tiglate was notably constant during the entire evaluation, as shown in Figure S9a.

2.2.3. Influence of IL Anion. Columns 1–4 contain identical amounts of [Ag⁺][NTf₂−] dissolved in the [BMIM⁺][NTf₂−], [BMIM⁺][NO₃−], [BMIM⁺][BF₄−], and [BMIM⁺][TfO−] ILs, respectively. Based on the comparison of initial retention factors of 1-hexene and 2-hexyne in Table 1, the order of silver(I) ion-olefin complexation strength was [Ag⁺][NTf₂−]/[BMIM⁺][BF₄−] (column 3) ≫ [Ag⁺][NTf₂−]/[BMIM⁺][TfO−] (column 4) > [Ag⁺][NTf₂−]/[BMIM⁺][NO₃−] (column 2). Figures 2 and S8 show that columns 3, 1, and 4 began to lose olefin retention at 110, 50, and 95 °C and completely lost selectivity for 1-hexene and 2-hexyne after exposure to 170, 95, and 155 °C, respectively. These results indicate that [Ag⁺][NTf₂−] was most stable in the [BMIM⁺][NTf₂−] IL. Among all applied gas streams, hydrogen tended to result in larger reduction of olefin retention factor. As shown in Figure S9a, the retention of methyl tiglate in columns 1 and 4 was relatively stable compared to 1-hexene and 2-hexyne.

2.3. Effects of Temperature and Hydrogen Gas on [Ag⁺][NTf₂−]/[DMIM⁺][NTf₂−] Mixture. Based on previous results, the [Ag⁺][NTf₂−]/[DMIM⁺][NTf₂−] IL mixture (column 14) was selected for further studies since it exhibited satisfactory silver(I) ion-olefin complexation with a remarkable stabilizing effect for silver(I) ions. Two replicate columns were prepared to independently study the effects of temperature and hydrogen exposure on silver(I) ion stability, with one column being exposed continuously to helium and the other to hydrogen. As shown in Figure 3, initial retention factors of 1-hexene, 2-hexyne, and methyl tiglate were measured at the first stage (A) of each graph with each heating stage held for 6 h and continued until olefin retention was lost.

The retention factors of 1-hexene and 2-hexyne were constant until heating the mixture to 155 °C under helium gas (stage J), as shown in Figure 3a. However, after heating at 170 °C (stage K), the retention factors significantly decreased. The decline was continuous until heating the mixture to 245 °C (stage P), where the retention factors of both 1-hexene and 2-hexyne converged to zero. Since hydrogen was not initially present in this system, the loss of silver(I) ion-olefin complexation capability of silver(I) ion can only be related to the elevated temperature. Upon hydrogen gas exposure, the retention of 1-hexene and 2-hexyne did not change until reaching 95 °C (stage F), began to decrease at 110 °C (stage...
hydrogen gas stream was further investigated at 35 and 110 °C. These temperature setpoints were chosen because silver(I) ions in this mixture were found to be stable at temperatures below 50 °C but vulnerable to change at temperatures over 95 °C (see Figure 3b). The retention factors of 1-hexene, 2-hexyne, and methyl tiglate were measured immediately after column preparation (the initial retention factor) and subsequently after every 6 h segment of exposure. Variation of the retention behavior for the probes upon exposing the columns to hydrogen at 35 °C (open symbols) and 110 °C (filled symbols) is shown in Figure 4. At 35 °C, the retention of all probes did not vary for 90 h of exposure, indicating that silver(I) ions were not affected by either the gas or temperature. However, at 110 °C, a decrease in the retention of 1-hexene and 2-hexyne was observed after approximately 6 h of exposure followed by a continual drop below 1.0 after 72 h of exposure. Variation in methyl tiglate retention was slightly different from the two other probes. As shown in Table S5, the retention factor of methyl tiglate after 90 h of hydrogen exposure at 110 °C was approximately 22.4% smaller than the initial retention factor. Compared to a 94.9 and 96.2% drop for 2-hexyne and 1-hexene, respectively, the decrease in methyl tiglate retention was relatively insignificant.

3. CONCLUSIONS

The effects of different exposure gas streams and temperatures on the temporal stability of silver(I) ion in IL solvents were studied. Chromatographic columns containing a thin layer of silver salt/IL mixtures were exposed to varying gas streams and increasing temperature conditions. The [Ag⁺][NTf₂⁻]/[DMIM⁺][NTf₂⁻] salt underwent more stable complexation with olefins in the [DMIM⁺][NTf₂⁻] IL compared to the [Ag⁺][TFO⁻] salt. In the [BMIM⁺][BF₄⁻] IL, neither [Ag⁺][NTf₂⁻] nor [Ag⁺][BF₄⁻] appeared to be stabilized despite their strong complexation with olefins. Silver(I) ions dissolved in ILs possessing longer alkyl chain substituents (i.e., [DMM⁺]) were found to be more favorable toward silver(I) ion-olefin complexation compared to ILs possessing shorter alkyl chains.

Figure 3. Variation of the retention factor of 1-hexene [○(green)], 2-hexyne [□(orange)], and methyl tiglate [◇(blue)] in [Ag⁺][NTf₂⁻]/[DMIM⁺][NTf₂⁻] (column 14) upon heating under exposure to constant (a) helium gas and (b) hydrogen gas. Temperatures applied for each heating stage are labeled with capital letters at the top of the plots and are as follows: (A) initial; (B) after 35 °C; (C) after 50 °C; (D) after 65 °C; (E) after 80 °C; (F) after 95 °C; (G) after 110 °C; (H) after 125 °C; (I) after 140 °C; (J) after 155 °C; (K) after 170 °C; (L) after 185 °C; (M) after 200 °C; (N) after 215 °C; (O) after 230 °C; and (P) after 245 °C. Retention factors were determined after every heating stage (6 h). Retention measurement conditions: carrier gas flow rate, 1 mL min⁻¹; oven temperature, 35 °C; inlet temperature, 150 °C; FID temperature, 160 °C.

Figure 4. Retention behavior change of methyl tiglate, 2-hexyne, and 1-hexene in [Ag⁺][NTf₂⁻]/[DMIM⁺][NTf₂⁻] (column 14) upon exposure to hydrogen gas stream at constant temperatures: at 35 °C, methyl tiglate [○(green)], 2-hexyne [◇(red)], and 1-hexene [□(blue)]; at 110 °C, methyl tiglate [■(red)], 2-hexyne [●(blue)], and 1-hexene [◇(green)]. Retention factors were determined after every 6 h of exposure, while the initial retention factor was measured immediately after column preparation. Retention measurement conditions: carrier gas flow rate, 1 mL min⁻¹; oven temperature, 35 °C; inlet temperature, 150 °C; FID temperature, 160 °C.
substituents (i.e., [BMIM+]); however, no difference in silver(I) ion stabilization was observed. Silver(I) ion-olefin complexation was relatively stronger in the [Ag+][NTf2−]/[BMIM+][BF4−] and [Ag+][NTf2−]/[BMIM+][TfO−] mixtures compared to the [Ag+][NTf2−]/[BMIM+][TfO−] and [Ag+][NTf2−]/[BMIM+][NO3−] mixtures. However, [Ag+][NTf2−] was most stable in the [NTf2−]-based ILs, while it was least stable in ILs containing the [BF4−] counter anion. The [Ag+][NTf2−]/[DMIM+][NTf2−] mixture was found to exhibit the most ideal composition for silver(I) ion-olefin complexation because of its high stability and increased olefin selectivity as silver(I) ions were stable until 155 and 110 °C under helium and hydrogen, respectively. Additionally, silver(I) ion-olefin complexation was unchanged for 90 h even upon continuous exposure to hydrogen at 35 °C. Results from this study demonstrate that the stability of silver(I) ions and their selectivity for olefins are highly dependent on the silver salt/IL composition and the operating conditions of the separation system.

4. EXPERIMENTAL SECTION

4.1. Materials and Reagents. Acetonitrile (99.9%), dichloromethane (99.8%), ethyl acetate (99.5%), 1-methylimidazole (99%), 1-bromocyclohexane (98%), hexane (99.7%), 1-hexene (99.7%), 2-hexene (99%), methyl tiglate (99%), PEG, silver nitrate ([Ag+][NO3−], 99%), [Ag+][NTf2−] (97%), silver trifluoromethanesulfonate ([Ag+][TfO−], 99%), silver trifluoromethanesulfonate ([Ag+][TfO−], 99%), silver trifluoromethanesulfonate ([Ag+][NO3−], 95%), [BMIM+][NO3−], 95%), [BMIM+][TfO−] (95%), and [BMIM+][BF4−] (97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium tetrafluoroborate ([Na+][BF4−], 97%) was purchased from Acros Organics (Morris Plains, NJ, USA). [Li+][NTf2−] (99.5%) salt was obtained from SynQuest Laboratories (Alachua, FL, USA). Naphthalene (98%) and untreated fused silica capillary tubing (I.D. 250 μm) were purchased from Supelco (Bellefonte, PA, USA). All chemicals were used as received.

4.2. Synthesis of ILs. The [BMIM+][NTf2−] IL was prepared by using a previously reported synthetic route. Briefly, [BMIM+][Cl−] was prepared by reacting 1 molar equiv of 1-methylimidazole with 1.5 molar equiv of 1-chlorobutane in 15 mL of acetonitrile under reflux (80 °C) for 24 h. Residual 1-chlorobutane was removed by evaporation, and the product was dissolved in 10 mL of water and washed five times with 5 mL of ethyl acetate. After removal of water under vacuum, the product was dried overnight. To 1.0 molar equiv of IL dissolved in 5 mL of water, 3.0 molar equiv of [Li+][NTf2−] was added and stirred at room temperature for 2 h. After removing the aqueous layer, the resulting [BMIM+][NTf2−] IL was dried under vacuum. Analogous synthetic routes were applied to synthesize the 1-decyI-3-methylimidazolium ([DMIM+]) [NTf2−] and [DMIM+][BF4−] ILs. For the [DMIM+][NTf2−] IL, 1-bromocyclohexane was used to prepare [DMIM+][Br−], followed by the metathesis reaction with [Li+][NTf2−]. The [DMIM+][BF4−] IL was synthesized by the anion exchange reaction of [DMIM+][Br−] and [Na+][BF4−]. Chemical structures of the ILs used in this study are shown in Table S1, and 1H NMR spectra of all synthesized ILs are available in Figures S1–S3 of the Supporting Information.

4.3. Preparation of Gas Chromatographic Columns and Probe Molecule Standards. All columns were prepared on segments of untreated fused silica capillary (0.25 mm internal diameter) using the static coating method. A coating solution with an IL concentration of 0.45% (w/v) in dichloromethane was used to prepare columns with a stationary phase film thickness of approximately 0.28 μm. For columns containing silver salts, a fixed concentration of each silver salt was added to the ILs, as shown in Table S2. The coated capillary columns were conditioned from 40 °C to 100 °C using a ramp of 1 °C min−1 and held isothermally at 100 °C for 2 h. Helium was used as a carrier gas at a constant flow of 1 mL min−1. Column efficiency was measured using naphthalene at 100 °C; efficiencies of columns ranged from 1500 to 3100 plates/meter. The composition of the coated stationary phases and the length of the prepared columns are shown in Table 1.

Probe molecule standards consisting of hexane, 1-hexene, and 2-hexyne were prepared by sealing 5 μL of each compound in separate 20 mL headspace vials. A standard solution of methyl tiglate was prepared in dichloromethane at a concentration of 1000 ppm. An injection volume of 1 μL was used for all probes.

4.4. Instrumentation. An Agilent Technologies (Santa Clara, CA, USA) 6850 gas chromatograph (GC) equipped with a flame ionization detector (FID) was employed to expose silver salt/IL mixtures (chromatographic columns) to a helium gas stream. Shimadzu (Tokyo, Japan) GC-17A and Agilent Technologies 6890N GCs were used to regulate nitrogen and hydrogen gases to the columns, respectively. A flow rate of 1 mL min−1 was applied for all gas exposure studies. The embedded oven programs in GCs were modified to control the temperature for column heating. After every exposure/heating event, the columns were installed on a separate Agilent Technologies 6850 GC equipped with FID to measure the retention properties of probe molecules. For experiments carried out under constant helium and hydrogen gases, the identical chromatographic system used for gas exposure was used to determine the retention properties. For all measurements, the oven, inlet, and FID temperatures were held at 35, 150, and 160 °C, respectively. A split ratio of 20:1 and a carrier gas (helium or hydrogen) flow rate of 1 mL min−1 were applied in all studies. The flow rates of hydrogen and air in the FID were held constant at 30 and 400 mL min−1, respectively. All retention measurements were obtained in triplicate. A Fisher Scientific (Fair Lawn, NJ, USA) Micro-master microscope was used to determine the solubility of the silver salt in PEG or IL solvents.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04854.

Description of silver (I) salt/PEG or IL solubility test; tables of ILs and PEG, silver (I) salts, and probe molecules used in the study; tables of olefin retention factor ratio between IL columns with/without [Ag+]-[NTf2−] and retention comparison for three probes in [Ag+][NTf2−]/[DMIM+][NTf2−] mixture (column 14) upon exposure to hydrogen gas and constant temperatures; 1H NMR spectra of the [BMIM+][NTf2−], [DMIM+][NTf2−], and [DMIM+][BF4−] ILs; solubility result of silver salts in IL and PEG solvents; photographs and microscopy images of silver salt/IL mixtures; plots of initial retention factor for methyl tiglate in neat IL and
[Ag⁺][NTf₂⁻]/IL columns; and change in the retention factors of 2-hexyne and methyl tiglate upon exposing various columns to different temperatures and gases (PDF)

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**Notes**

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**REFERENCES**


