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Potential of Silver-Based Room-Temperature Ionic Liquids for Ethylene/Ethane Separation

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The potential of room-temperature ionic liquids (RTILs) in separating ethylene from ethane is investigated. The absorption of olefins is enhanced by chemical absorption via π -complex formation with a transition-metal cation added to a standard RTIL. The effects of the ionic liquid structure of silver-based RTILs that contain Ag(I) salts (AgNO_3 , $\text{Ag}[\text{TfO}]$, and $\text{Ag}[\text{Tf}_2\text{N}]$) on gas absorption and solvent stability are investigated. The absorption isotherms of C_2H_4 and C_2H_6 into standard RTILs and designed silver-based RTILs were measured with a gravimetric balance between 303 and 333 K and up to 10 bar. C_2H_4 absorption was chemically enhanced in the silver-based RTILs and was considerably higher than that in the standard RTILs. Absorption of C_2H_6 in the silver-based RTILs is based on physical interactions only. The olefin/paraffin selectivity at a pressure of 1 bar was ~ 30 – 50 higher in the silver-based RTILs than in standard ionic liquids.

1. Introduction

The separation of olefins from paraffins is an essential, but costly, separation in the chemical and petrochemical industry.^{1–6} Generally, this separation can be performed using low-temperature (high-pressure) distillation, physical and chemical adsorption, reactive absorption, and membrane separation.^{7–11} Despite the high energy and capital demands associated with low-temperature distillation, this is the prevailing technology, because of its recognized efficiency and reliability.¹¹ The energy required to separate olefin/paraffin mixtures via cryogenic distillation was estimated to be $\sim 130 \times 10^9$ MJ/yr.⁸ The energy requirements of the process could potentially be reduced by separating the olefin from the paraffin via reactive absorption.⁸

Olefins can form reversible complexes with transition-metal cations via a π -bond complex formation mechanism that is described elsewhere.^{1–4,8,10–12} In the complex formation, the olefin and the metal cation work as the electron donor and the acceptor, respectively. Usually, silver and copper are the metals of choice for the reactive absorption of olefins; however, in theory, all transition metals can be used. The complex formed by the olefinic gas with either Ag(I) and Cu(I) can easily be reversed by pressure and temperature swing and both of the metals are relatively inexpensive.^{1–3,7,8,10–12} The solution formed by a salt of the transition-metal cation and a polar solvent, such as water and ethylene glycol, is usually the source of the metal cation that is used as a reactive agent.^{8,11,12} However, the affinity for the olefinic gas in a highly polar solvent is low and the high degree of solvation is equivalent to a reduced availability of the metal cation for reaction with the olefin.^{5,13–17} In addition, the high degree of solvation is associated to a higher metal cation instability.⁸ Furthermore, in the case of using a water-containing solvent, the removal of water from the treated stream is compulsory, particularly if the olefin is sent to a polyolefin plant. The production of polyolefins requires olefin streams of high purity.^{8–12} The traditional operations that require drying of the treated olefin stream exclude the use of aqueous or water-based solvents, given the negative impact in the total energy and economic balance resulting from additional separations.¹¹

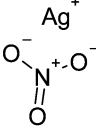
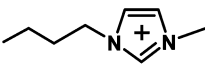
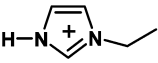
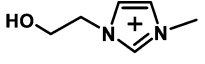
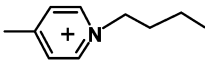
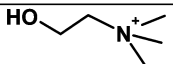
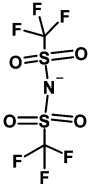
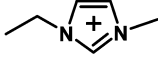
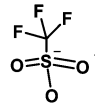
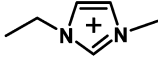
Although the paraffin/olefin separation by chemical absorption is feasible, it is not positioned yet in the industry, because of the instability of the metal cation of the solvents and the wide variety of contaminants in the petrochemical streams. The selective olefin absorption and the stability of the metal cation (complexing agent) are the main concerns for achieving a reliable solvent. Traditional solvents are not capable of dealing with these requirements simultaneously, given the effect of other gases, impurities, and the usual plant operating conditions. Hence, irreversible loss of the reactive agent is frequently observed.

Because of their dual organic and ionic character, room-temperature ionic liquids (RTILs) may possibly overcome these drawbacks, which, until now, have been exhibited by conventional solvent systems. Moreover, RTILs have advantageous properties, such as a negligible volatility, which enables a relatively easy recovery, a wide range of polarities, and a large liquidus range. RTILs can absorb different olefin and paraffin gases.^{18–24} Ortiz et al. reported the selective absorption of propylene from propane using a solvent formed by silver tetrafluoroborate (0.25 M) dissolved into 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{bmim}]\text{BF}_4$).¹⁸ The selectivity of the ionic liquid with the Ag^+ cation was at least eight times higher than that of $[\text{bmim}]\text{BF}_4$ at 298 K. For an analogous gas separation, Huang et al. synthesized several ionic liquids with the $[\text{Tf}_2\text{N}]^-$ anion that contain silver complexes in the cation.¹⁹ These ionic liquids were used to impregnate membranes for the separation of hexene/hexane, pentene/pentane, and isoprene/pentane. The authors reported a high olefin/paraffin selectivity, ~ 500 , but a low flux, $\sim 2 \times 10^{-5} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ at $\Delta P = 111 \text{ kPa}$. The selectivity is calculated as the ratio between the permeance of the olefin to that of the paraffin.¹⁹ Furthermore, a patent of a method for the separation of olefins from non-olefins (paraffins, cycloparaffins, oxygenates, and aromatics), using a dispersion of metal salts in ionic liquids, was found.²⁰ This patent claims that olefins are separated from a recycle stream in a Fischer–Tropsch synthesis and that acetylene is removed with a nickel salt.

A variety of copper and silver salts is used and olefins are recovered by desorption using heat or pressure swing. Some of the copper- and silver-containing salts that are used in olefin/paraffin separations are copper(I) chloride (CuCl , commonly called cuprous chloride), copper(I) bromide (CuBr), cuprous

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Table 1. Designed Silver-Based Room-Temperature Ionic Liquids (RTILs)

| | Ag-based RTIL | Salt | Ionic liquid | Ionic Liquid Cation | [Metal] ⁺ mol/L | Mol % |
|---|-------------------------------|--|---------------------------|--|-------------------------------|--------|
| a | [bmim]NO ₃ -Ag |  | [bmim]NO ₃ |  | 3.3 | 40 |
| b | [H-eim]NO ₃ -Ag | | [H-eim]NO ₃ |  | 4.4 | 40 |
| c | [HO-emim]NO ₃ -Ag | | [HO-emim]NO ₃ |  | 2.1 | 25 |
| d | [4-mebupy]NO ₃ -Ag | | [4-mebupy]NO ₃ |  | 1.2 | 20 |
| e | [chol]NO ₃ -Ag | | [chol]NO ₃ |  | 2.2 | 20 |
| f | [emim][Tf ₂ N]-Ag | Ag[Tf ₂ N]  | [emim][Tf ₂ N] |  | 0.45, 1.8 | 10, 40 |
| g | [emim][TfO]-Ag | Ag[TfO]  | [emim][TfO] |  | 1.2 | 20 |

trifluoroacetate (Cu[TFA]), copper(I) nitrate (CuNO₃), silver nitrate (AgNO₃), silver tetrafluoroborate (AgBF₄), silver trifluoromethane sulfonate (Ag[TfO]), and silver trifluoroacetate (Ag[TFA]).^{1–5,7–12} Solvents with F[–] and Cl[–] ions are not preferred, because of the equipment corrosion and hazards associated with the use of halocarbons and also with the presence of HCl or HF formed by side reactions and degradation of the solvent.^{8,11,12} However, both the available solid salts source of the transition-metal cation and most of the purchasable ionic liquids contain those compounds in their structure.

Because selective and reversible absorption of olefins is possible with silver salts, silver-based RTILs are expected to be suitable solvents for ethylene/ethane separations without the disadvantages of conventional solvents. The goal of this work is to design specific silver-containing ionic liquids for an improved separation of ethylene and ethane. The results of the ethylene/ethane separation with silver-based RTILs are compared to standard RTILs and conventional silver salt solutions.

2. Experimental Methods

2.1. Chemicals. Ethane (C₂H₆) was obtained from Praxair (purity of 99.99%) and had a water content of <5 ppmv. Ethylene (C₂H₄) was purchased from Hoekloos (purity of >99.9%). The RTILs 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF₄, CAS No. 174501-65-6, high purity, 0.001 water mass fraction), 1-butyl-3-methylimidazolium dicyanamide ([bmim][DCA], CAS No. 448245-52-1, grade purum ≥ 0.97, with a water content of ≤ 2000 ppm), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆, CAS No. 174501-64-5, high purity, with a water mass fraction of 0.001), and *N*-butyl-4-methylpyridinium tetrafluoroborate ([mebupy]BF₄, CAS No. 343952-33-0, synthesis quality, water content of <10000 ppm)

were purchased from Merck. The RTILs 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonamide) ([emim][Tf₂N]), CAS No. 174899-82-2, purity assay ≥ 0.98 and water ≤ 0.5%, and 1-butyl-3-methylimidazolium thiocyanate ([bmim]SCN, CAS No. 344790-87-0, purity assay ≥ 0.95, water ≤ 10000 ppm and chloride content [Cl[–]] ≤ 10000 ppm), and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [emim][TfO], CAS No. 145022-44-2, purity assay > 0.98 and water ≤ 0.5%) were produced by BASF and obtained from Sigma–Aldrich. The RTILs 1-butyl-3-methylimidazolium methylsulfate ([bmim]CH₃SO₄, CAS No. 401788-98-5, purity assay > 0.95), and 1-butyl-3-methylimidazolium nitrate ([bmim]NO₃, CAS No. 179075-88-8, purity assay > 0.95) were produced by BASF and purchased from Fluka. The RTIL *N*-butyl-4-methylpyridinium thiocyanate ([mebupy]SCN) was obtained from IoLiTec (purity of 98%).

All RTILs were used after drying in a rotary evaporator under vacuum (10^{–3} bar) and 363 K for at least 12 h.

The silver-based RTILs were prepared by Jan de With of Shell Global Solutions in Amsterdam, The Netherlands. The supplier of the silver salts was Sigma–Aldrich: AgNO₃ (ACS grade, >99%) and AgTfO (>99%). AgTf₂N was synthesized from Ag₂CO₃ (Aldrich, >99%) and HTf₂N (Aldrich, 95%). The prepared solvents were kept dry and in dark conditions, and they were used without further treatment. The structures of the ionic liquids used as solution media for each of the Ag(I) salts used are presented in Table 1. The viscosities of the silver-based solvents were considerably higher (a factor of ~2–4), compared to the original ionic liquids.

RTIL solvents with the AgNO₃ salt were the first choice, given its documented chemistry, performance, and reliability, as well as its relatively low price. The ionic liquid 1-butyl-3-

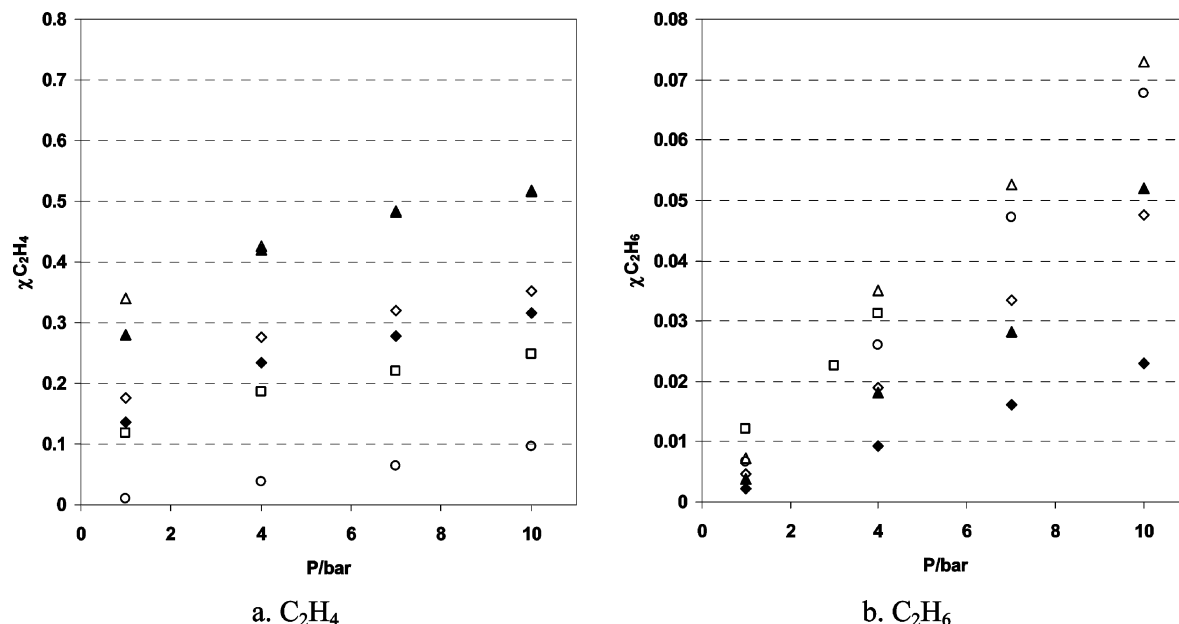


Figure 1. (a) C_2H_4 and (b) C_2H_6 absorption at 303 and 333 K in RTIL solvents with $Ag[Tf_2N]$ and $Ag[TfO]$. The symbols indicate the following: (Δ) $[emim][Tf_2N]$ -Ag, 1.8 N, 303 K; (\blacktriangle) $[emim][Tf_2N]$ -Ag, 1.8 N, 333 K; (\square) $[emim][Tf_2N]$ -Ag, 0.45 N, 303 K; (\diamond) $[emim][TfO]$ -Ag, 1.2 N, 303 K; (\blacklozenge) $[emim][TfO]$ -Ag, 1.2 N, 333 K; and (\circ) $[emim][Tf_2N]$, 303 K.

methylimidazolium nitrate ($[bmim]NO_3$) is used to solvate the silver nitrate ($AgNO_3$) salt (entry a in Table 1). To examine the influence of the cationic structure of the imidazolium, two other structures were used (see entries b and c in Table 1). The effect of using a different type of ionic liquid cation is studied in the solvent design, including pyridinium and choline cations (see entries d and e, respectively, in Table 1).

Because imidazolium liquids with the amide ($[Tf_2N]^-$) anion exhibit a high affinity for C_2H_4 and C_2H_6 , these are also considered.^{23,24} The solvent is prepared from the IL $[emim][Tf_2N]$ and the dissolved solid $Ag[Tf_2N]$ salt (see entry f in Table 1).

A relatively inexpensive and stable salt that can be used as source of $Ag(I)$ is silver trifluoromethanesulfonate ($Ag[TfO]$). In addition, the availability of $[emim][TfO]$, which is an imidazolium liquid with a similar anion, enables the design of a RTIL-based solvent (see g in Table 1).

2.2. Equipment. The absorption isotherms of C_2H_4 and C_2H_6 were measured with an Intelligent Gravimetric Analyzer (IGA 003, Hiden Analytical) at temperatures in the range of 303–333 K and pressures up to ~ 10 bar. The gravimetric balance is symmetric, and the components on each side, sample and counterweight, are placed in a pressurized stainless steel cylindrical reactor. The ionic-liquid-based solvent, typically 50–70 mg, was loaded in the gravimetric microbalance, dried, and degassed at 343 K and 10^{-3} bar, using a vacuum pump (Baltzers TCP 121) for a period of minimum 12 h, until the rate of change in weight was <0.001 mg/h. The temperature of the sample was kept constant (± 0.1 K) with a regulated external thermostat bath (Julabo F25 MW) filled with oil, which was coupled to a jacket of both sample and reference side of the gravimetric balance. After the sample was dried, the thermostat bath was brought to the experimental temperature. The system was kept under vacuum until the mass and temperature of the sample were constant for at least one hour. Subsequently, the RTIL-based solvent was left in contact with the gas to be measured, either C_2H_4 or C_2H_6 . The pressurized vessel with the solvent was filled with the measured gas until the set pressure was attained, and, afterward, the increment on weight was

monitored. The ionic-liquid solvent and the gas attained equilibrium when the weight change observed throughout a period of time was <0.001 mg/h.

The time required to attain equilibrium at each pressure level was strongly dependent on the nature of the ionic liquid. Intervals of time larger than 10 h were allowed to reach equilibrium at each pressure step. In the solubility calculations, the effects from buoyancy and equipment sensitivity were taken into consideration. The total uncertainty in the solubility data due to both systematic correction factors and the buoyancy was lower than ± 0.001 for C_2H_4 and ± 0.002 for C_2H_6 (in mole fraction of the absorbed gases). The densities of C_2H_4 and C_2H_6 were obtained from the NIST 69 database for each temperature and pressure measured.²⁵ The density of the silver-based ionic liquids solvents was determined using a Anton Paar Model DMA 5000 densimeter. The standard deviation of the measurements was $<2.0 \times 10^{-5}$ g/cm³.

3. Results and Discussion

3.1. Effects of Silver-Based RTIL Solvents. The solubility of C_2H_4 and C_2H_6 into the silver-based RTILs that contain $Ag[Tf_2N]$ or $Ag[TfO]$ are plotted in Figure 1. Note that the magnitude of the scale of the “y-axis” of C_2H_4 is 10 times greater than that of C_2H_6 . Comparing Figures 1a and 1b, it is apparent that the solubility of ethylene is higher than that of ethane in the studied ionic liquids.

The absorption of C_2H_4 is enhanced when the designed silver-based RTILs are used. Figure 1a shows that a higher content of $Ag(I)$ cation provides a higher C_2H_4 capacity to the solvent. Compared to the standard $[emim][Tf_2N]$, the amount of C_2H_4 absorbed by the solvent containing $Ag(I)$ at 0.45 N at 1 bar is a factor of 12.5 higher than that in the standard ionic liquid and a factor of 2.5 higher at 10 bar. The absorption of C_2H_4 was increased more than 35 times at 1 bar when a higher concentration of metallic cation $Ag(I)$ at 1.8 N was used (and more than five times greater at 10 bar).

The C_2H_4 absorption isotherms in the silver-based RTILs that contain $Ag[Tf_2N]$ show a steep increase with pressure, up to

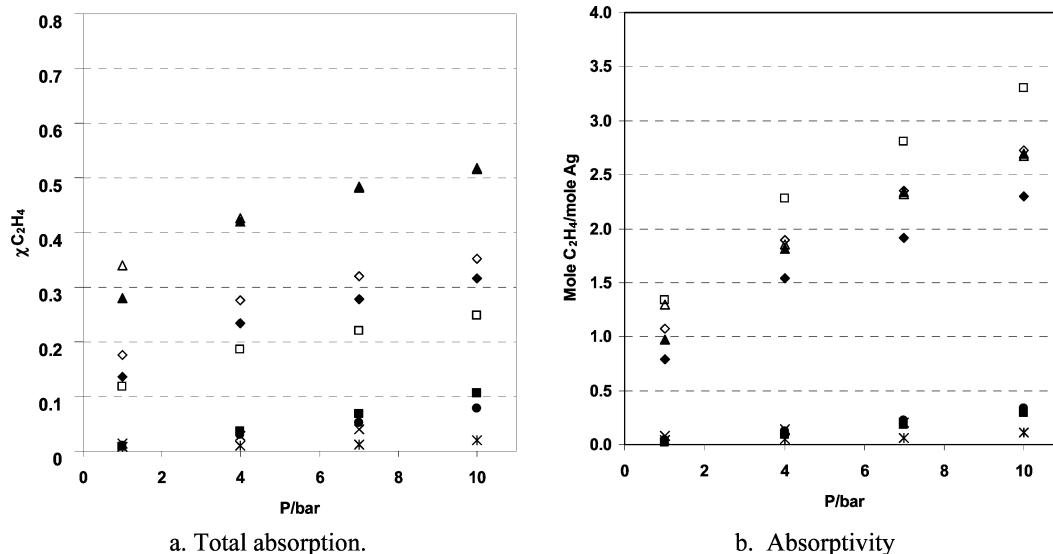


Figure 2. Absorption of C₂H₄ in silver-based RTILs with several anions at 303 and 333 K: (a) total absorption of C₂H₄ (expressed in molar fraction), and (b) amount of Ag(I) used (expressed in terms of moles of C₂H₄ absorbed per mole of Ag(I) in the solvent). The symbols indicate the following RTILs: (□) [emim][Tf₂N]-Ag, 0.45 N, 303 K; (Δ) [emim][Tf₂N]-Ag, 1.8 N, 303 K; (▲) [emim][Tf₂N]-Ag, 1.8 N, 333 K; (◇) [emim][TfO]-Ag, 1.2 N, 303 K; (◆) [emim][TfO]-Ag, 1.2 N, 333 K; (■) [H-emim]NO₃-Ag, 4.4 N, 333 K; (●) [HO-emim]NO₃-Ag, 2.1 N, 333 K; (×) [4-mebupy]NO₃-Ag, 1.2 N, 333 K; and (*) [chol]NO₃-Ag, 2.2 N, 333 K.

~2 bar, and then a linear increase with pressure, indicating that chemical absorption of C₂H₄ is occurring. Most likely, the absorption of C₂H₄ is enhanced by the formation of the olefin–metal complex. In contrast, Figure 1b shows that the C₂H₆ absorption increases linearly with pressure, indicating that physical mechanisms direct the absorption of C₂H₆ in the silver-based RTILs that contain Ag[Tf₂N] and Ag[TfO]. As expected, the absorption of C₂H₆ is not enhanced by the addition of the Ag(I) cation. For the two tested Ag[Tf₂N]-containing solvents, the amount of C₂H₆ absorbed remained almost the same as that in the standard [emim][Tf₂N].

The absorption of C₂H₄ in the silver-based RTILs decreases when the temperature is increased, as can be seen in Figure 1a. The amount of C₂H₄ absorbed into [emim][TfO]-Ag, 1.2 N, at 303 K is higher than that at 333 K. Unexpectedly, the absorption of C₂H₄ into [emim][Tf₂N]-Ag, 1.8 N, does not show a significant reduction when temperature is increased from 303 K to 333 K throughout the pressure range. Only at 1 bar is the measured C₂H₄ absorption at 333 K evidently lower than the value measured at 303 K.

3.2. Anion Effect. The C₂H₄ absorption results are plotted in Figures 1 and 2. The silver-based RTILs with a larger C₂H₄ capacity are those in which the added metal cation, Ag(I), was obtained from either Ag[Tf₂N] or Ag[TfO] (see Figure 2). The solvents with Ag(I) from AgNO₃ absorbed significantly lower amounts of C₂H₄, as depicted in Figure 2. The solvent [bmim]NO₃-Ag, 3.3 N, was unstable. At C₂H₄ absorption, the silver precipitated and formation of other stable salts was observed. Also, the solvent [H-emim]NO₃-Ag, 4.4 N, was unstable during C₂H₄ absorption and, furthermore, was corrosive.

The superior capacity exhibited by the solvents with [Tf₂N][−] and [TfO][−] anions can be attributed to the lower degree of ionic association created within the ionic liquid and with Ag(I). The interaction of the amide ([Tf₂N][−]) anion with organic cations is weak and, therefore, the lattice energy of the liquid salt is relatively low.²⁶ In the amide anion, the charge of the nitrogen is largely delocalized on the S atoms, but the charge is only slightly delocalized on the two O atoms. Consequently, the delocalized charge is shielded in the molecule and the strength of the ionic interactions with the surrounding cations is

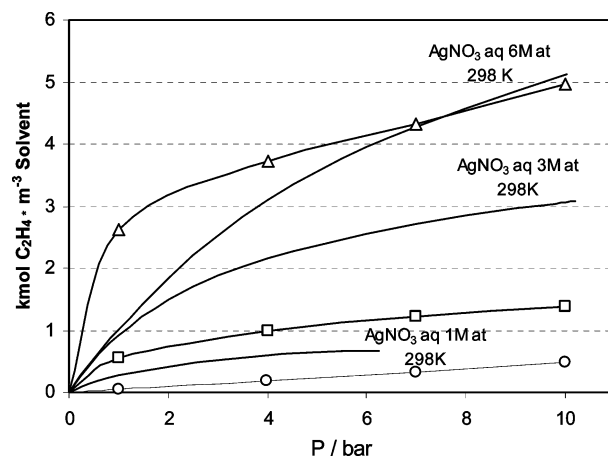


Figure 3. Volumetric C₂H₄ load of silver-based RTIL at 303 K and AgNO₃ aqueous solutions. The symbols indicate (Δ) [emim][Tf₂N]-Ag, 1.8 N; (□) [emim][Tf₂N]-Ag, 0.45 N; and (○) [emim][Tf₂N]. The lines indicate the C₂H₄ solvent load in AgNO₃ at 298 K. Solubility data of C₂H₄ in AgNO₃ were taken from Keller and Marcinkowsky,⁷ Wentink,¹⁷ and Cho et al.¹³

reduced.^{27,28} Hence, the metal cation will be more available for forming a complex with C₂H₄. Because of the lower Ag(I) content, the absorption capacity per mole Ag(I) is higher for [emim][Tf₂N]-Ag, 0.45 N, than for [emim][Tf₂N]-Ag, 1.8 N. Tokuda et al. found with imidazolium based ionic liquids that ionic association of the trifluoromethane sulfonate ([TfO][−]) anion is lower than that of the amide anion and much more lower than BF₄[−].²⁹

3.3. C₂H₄ Absorption in Silver-Based RTILs and Aqueous AgNO₃ Solutions. The volumetric C₂H₄ capacity of the Ag[Tf₂N]-containing RTILs is plotted in Figure 3, together with those reported for aqueous AgNO₃ solutions at ~300 K, because AgNO₃ solutions are the ones used most often for olefin/paraffin separations.

It is observed that the absorption of C₂H₄ in the [emim][Tf₂N]-Ag-based solvents are comparable to the gas loads obtained for aqueous solutions with much-higher concentrations of silver nitrate. This is due to the more-efficient utilization of the Ag(I) ions in the RTILs for complexation, as is illustrated by Figure

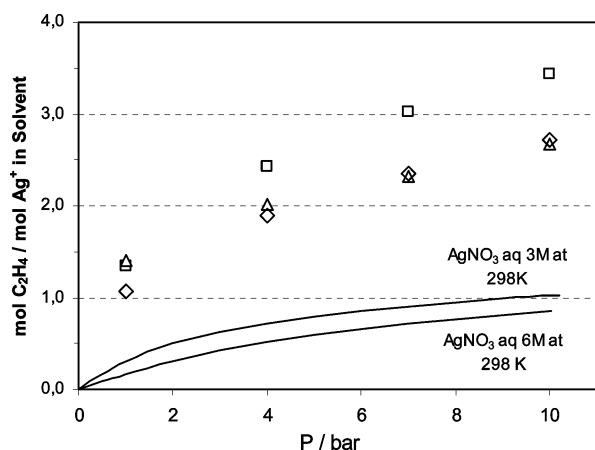


Figure 4. C_2H_4 absorbed per Ag(I) cation present in silver-based RTILs at 303 K and AgNO_3 aqueous solutions. The symbols indicate the following silver-based RTILs: (\square) $[\text{emim}][\text{Tf}_2\text{N}]\text{-Ag}$, 0.45 N; (Δ) $[\text{emim}][\text{Tf}_2\text{N}]\text{-Ag}$, 1.8 N; and (\diamond) $[\text{emim}][\text{TfO}]\text{-Ag}$, 1.2 N. The lines indicate the absorptivity of C_2H_4 in AgNO_3 at 298 K. AgNO_3 data were taken from Keller and Marcinkowsky.⁷

4. The Ag(I) ions in aqueous AgNO_3 solutions are surrounded by water molecules, whereas the Ag(I) ions in RTILs are not, which makes them more accessible. The highest ethylene absorption is seen in $[\text{emim}][\text{Tf}_2\text{N}]\text{-Ag}$, 1.8 N, up to a pressure of 7 bar and is higher than that in a 6 M AgNO_3 solution. The ethylene absorption in the 6 M AgNO_3 solution is slightly higher only at pressures above 7 bar.

The high use of silver by the RTIL-based solvents plotted in Figure 4 may be explained by the efficient combination of the chemical reactive capture and the higher physical absorption capacity of the bulky ionic liquids. The high affinity of the functional groups contained in the $[\text{TfO}]^-$ anion with the olefin increases the absorption potential of the solvent. In the case of $[\text{Tf}_2\text{N}]^-$, it is known that its highly nonlocalized anion charge facilitates gas absorption.

The enthalpy of C_2H_4 solution in $[\text{emim}][\text{TfO}]\text{-Ag}$, 1.2 N, was estimated using the Gibbs–Helmholtz relation (eq 1).³⁰

$$\left[\frac{\partial \ln P}{\partial (1/T)} \right]_x = -\frac{\Delta H}{R} \quad (1)$$

The enthalpy of absorption is determined from the slope of the plot of the logarithm of the pressure needed to reach the same concentration of C_2H_4 in the silver-based RTIL versus the inverse of the corresponding temperature ($1/T$). The calculated enthalpy of C_2H_4 dissolution in the $[\text{emim}][\text{TfO}]\text{-Ag}$, 1.2 N, is presented in Figure 5.

As depicted in Figure 5, the calculated absorption enthalpy is -22.6 kJ/mol at a low C_2H_4 solvent load ($\chi \approx 0.17$), caused by chemical absorption. At higher load ($\chi \approx 0.29$), the enthalpy of C_2H_4 absorption is approximately -11.2 kJ/mol , because of physical absorption. On average, the C_2H_4 enthalpy of absorption in $[\text{emim}][\text{TfO}]\text{-Ag}$, 1.2 N, is slightly lower than the reported absorption enthalpy in a 6 M AgNO_3 solution, which is roughly -25 kJ/mol (mainly chemical absorption).^{7,13} From the negative values of the “y”-axis in the plot, it can be concluded that the absorption of ethylene is an exothermic process, which is consistent with the behavior of the ethylene solubility with temperature. The solubility decreases as the temperature increases, as is observed in Figure 2.

At the higher load of ethylene in the solvent ($\chi_{\text{C}_2\text{H}_4} \approx 0.29$), the magnitude of the enthalpy of solution is $\sim 50\%$ lower than that at the lower ethylene solvent load plotted ($\chi_{\text{C}_2\text{H}_4} \approx 0.17$).

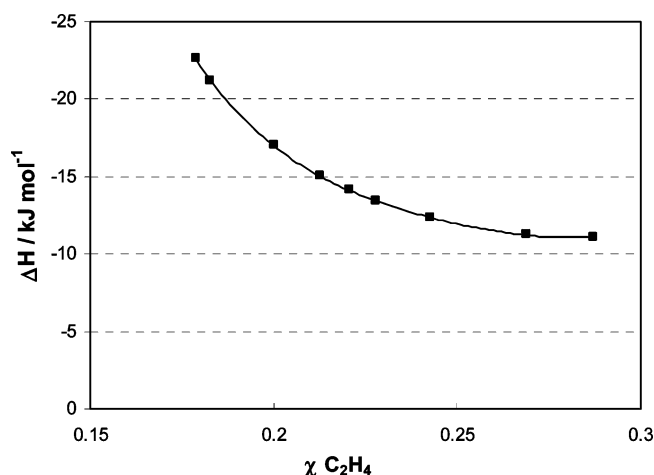


Figure 5. Enthalpy of solution for C_2H_4 in $[\text{emim}][\text{TfO}]\text{-Ag}$, 1.2 N.

This is consistent with the mixing effects from the reactive formation of the π -complex between the ethylene and the Ag(I) cations present in the liquid. At the lower ethylene load, the concentration of Ag(I) cations available in the liquid is higher than the concentration of Ag(I) cations at the higher solvent gas load, because part of the initial concentration of Ag(I) cations has already been used by forming the silver–olefin complex with the absorbed ethylene. In other words, a higher enthalpy of solution is related to a higher concentration of Ag(I) cations available in the liquid.

The energy required to reverse the olefin–metal complex (during solvent regeneration) is higher when the concentration of Ag(I) cations in the solvent is higher.

3.4. $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ Selectivity. The molar selectivity toward ethylene is calculated from the individual gas absorption measurements, according to eq 2.

$$S_{\text{C}_2\text{H}_4/\text{C}_2\text{H}_6} = \left(\frac{\text{moles of } \text{C}_2\text{H}_4/\text{mole of RTIL}}{\text{moles of } \text{C}_2\text{H}_6/\text{mole of RTIL}} \right)_p = \left(\frac{\text{moles of } \text{C}_2\text{H}_4}{\text{moles of } \text{C}_2\text{H}_6} \right) \quad (2)$$

The ethylene/ethane selectivity provided by the $\text{Ag}[\text{Tf}_2\text{N}]\text{-}$ and $\text{Ag}[\text{TfO}]\text{-}$ containing RTILs is plotted in Figure 6. The selectivity obtained with these RTILs is considerably greater than that of the standard ionic liquids, as can be seen in Figure 6 and Table 2.³¹ Camper found ethylene/ethane selectivities to be of the same order (1.3–2.0, calculated from the Henry constants at 313 K).³²

The calculated selectivity for the silver-based solvents $[\text{emim}][\text{TfO}]$ and $[\text{emim}][\text{Tf}_2\text{N}]$ is higher at 333 K than that at 303 K. The physical absorption of C_2H_6 decreases as the temperature increases, but at a higher temperature, the accessibility of the Ag(I) ions in the ionic liquid is larger, thereby enhancing the chemical absorption of C_2H_4 . The selectivity decreases with an increment in pressure, which is also an evidence for the absorption by chemical mechanism.

A higher selectivity is calculated for the IL $[\text{emim}][\text{Tf}_2\text{N}]\text{-Ag}$, 1.8 N, than for $[\text{emim}][\text{Tf}_2\text{N}]\text{-Ag}$, 0.45 N, which is according to expectations, because the first IL contains a larger amount of Ag(I) cations. The selectivity calculated for $[\text{emim}][\text{Tf}_2\text{N}]\text{-Ag}$, 0.45 N, is close to 10 at 1 bar, which is of the same order as that reported by Ortiz et al. for the separation of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ with $[\text{bmim}]\text{BF}_4$ with 0.25 M AgBF_4 at 333 K.²¹

Ho et al. used an absorption solvent formed by cuprous diketone in α -methylstyrene and reported a separation factor

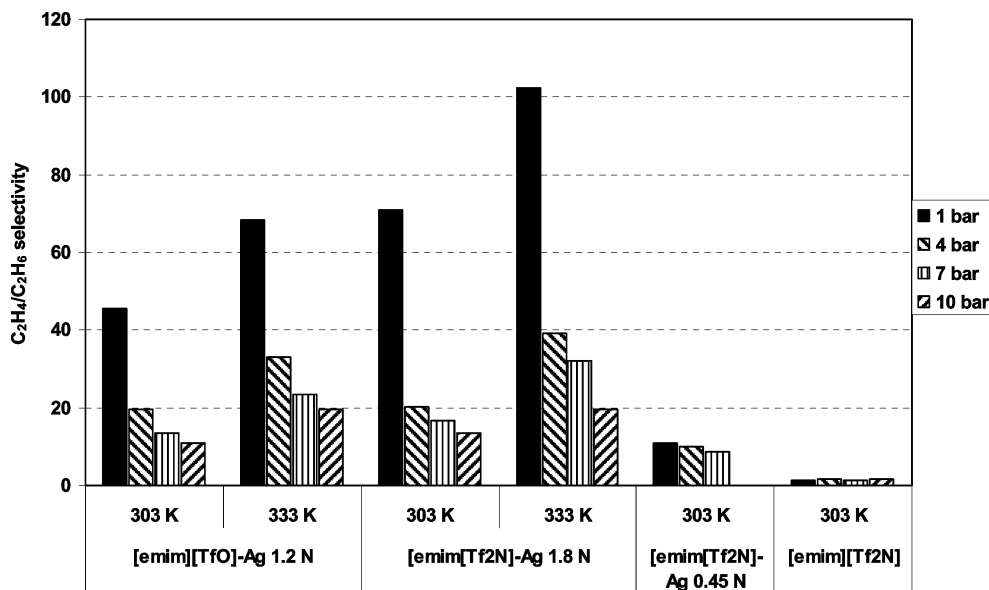


Figure 6. C₂H₄/C₂H₆ selectivity in Ag[Tf₂N]- and Ag[TfO]-containing RTIL-based solvents.

Table 2. C₂H₄/C₂H₆ Selectivity in Standard RTILs at 303 K at Various Pressures^a

| compound | Selectivity | | | |
|---------------------------------------|-------------|-------|-------|--------|
| | 1 bar | 4 bar | 7 bar | 10 bar |
| [bmim]BF ₄ | 2.0 | 2.0 | 2.0 | 2.1 |
| [4-mebupy]BF ₄ | 2.8 | 2.9 | 2.9 | 3.0 |
| [bmim]SCN | 1.0 | 1.5 | 1.6 | 1.5 |
| [4-mebupy]SCN | 0.9 | 1.6 | 1.6 | 1.4 |
| [bmim][DCA] | 2.1 | 2.2 | 2.2 | 2.3 |
| [bmim]CH ₃ SO ₄ | 2.3 | 2.0 | 1.9 | 1.6 |
| [bmim]PF ₆ | 2.3 | 2.0 | 2.6 | 2.5 |
| [emim][Tf ₂ N] | 1.4 | 1.5 | 1.4 | 1.5 |

^a Data taken from ref 31.

of 17/1 for C₂H₄/C₂H₆.⁵ Cho et al. used aqueous AgNO₃ as a solvent at 298 K and calculated a C₂H₄/C₂H₆ selectivity of 41 and 112, respectively, for solvents with a AgNO₃ concentration of 1 and 6 M.¹³

The C₂H₄/C₂H₆ selectivity calculated for the silver-based RTILs with [TfO][−] and [Tf₂N][−] as the anion, with a Ag(I) concentration of 1.2 and 1.8 N, respectively, at 333 K is comparable to that reported for aqueous 6 M AgNO₃ at 298 K and at least four times higher than that achieved by the solvent with cuprous diketonate.

4. Conclusions

Silver-containing room-temperature ionic liquids (RTILs) perform better than standard ionic liquids in the separation of ethylene/ethane. The highest C₂H₄/C₂H₆ selectivity is achieved with the silver-based ionic liquids [emim][TfO]-Ag, 1.2 N, and [emim][Tf₂N]-Ag, 1.8 N: ~45–70 at 303 K and ~70–100 at 333 K.

The improvement of the C₂H₄ absorption is due to chemical complexation of the olefin with a transition-metal cation. The absorption of C₂H₆ is achieved by physical interaction only. The highest C₂H₄ absorption capacity is obtained with the ionic liquids that contained [Tf₂N][−] and [TfO][−] as the anion and using a salt with the same anion as the source of Ag(I).

The absorption capacity of C₂H₄ in [emim][Tf₂N]-Ag, 1.8 N, and [emim][TfO]-Ag, 1.2 N, at 303 K is comparable to that of a 6 M AgNO₃ solution at 298 K. The C₂H₄/C₂H₆ selectivity with an ionic liquid without Ag⁺, [emim][Tf₂N], is ~1.5 at 303

K. The C₂H₄/C₂H₆ selectivity in silver-based ionic liquids is comparable to those in aqueous AgNO₃ solutions: 41 (1 M) and 112 (6 M), but ionic liquids exhibit a much higher absorption rate per mole of Ag(I) cations than aqueous AgNO₃ solutions.

The low volatility of the silver-based RTILs can be a key factor in the selection of the solvent for olefin/paraffin separations. The feed to the hydrocarbon fractionation unit in a refinery or a cracker is dried upstream of the ethylene/ethane separation; therefore, the hydrocarbon feed gases contain no water. The negative impact on the process economy caused by the required water removal from the gas after the separation can be avoided using an RTIL-based solvent.

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