Polymeric ionic liquids containing copper(I) and copper(II) ions as gas chromatographic stationary phases for olefin separations

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Abstract

Copper(I) ions (Cu^+) are used in olefin separations due to their olefin complexing ability and low cost, but their instability in the presence of water and gases limits their widespread use. Ionic liquids (ILs) have emerged as stabilizers of Cu^+ ions and prevent their degradation, providing high olefin separation efficiency. There is limited understanding into the role that polymeric ionic liquids (PILs), which possess similar structural characteristics to ILs, have on Cu^+ ion-olefin interactions. Moreover, copper ions with diverse oxidation states, including Cu^+ and Cu^{2+} ions, have been rarely employed for olefin separations. In this study, gas chromatography (GC) is used to investigate the interaction strength of olefins to stationary phases composed of the 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($[C_6MIM^+][NTf_2^-]$) IL and the poly(1-hexyl-3-vinylimidazolium $[NTf_2^-]$) (poly($[C_6VIM^+][NTf_2^-]$)) PIL containing monovalent and divalent copper salts (i.e., $[Cu^+][NTf_2^-]$ and $[Cu^{2+}]2[NTf_2^-]$). The chromatographic retention of alkenes, alkynes, dienes, and aromatic compounds was examined. Incorporation of the $[Cu^{2+}]2[NTf_2^-]$ salt into a stationary phase comprised of poly(dimethylsiloxane) resulted in strong retention of olefins, while its addition to the $[C_6MIM^+][NTf_2^-]$ IL and poly($[C_6VIM^+][NTf_2^-]$) PIL allowed for the interaction strength to be modulated. Olefins exhibited greater affinities toward IL and PIL stationary phases containing the $[Cu^{2+}]2[NTf_2^-]$ salt compared to those with the $[Cu^+][NTf_2^-]$ salt. Elimination of water from both copper salts was observed to be an important factor in promoting olefin interactions, as evidenced by increased olefin retention upon exposure of the stationary phases to high temperatures. To evaluate the long-term thermal stability of the stationary phase, chromatographic retention of probes was measured on the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase after its exposure to helium at a temperature of 110 °C.

Keywords: gas chromatography; olefin separations; copper-mediated separations; ionic liquids; polymeric ionic liquids.

1. Introduction

Transition metals are known to form complexes with unsaturated hydrocarbons and have been used for the separation of light olefins from paraffins. [1–5] Among these, silver (Ag^+) and copper (Cu^+) ions are capable of withdrawing electrons from π-bonds of olefins to their vacant s-orbitals while back-donating electrons to π-bonds from their filled d-orbitals to form a reversible complex.[6] The moderate electronegativity of Ag^+ and Cu^+ ions allows for reversible olefin complexation; additionally, their cost-effectiveness in relation to other metals has led to their widespread use as a carrier and pseudophase for olefin separations in facilitated transport membranes and gas chromatography (GC) studies, respectively. [7–11]

Despite the advantageous characteristics of Cu^+ and Ag^+ ions, a significant challenge arises from their susceptibility in undergoing irreversible reactions with components that are often present in separation streams, thereby impeding the selective separation of olefins from paraffins. [12] The absence of a stabilizing ligand on Cu^+ ion may give rise to disproportionation of Cu^+ ion and irreversible reaction with oxygen and water, [8] while the Ag^+ ion can be reduced by reducing agents such as hydrogen peroxide and hydrogen gas. The introduction of hydrogen sulfide, a common impurity associated with the thermal cracking of hydrocarbons, can result in the formation of insoluble copper and silver sulfides. [12,13] Acetylenes are capable of undergoing irreversible reactions with Cu^+ ions resulting in the formation of unstable and shock-sensitive hazardous copper acetylide or silver acetylide compounds. Hence, numerous studies have explored the stabilization of Cu^+ and Ag^+ ions as a critical factor for enhancing the efficiency of olefin separations; [10,14–18] in particular, Cu^+ ions are attractive in olefin separations due to their comparatively lower cost. [19–22] For example, Miller examined the performance of an aqueous copper(I) nitrate ($[Cu^+][NO_3^-]$)

ethanolamine solution in the Imperial Chemical Industries olefin recovery process and contrasted its effectiveness with that of silver(I) tetrafluoroborate ($[Ag^+][BF_4^-]$). A notable cost difference was observed (based on prices in 1969), with $[Ag^+][BF_4^-]$ being approximately 60 times more expensive than the Cu_2O salt. [19]

To achieve efficient separation of olefins through the stabilization of Cu^+ ions, investigations have studied media that provide stable copper(I) complexes. [23–27] Polystyrene resins with various amino groups were modified by incorporating cuprous chloride ($[Cu^+][Cl^-]$) as an enhancer in the separation of ethylene. The presence of primary and secondary amino groups within the polystyrene resin notably enhanced the adsorption of ethylene by $[Cu^+][Cl^-]$, whereas the polystyrene resin containing tertiary amino groups exhibited diminished ethylene selectivity. The results revealed that ethylene undergoes adsorption through coordination to the Cu^+ ion within the copper-amino complex.[23] Separation of isoprene from n-pentane was achieved by an aqueous Cu^+ ion/pyridine/HNO_3 system, prepared from comproportionation of Cu(0) and $[Cu^{2+}]2[NO_3^-]\cdot 3H_2O$, followed by stabilization of Cu^+ ion by coordination to pyridine in the presence of HNO_3. [24] Enhanced absorption of ethylene over ethane was investigated using $[Cu^+][Cl^-]$ and cuprous bromide ($[Cu^+][Br^-]$), followed by the addition of aniline and N-methyl-2-pyrrolidone (NMP) as ligands to stabilize Cu^+ ions. [25] The $[Cu^+][Cl^-]$-aniline-NMP system was characterized by infrared (IR) spectroscopy and proton nuclear magnetic resonance (^1H NMR) spectroscopy and revealed reduced π-backbonding between Cu^+ ion and ethylene. More specifically, the aniline ligand was observed to compete with ethylene for coordination to Cu^+ ion, and thus reduced the capacity of ethylene absorption but enhanced the stability of the complex. [26] The sorbent, consisting of Cu^+ ions and fluorinated bis(pyrazolyl)borate as a ligand, was employed in the separation of propylene from a propylene/propane mixture. Separation of propylene involved the selective extraction of propylene by a Cu^+ ion-complex and subsequent desorption of propylene at 40 °C. [27] Impregnating a choline chloride-glycerol deep eutectic solvent (DES) combined with $[Cu^+][Cl^-]$ into a microporous nylon membrane resulted in enhanced solubility, diffusivity, and selectivity for ethylene over ethane. [28]

Ionic liquids (ILs) have emerged as solvents for the stabilization of Cu^+ ions due to favorable characteristics including low vapor pressure, high thermal stability, and the ability to employ numerous cation/anion combinations. [29,30] The respective $[Cu^+][Cl^-]$/1-butyl-3-methylimidazolium chloride ($[C_4MIM^+][Cl^-]$) IL and $[Ag^+][BF_4^-]/[C_4MIM^+][BF_4^-]$ IL was employed for the adsorption of 1-butene over butane. The results revealed that the adsorption capacity for 1-butene in the $[Cu^+][Cl^-]/[C_4MIM^+][Cl^-]$ IL system was lower [31] and subsequent investigations into the $[Cu^+][Cl^-]/[C_4MIM^+][Cl^-]$ IL system demonstrated comparable capability for propylene absorption to Ag^+-based ILs. [21] Notably, the $[Cu^+][Cl^-]/[C_4MIM^+][Cl^-]$ IL showed the highest capability for propylene absorption among other Cu^+ ion-based ILs, exhibiting a rate of 0.40 mol of propylene per kilogram of IL compared to copper thiocyanate ($[Cu^+][SCN^-]$)/tricaprylmethylammonium $[SCN^-]$ ($[A336^+][SCN^-]$) and $[Cu^+][Cl^-]$/N-methylpyrrolidone $[Cl^-]$ ($[HNMP^+][Cl^-]$) ILs, which absorbed propylene at 0.37 and 0.17 mol/kg, respectively. The selectivity obtained by the $[Cu^+][Cl^-]/[C_4MIM^+][Cl^-]$ IL system for propylene over propane reached 13.0 at 298 K, while the $[Cu^+][SCN^-]/[A336^+][SCN^-]$ IL (2.5) and $[Cu^+][Cl^-]/[HNMP^+][Cl^-]$ ILs (6.5) produced relatively lower propylene selectivity at the same temperature. [21] A separate study investigated the enhancement of propylene adsorption by introducing $[Cu^+][Cl^-]$ and $[Cu^+][Br^-]$ into the 1-ethyl-3-methylimidazolium $[C_2MIM^+][Br^-]$ and $[C_4MIM^+][Br^-]$ ILs. [20] The greatest propylene absorption capacity was observed when employing IL cations featuring longer alkyl substituents and the Cu^{+} cation paired with the $[Br^{-}]$ anion. Solubility of propylene in the $[Cu^{+}][Br^{-}]/[C_4MIM^{+}][Br^{-}]$ IL mixture was comparable with other studies utilizing $[Ag^{+}][BF_4^{-}]$ and the $[C_4MIM^{+}][BF_4^{-}]$ IL. [20] A comparable investigation using the $[Cu^{+}][Cl^{-}]/[C_4MIM^{+}][Cl^{-}]$ IL mixture, supported by a microporous polyvinylidene fluoride membrane, also produced an ethylene/ethane selectivity (11.8) similar to that of an Ag^{+}-based polymeric membrane and polymer electrolyte membrane. [22]

Similar to the Cu^{+} ion-complexation method utilized in olefin separations, attempts have been made to develop olefin separation systems utilizing Cu^{+} ions originating from $[Cu^{2+}]2[NTf_2^{-}]$ salts. [12,32] The $[Cu^{2+}]2[BF_4^{-}]$ salt was employed due to the limited solubility of the $[Cu^{+}][NTf_2^{-}]$ salt in the polyether-polyamide block copolymer/solvent system and used as a membrane for separating ethylene from ethane. [12] Poly(ethylene) glycol was employed as a medium for incorporating $[Cu^{2+}]2[BF_4^{-}]$ and $[Cu^{2+}]2[Cl^{-}]$ salts to extract 1-decene, owing to its propensity to reduce Cu^{2+} to Cu^{+} ions. [32] Nevertheless, a limited number of investigations have employed Cu^{2+} ion-ligand complexes as a direct metal source for the separation of unsaturated hydrocarbons involving the formation of charge-transfer complexes with π-electron acceptor metal ions. [33–38] Wasiak utilized phosphinated silica infused with $[Cu^{2+}]2[Cl^{-}]$ and $[Cu^{2+}]2[Br^{-}]$ to separate olefins by GC. Chromatographic retention of unsaturated hydrocarbons (C_5-C_7) and aromatic compounds was measured using columns packed with silica featuring the diphenyl-phosphine (PPh_2) ligand coordinated with the Cu^{2+} ion. The retention factor of 1,4-cyclohexadiene on the PPh_2 silica column increased when the $[Cu^{2+}]2[Cl^{-}]$ and $[Cu^{2+}]2[Br^{-}]$ salts were incorporated in the stationary phase. [35] A similar investigation was conducted by utilizing the $[Cu^{2+}]2[Cl^{-}]$ salt and 2-cyanoethyltriethoxysilane to promote interactions with olefins. [36]

Interactions between Cu^{2+} ion-IL systems and unsaturated hydrocarbons remain unexplored, and the long-term stability of Cu^{2+} ions within ILs has never been assessed. This study examines the $[Cu^{2+}]2[NTf_2^-]$ salt dissolved in imidazolium-based IL as a stationary phase in GC for the separation of olefins and paraffins. The interaction strength IL stationary phases containing the $[Cu^{2+}]2[NTf_2^-]$ salts for olefins is compared with those containing monovalent copper salts (e.g., $[Cu^+][NTf_2^-]$). Polymeric ionic liquids (PILs) were also studied as stationary phases by incorporation of Cu^+ and Cu^{2+} ions, exploiting their high thermal and chemical stability as well as unique solvation characteristics that originate from both ILs and their polymeric analogs. [39,40] A comparison of $[Cu^+][NTf_2^-]$-olefin interactions for different stationary phases was explored by examining the $[C_6MIM^+][NTf_2^-]$ IL, poly($[C_6VIM^+][NTf_2^-]$) PIL and a PIL crosslinked with the 1,12-di(3-vinylimidazolium)dodecane $2[NTf_2^-]$ crosslinker ($[C_{12}(VIM)_2{}^{2+}]2[NTf_2^-]$). Chromatographic retention of olefins was also examined with the $[Cu^{2+}]2[NTf_2^-]$ salt in the $[C_6MIM^+][NTf_2^-]$ IL and poly($[C_6VIM^+][NTf_2^-]$) PIL. Furthermore, the influence of elevated temperatures on the selectivity of $[Cu^{2+}]2[NTf_2^-]$-containing stationary phases was carried out, particularly with regard to water removal.

2. Materials and methods

2.1. Materials

Copper(I) bis[(trifluoromethyl)sulfonyl]imide ($[Cu^+][NTf_2^-]$) was purchased from Thermo Scientific Chemicals (Waltham, MA, USA). Copper(II) $[NTf_2^-]$ ($[Cu^{2+}]2[NTf_2^-]$), 2-octyne (99%), and methyl tiglate (98%) were purchased from TCI Chemicals (Portland, OR, USA). $[Cu^{2+}]2[NTf_2^-]\cdot H_2O$, hexane (99%), 1-hexene (99%), *cis*-2-hexene (95%), 2-hexyne (99%), *cis*-1,4-hexadiene (99%), 3-methyl-1,4-pentadiene (99%), 2,3-dimethyl-1,3-butadiene (99%), cyclohexane (99%), cyclohexene (99%), 1,4-cyclohexadiene (97%), benzene (99%), octane (99%), *trans*-2-octene (97%), 4-octyne (99%), *o*-xylene (99%), *p*-xylene (99%), *m*-xylene (99%), ethylbenzene (99%), nonane (99%), 1-nonene (99%), 1,8-nonadiene (99%), allylbenzene (98%), terpinolene (99%), *γ*-terpinene (99%), 4-phenyl-1-butene (99%), phenylacetylene (98%), benzaldehyde (98%), azobisisobutyronitrile (AIBN, 95%), $[Li^+][NTf_2^-]$ (99 %), 1-methylimidazole (99%), 1-vinylimidazole (99%), 1-bromohexane (98%), and 1,12-dibromododecane (98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The compounds 1-hexyne (98%), 3-hexyne (99%), and 1,5-hexadiene (98%) were obtained from Alfa Aesar (Ward Hill, MA, USA). Styrene (99%) was procured from Oakwood Chemical (Estill, SC, USA.). OV-101 (100% poly(dimethylsiloxane)) was obtained from Ohio Valley Specialty Company (Marietta, OH, USA). Untreated fused silica capillary tubing (250 μm I.D.) was purchased from Supelco (Bellefonte, PA, USA).

2.2. Preparation of GC columns and IL polymerization

Preparation of all ILs, IL monomers, and IL crosslinkers is described in the Supporting Information using previously published synthetic routes. [41,42] The chemical composition and molecular weights of the stationary phase materials are detailed in Table S1. ^{1}H NMR spectra are provided in Figures S1−S3 in the Supporting Information. [41–43] Gas chromatographic capillary tubing with a length of 5.0 m and an inner diameter of 0.25 mm was used in the study for the preparation of all chromatographic columns. The columns were prepared by coating the copper-containing stationary phase on the inner surface of untreated fused silica tubing using the static coating method. [44] To achieve a film thickness of 0.28 μm, a solution comprised of 0.448% (w/v) of IL, IL monomer or OV-101 was dissolved in 5% (v/v) methanol and 95% (v/v) dichloromethane. All copper-containing columns prepared in this study are listed in Table 1.

2.2.1. Cu^+ ion-containing IL, PIL and crosslinked PIL stationary phases

The Cu^+ ion-containing columns were prepared using the $[Cu^+][NTf_2^-]$ salt dried by rotary evaporation at 50 °C for 10 h. The $[Cu^+][NTf_2^-]$ salt was significantly hygroscopic and observed to readily absorb water from the atmosphere, resulting in a liquid with a blue color. Removal of water from the salt resulted in the appearance of a white-colored crystal. The dried $[Cu^+][NTf_2^-]$ salt was added to the IL, IL monomer, or IL monomer and a crosslinker, followed by dissolving the mixture in dichloromethane containing 5% (v/v) methanol in order to prepare coating solutions used to produce columns 1-7 in Table 1. A thermal initiator, AIBN, was added at 3% by weight of the stationary phase to the coating solution and polymerized after coating to obtain the PIL columns (columns **2**, **3**, **6**, and **7** in Table 1). Polymerization was performed by filling the coated column with nitrogen gas for 1 h at a flow of 1 mL min^{-1} at room temperature, followed by sealing both ends and heating in a GC oven from 40 °C to 80 °C at 1 °C min^{-1} and finally subjecting it to an isothermal hold at 80 °C for 15 h. [43] Utilizing an identical polymerization methodology as mentioned above, a column incorporating AIBN (column **5**) and consisting of the IL in place of the IL monomer was also produced.

2.2.2. Cu^{2+} ion-containing IL and PIL stationary phases

Water was removed from the $[Cu^{2+}]2[NTf_2^-]\cdot H_2O$ reagent by heating to 100 °C for 5 h, yielding a pale blue compound ($[Cu^{2+}]2[NTf_2^-]$). A PIL column incorporating Cu^{2+} ion (column **10**) was prepared through polymerization of IL monomer in the presence of 12 wt%

Cu^{2+} and 3 wt% AIBN, and then heated at 80 °C for 15 h in a round-bottom flask using ethanol as a solvent. [45] The number of moles of Cu^{2+} ions incorporated into the IL or PIL was equivalent to half the number of moles of Cu^{+} ions incorporated into the IL or PIL, as described in Section 2.3.1. Ethanol was evaporated after polymerization and was followed by the addition of dichloromethane solution containing 5% v/v methanol to the flask to produce a coating solution (0.448% w/v) used for preparing the column. Using an identical method, an IL column containing Cu^{2+} ions (column **8**) was prepared as a control. To examine the effect of AIBN on the $[Cu^{2+}]2[NTf_2^-]$ salt, a mixture of IL, $[Cu^{2+}]2[NTf_2^-]$ and AIBN was prepared, using the same column preparation mentioned above to produce column **9**. Column **11** was prepared by mixing anhydrous $[Cu^{2+}]2[NTf_2^-]$ with IL, while columns **12** and **13** were produced using the OV-101 stationary phase.

After stationary phase and column preparation, all capillary columns underwent column conditioning by exposing the columns to helium gas at a flow rate of 1 mL min^{-1} using temperatures ranging from 50 °C to 100 °C at a ramp of 5 °C min^{-1}. The columns were then held isothermally at 100 °C for 20 min. The chromatographic efficiency of the conditioned columns was assessed using naphthalene at 100 °C, and the measured efficiencies ranged from 1500 to 2400 plates/meter.

2.3. Instrumentation

Chromatographic retention times of probe molecules were measured using Agilent Technologies (Santa Clara, CA, USA) 6850A, 6890N, and 7890N GCs equipped with a flame ionization detector (FID). A 1 μL volume of analytes was injected using a Hamilton 701 N 10 μL syringe at a 20:1 split ratio with the injector maintained at 150 °C. Each sample (3.0 μL) was contained in a 5 mL headspace vial. Helium served as the carrier gas, with a constant flow rate of 1 mL min^{-1}. The oven temperature was held at 35 °C for all measurements. The FID was maintained at 160 °C with hydrogen and air supplied at 30 mL min^{-1} and 300 mL min^{-1}, respectively.

3. Results and discussion

3.1. Comparison of olefin separation performance for imidazolium-based IL GC stationary phases containing Cu$^+$ ions

In the study of olefin separations within the Cu$^+$ ion-IL system, chromatographic retention of olefins (based on the retention factor) on the neat IL stationary phase (column **1** in Table 1) served as a control. To examine the impact of polymerization of the IL stationary phase and its effect on olefin separation, a comparison was made between the IL and a linear PIL stationary phase, represented by the neat PIL (column **2**). Crosslinking of the PIL stationary phase was evaluated by measuring the retention factor of olefins on the neat xPIL stationary phase (column **3**), in which the $[C_{12}(VIM)_2^{2+}]2[NTf_2^-]$ IL served as a crosslinker. Retention factors of olefins measured from respective IL and PIL stationary phases were compared to those obtained on stationary phases incorporating the $[Cu^+][NTf_2^-]$ salt, namely, the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL (column **4**), $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL (column **6**), and $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]/[C_{12}(VIM)_2^{2+}]2[NTf_2^-]$) PIL (column **7**), respectively. The $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase containing AIBN (column **4**) was tested to examine the effect of Cu$^+$ ion reduction by the thermal initiator during the IL and PIL column preparation process. To explore changes in olefin separation upon incorporation of the $[Cu^+][NTf_2^-]$ salts, the stationary phases were initially tested with 4-octyne, and its retention was systematically compared across the stationary phases. As shown in Figure 1, the incorporation of Cu^+ ions in the stationary phases led to increased retention of 4-octyne; its retention factor on the neat IL (1.66), neat PIL (1.73), and neat xPIL (1.61) exhibited a 1.46-fold, 1.38-fold and 1.61-fold increase, respectively. In contrast, the retention factor for 4-octyne on the AIBN/$[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase (1.75) remained largely unchanged compared to that observed on the neat IL (1.66).

The impact of heating stationary phases containing Cu^+ ions (columns **4**-**7** in Table 1) was examined. Retention factors of 4-octyne were measured after subjecting the columns to 110 °C for 10 h under helium gas. As shown in Figure 1, the retention factor of 4-octyne on the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL (2.43) increased by 3.41-fold after the heating procedure (8.28), which may be attributed to the removal of water from the $[Cu^+][NTf_2^-]$ salt. [46] In contrast, the retention factor of 4-octyne on the AIBN/$[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase (1.75) showed a slight increase after heating (1.96), indicating that the reduction of Cu^+ ions to Cu(0) by AIBN may result in a lower concentration of Cu^+ ions, and therefore a decrease in the amount of water absorption by Cu^+ ions. Due to the reduction of Cu^+ ions within the PIL column during polymerization, the retention factor of 4-octyne on the $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL stationary phase (2.39) was largely unchanged after heating. However, the retention factor of 4-octyne on the $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]/[C_{12}(VIM)_2^{2+}]2[NTf_2^-]$) PIL increased from 2.59 to 4.12 after the heating process, suggesting that the reduction of Cu^+ ions resulted in weaker Cu^+ ion-olefin interactions that can be mitigated by crosslinking of the PIL.

3.1.1. Interaction of Cu^+ ions with π-bonds in unsaturated hydrocarbons

To investigate the interaction of Cu^+ ions and olefins with varied chemical structure, retention factors of alkanes, alkenes, alkynes, and dienes were measured on Cu^+ ion-containing stationary phases and compared to the neat IL (or PIL) stationary phases. Alkanes exhibited very little change in retention upon incorporation of Cu^+ ions into the IL (or PIL) stationary phase, as shown in Figure 2 (a). Alkenes possessing six or eight carbons including 1-hexene, *cis*-2-hexene and *trans*-2-octene exhibited no change in retention for the stationary phases containing Cu^+ ions and neat IL (or PIL) stationary phases; however, only 1-nonene exhibited a change in retention factor from 1.46 on the neat IL (column **1**) to 2.54 using the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL.

Retention factors of alkynes including 1-hexyne, 2-hexyne, 3-hexyne, 2-octyne and 4-octyne substantially increased when Cu^+ ion was added to the stationary phases, as shown in Figure 2 (c). For example, the retention factor of 2-octyne increased by a factor of 4.0 (2.50 to 10.04) while 2-hexyne increased by a factor of 3.7 (0.48 to 1.76) using the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase (column **4**) compared to neat IL (column **1**). Crosslinking of the PIL was observed to enhance Cu^+ ion-olefin interactions, where an increase in the retention factor of 2-octyne from 2.39 on the neat xPIL (column **3**) to 5.23 on the $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]/[C_{12}(VIM)_2^{2+}]2[NTf_2^-]$) PIL (column **7**) was observed, while the retention factor of 2-octyne on the neat PIL (column **2**) was 2.61 and increased slightly to 3.06 on the $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL stationary phase (column **6**). Isomers of hexyne exhibited varied retention depending on the position of the triple bond within the chemical structure; for example, the retention factors of 1-hexyne, 2-hexyne, and 3-hexyne on the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase increased from 1.25 to 1.76 and finally to 2.02, respectively. The analyte 1-hexyne exhibited the weakest interaction with

Cu^+ ions among the hexyne isomers and appears to contradict prior studies where 1-hexyne experienced reduced steric hindrance compared to other hexyne isomers upon interaction with Ag^+ ions. [41,47]

Dienes featuring terminal double bonds, such as 1,5-hexadiene and 1,8-nonadiene, exhibited strong Cu^+ ion-olefin interactions in contrast to other isomeric dienes such as *cis*-1,4-hexadiene, 3-methyl-1,4-pentadiene and 2,3-dimethyl-1,3-butadiene, as shown in Figure 2 (b). For example, the retention factor of 1,5-hexadiene increased significantly from 0.16 to 6.44 when Cu^+ ion was added to the IL (column **4**) and increased from 0.16 to 5.17 when Cu^+ ion was introduced to the xPIL stationary phase (column **7**). The analyte *cis*-1,4-hexadiene exhibited a slight increase from 0.21 to 0.39 and from 0.21 to 0.29, respectively, under the same conditions. Retention factors of 2,3-dimethyl-1,3-butadiene measured on stationary phases containing Cu^+ ions (columns **4**, **5**, **6**, and **7**) remained unchanged when compared to those of the neat IL (or PIL) stationary phases (columns **1**, **2**, and **3**). This observation suggests that the presence of methyl substituents in the diene may impede interactions between Cu^+ ions and the terminal C=C bonds of dienes.

In general, olefins measured on the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase exhibited higher retention factors than those assessed on the AIBN/$[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL. This difference is illustrated in Figure 2, which reveals the influence of AIBN on the resulting concentration of Cu^+ ions in the stationary phase. Notably, there is a lack of prior studies that have directly investigated the reaction of Cu^+ ions with radicals generated from AIBN, and may be attributed to Cu^+ ions in cuprous salts undergoing rapid disproportionation to Cu^{2+} ion and Cu(0) in polar or IL solvents. [48] Research efforts have focused on the reduction of Cu^{2+} to Cu^+ ions through the application of AIBN, [49–52] as well as the conversion of Cu^{2+} ions to copper nanoparticles utilizing free radicals generated from a photoinitiator. [53] Ag^+ ion, possessing similar characteristics to Cu^+ ion as a group 11 transition metal, has been reported to be reduced to zero-valent silver by the AIBN initiator in previous studies. [41,54,55] Consequently, it is plausible that Cu^+ ion undergoes a similar reduction facilitated by AIBN, resulting in decreased olefin retention factors. Similarly, the retention factors of olefins acquired from the $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL stationary phase (column **6**), which employed AIBN during the polymerization process, were largely unchanged when compared to those obtained from the neat PIL (column **2**). However, when Cu^+ ion was added to the crosslinked PIL stationary phase (column **7**), a significant increase in olefin retention was observed, compared to linear PIL (column **6**), indicating that the crosslinker in the PIL plays a role in facilitating Cu^+ ion-olefin interactions.

3.1.2. Interaction of Cu^+ ions with π-bonds within cyclic hydrocarbons

Interactions between Cu^+ ion and C=C bonds within a group of cyclic hydrocarbons were explored by measuring the chromatographic retention of cyclohexane, cyclohexene, 1,4-cyclohexadiene, terpinolene, and *γ*-terpinene, as shown in Figure 3. Retention factors of cyclohexene on the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase (0.48) and neat IL (0.39) were exceptionally low. Similarly, retention factors for cyclohexadiene (1.09) obtained on the Cu^+ ion-containing IL stationary phase were similar to the neat IL (0.85). The retention factor of terpinolene on the IL (12.75) increased by 1.6% when Cu^+ ion was added into the IL stationary phase with 3% AIBN (12.95), and increased slightly by 5.6% in the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase (13.46). These results suggest that the Cu^+ ion content in the stationary phases has no significant impact on the variation of retention factor for cyclic hydrocarbons possessing C=C bonds, indicating a lack of complexation between Cu^+

ions and the π-bonds within cyclic hydrocarbons. Interactions of these probe molecules appear to be stronger with the IL (or PIL) stationary phase.

3.1.3. Interaction of Cu^+ ions with π-bonds within aromatic compounds

Chromatographic retention of aromatic compounds possessing a single aromatic ring were measured on Cu^+ ion-containing IL and PIL stationary phases. The analytes *o*-, *m*- and *p*-xylene and benzaldehyde are shown in Figure 4 (a) and the effect of benzene substituents featuring π-bonds on Cu^+ ion-olefin interactions was investigated by measuring retention factors of styrene, ethylbenzene, allylbenzene, 4-phenyl-1-butene, and phenylacetylene, as shown in Figure 4 (b). Retention factors for all xylene isomers in Figure 4 (a) did not change after Cu^+ ions were incorporated into the IL-based stationary phase. For example, the retention factor of *o*-xylene was 11.28 on the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL and 11.34 on the neat IL stationary phase. The retention factor of *o*-xylene on the neat PIL (12.06) decreased by 16.9% on the $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL (10.02), indicating that the predominant interactions are likely linked to the IL (or PIL) composition of the stationary phase.

Figure 4 (b) shows the retention factors of styrene, ethylbenzene, allylbenzene, 4-phenyl-1-butene, and phenylacetylene which indicate the interaction strength between Cu^+ ion and benzene in the presence of substituents featuring C=C bonds. Increasing the distance between the benzene ring and the C=C bonds of the substituent impacts the flexibility of the carbon chain substituents, which may also reduce the steric hindrance on C=C bonds of substituent, thereby facilitating interactions between the C=C bond of the benzene substituent and the Cu^+ ion. For example, styrene and allylbenzene exhibited increased retention factors of 11.8% (17.11 to 19.13) and 22.4% (17.75 to 21.73), respectively, upon addition of Cu^+ ion to the IL stationary phase. Moreover, the retention factor of 4-phenyl-1-butene increased significantly (by 53.2%) from 35.68 to 54.68. Aromatic analytes were found to retain more strongly compared to linear hydrocarbons possessing π-bonds in both IL and PIL stationary phases due to π-π interactions between the benzene ring and the imidazolium moiety within the IL and PIL stationary phases, as shown in Figure 4.

3.2. Comparison of olefin separation on IL and PIL stationary phases containing Cu^{2+} ions after heating

To compare the interaction of hydrocarbons with Cu^+ and Cu^{2+} ions, retention characteristics of analytes were measured on stationary phases containing $[Cu^+][NTf_2^-]$ and $[Cu^{2+}]2[NTf_2^-]$ salts. Results from the previous section indicated that the presence of AIBN during preparation of the Cu^+ ion-containing stationary phases led to lower retention of olefins compared to the stationary phases prepared without AIBN. This drop in olefin retention may be attributed to the AIBN-induced reduction of Cu^+ ions in the stationary phase, resulting in weaker Cu^+ ion-olefin interactions. Consequently, an effort was made to preserve Cu^+ ion-olefin interactions by employing AIBN as a reducing agent to convert Cu^{2+} ions to Cu^+ ions during the polymerization process. [49–52] For the PIL stationary phase containing the $[Cu^{2+}]2[NTf_2^-]$ salt (column **10**), significant increase in olefin retention was observed compared to the $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL (column **6**). As shown in Figure 2 (a), the retention factor of 1-nonene on the $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL stationary phase was 1.39; however, on the $[Cu^{2+}]2[NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL (Figure 5 (a)), the retention factor of 1-nonene spiked to 14.84 and further increased to 42.64 following heat treatment, further highlighting the substantial increase in olefin retention on the $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL and $[Cu^{2+}]2[NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL stationary phases despite the molar quantity of Cu^{2+} ions used in the stationary phase being half that of Cu^+ ions.

Figures 6-8 and Figures S1-S2 (supporting information) show results of Cu^{2+} ion-olefin interactions and a comparison of olefin retention on the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL and $[Cu^{2+}]2[NTf_2^-]$/OV-101 stationary phases. The impact of AIBN on the reduction of Cu^{2+} ions within the stationary phases was assessed by comparing the retention of olefins on the Cu^{2+} ion-containing IL with those in the presence of AIBN. Stationary phases containing Cu^{2+} ions were subjected to a 1-hour helium exposure step at temperatures of 110, 125, 140, and 155 °C, respectively. Subsequent measurements were conducted to measure the retention factors of all probe molecules, and the data were compared to those obtained prior to column heating. This heating process aimed to uncover the influence of water that remains in the stationary phase on the chromatographic retention of olefins.

3.2.1. Interaction of Cu^{2+} ions with π-bonds within unsaturated hydrocarbons

The Cu^{2+} ion-containing IL (and PIL) stationary phases following heat treatment were found to have stronger retention of alkenes, alkynes, and dienes, as shown in Figure 5. The observed trends are analogous to those for Cu^+ ions-containing stationary phases in Figure 1; however, columns possessing Cu^{2+} ions showed notably greater interaction strength with olefins, as shown in Figure 5 (c). The retention factor of 4-octyne on the neat IL stationary phase (1.66) exhibited a 1.46-fold increase on the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL before heating (2.43) and a 5.0-fold increase after heating (8.28). In the case of the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL, the retention factor increased by 120-fold before heating (199.16) and a 439-fold increase was observed after heating (729.18) compared to neat IL (1.66).

Increased olefin retention on stationary phases containing Cu^{2+} ions upon heating can be attributed to the following two potential factors: (1) formation of Cu^+ ions from Cu^{2+} ions in IL (or PIL), and/or (2) removal of water. To validate whether Cu^{2+} ions exclusively interact with olefins or undergo conversion to Cu^+ ions in the presence of ILs, Cu^{2+} ions were added to a non-polar and non-ionic stationary phase, OV-101. As shown in Figure S4 (a), the column containing Cu^{2+} ions in OV-101 provided high retention of 1-hexene (retention factor of 175.17), suggesting that Cu^{2+} ions alone can interact with olefins without the IL. Chromatographic peaks for the majority of olefins measured from the $[Cu^{2+}]2[NTf_2^-]$/OV-101 stationary phase could not be detected and may be due to the strong adsorption of olefins on Cu^{2+} ions incorporated in the OV-101 stationary phase. Chromatographic peaks corresponding to 1-hexene and *cis*-2-hexene were identified on the $[Cu^{2+}]2[NTf_2^-]$/OV-101 stationary phase, but alkynes and dienes were not detected, as shown in Figure S4 (b) and (c). The retention factor of 1-hexene on the $[Cu^{2+}]2[NTf_2^-]$/OV-101 stationary phase (175.17) exhibited a slight decrease of 4.3% after heating (167.68). Limited solubility of the $[Cu^{2+}]2[NTf_2^-]$ salt in OV-101 was observed during preparation of the coating solution. Consequently, chromatographic peaks of 1-hexene that exhibited tailing and flattening profiles were observed and may be attributed to excessively strong adsorption of 1-hexene on Cu^{2+} ions in OV-101, thereby limiting the number of active sites of Cu^{2+} ion to interact with other 1-hexene molecules.

Retention factors of 1-hexene, *cis*-2-hexene, and *trans*-2-octene on the neat IL (or PIL) stationary phases and those containing Cu^+ ions showed very little differences in Figure 2 (a); however, retention factors with Cu^{2+} ions in Figure 5 (a) shows that the strongest interaction was between Cu^{2+} ions and alkenes. For example, the retention factor of 1-hexene on the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase was 10.09 (Figure 5 (a)) while that on the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL was 0.21 (Figure 2 (a)). The retention factor of 1-hexene was reduced to 5.42 on the AIBN/$[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL, compared to that of the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL (10.09). This observation reinforces the assertion that Cu^{2+} ions can interact with olefins and that AIBN acts as a reducing agent, thereby leading to a reduction in the amount of Cu^{2+} ions within the stationary phase.

Following a similar trend to the results for alkenes, retention factors of dienes increased significantly for the IL (or PIL) when Cu^+ ions in the stationary phases were replaced by Cu^{2+} ions. Notably, the retention factor of *cis*-1,4-hexadiene was 0.39 (Figure 2 (b)) on the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL and increased significantly to 54.73 (Figure 5 (b)) on the IL stationary phase containing $[Cu^{2+}]2[NTf_2^-]$. This also applied to the PIL, where the retention factor of *cis*-1,4-hexadiene was 0.2 on the $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL (Figure 2 (b)) and increased to 21.33 on the $[Cu^{2+}]2[NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL stationary phase (Figure 5 (b)). Hexynes, exhibiting weak interaction with the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL and $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL stationary phases, were similarly observed to interact more strongly on the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL and $[Cu^{2+}]2[NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL stationary phase. In the case of Cu^+ and Cu^{2+} ions in the IL, the retention factor of 2-hexyne was 1.76 in the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL (Figure 2 (c)) and 0.48 in the neat IL stationary phase, but rose drastically to 158.29 in the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL (Figure 5 (c)). In the case of Cu^+ and Cu^{2+} ions in the PIL stationary phase, the retention factor of 2-hexyne was 0.56 for the $[Cu^+][NTf_2]$/PIL (Figure 2 (c)) and 0.50 on the neat PIL stationary phase, but rose to 66.74 on the $[Cu^{2+}]2[NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL (Figure 5 (c)).

3.2.2. Interaction of Cu^{2+} ions with π-bonds within cyclic hydrocarbons

Chromatographic retention of cyclic hydrocarbons did not vary significantly between the neat IL (and PIL) stationary phases and those incorporating $[Cu^+][NTf_2^-]$ salts, as shown in Figure 3. The π-complexation between Cu^+ ion and cyclic hydrocarbons was thought to be sterically hindered by their ring structure, with interactions predominantly involving the IL (or PIL) stationary phase, rather than the Cu^+ ions. In contrast, the Cu^{2+} ion-containing IL (or PIL) stationary phases produced stronger retention of cyclic hydrocarbons compared to the neat IL (or PIL) stationary phases, as shown in Figure 6. For example, the retention factor of cyclohexene on the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase (11.50) increased substantially (29.49-fold) in comparison to the neat IL (0.39). The retention factor for cyclohexadiene showed a 36-fold increase on the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase (30.52) compared to that on the neat IL (0.85). Retention factors for terpinolene (12.74) and γ-terpinene (12.17) on the neat IL stationary phase increased to 140.34 and 132.50, respectively, on the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL (Figure 6), with no significant difference observed in the IL stationary phase containing $[Cu^+][NTf_2]$ (Figure 3). Furthermore, chromatographic peaks corresponding to cyclic hydrocarbons with C=C double bonds were not detected on the $[Cu^{2+}]2[NTf_2^-]$/OV-101 stationary phase due to strong interactions with Cu^{2+} ions. The observed retention factor for cyclohexane (1.07) closely resembles that measured on the unmodified OV-101 stationary phase (1.10), as shown in Figure S5 (a).

3.2.3. Interaction of Cu^{2+} ions with π-bonds within aromatic compounds

Alkyl substituents appended to aromatic analytes play a critical role in their interaction with Cu^+ and Cu^{2+} ions. Figure 4 (b) illustrates that an increase in the distance between the aromatic ring and the double bond on the substituent leads to enhanced interactions with the

$[Cu^+][NTf_2^-]$ salt, and stronger chromatographic retention. A similar trend is observed for the $[Cu^{2+}]2[NTf_2^-]$ salt, as shown in Figure 7(b), where the strength of the Cu^{2+} ion-olefin interaction in the IL follows the order: 4-phenyl-butene > allylbenzene > styrene, with these probes exhibiting higher retention factors.

Figure 7(b) reveals a substantial increase in the retention of styrene on the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL, with retention factors ranging from 77.38 (before heating) to 208.49 (after heating). This is markedly different from the retention factor of styrene on the neat IL stationary phase (17.11). Similarly, the retention factor of allylbenzene on the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL increased significantly from 182.57 (before heating) to 449.55 (after heating), surpassing that measured from the $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase (21.73). Notably, the retention factor of 4-phenyl-butene on the Cu^{2+}/ IL was 637.81 before heat treatment; however, the chromatographic peak corresponding to 4-phenyl-butene was not observed after heating.

Heat treatment of the stationary phases containing Cu^{2+} ions had no discernable impact on the retention of aromatic compounds lacking allyl or vinyl substituents. Furthermore, following the removal of water, no discernible interaction between Cu^{2+} ions and olefins was detected; moreover, predominant interactions appeared to take place between the benzene ring and the imidazolium moiety within the IL and PIL stationary phase. As illustrated in Figure 7(a), the retention factor of *o*-xylene on the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL changed very little before and after column heating. Incorporation of Cu^{2+} ions to the OV-101 stationary phase appears to enhance interactions with aromatic compounds (Figure S5 (b) and (c)), leading to a significant difference in xylene retention between neat the OV-101 and the $[Cu^{2+}]2[NTf_2^-]$/OV-101 stationary phases. For example, the retention factor of *o*-xylene increased from 8.67 on the neat OV-101 stationary phase to 4.18 times (36.26) in the

$[Cu^{2+}]2[NTf_2^-]$/OV-101 before heating and 5.31 times (46.04) on the $[Cu^{2+}]2[NTf_2^-]$/OV-101 stationary phase after heating, respectively.

3.3. Variation in the strength of Cu^{2+} ion-olefin interactions with increasing heating temperature of the stationary phases

To ascertain the optimal heating conditions for inducing the strongest Cu^{2+} ion-olefin interactions in the stationary phase, they were subjected to continuous heating in a GC oven. Stationary phases containing Cu^{2+} ions were subjected to helium exposure and incrementally heated for 1 hour at varying temperatures, increasing by 15 °C intervals, and ranging from 110 to 305 °C. The retention factor of 1-hexyne was measured following each heating stage and showed increased retention as the Cu^{2+} ion-containing stationary phases were exposed to higher temperatures, as depicted in Figure S6. For example, the retention factor of 1-hexyne on the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase was 31.03 before heating and increased to 101.31 after the stationary phase was exposed to 155 °C. The chromatographic peak corresponding to 1-hexyne disappeared when the column was exposed to temperatures exceeding 155 °C and is likely due to the strong adsorption of 1-hexyne onto the Cu^{2+} ion following water removal. Specifically, 1-hexyne did not elute from the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase when exposed to temperatures of 170 °C, nor from the AIBN/$[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase at temperatures of 200 °C. Similarly, 1-hexyne did not elute from the $[Cu^{2+}]2[NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL stationary phase when exposed to temperatures of 155 °C. The chromatographic peaks of 1-hexyne reappeared after exposing the stationary phases to 275 °C.

Due to the adsorption of 1-hexyne onto the stationary phase, the retention factor of 2-hexyne was measured after exposing the stationary phase to 155 °C, as shown in Figure 8. Each column demanded a unique exposure temperature to achieve the maximum retention of 2-hexyne: 212.1 at 185 °C for the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL, 108.1 at 215 °C for the AIBN/$[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL, and 67.2 at 170 °C for the $[Cu^{2+}]2[NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL stationary phase. After reaching a temperature corresponding to the maximum retention for 2-hexyne, thermal degradation of each stationary phase was observed, resulting in decreased retention after the subsequent temperature exposure. The temperature at which the maximum retention of olefin was observed indicates a balance between stationary phase degradation and exhaustive water removal within the columns. Consequently, the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL efficiently facilitated activation of Cu^{2+} ions at lower temperatures and exhibited enhanced interactions with olefins compared to the $[Cu^{2+}]2[NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL. As a supplement to the above experiment, an investigation into the long-term thermal stability of the stationary phase was conducted using the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase.

3.4. Variation in the strength of Cu^{2+} ion-olefin interactions upon constant heating of the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase

To understand the impact of heating on the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase (column **11**) at a constant temperature, representative probe molecules including hexane, 1-hexane, *cis*-2-hexene, 1-hexyne, 2-hexyne, *o*-xylene, and methyl tiglate were studied. The column underwent continuous helium gas exposure at an oven temperature of 110 °C, with temperature conditions set to an isothermal temperature of 35 °C for each retention time measurement on the same GC instrument. Measurements were taken at 1-hour intervals during the initial 4 h of exposure at 110 °C. Subsequently, measurements were taken at 2-hour intervals until 20 h, followed by measurements at 8-hour intervals until 76 h, and then at 16-hour intervals until 476 h had elapsed. The Cu^{2+} ion-IL utilizing anhydrous $[Cu^{2+}]2[NTf_2^-]$ salt (column **11**) was employed instead of the $[Cu^{2+}]2[NTf_2^-]\cdot H_2O$ salt, accounting for the potential deformation of $[Cu^{2+}]2[NTf_2^-]\cdot H_2O$ in the drying procedure prior to its addition to the IL. The $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase featuring the anhydrous salt exhibited significant retention of 2-hexyne after heating, comparable to that prepared from the $[Cu^{2+}]2[NTf_2^-]\cdot H_2O$ salt. Nevertheless, the heating time required at 110 °C to achieve the maximum retention of 2-hexyne was longer compared to that required at temperatures above 155 °C. For example, the retention factor of 2-hexyne in Figure 9 (a) exhibited an upward trend with increased exposure time until reaching 108 h, after which it stabilized and showed little variation up to 476 h. The 1-hexyne analyte did not elute from the column after exposing the column for 18 h, and this phenomenon continued until 476 h had elapsed. The retention factor of methyl tiglate decreased from 22.62 to 19.32 after 3 hours of exposure due to water removal and then remained consistent, as shown in Figure 9 (b). Meanwhile, *o*-xylene exhibited constant retention throughout the exposure, indicating its more dominant interaction with the IL. The variation in retention for alkenes is presented in Figure 9 (c), indicating that alkenes consistently exhibited higher retention than alkanes, even after exposure. For example, hexane consistently exhibited negligible retention due to the absence of π-bonds within its chemical structure, whereas the retention factor of both 1-hexene and *cis*-2-hexene increased as the exposure times were lengthened, peaking at an exposure time of 108 h. After an exposure time of 108 h, 1-hexene exhibited a slightly higher retention factor of 2.65 compared to *cis*-2-hexene's retention factor of 1.35. The retention factors remained stable for both alkenes until 476 h of exposure. Overall, the $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase exhibited constant retention for olefins, including 2-hexyne, 1-hexene, and *cis*-2-hexene, even after exposure to 110 °C. The approach (outlined in Section 3.4) and results from a previous study

[46] suggest that activating the Cu^{2+} ion at elevated temperatures above 140 °C could expedite this process.

4. Conclusions

This study investigated $[Cu^{+}][NTf_2^{-}]$ and $[Cu^{2+}]2[NTf_2^{-}]$ salts for the separation of olefins through their interactions with the π-bonds of hydrocarbons, by introducing the copper salts into imidazolium-based IL and PIL stationary phases and measuring olefin retention using GC. Reduction of both $[Cu^{+}][NTf_2^{-}]$ and $[Cu^{2+}]2[NTf_2^{-}]$ salts associated with the addition of free radical initiator during preparation of the stationary phases was indirectly observed by the decreased retention of hydrocarbons featuring carbon-carbon double or triple bonds, including alkenes, alkynes, and dienes. When the $[Cu^{+}][NTf_2^{-}]$ salt was introduced into the crosslinked PIL, it exhibited increased olefin retention compared to that of the PIL stationary phase. Stationary phases containing the $[Cu^{2+}]2[NTf_2^{-}]$ salt undergo more strong interaction with olefins than those containing $[Cu^{+}][NTf_2^{-}]$; the retention factor of 1-hexene in the $[Cu^{2+}]2[NTf_2^{-}]/[C_6MIM^{+}][NTf_2^{-}]$ IL exhibited a 48.0-fold increase compared to that in $[Cu^{+}][NTf_2^{-}]/[C_6MIM^{+}][NTf_2^{-}]$ IL. Utilization of imidazolium-based IL and PILs, when contrasted with the OV-101 stationary phase, permitted modulation of olefin interaction using Cu^{2+} ions, enabling their application as stationary phases for olefin separations. The effect of heating, due to the removal of water from the Cu^{2+} ion-containing stationary phase, led to increased retention of hydrocarbons containing carbon-carbon double or triple bonds. Identifying the optimal temperature for heating the stationary phase is required to balance the full activation of Cu^{2+} ions by completely removing water and degradation of the GC stationary phase. Furthermore, it is essential to explore the optimal temperature that facilitates elution of strongly adsorbing olefins, such as 1-hexyne and 1,5-hexadiene, from Cu^{2+} ions in order to reduce the duration of the separations process. Crosslinking of the PIL stationary phase led to enhanced Cu^+ ion-olefin interactions compared to their non-crosslinked, linear counterparts even in the presence of a reducing agent.

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Table 1. Composition of copper salts and ILs/PILs examined in this study as chromatographic stationary phases.

No.	**Copper Salt**	**Stationary Phase (SP)**	**Copper Salt Concentration in SP (wt%)**
1	-	$[C_6MIM^+][NTf_2^-]$	0.0
2	-	poly($[C_6VIM^+][NTf_2^-]$)	0.0
3	-	poly($[C_6VIM^+][NTf_2^-]/[C_{12}(VIM)_2^{2+}]2[NTf_2^-]$) (2:1 w/w)	0.0
4	$[Cu^+][NTf_2^-]$	$[C_6MIM^+][NTf_2^-]$	13.3
5	$[Cu^+][NTf_2^-]$	$[C_6MIM^+][NTf_2^-]$, 3% AIBN	13.3
6	$[Cu^+][NTf_2^-]$	poly($[C_6VIM^+][NTf_2^-]$)	13.3
7	$[Cu^+][NTf_2^-]$	poly($[C_6VIM^+][NTf_2^-]/[C_{12}(VIM)_2^{2+}]2[NTf_2^-]$) (2:1 w/w)	13.3
8	$[Cu^{2+}]2[NTf_2^-]$	$[C_6MIM^+][NTf_2^-]$	12.0
9	$[Cu^{2+}]2[NTf_2^-]$	$[C_6MIM^+][NTf_2^-]$, 3% AIBN	12.0
10	$[Cu^{2+}]2[NTf_2^-]$	poly($[C_6VIM^+][NTf_2^-]$)	12.0
11	$[Cu^{2+}]2[NTf_2^-]$	$[C_6MIM^+][NTf_2^-]$	12.0
12	-	OV-101	0.0
13	$[Cu^{2+}]2[NTf_2^-]$	OV-101	12.0

Figure Legends

Figure 1. Retention factors of 4-octyne after exposing IL and PIL stationary phases containing Cu(I) ion at 110 °C. The stationary phases included: $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL (column 4) after heating (filled black) and before heating (patterned black), and neat IL (column 1, hollow black); $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL with AIBN (column 5) after heating (filled gray) and before heating (patterned gray); $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL (column 6) after heating (filled blue) and before heating (patterned blue), and neat PIL (column 2, hollow blue); $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]/[C_{12}(VIM)_2^{2+}]2[NTf_2^-]$) PIL (column 7) after heating (filled purple) and before heating (patterned purple), and neat crosslinked PIL (column 3, hollow purple). Retention measurement condition: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 35 °C; inlet temperature, 150 °C; FID temperature 160 °C. Column heating condition: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 110 °C for 10 h.

Figure 2. Retention factors of (a) alkanes and alkenes; (b) dienes (*cis*-1,4-hexadiene, 1,5-hexadiene, 3-methyl-1,4-pentadiene, 2,3-dimethyl-1,3-butadiene, and 1,8-nonadiene); and (c) alkynes (1-hexyne, 2-hexyne, 3-hexyne, 2-octyne, 4-octyne) were collected from ILs and PILs containing the $[Cu^+][NTf_2^-]$ salt. The stationary phases included: $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL after heating (column 4, filled black) and neat IL (column 1, hollow black); $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL with AIBN after heating (column 5, filled gray); $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL (column 6, filled blue) and neat PIL (column 2, hollow blue); $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]/[C_{12}(VIM)_2^{2+}]2[NTf_2^-]$) PIL after heating (column 7, filled purple) and neat crosslinked PIL (column 3, hollow purple).
Retention measurement conditions: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 35 °C; inlet temperature, 150 °C; FID temperature 160 °C. Column heating condition: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 110 °C for 10 h.

Figure 3. Comparison of cyclohexane, cyclohexene, 1,4-cyclohexadiene, terpinolene, and *γ*-terpinene retention measured from ILs and PILs containing the $[Cu^+][NTf_2^-]$ salt. The stationary phases included: $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL after heating (column 4, filled black) and neat IL (column 1, hollow black); $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL with AIBN after heating (column 5, filled gray); $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL (column 6, filled blue) and neat PIL (column 2, hollow blue); $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]/[C_{12}(VIM)_2^{2+}]2[NTf_2^-]$) PIL after heating (column 7, filled purple) and neat crosslinked PIL (column 3, hollow purple).
Retention measurement conditions: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 35 °C; inlet temperature, 150 °C; FID temperature 160 °C. Column heating condition: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 110 °C for 10 h.

Figure 4. Comparison of aromatic compound retention measured from ILs and PILs containing the $[Cu^+][NTf_2^-]$ salt: (a) benzene, *o*-xylene, *m*-xylene, *p*-xylene, and benzaldehyde; and (b) styrene, ethylbenzene, allylbenzene, 4-phenyl-1-butene, and phenylacetylene. The stationary phases included: $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL after heating (column 4, filled black) and neat IL (column 1, hollow black); $[Cu^+][NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL with AIBN after heating (column 5, filled gray); $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]$) PIL (column 6, filled blue) and neat PIL (column 2, hollow blue); $[Cu^+][NTf_2^-]$/poly($[C_6VIM^+][NTf_2^-]/[C_{12}(VIM)_2^{2+}]2[NTf_2^-]$) PIL after heating (column 7, filled purple) and neat crosslinked PIL (column 3, hollow purple).

Retention measurement conditions: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 35 °C; inlet temperature, 150 °C; FID temperature 160 °C. Column heating condition: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 110 °C for 10 h.

Figure 5. Retention factors of (a) alkanes and alkenes; (b) dienes (*cis*-1,4-hexadiene, 1,5-hexadiene, 3-methyl-1,4-pentadiene, 2,3-dimethyl-1,3-butadiene, and 1,8-nonadiene); and (c) alkynes (1-hexyne, 2-hexyne, 3-hexyne, 2-octyne, 4-octyne) were collected from ILs and PILs containing the [Cu^{2+}]2[NTf_2^-] salt. The stationary phases included: [Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-] IL (column 8) after heating (filled black) and before heating (patterned black), and neat IL (column 1, hollow black); [Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-] IL with AIBN (column 9) after heating (filled gray) and before heating (patterned gray); [Cu^{2+}]2[NTf_2^-]/poly([C_6VIM^+][NTf_2^-]) PIL (column 10) after heating (filled blue) and before heating (patterned blue), and neat PIL (column 2, hollow blue). Retention measurement conditions: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 35 °C; inlet temperature, 150 °C; FID temperature 160 °C. Column heating condition: carrier gas flow rate, 1 mL min^{-1}; oven temperature, for 1 h each at 110, 125, 140 and 155 °C.

Figure 6. Comparison of cyclohexane, cyclohexene, 1,4-cyclohexadiene, terpinolene, and *γ*-terpinene retention measured from ILs and PILs containing the [Cu^{2+}]2[NTf_2^-] salt. The stationary phases included: [Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-] IL (column 8) after heating (filled black) and before heating (patterned black), and neat IL (column 1, hollow black); [Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-] IL with AIBN (column 9) after heating (filled gray) and before heating (patterned gray); [Cu^{2+}]2[NTf_2^-]/poly([C_6VIM^+][NTf_2^-]) PIL (column 10) after heating (filled blue) and before heating (patterned blue), and neat PIL (column 2, hollow blue). Retention measurement conditions: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 35 °C; inlet temperature, 150 °C; FID temperature 160 °C. Column heating condition: carrier gas flow rate, 1 mL min^{-1}; oven temperature, for 1 h each at 110, 125, 140 and 155 °C.

Figure 7. Comparison of aromatic compound retention measured from ILs and PILs containing the [Cu^{2+}]2[NTf_2^-] salt: (a) benzene, *o*-xylene, *m*-xylene, *p*-xylene, and benzaldehyde; and (b) styrene, ethylbenzene, allylbenzene, 4-phenyl-1-butene, and phenylacetylene. The stationary phases included: [Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-] IL (column 8) after heating (filled black) and before heating (patterned black), and neat IL (column 1, hollow black); [Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-] IL with AIBN (column 9) after heating (filled gray) and before heating (patterned gray); [Cu^{2+}]2[NTf_2^-]/poly([C_6VIM^+][NTf_2^-]) PIL (column 10) after heating (filled blue) and before heating (patterned blue), and neat PIL (column 2, hollow blue). Retention measurement conditions: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 35 °C; inlet temperature, 150 °C; FID temperature 160 °C. Column heating condition: carrier gas flow rate, 1 mL min^{-1}; oven temperature, for 1 h each at 110, 125, 140 and 155 °C.

Figure 8. Variation in 2-hexyne retention measured from ILs and PILs containing the [Cu^{2+}]2[NTf_2^-] salt. The stationary phases included: [Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-] IL (column 8, black); [Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-] IL with AIBN (column 9, gray); [Cu^{2+}]2[NTf_2^-]/poly([C_6VIM^+][NTf_2^-]) PIL (column 10, blue) Retention measurement conditions: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 35 °C; inlet temperature,

150 °C; FID temperature 160 °C. Column heating conditions: helium carrier gas flow rate, 1 mL min^{-1}; oven temperature, for 1 h each at temperature.

Figure 9. Retention variation of (a) 1-hexyne (blue) and 2-hexyne (purple); (b) methyl tiglate (green) and *o*-xylene (pink); and (c) 1-hexene (red), *cis*-2-hexene (yellow), and hexane (gray), measured from $[Cu^{2+}]2[NTf_2^-]/[C_6MIM^+][NTf_2^-]$ IL stationary phase (column 8) upon exposure to a helium gas stream at constant temperatures at 110 °C. Retention measurement conditions: carrier gas flow rate, 1 mL min^{-1}; oven temperature, 35 °C; inlet temperature, 150 °C; FID temperature 160 °C.