

# Deconvoluting the Combined Effects of Gas Composition and Temperature on Olefin Selectivity for Separations Using Silver(I) Ions in Ionic Liquids

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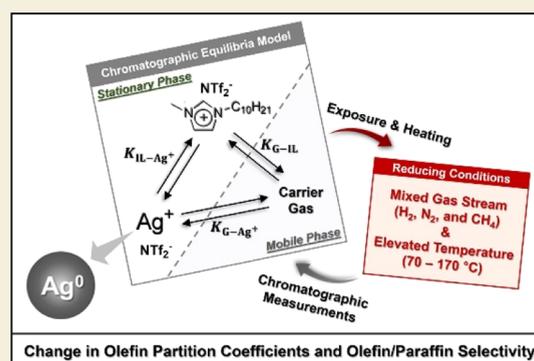
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**ABSTRACT:** Silver(I) ions have the propensity of undergoing reduction to form metallic silver within olefin/paraffin separation systems when they are subjected to hydrogen at elevated temperatures. Ionic liquids (ILs) are versatile solvents known for their low vapor pressure, high thermal stability, and structural tunability and have been shown to minimize hydrogen-induced reduction of silver(I) ions when employed as solvents. In the development of robust separation platforms that employ silver(I) ions, it is essential to deploy reliable approaches capable of measuring and assessing the factors that lower the overall separation performance. In this study, silver(I) ions dissolved in an imidazolium-based IL are subjected to mixed gas streams composed of hydrogen, nitrogen, and methane under varying temperatures. Using inverse gas chromatography, a total of 44 columns with stationary phases containing four different concentrations of silver(I) bis[(trifluoromethyl)sulfonyl]imide ( $[\text{Ag}^+][\text{NTf}_2^-]$ ) dissolved in the 1-decyl-3-methylimidazolium ( $[\text{C}_{10}\text{MIM}^+]$ )  $[\text{NTf}_2^-]$  IL were used to measure partition coefficients of olefins and paraffins, as well as aromatics, esters, and ketones. Upon exposing the stationary phases to mixed gases at elevated temperatures, olefin partitioning between the silver(I) ion pseudophase and the two other phases (i.e., carrier gas and IL stationary phase) was observed to decrease over time, while partitioning between the IL stationary phase and carrier gas remained unchanged. It was found that exposure gases composed of 5.0 to 85.0 mol % hydrogen and temperatures ranging from 95 to 130 °C resulted in a remarkable acceleration of silver(I) ion reduction and an approximate 36.4–61.3% decrease in olefin partitioning between the silver(I) ion pseudophase and both the carrier gas and IL stationary phase after 60 h. While binary mixtures of hydrogen and nitrogen resulted in a continuous decrease in silver(I) ion–olefin complexation capability, a ternary gas mixture produced varied silver(I) ion reduction kinetics.

**KEYWORDS:** olefin/paraffin separation, ionic liquids, silver(I) ion reduction, mixed gas atmosphere, temperature, partition coefficient, gas chromatography



## INTRODUCTION

The separation of light olefins from structurally similar paraffins is challenging since these molecules often possess nearly indistinguishable physicochemical properties.<sup>1,2</sup> To improve olefin/paraffin selectivity in gas separation systems such as facilitated transport membranes (FTMs) and gas chromatography (GC), the silver(I) ion has been used as an additive since it may undergo reversible and selective complexation with olefins via electron donation from the filled  $\pi$ -orbital of olefin to the  $s$  orbital of the silver(I) ion and subsequent back donation of electrons from the  $d$  orbital of silver to the empty antibonding  $\pi$ -orbital of the olefin.<sup>3,4</sup> As an example, a liquid-FTM contactor composed of a nonporous membrane module and aqueous silver nitrate ( $[\text{Ag}^+][\text{NO}_3^-]$ ) solution was employed in the separation of ethylene from an ethylene/ethane mixture.<sup>5</sup> By continuously supplying the feed gas mixture (64/36 vol % of ethylene and ethane) and aqueous  $[\text{Ag}^+][\text{NO}_3^-]$  solution to each channel, ethylene/ethane

selectivities of up to 562 were achieved. Kovvali and co-workers have prepared immobilized liquid membranes immersed in  $[\text{Ag}^+][\text{NO}_3^-]$ /glycerol solutions and reported their performance in the separation of 1-butene from  $n$ -butane.<sup>6</sup> As higher silver(I) ion concentrations within the membrane system were employed, a linear increase in 1-butene/ $n$ -butane selectivity was observed, with the highest selectivity of 850 being achieved using a membrane containing 7.5 M of silver(I) ions.

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To successfully exploit the olefin complexation capability of silver(I) ions in gas separation systems, the selection of appropriate solvents is critical. Solvents such as water and methanol have been used previously as they generally exhibit high solubility of silver(I) salts.<sup>7–10</sup> However, at elevated temperatures, these solvents can undergo volatilization, resulting in decreased separation performance.<sup>11</sup> Ionic liquids (ILs) are versatile nonmolecular solvents possessing low vapor pressure and high thermal stability and can be structurally tuned using various cation and anion combinations.<sup>12</sup> ILs have been used to dissolve silver(I) salts and facilitate olefin complexation in olefin/paraffin separation systems. Galán Sánchez and co-workers have investigated the ethylene/ethane absorption properties of various silver(I) salt/IL solutions, where ILs such as 1-butyl-3-methylimidazolium ( $[\text{C}_4\text{MIM}^+]$ )  $[\text{NO}_3^-]$ , 1-butyl-4-methylpyridinium  $[\text{NO}_3^-]$ , choline  $[\text{NO}_3^-]$ , 1-ethyl-3-methylimidazolium triflate ( $[\text{C}_2\text{MIM}^+][\text{TfO}^-]$ ), and  $[\text{C}_2\text{MIM}^+]$  bis[(trifluoromethyl)sulfonyl]imide ( $[\text{NTf}_2^-]$ ) were impregnated with silver(I) salts such as  $[\text{Ag}^+][\text{NO}_3^-]$ ,  $[\text{Ag}^+][\text{TfO}^-]$ , and  $[\text{Ag}^+][\text{NTf}_2^-]$ .<sup>13</sup> Among the examined mixtures, the  $[\text{Ag}^+][\text{NTf}_2^-]/[\text{C}_2\text{MIM}^+][\text{NTf}_2^-]$  composition produced an ethylene/ethane selectivity exceeding 100. Nan and co-workers have employed silver-containing ILs as GC stationary phases.<sup>14</sup> Compared to the conventional  $[\text{C}_4\text{MIM}^+][\text{NTf}_2^-]$  IL, a mixed-ligand silver-based IL  $\{[\text{Ag}^+(1\text{-butylimidazole}) (1\text{-methylimidazole})][\text{NTf}_2^-]\}$  exhibited higher 1-hexene/*n*-hexane selectivity when impregnated with  $[\text{Ag}^+][\text{NTf}_2^-]$ .

Although the exploitation of silver(I) ion–olefin complexation in olefin/paraffin separation systems may provide advantages, such as promising selectivity and lacking necessity for the analyte phase change (i.e., from gas to liquid), resulting in less energy consumption,<sup>15,16</sup> it has not been fully realized in industrial platforms due to the propensity of undesirable silver(I) ion reduction and precipitation of metallic silver within the process line.<sup>17–19</sup> Previous studies have reported that various reducing gases such as hydrogen, acetylene, and hydrogen sulfide can facilitate silver(I) ion reduction to metallic silver, resulting in decreased olefin complexation capability.<sup>20,21</sup> Specifically, hydrogen was found to cause silver(I) ion poisoning as it is commonly present in feed gas streams.<sup>17,22</sup> To improve the stability of the dissolved silver(I) ion and facilitate its selective olefin complexation, numerous solvents have been studied. For example, Davenport and co-workers have synthesized polymer electrolyte membranes composed of 50 wt % of  $[\text{Ag}^+][\text{NTf}_2^-]$  and crosslinked poly(ethylene glycol) diacrylate for ethylene/ethane separation.<sup>23</sup> The membrane maintained 90% of its initial ethylene/ethane selectivity for over 10 weeks even after permeation with pure hydrogen at 4 bar and 35 °C. ILs have also been shown to provide a stabilizing effect on silver(I) ions. FTMs consisting of  $[\text{Ag}^+][\text{NTf}_2^-]$  and the 1-hexyl-2,3-dimethylimidazolium  $[\text{NTf}_2^-]$  IL exhibited consistent propylene/propane selectivity for 4 days of pure hydrogen exposure at 35 °C.<sup>24</sup> Moreover, GC stationary phases containing the 1-decyl-3-methylimidazolium ( $[\text{C}_{10}\text{MIM}^+]$ )  $[\text{NTf}_2^-]$  IL impregnated with dissolved  $[\text{Ag}^+][\text{NTf}_2^-]$  were also discovered to mitigate the reduction of silver(I) ion by pure hydrogen carrier gas at temperatures up to 95 °C.<sup>25</sup> These observations are likely due to the presence of multiple  $[\text{NTf}_2^-]$  IL anions surrounding the silver(I) ion, resulting in its protection from hydrogen-mediated reduction.<sup>26</sup>

A fundamental understanding of the silver(I) ion reduction mechanism that occurs in IL solvents has not been fully achieved. Our group recently developed a chromatographic three-phase equilibria model to measure the partitioning of olefins and paraffins between the carrier gas, IL stationary phase, and silver(I) ion pseudophase.<sup>27</sup> From the model, three analyte partition coefficients between the IL and carrier gas phase, silver(I) ion pseudophase and carrier gas phase, and silver(I) ion pseudophase and IL stationary phase were determined. An advantage of the chromatographic platform is that it can be used to investigate the loss of olefin selectivity for silver(I) ion-containing separation systems when exposed to conditions that favor silver(I) ion reduction. For example, the effects of elevated temperature and reducing gas streams on the performance of silver(I) ion-based separation systems can be simultaneously evaluated by monitoring the change of analyte partition coefficients over time.

This study investigates the effects of mixed gas streams on the gradual loss of silver(I) ion–olefin selectivity in an IL solvent at elevated temperatures using inverse gas chromatography (IGC). Chromatographic columns featuring stationary phases with varying amounts of  $[\text{Ag}^+][\text{NTf}_2^-]$  dissolved in the  $[\text{C}_{10}\text{MIM}^+][\text{NTf}_2^-]$  IL are used to determine partition coefficients of various analytes, including alkanes, alkenes, alkynes, aromatics, esters, and ketones. Heating the stationary phases to temperatures ranging from 70 to 170 °C under continuous exposure to binary and ternary mixed gas streams containing hydrogen, nitrogen, and methane resulted in the temporal decrease of analyte partition coefficients. By comparing the variation of analyte retention factors and partition coefficients over time, the loss of olefin/paraffin separation performance in the mixed gas environment can be quantitatively evaluated. Results from this study are important in identifying optimal feed gas compositions and temperatures for separation systems composed of silver(I) salt and imidazolium-based ILs to attain the highest olefin selectivity. In addition, this study showcases the versatility of IGC in permitting exposure of stationary phases to mixed gases and varied temperature conditions, while facilitating the measurement of intermolecular interactions and their variation over time.

## EXPERIMENTAL SECTION

### Materials and Reagents

Acetonitrile (99.9%), dichloromethane (99.8%), 1-bromodecane (98%), ethyl acetate (99.5%), 1-methylimidazole (99%), nonane (99%), 2-hexanone (99%), methyl tiglate (99%), *n*-hexane (99.7%), 1-hexene (99.8%), *cis*-1,4-hexadiene (99%), 2,3-dimethyl-1,3-butadiene (98%), 2-hexyne (99%), benzene (99.8%), toluene (99.5%), *o*-xylene (99.8%), *m*-xylene (99%), *p*-xylene (99%), ethylbenzene (99.8%), 1-nonene (96%), and  $[\text{Ag}^+][\text{NTf}_2^-]$  (97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Compounds 3-hexyne (99%) and *cis*-2-hexene (96%) were purchased from Alfa Aesar (Tewksbury, MA, USA). Lithium bis[(trifluoromethyl)sulfonyl]imide ( $[\text{Li}^+][\text{NTf}_2^-]$ , 99.5%) salt was purchased from SynQuest Laboratories (Alachua, FL, USA). Untreated fused silica capillary tubing (I.D. 250  $\mu\text{m}$ ) and naphthalene (98%) were purchased from Supelco (Bellefonte, PA, USA). Cylinders containing custom gas mixtures (ultra-high purity, 99.999%) of hydrogen/nitrogen, hydrogen/helium, and hydrogen/methane/nitrogen were purchased from Airgas, Inc. (Des Moines, IA, USA). All chemicals were used as received without further purification.

## Instrumentation

An Agilent Technologies (Santa Clara, CA, USA) 6850 gas chromatograph equipped with a flame ionization detector (FID) was used to expose silver(I) salt/IL mixtures as chromatographic stationary phases to mixed gas streams. A flow rate of 1 mL min<sup>-1</sup> was applied for all gas exposure studies. The embedded GC oven program was modified to control the temperature for column heating. After every exposure/heating event, columns were installed into an Agilent Technologies 6850 gas chromatograph equipped with an FID to measure the retention times of analytes. For all measurements, the inlet, oven, and FID were held at 150 °C, 35 °C, and 160 °C, respectively. Helium was used as a carrier gas at a flow rate of 1 mL min<sup>-1</sup> and a split ratio of 7:1. Flow rates of hydrogen and air in the FID were held constant at 30 and 400 mL min<sup>-1</sup>, respectively.

A Rigaku 600 Miniflex with Cu-K $\alpha$  radiation ( $\lambda = 1.54059 \text{ \AA}$ ) and a Ni-K $\beta$  filter was used to perform powder X-ray diffraction (XRD) analysis on the recovered silver compounds. Sample holders composed of zero-background silicon plates were used to measure XRD patterns of the examined samples.

## Synthesis of the [C<sub>10</sub>MIM<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] IL

The [C<sub>10</sub>MIM<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] IL was prepared using a previously reported synthetic route.<sup>14</sup> Briefly, 1.0 molar equivalent of 1-methylimidazole and 1.5 molar equivalents of 1-bromodecane were reacted in 10 mL of acetonitrile under reflux at 80 °C for 24 h. After removing the solvent and residual 1-bromodecane by reduced pressure evaporation, the product was dissolved in 10 mL of deionized water and washed with 5 mL of ethyl acetate. This washing procedure was repeated five times. Deionized water was removed by evaporation, and the [C<sub>10</sub>MIM<sup>+</sup>][Br<sup>-</sup>] IL product was further dried overnight under vacuum. To produce an IL consisting of the [NTf<sub>2</sub><sup>-</sup>] anion, 1.0 molar equivalent of the [C<sub>10</sub>MIM<sup>+</sup>][Br<sup>-</sup>] IL and 3.0 molar equivalents of [Li<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] were dissolved in 5 mL of deionized water and stirred at room temperature for 2 h. The [C<sub>10</sub>MIM<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] IL was obtained as a separate layer and dried under vacuum before use.

## Preparation of GC Columns, Reduced Silver(I) Ion Compounds, and Analyte Standards

Segments of untreated fused silica capillary (0.25 mm ID) were used to prepare all chromatographic columns using the static coating method.<sup>28</sup> For reduced silver recovery experiments, a neat silver(I) salt (without IL solvent) was prepared as a stationary phase and coated on the inner wall of the capillary column. A coating solution containing a [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] concentration of 0.96% (w/v) in a dichloromethane/methanol mixture (95/5 vol %) provided an approximate stationary film thickness of 0.60  $\mu\text{m}$ . Similarly, columns with stationary phases containing the IL impregnated with varying amounts of [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] were also prepared. A coating solution with an IL concentration of 0.45% (w/v) dissolved in pure dichloromethane resulted in an approximate stationary phase film thickness of 0.28  $\mu\text{m}$ . A total of 44 chromatographic columns, except those used for reduced silver recovery experiments, were conditioned using a temperature program of 40 to 100 °C at a ramp of 1 °C min<sup>-1</sup> and held at 100 °C for 2 h. Helium was employed as a carrier gas with a flow rate of 1 mL min<sup>-1</sup>. Naphthalene was used to measure the efficiency of all conditioned columns at 100 °C with column efficiencies ranging from 1550 to 2950 plates/meter.

Upon the completion of reduction for columns containing neat [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] and the [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>]/[C<sub>10</sub>MIM<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] IL mixture, deionized water was filled into the capillaries, followed by 2 h of ultrasonication with rubber septa sealing both ends of the capillaries. Mixtures of the product and deionized water were recovered from each column by the application of gentle pressure using a 3 mL syringe. Deionized water was removed by reduced pressure evaporation, and the reduced products were further dried overnight under vacuum prior to XRD characterization.

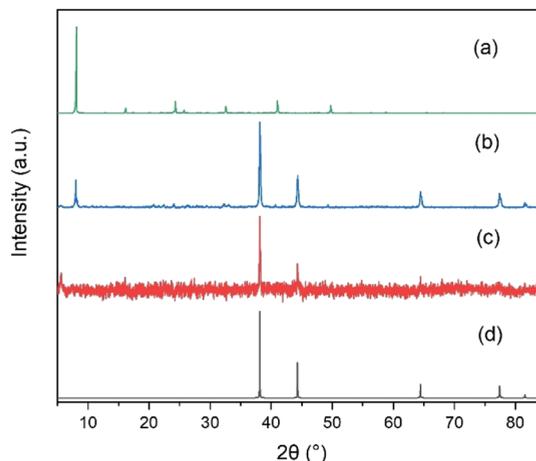
In separate 20 mL headspace vials, 5  $\mu\text{L}$  of each analyte was transferred using a 25  $\mu\text{L}$  gas-tight syringe and sealed to prepare standards for all retention measurements. An injection volume of 1  $\mu\text{L}$

was used for all GC measurements, and all retention measurements were obtained in triplicate.

## RESULTS AND DISCUSSION

### Hydrogen-Promoted Reduction of the Silver(I) Ion in the [C<sub>10</sub>MIM<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] IL

Metallic silver formed by the hydrogen-promoted reduction of the silver(I) ion in olefin/paraffin separation systems has been characterized by various methods, including color change observation,<sup>21</sup> microscopic analysis,<sup>29,30</sup> X-ray photoelectron spectroscopy,<sup>23</sup> and powder XRD analysis.<sup>26,31,32</sup> To confirm that the silver(I) ion dissolved in an IL undergoes hydrogen-mediated reduction to metallic silver, neat [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] and the [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>]/[C<sub>10</sub>MIM<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] IL mixture were both reduced, and the products characterized by powder XRD analysis. Figure S1 in the Supporting Information describes all procedures used to perform in-column silver(I) ion reduction. For the reduced neat [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>], chromatographic columns were coated with a thin layer of neat [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>], as described in the Experimental Section. To prepare the reduced [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] dissolved in the IL solvent, a stationary phase containing 50 wt % of [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] dissolved in the [C<sub>10</sub>MIM<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] IL was coated onto capillary columns. After exposing the columns to a pure hydrogen gas stream at 200 °C for 120 h, the stationary phase was recovered from each set of columns and characterized by powder XRD (see the Experimental Section). Although no previous literature reports have discussed thermal degradation of the [C<sub>10</sub>MIM<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] IL under these conditions (i.e., heating at 200 °C under a hydrogen atmosphere for 120 h), the IL portion of the stationary phase was not considered to affect the results of silver(I) ion reduction in this study as imidazolium-based ILs are generally stable at these temperatures.<sup>33,34</sup> The resulting XRD spectra of [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] before and after hydrogen-induced reduction are shown in Figure 1. The neat [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] exhibits strong crystalline peaks centered at 2 $\theta$  values of 7.8°, 15.6°, 23.4°, 31.4°, 39.5°, and 47.9°. However, these crystalline peaks were not observed in the spectrum of the reduced [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>]. Instead, new peaks at 2 $\theta$  values of 38.1°, 44.2°, 64.4°, and 77.3° appeared, indicating that the

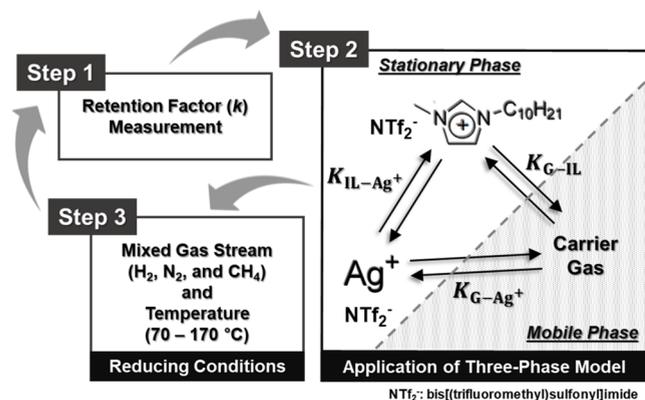


**Figure 1.** Comparison of powder XRD spectra before and after hydrogen-promoted reduction of the silver(I) salt. Sample information: neat [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>], (a); reduced neat [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>], (b); reduced [Ag<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>]/[C<sub>10</sub>MIM<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] IL, (c); and silver reference, (d).

diffraction characteristics of neat  $[\text{Ag}^+][\text{NTf}_2^-]$  were completely changed upon exposure to pure hydrogen gas under elevated temperatures. The diffraction pattern of reduced  $[\text{Ag}^+][\text{NTf}_2^-]$  was found to be analogous to that of a silver reference, confirming that the product of hydrogen-promoted silver(I) ion reduction is metallic silver.<sup>35</sup> Furthermore, crystalline peaks at  $2\theta$  values observed for reduced  $[\text{Ag}^+][\text{NTf}_2^-]$  and reduced  $[\text{Ag}^+][\text{NTf}_2^-]/[\text{C}_{10}\text{MIM}^+][\text{NTf}_2^-]$  ILs (Figure 1b,c) were identical to each other, indicating that the silver(I) ion dissolved in the IL solvent is also reduced to metallic silver by hydrogen gas. These results are in good agreement with a previous FTM study that performed XRD characterization on dark-colored particles produced from reducing  $[\text{Ag}^+][\text{NO}_3^-]/1\text{-hexyl-3-methylimidazolium} [\text{NO}_3^-]$  using hydrogen.<sup>26</sup>

### Selection of the Silver(I) Ion Concentration Working Range and Mixed Gas Compositions

As the three-phase chromatographic equilibria model enables quantitative evaluation of analyte partitioning within a separation system, it can be exploited to monitor the gradual reduction of the silver(I) ion, as detailed in Figure 2. Initially,



**Figure 2.** Schematic describing the application of the three-phase equilibria model in monitoring the loss of silver(I) ion–olefin selectivity. Initial chromatographic retention of analytes on the  $[\text{Ag}^+][\text{NTf}_2^-]/[\text{C}_{10}\text{MIM}^+][\text{NTf}_2^-]$  stationary phases were measured by GC (Step 1). The three-phase equilibria model was applied to determine partition coefficients of  $K_{\text{G-IL}}$ ,  $K_{\text{G-Ag}^+}$ , and  $K_{\text{IL-Ag}^+}$  (Step 2). The stationary phases were then exposed to reducing conditions (Step 3). Steps (1) and (2) are repeated to obtain the partition coefficients after silver(I) ion reduction.

retention factors ( $k$ ) of analytes, defined as  $k = (t_R - t_0)/t_0$ , where  $t_R$  is the analyte retention time and  $t_0$  is the dead time of propane,<sup>36</sup> were measured chromatographically (Step 1), followed by the determination of partition coefficients using the equilibria model (Step 2). In the chromatographic three-phase equilibria model, analyte retention by the silver(I) ion-containing IL stationary phase is described by the combined contribution of three analyte partition coefficients, including  $K_{\text{G-IL}}$  between the IL and carrier gas,  $K_{\text{G-Ag}^+}$  between the silver(I) ion pseudophase and carrier gas, and  $K_{\text{IL-Ag}^+}$  between the silver(I) ion pseudophase and IL.<sup>27</sup> The relationship between chromatographic retention of an analyte and the three partition coefficients can be described by eq 1,

$$K = v_p K_{\text{G-IL}} (K_{\text{IL-Ag}^+} - 1) C_{\text{Ag}^+} + K_{\text{G-IL}} \quad (1)$$

where  $K$  is the apparent partition coefficient,  $v_p$  is the partial specific volume of silver(I) salt, and  $C_{\text{Ag}^+}$  is the concentration of silver(I) ions. A full derivation of eq 1 can be found in the Supporting Information. From a plot of  $K$  versus  $C_{\text{Ag}^+}$  according to eq 1,  $K_{\text{G-IL}}$  and  $K_{\text{IL-Ag}^+}$  can be obtained from the y-intercept and slope of the plot, respectively. The constant  $K_{\text{G-Ag}^+}$  can be calculated by multiplying  $K_{\text{G-IL}}$  and  $K_{\text{IL-Ag}^+}$  (see the Supporting Information). Upon exposing the columns to reducing conditions (Step 3), steps 1 and 2 were repeated to provide a new set of partition coefficients.

Stationary phases containing up to 0.495 M  $[\text{Ag}^+][\text{NTf}_2^-]$  dissolved in the  $[\text{C}_{10}\text{MIM}^+][\text{NTf}_2^-]$  IL were applied in this study as a linear correlation between olefin retention and silver(I) ion concentration was previously observed below a silver(I) salt concentration of 0.518 M.<sup>27</sup> Table 1 lists the

**Table 1.** List of Stationary Phases Examined in This Study Containing Varying Concentrations of the Silver(I) Salt Dissolved in an IL Solvent

label	silver(I) salt	IL solvent	molar ratio <sup>a</sup>	silver(I) salt concentration <sup>b</sup> (M)
N1	$[\text{Ag}^+][\text{NTf}_2^-]$	$[\text{C}_{10}\text{MIM}^+][\text{NTf}_2^-]$	1:5.4	0.495
N2	$[\text{Ag}^+][\text{NTf}_2^-]$	$[\text{C}_{10}\text{MIM}^+][\text{NTf}_2^-]$	1:7.6	0.348
N3	$[\text{Ag}^+][\text{NTf}_2^-]$	$[\text{C}_{10}\text{MIM}^+][\text{NTf}_2^-]$	1:16.3	0.163
N4	- <sup>c</sup>	$[\text{C}_{10}\text{MIM}^+][\text{NTf}_2^-]$	0:1.0	0.000

<sup>a</sup>Molar ratio between the silver(I) salt and the IL solvent. <sup>b</sup>Molarity of the silver(I) ion in the IL solvent. <sup>c</sup>Not added.

composition of all silver(I) ion-containing stationary phases examined in this study. In previous studies, a pure hydrogen gas stream was subjected to silver(I) ion-containing FTMs and GC stationary phases to accelerate the reduction of silver(I) ions and the formation of metallic silver.<sup>21,24,25</sup> However, to better simulate silver(I) ion reduction conditions that occur in industrial settings, the effect of mixed gas streams needs to be examined as real feed gas consists of multiple components, such as hydrogen, nitrogen, methane, olefins, and paraffins.<sup>37</sup> By applying gas mixtures of hydrogen/nitrogen, hydrogen/nitrogen/methane, and hydrogen/helium containing 5.19 to 85.00 mol % of hydrogen while simultaneously monitoring the gradual loss of olefin selectivity for the silver(I) salt/IL stationary phases, the effect of different gas mixture compositions on silver(I) ion reduction can be systematically studied. The composition of gas mixtures examined in this study is provided in Table S1.

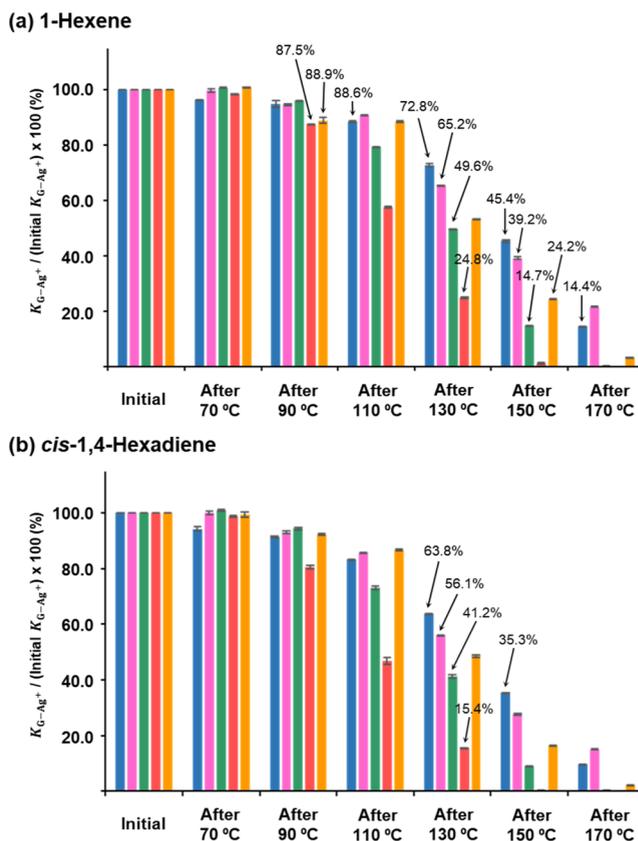
### Effect of Temperature on Silver(I) Ion Reduction

In addition to hydrogen catalyzing the reduction of the silver(I) ion, temperature is also known to affect the stability of silver(I) ion-containing separation systems.<sup>38,39</sup> For example, the observed selectivity of 1-hexene versus *n*-hexane measured using GC stationary phases containing  $[\text{Ag}^+][\text{NTf}_2^-]$  in the  $[\text{C}_{10}\text{MIM}^+][\text{NTf}_2^-]$  IL was found to be constant until the mixture was heated to 95 °C under pure hydrogen gas.<sup>25</sup> However, olefin selectivity was observed to decrease when the stationary phases were heated to 110 °C and reached nearly zero after heating at 170 °C.

For each mixed gas composition applied, the heating condition used in the column exposure experiments was

optimized. Immediately after preparing column replicates (N1–N4 in Table 1), initial retention factors for 17 analytes possessing similar molecular structures but different  $\pi$ -bonding characters were measured, followed by the construction of plots relating  $K$  and  $C_{Ag^+}$ . Upon determining the initial partition coefficients of each analyte using the three-phase equilibria model, each column set was further exposed to the mixed gas streams at 70 °C for 12 h, followed by additional measurement of analyte retention factors and calculation of partition coefficients. This process was repeated using 20 °C increments of temperature until the stationary phases were observed to completely lose olefin/paraffin selectivity. Chromatograms demonstrating changes in the retention of six representative analytes on the 0.348 M  $[Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$  IL column (N2, see Table 1) obtained after heating at varying temperatures under 5/95 and 50/50 mol % of hydrogen/nitrogen streams are shown in Figures S2 and S3, respectively.

The silver(I) ion-containing IL stationary phase revealed negligible interaction with *n*-hexane, resulting in retention factors lower than 0.3 throughout this study. Retention factors for 1-hexene and 2-hexyne measured after each heating event under various mixed gas compositions are listed in Tables S2 and S3 in the Supporting Information, respectively. Based on these values, plots of  $K$  versus  $C_{Ag^+}$  for 1-hexene (a) and 2-hexyne (b) and the observed variation upon heating under a gas stream composed of 5/95 mol % of hydrogen/nitrogen were constructed, as shown in Figure S4. As expected, a more significant decrease in the slopes of the plots for both 1-hexene and 2-hexyne was observed when the stationary phases were heated to higher temperatures. Tables S4–S8 in the Supporting Information list the analyte partition coefficients ( $K_{G-IL}$ ,  $K_{IL-Ag^+}$ , and  $K_{G-Ag^+}$ ) obtained for different exposure gas mixtures under varying temperature conditions. In general, the  $K_{G-IL}$  values for analytes did not change remarkably throughout the gas exposure experiments, indicating that analyte partitioning between the bulk IL stationary phase and carrier gas phase was not affected by the reducing environment. For analytes possessing one double bond (e.g., 1-hexene, *cis*-2-hexene, and 1-nonene), the  $K_{IL-Ag^+}$  and  $K_{G-Ag^+}$  values remained almost constant when the  $[Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$  IL stationary phases were heated to 70 and 90 °C under most of the exposure gas compositions, except for the cases of 85/15 mol % of hydrogen/nitrogen and 25/25/50 mol % of hydrogen/methane/nitrogen where drops of 12.5 and 11.1%, respectively, were observed. However, values for  $K_{IL-Ag^+}$  and  $K_{G-Ag^+}$  began to decrease significantly at temperatures above 110 °C for all systems. For example, the  $K_{G-Ag^+}$  value of 1-hexene after exposure to 5/95 mol % of hydrogen/nitrogen at 110 °C for 12 h was approximately 88.6% of the initial value, as shown in Figure 3a. At higher temperatures, the  $K_{G-Ag^+}$  values continued to decrease and reached approximately 14.4% of the initial value upon heating to 170 °C. This may be due to the increased solubility of hydrogen in the 1-alkyl-3-methylimidazolium  $[NTf_2^-]$  ILs at elevated temperatures.<sup>40,41</sup> As more hydrogen molecules are dissolved in the  $[Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$  IL mixtures upon heating, the rate of hydrogen-induced reduction of silver(I) ions is accelerated, resulting in a greater loss of olefin selectivity. Interestingly, partition coefficients of *cis*-1,4-hexadiene tended to drop more steeply compared to that of

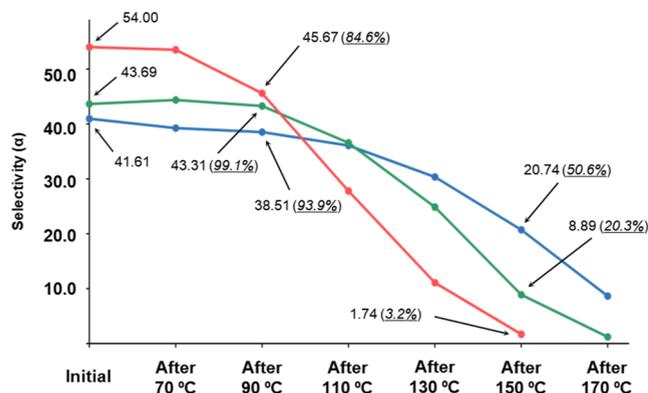


**Figure 3.** Plots describing the changes in  $K_{G-Ag^+}$  of 1-hexene (a) and *cis*-1,4-hexadiene (b) relative to the initial  $K_{G-Ag^+}$  values under different reducing conditions after exposure to mixed gases with varying hydrogen, nitrogen, and methane contents. Initial  $K_{G-Ag^+}$  values were obtained immediately after preparing the  $[Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$  IL columns. Mixed gas compositions for column exposure: 5/95 mol % of hydrogen/nitrogen, MG1 (Blue ■); 15/85 mol % of hydrogen/nitrogen, MG2 (Pink ■); 50/50 mol % of hydrogen/nitrogen, MG3 (Green ■); 85/15 mol % of hydrogen/nitrogen, MG4 (Red ■); and 25/50/25 mol % of hydrogen/nitrogen/methane, MG5 (Orange ■). Every exposure/heating stage was held for 12 h.

1-hexene. For example, the  $K_{G-Ag^+}$  values of 1-hexene determined after exposure to 5/95 mol % of hydrogen/nitrogen at 130 and 150 °C were approximately 72.8 and 45.4% of the initial value, respectively (see Figure 3a). Under the same mixed gas stream, the  $K_{G-Ag^+}$  values of *cis*-1,4-hexadiene reached approximately 63.8 and 35.3% of the initial  $K_{G-Ag^+}$  value at 130 and 150 °C, respectively, as shown in Figure 3b. These observations can be attributed to the multiple double bonds in *cis*-1,4-hexadiene that enable its stronger partitioning to the silver(I) ion pseudophase over the carrier gas than 1-hexene.<sup>27</sup> As the overall retention of *cis*-1,4-hexadiene on the stationary phase is affected more by the presence of the silver(I) ion pseudophase than that of 1-hexene, the decrease in the  $K_{IL-Ag^+}$  and  $K_{G-Ag^+}$  values is much more significant.

When the composition of the binary gas mixture was varied, the  $K_{G-Ag^+}$  values of 1-hexene decreased when the hydrogen content in the gas stream was increased, as shown in Figure 3a. Heating the columns to 130 °C under a binary mixture composed of 15 mol % hydrogen and 85 mol % nitrogen

resulted in a  $K_{G-Ag^+}$  value for 1-hexene that was approximately 65.2% of the initial value, while those obtained under 50/50 and 85/15 mol % of hydrogen/nitrogen were 49.6 and 24.8% of the initial  $K_{G-Ag^+}$  values, respectively. These observations agree with previous studies that described pure hydrogen playing a larger role in the reduction of the silver(I) ion than pure nitrogen at temperatures higher than 110 °C.<sup>25</sup> Similar trends were observed in the selectivity between 1-hexene and *n*-hexane. Selectivity ( $\alpha$ ) is a measure of the peak-to-peak separation between two analytes; higher selectivity values indicate that a system is able to better separate two analytes and is calculated by taking the ratio of retention factors for two analytes.<sup>36</sup> The  $[Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$  IL stationary phases were able to preserve the selectivity of 1-hexene and *n*-hexane at higher temperatures when exposed to gas compositions containing lower amounts of hydrogen. For example, when heating the replicate N1 columns (0.495 M  $[Ag^+][NTf_2^-]$  dissolved in the  $[C_{10}MIM^+][NTf_2^-]$  IL) to 90 °C, binary mixtures of 5/95 and 50/50 mol % hydrogen/nitrogen revealed a loss of selectivity of less than 7.0%, while columns exposed to 85/15 mol % hydrogen/nitrogen resulted in a 15.4% decrease, as shown in Figure 4. After heating the



**Figure 4.** Plots showing the changes in selectivity between 1-hexene and *n*-hexane in the 0.495 M  $[Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$  IL columns upon heating at elevated temperatures under binary mixed gas streams of hydrogen and nitrogen. Mixed gas compositions applied: 5/95 mol % of hydrogen/nitrogen, MG1 (blue); 50/50 mol % of hydrogen/nitrogen, MG3 (green); and 85/15 mol % of hydrogen/nitrogen, MG4 (red). The values in parentheses are relative ratios compared to the initial selectivities. Every heating event was held for 12 h. Retention measurement conditions: injection volume, 1  $\mu$ L; split ratio, 7:1; carrier gas flow rate, 1 mL min<sup>-1</sup>; oven temperature, 35 °C; inlet temperature, 150 °C; and FID temperature, 160 °C.

identical N1 columns to 150 °C, the gas mixture of 85 mol % hydrogen and 15 mol % nitrogen only retained 3.2% of its selectivity between 1-hexene and *n*-hexane, while the 50/50 and 5/95 mol % hydrogen/nitrogen compositions retained 20.3 and 50.6% of their initial selectivity values, respectively.

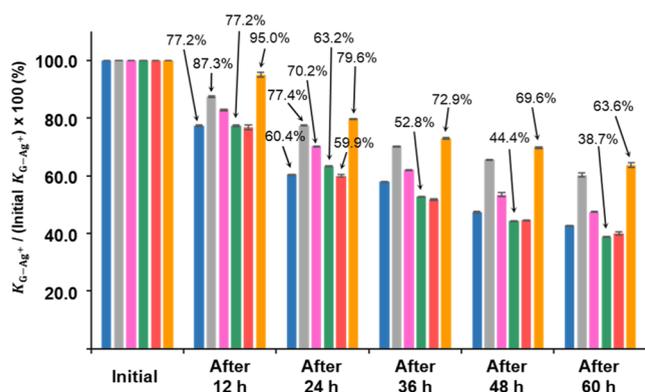
As expected, analytes possessing a multiple  $\pi$ -bonding character revealed a more pronounced decrease in the  $K_{IL-Ag^+}$  and  $K_{G-Ag^+}$  values than analytes containing one  $\pi$ -bond when exposed to gas streams containing a higher proportion of hydrogen at elevated temperatures. For example, the  $K_{G-Ag^+}$  values of *cis*-1,4-hexadiene after heating at 130 °C under 15/85, 50/50, and 85/15 mol % of hydrogen/nitrogen were approximately 56.1, 41.2, and 15.4% of the initial values,

respectively (see Figure 3b). A ternary gas mixture composed of hydrogen/methane/nitrogen (25/25/50 mol %) was also observed to produce a decrease in the  $K_{IL-Ag^+}$  and  $K_{G-Ag^+}$  values for analytes with a  $\pi$ -bonding character. Interestingly, the decrease tended to be higher than that of the 15/85 mol % of hydrogen/nitrogen gas stream but lower than that of the 50/50 mol % hydrogen/nitrogen mixture. For example, the  $K_{G-Ag^+}$  value of 1-hexene upon heating to 150 °C under 25/25/50 mol % of hydrogen/methane/nitrogen decreased by 75.8% from the initial value, while the drops under 15/85 and 50/50 mol % of hydrogen/nitrogen streams were approximately 60.8 and 85.3%, respectively. These results show that hydrogen remains capable of promoting the reduction of silver(I) ions at elevated temperatures even when it is part of a ternary mixture of other gases.

### Silver(I) Ion Reduction upon Exposure to Mixed Gas Streams at Fixed Temperatures

Based on the previous results, heating conditions that resulted in an approximate 15% decrease in the  $K_{G-Ag^+}$  values relative to the initial  $K_{G-Ag^+}$  values were selected from a temperature range of 95–130 °C for each gas mixture and applied to monitor the loss of olefin/paraffin selectivity over time. Measurements of initial retention factors for all analytes were performed on replicate columns of N1–N4 (Table 1), followed by the determination of initial partition coefficients using the three-phase equilibria model. After exposing each column set to the mixed gas streams at selected temperatures for 12 h, a new set of analyte retention factors and partition coefficients were determined. This process was repeated until the total exposure time reached 60 h.

The partition coefficients for each analyte determined from these experiments are shown in Tables S9–S14 of the Supporting Information. As expected, no significant change in the values of  $K_{G-IL}$  was observed, while the  $K_{IL-Ag^+}$  and  $K_{G-Ag^+}$  values decreased continuously throughout the exposure time course. Similar to the results from the previous section, the extent of decrease in the  $K_{IL-Ag^+}$  and  $K_{G-Ag^+}$  values was dependent on both the content of hydrogen in the exposure gas mixture and the heating temperature. For example, the relative  $K_{G-Ag^+}$  value of 2-hexyne decreased to 60.4% of the initial value after exposing columns to the 5/95 mol % hydrogen/nitrogen mixture at 130 °C for 24 h, as shown in Figure 5. Likewise, heating the stationary phases to 125, 115, and 95 °C under 15/85, 50/50, 85/15 mol % of a hydrogen/nitrogen gas stream, respectively, for 24 h resulted in a comparable decrease in the  $K_{G-Ag^+}$  values of 2-hexyne. When a higher hydrogen content was present in the exposure gas mixture stream, a lower temperature was required to produce a similar loss of silver(I) ion–olefin. It was also observed that variations in the  $K_{IL-Ag^+}$  and  $K_{G-Ag^+}$  values for olefins tended to be smaller as the heating/exposure experiments proceeded under binary gas mixtures of hydrogen and nitrogen. As an example, the  $K_{G-Ag^+}$  value of 2-hexyne obtained after exposing the columns to 50/50 mol % of hydrogen/nitrogen at 115 °C for 12 h dropped by 22.8% from the initial  $K_{G-Ag^+}$  value. After 24 and 36 h under the identical exposure and heating conditions, further decreases of 14.0 and 10.4%, respectively, were observed. Finally, decreases in the  $K_{G-Ag^+}$  values became even smaller and decreases of 8.4 and 5.7% were obtained after



**Figure 5.** Change in the  $K_{G-Ag^+}$  value for 2-hexyne compared to the initial  $K_{G-Ag^+}$  values upon exposure to different mixed gases at fixed temperatures. Initial partition coefficients were determined immediately after preparing the  $[Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$  IL columns. Mixed gas exposure/heating conditions: 5/95 mol % of hydrogen/nitrogen, MG1, at 130 °C (Blue ■); 5/95 mol % of hydrogen/helium, MG6, at 130 °C (Gray ■); 15/85 mol % of hydrogen/nitrogen, MG2, at 125 °C (Pink ■); 50/50 mol % of hydrogen/nitrogen, MG3, at 115 °C (Green ■); 85/15 mol % of hydrogen/nitrogen, MG4, at 95 °C (Red ■); and 25/50/25 mol % of hydrogen/nitrogen/methane, MG5, at 120 °C (Orange ■).

48 and 60 h, respectively. This may be due to the limited kinetics of the silver(I) ion–hydrogen reaction within the stagnant chromatographic platform.<sup>42</sup>

Replacing the nitrogen portion of the exposure gas mixture with helium resulted in less significant changes in the  $K_{IL-Ag^+}$  and  $K_{G-Ag^+}$  values. For example, the  $K_{G-Ag^+}$  values of 2-hexyne upon exposure to 5/95 mol % of hydrogen/nitrogen and 5/95 mol % of hydrogen/helium at 130 °C for 12 h were 77.2 and 87.3% of the initial  $K_{G-Ag^+}$  values, respectively, as shown in Figure 5. After 24 h of the mixed gas exposure under the same conditions, the  $K_{G-Ag^+}$  values further decreased to 60.4% (5/95 mol % of hydrogen/nitrogen) and 77.4% (5/95 mol % of hydrogen/helium) of the initial  $K_{G-Ag^+}$  values. A Welch's *t*-test on these data sets confirms that the compared mean values are statistically different from each other at the 95% confidence level.<sup>43,44</sup> These results may be due to a difference in the solubility of nitrogen and helium in imidazolium-based ILs at elevated temperatures.<sup>41,45</sup> Helium and hydrogen may compete for dissolution in the  $[Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$  IL mixtures at 130 °C as both of these gases are reported to have greater solubilities in imidazolium-based ILs at higher temperatures. As a result, the number of moles of hydrogen available for promoting the reduction of silver(I) ions may be lower than the case where the binary mixture of hydrogen and nitrogen is applied.

Similar to the binary mixtures, a continuous loss in silver(I) ion–olefin complexation capability was also observed for the ternary mixture of hydrogen/nitrogen/methane (25/50/25 mol %). However, changes in the  $K_{IL-Ag^+}$  and  $K_{G-Ag^+}$  values were rather irregular compared to data obtained from exposure by the binary gas mixtures, where smaller decreases in these values were observed under prolonged exposure and heating times. When the columns were exposed to 25/50/25 mol % of hydrogen/nitrogen/methane at 120 °C for 12 h, an approximate 5.0% decrease in the  $K_{G-Ag^+}$  value of 2-hexyne was observed relative to its initial value. After 24 and 36 h of

heating and exposure under the identical conditions, the  $K_{G-Ag^+}$  values further decreased by 15.4 and 6.7%, respectively. A continuous decrease was also observed in the selectivity of 2-hexyne and *n*-hexane, as shown in Figure S5. When replicate N1 columns (0.495 M  $[Ag^+][NTf_2^-]$  dissolved in the  $[C_{10}MIM^+][NTf_2^-]$  IL) were heated and exposed to the binary mixtures of hydrogen and nitrogen, the 2-hexyne/*n*-hexane selectivity decreased the most after first 12 h, followed by less significant drops throughout the remainder of the time course. However, the ternary gas mixture of hydrogen/nitrogen/methane (25/50/25 mol %) resulted in unpredictable variations in selectivity. For example, the 2-hexyne/*n*-hexane selectivity increased by 3.8% after 12 h of heating and exposure and then proceeded to decrease by approximately 12.3% after 24 h. These trends may be attributed to the higher complexity of the ternary mixture relative to that of the studied binary mixtures as overall hydrogen solubility in imidazolium-based ILs can be significantly affected by the presence of another gas.<sup>46</sup> As a result, the loss of olefin selectivity by hydrogen-promoted reduction of silver(I) ions in the  $[C_{10}MIM^+][NTf_2^-]$  IL can vary over time.

## CONCLUSIONS

In this work, a gradual loss of olefin separation capability induced by the reduction of the silver(I) ion in silver(I) ion/IL mixtures was studied using IGC. Chromatographic columns featuring stationary phases with either neat  $[Ag^+][NTf_2^-]$  or  $[Ag^+][NTf_2^-]$  dissolved in the  $[C_{10}MIM^+][NTf_2^-]$  IL were reduced under a pure hydrogen stream at 200 °C for 120 h. Using XRD, it was proven that both neat  $[Ag^+][NTf_2^-]$  and the  $[Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$  IL mixture undergo reduction to form metallic silver. Exposing the  $[Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$  IL-based stationary phases to binary or ternary gas mixtures of hydrogen, nitrogen, and methane at increasing temperatures resulted in a loss of silver(I) ion–olefin complexation. In all of the examined cases, the  $K_{G-IL}$  values remained constant, suggesting that analyte equilibria between the IL and carrier gas phase are not affected by the reducing conditions of the gas stream. However, the  $K_{IL-Ag^+}$  and  $K_{G-Ag^+}$  values for olefins tended to decrease more remarkably at temperatures above 110 °C and reached 0.1–21.6% of the initial values upon heating to 170 °C. When binary mixtures (5/95 mol %) of hydrogen/nitrogen and hydrogen/helium were compared, the latter composition provided a less significant decrease in olefin partitioning between the silver(I) ion pseudophase and the two other phases. A ternary gas mixture of hydrogen/nitrogen/methane also resulted in a continuous loss of silver(I) ion–olefin complexation capability; however, the trend was somewhat irregular compared to binary mixtures and may be attributed to its higher complexity. This study demonstrates that environmental factors affecting the reduction of the silver(I) ion dissolved in an IL solvent can be measured chromatographically, allowing for the determination of analyte partition coefficients and their change over time between different components of the chromatographic system. Experimental conditions including the mixed gas stream composition and temperature were customized using the IGC platform, extending its applicability in measuring highly specific molecular level interactions under varying conditions. Similar approaches may be useful to further delineate environmental effects in more complicated systems, including mixed gas

systems of greater complexity and/or gases containing water vapor. The versatility of IGC provides a measurement platform, allowing for a better understanding into the complex interplay of temperature, gas composition, and water on the utilization of silver(I) ion-containing ILs in olefin/paraffin separations.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmesureciau.2c00052>.

Derivation of the three-phase equilibria model equations, gas mixtures applied in stationary phase exposure experiments, 1-hexene and 2-hexyne retention factors under different mixed gas streams at varying temperatures, determined analyte partition coefficients under different mixed gas streams at varying temperatures, determined analyte partition coefficients under different mixed gas streams at fixed temperatures, schematic illustrating the procedures for characterizing in-column reduction products, chromatograms demonstrating changes in retention time of six representative analytes on the  $[\text{Ag}^+][\text{NTf}_2^-]/[\text{C}_{10}\text{MIM}^+][\text{NTf}_2^-]$  IL columns after heating at different temperatures under two different hydrogen/nitrogen mixed gas streams, plots of  $K$  of 1-hexene and 2-hexyne versus silver(I) ion concentration in the  $[\text{Ag}^+][\text{NTf}_2^-]/[\text{C}_{10}\text{MIM}^+][\text{NTf}_2^-]$  stationary phases, and plots showing changes in selectivity between 2-hexyne and  $n$ -hexane in the 0.495 M  $[\text{Ag}^+][\text{NTf}_2^-]/[\text{C}_{10}\text{MIM}^+][\text{NTf}_2^-]$  stationary phases upon exposure to various mixed gas streams at fixed temperatures (PDF)

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### Author Contributions

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(supporting); **Emily A. Smith** project administration (supporting), supervision (supporting), writing-review & editing (supporting); **Jared L. Anderson** conceptualization (lead), project administration (lead), supervision (lead), writing-review & editing (lead).

### Notes

The authors declare no competing financial interest.

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