

Reactive Ionic Liquid Media for the Separation of Propylene/Propane Gaseous Mixtures

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Designed room temperature ionic liquids (RTILs) containing silver salt are presented as reactive media in separating propylene/propane gas mixtures. Solubilities of propylene and propane in the reactive media, silver tetrafluoroborate (AgBF_4) dissolved in 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF_4) and *N*-butyl-4-methylpyridinium tetrafluoroborate (BmpyBF_4), were investigated as a function of silver ion concentration, temperature, and pressure. Equilibrium data were obtained working in a temperature range between 278 and 318 K and at pressures up to 6 bar. Propylene absorption was chemically enhanced in the silver-based RTILs and was considerably higher than that in the standard RTILs. Absorption of propane in the silver-based RTILs is based on physical interactions only. A simple mathematical model based on the formation of complex species with different stoichiometry has been developed in order to describe the total propylene absorption, and the model was validated with experimental data obtained working with different concentrations of silver salt (between 0.1 and 1 M). The model parameters, equilibrium constants ($K_{\text{Eq},1} f(T)$ and $K_{\text{Eq},2} f(T)$), and enthalpies of complexation ($\Delta H_{r,1}$, $\Delta H_{r,2}$) were obtained. Thermal stability of the silver ions was analyzed and to be found dependent on the silver salt concentration. Complete regeneration of the reaction media was possible at a temperature of 313 K and 20 mbar of pressure.

1. Introduction

Industrial olefin/paraffin separations heavily rely upon energy intensive distillation-based technologies, which represent a class of the most important and also the most costly processes in the chemical industry. Development of economically viable propylene/propane separation processes is becoming increasingly important, but it is extremely challenging due to the physico-chemical similarities between those two molecules.^{1–4} Among a number of alternatives separation processes, reactive absorption of olefins from an olefin/paraffin mixture using a silver salt solution as absorption liquid may be attractive in this respect.^{5–10}

Reactive absorption of olefins with transition metals in aqueous and organic media has been extensively studied in the literature. The advantage of chemical complexation of olefins with transition metals is that the bonds formed are stronger than those due to van der Waals forces alone, so it is possible to achieve high selectivity and high capacity for the component to be bounded; at the same time, the bonds are still weak enough to be broken by using simple engineering operations such as raising the temperature or decreasing the pressure.⁶ However, there are a number of disadvantages associated to the absorption solvent related to the selective olefin absorption, stability of the transition metal, solvent losses, and maximum temperature conditions that can be used. So that solvents with high olefin-capacity, selectivity, and resistance to contaminants and process conditions are still desired.¹¹

Room-temperature ionic liquids (RTILs) have been demonstrated to be excellent solvents for many reactions involving gaseous reactants entering the RTIL solution because of its ionic

and organic character together with its renowned and remarkable properties. RTILs are salts composed exclusively of ions that remain in the liquid phase at or below 373 K. RTILs are compounds that have negligible vapor pressure, high chemical and thermal stability, and relatively large electrochemical windows. They can be water-soluble depending on the hydrophilicity of the ionic moieties. Polarity and hydrophilicity/hydrophobicity can be tuned by a suitable combination of cation and anion; therefore they have been termed “designer solvents”. Therefore, these aforementioned characteristics make RTILs potential substitutes for organic solvents as separating agents and media for reactions or electrochemical process.^{11–20} Their lack of volatility gives ionic liquids the feature that they can perform clean gas separations without any loss of solvent or contamination of the gas stream. However, some major issues yet to be addressed are mixture viscosities, oxidation stability especially for a Ag(I)-based system, high degree of paraffin solubility, and resistance to impurities such as acetylene and hydrogen sulfide.

If transition metal salts are dissolved or suspended in ionic liquids, a more effective solvent system for the separation is expected. Silver ions or complexing agents can be added or “doped” into ionic liquids. RTILs can be used to control the interaction between the silver cation (Ag^+) and its counteranion (X^-) in a RTILs/silver salt system, with the result that the silver cation becomes chemically more active in forming silver–olefin complexes.²¹

Improvement of the solvent potential of the ionic liquid for the olefin/paraffin separation has not been extensively explored. In a previous work the silver salt AgBF_4 (0.25 M) was dissolved in BmimBF_4 and the total propylene absorption was determined.¹² Galán et al.¹¹ presented the effects of the type of cations and anions in Ag-based RTIL structure on the absorption of ethylene and ethane between 303 and 333 K and up to 10 bar, obtaining the highest ethylene absorption values with the

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ionic liquids that contained $[\text{Tf}_2\text{N}]^-$ and $[\text{TfO}]^-$ as the anion and using a salt with the same anion as the source of Ag^+ . Munson et al.¹⁶ tested the solubility of Ag^+ and Cu^+ salts in some ionic liquids and the separation of *n*-butene/butane mixtures. Facilitated transport in SILMs is also possible through the incorporation of silver carriers.^{21,22} Kang et al.²³ reported the propylene/propane separation using facilitated transport with silver nanoparticles in BmimBF₄-membranes. Huang et al.²⁴ synthesized several ionic liquids that contain silver complexes in the cation, which were used to impregnate membranes and obtained high olefin/paraffin selectivity, ~500.

The main objective of this work is to investigate the absorption of propylene–propane mixtures in Ag^+ –RTILs media. As reported in Galán et al.¹¹ for $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ separation, in the designed RTIL-based solvents, the structure of the ionic liquid cation plays an important role in the stabilization of the metal cation in the solvent. The effect of the cation on the solvent capacity and stability can only be studied when different cation structures are combined with the same anion. Therefore, having selected AgBF_4 as silver salt, in order to examine the possible influence of the cation structure, two RTILs were chosen where the anion BF_4^- was bonded to two different cations from the main families (imidazolium and pyridinium). In the current paper we present the experimental and theoretical study of the solubility of the gaseous components in the ionic liquids containing different concentrations of silver salt as a function of temperature and pressure.

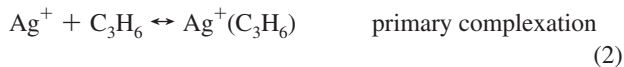
2. Theoretical Considerations

Equilibrium curves for propylene and propane gases generated with silver-free ionic liquids found both gases to exhibit ideal Henry's law behavior at low pressures. For physical solubility, the Henry's law constant can be defined as

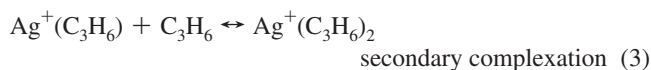
$$H_i = \frac{C_i}{P_i} \quad (1)$$

where C_i is the concentration of the gas in the liquid phase, and P_i is the partial pressure of the gas. Since propane is not able to form a complex with the silver ions, the only absorption is due to physical solubility and it can be described by the Henry's law in reactive media too.

To successfully describe the absorption process of propylene with physical and chemical effects, an equilibrium model was developed. The reactive capture of C_3H_6 with a RTIL-based solvent that contains silver(I) ions can proceed with the formation of the primary reversible π -complex between the C_3H_6 and the ions and it is described by the following reaction:



Under certain conditions (high silver loading, high propylene partial pressure, and low temperature), organometallic complexes with different stoichiometries can exist: the secondary complex (1:2 silver–olefin) and the tertiary complex (2:1). The secondary and tertiary complex species are formed through consecutive reactions of the primary complex with another molecule of propylene or silver ion, respectively.¹⁰ In a previous work, after analysis of the experimental results, no evidence was found that significant amounts of this tertiary complex had been formed, in contrast to secondary complexes.¹² The secondary complex is formed through a consecutive reaction of the primary complex with another propylene molecule:



The equilibrium constants are defined as

$$K_{\text{Eq},1} = \frac{[\text{Ag}^+(\text{C}_3\text{H}_6)]}{[\text{Ag}^+][\text{C}_3\text{H}_6]} \quad (4a)$$

$$K_{\text{Eq},2} = \frac{[\text{Ag}^+(\text{C}_3\text{H}_6)_2]}{[\text{Ag}^+(\text{C}_3\text{H}_6)][\text{C}_3\text{H}_6]} \quad (4b)$$

The concentration of dissolved propylene in the liquid phase in eqs 4a and 4b is obtained from eq 1. The total propylene solubility is the sum of physically dissolved propylene and the chemical complexation with silver:

$$[\text{C}_3\text{H}_6]^T = [\text{C}_3\text{H}_6] + [\text{Ag}^+(\text{C}_3\text{H}_6)] + 2[\text{Ag}^+(\text{C}_3\text{H}_6)_2] \quad (5)$$

Combining eq 5 with eqs 1 and 4a and 4b gives

$$[\text{C}_3\text{H}_6]^T = H_{\text{C}_3\text{H}_6} P_{\text{C}_3\text{H}_6} (1 + K_{\text{Eq},1}[\text{Ag}^+] + 2K_{\text{Eq},1}K_{\text{Eq},2}(H_{\text{C}_3\text{H}_6})[\text{Ag}^+]) \quad (6)$$

The concentration of free silver can be calculated from a total silver balance,

$$[\text{Ag}^+] = [\text{Ag}^+]^T - ([\text{Ag}^+(\text{C}_3\text{H}_6)] + [\text{Ag}^+(\text{C}_3\text{H}_6)_2]) \quad (7)$$

Combining eq 7 with eqs 1 and 4a and 4b yields after rewriting

$$[\text{Ag}^+] = \frac{[\text{Ag}^+]^T}{(1 + K_{\text{Eq},1}P_{\text{C}_3\text{H}_6}H_{\text{C}_3\text{H}_6} + K_{\text{Eq},1}K_{\text{Eq},2}(P_{\text{C}_3\text{H}_6}H_{\text{C}_3\text{H}_6})^2)} \quad (8)$$

Combining eqs 6 and 8 gives the total propylene solubility as a function of the pressure and concentration of the silver metal. The thermodynamic selectivity at equilibrium is defined here as the ratio at equilibrium of absorbed propylene to propane.

$$\text{selectivity} = \frac{([\text{C}_3\text{H}_6]^T/[\text{C}_3\text{H}_8]^T)}{(P_{\text{C}_3\text{H}_6}/P_{\text{C}_3\text{H}_8})} \quad (9)$$

The temperature dependencies of the Henry's law constants and selectivity for gases were studied using a Van't Hoff type equation:²⁵

$$H(T) = H_0 e^{-\Delta H_{\text{sol}}/(RT)} \quad (10)$$

The dependency with temperature of the equilibrium constants for the complexation reactions ($K_{\text{Eq},1}$, $K_{\text{Eq},2}$) can be described by the Van't Hoff equation,

$$\frac{d \ln K_{\text{Eq}}}{d(1/T)} = \frac{\Delta H_r}{R} \quad (11)$$

where T is the temperature (K), ΔH_r is the enthalpy of complexation (kJ mol^{-1}), and R is the gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$).

3. Experimental Section

3.1. Materials. Propylene and propane gases were purchased from Praxair and their purity was of 99.5%. The RTILs used in

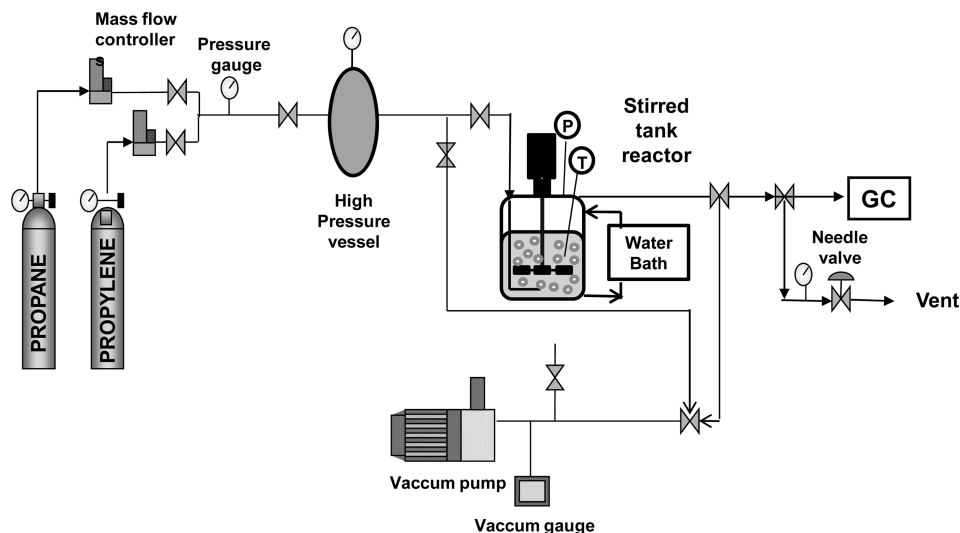


Figure 1. Experimental setup.

this study were 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF₄) from Iolitec, with a minimum purity of 99% and residual halide content less than 500 ppm, and *N*-butyl-4-methylpyridinium tetrafluoroborate (BmpyBF₄), synthesis quality purchased from Merck. Reactive media were prepared using silver tetrafluoroborate (AgBF₄) of 99% purity (Apollo Scientific Ltd.) dissolved in the RTIL at room temperature. All chemicals were used as received.

3.2. Apparatus and Measurements. A diagram of the apparatus used for the measurements of the gases' solubilities is included in Figure 1. The equipment consisted of a stainless steel vessel (upper chamber, 66 mL) used to transfer a known amount of gas into a stainless steel autoclave (lower chamber) for gas–liquid contacting. The temperature of the system is controlled by fluid circulation in conjunction with computer controlled electric heating. The temperature was monitored with a type K thermocouple (Assy) placed inside the lower chamber and automatically maintained within 0.1 K of the set-point. The pressure in the upper chamber is measured by a digital pressure gauge (Omega Engineering DPG1000B-30 V100G with an accuracy of ± 0.017 bar), and the autoclave pressure was measured with a pressure transducer (Hirschmann12B-GDM0–25 bar with an accuracy of ± 0.001 bar). The experimental setup is described in detail elsewhere.¹² Final compositions in mixed gas streams of propylene/propane were analyzed using a HP 6890 gas chromatograph (Agilent) equipped with an autosampling gas valve, a TCD detector, and a semicapillary column (length 50 m, nominal diameter 0.53 mm, model HP AIS).

3.3. Procedure. To begin the absorption experiments, 15 mL of the reactive silver–ionic liquid mixture was added to the autoclave. Air was removed from both the upper and the lower chambers by a vacuum pump (<2 mbar). The valve was closed, separating the two chambers. Then, a gas sample was injected into the upper chamber to a desired pressure (P_{upp}), which was the initial pressure. After the gas was charged, the stirrer was turned on (1500 rpm) and the silver–RTIL mixture was constantly stirred throughout the experiment. The equipment was allowed to stand undisturbed until the temperature was equilibrated. This procedure took between 2 and 3 h. The equilibrium process began adding the solute gas to the autoclave when the valve was opened. The system pressure changed with time due to the system approaching equilibrium, the pressure and temperature readings were recorded in 1-min intervals until the pressure was

Table 1. Henry's Constants (mol/(L bar)) at Different Temperatures and Parameter Values for Equation 10

temperature (K)	BmimBF ₄		BmpyBF ₄	
	propylene	propane	propylene	propane
278	0.145	0.059		
288	0.103	0.045	0.103	0.047
298	0.069	0.028	0.080	0.034
308	0.055	0.022	0.064	0.024
318	0.039	0.011		

gas	H_0 (mol L ⁻¹ bar ⁻¹)	ΔH_{sol} (kJ mol ⁻¹)	H_0 (mol L ⁻¹ bar ⁻¹)	ΔH_{sol} (kJ mol ⁻¹)
propylene	4.28×10^{-6}	-24.10	6.14×10^{-5}	-17.77
propane	1.84×10^{-7}	-29.50	1.52×10^{-6}	-24.76

consistent for 10 consecutive intervals, equilibration time varied between 30 and 90 min. The final pressure difference and compositions, after accounting for the increase in volume, were used to determine the number of moles of gas absorbed.¹² Once the final equilibrium conditions were recorded, the stirrer was stopped, and the solutions were either regenerated or kept for a subsequent absorption or desorption experiment.

4. Results and Discussion

4.1. Physical Solubility in RTILs. To determine the potential of room temperature ionic liquids as a solvent for propylene/propane separation and evaluate the physical solubility of both gases, silver-free RTILs were used as absorption media. Equilibrium curves for propylene and propane gases generated with this silver-free ionic liquid showed both gases to exhibit ideal Henry's law behavior. The solubility line for propane had a lower slope than that for propylene due to the RTILs natural affinity for the olefin (intermolecular forces). Owing to their higher polarizability, unsaturated hydrocarbons experience a stronger solvation in ILs compared to saturated hydrocarbons.¹³

As expected, in both cases the gas solubility increased linearly with the system pressure and decreased with the system temperature. The experimental Henry's constants were found from the slope of the fitting of experimental data to a straight line using a least-squares method. Table 1 collects the experimental Henry's constants for propane and propylene in BmimBF₄ and BmpyBF₄ at different temperatures and the characteristic parameters of the dependency on temperature (H_0) and the standard solvation enthalpy for gas-to-liquid transfer (ΔH_{sol}). A good agreement is obtained between the values of

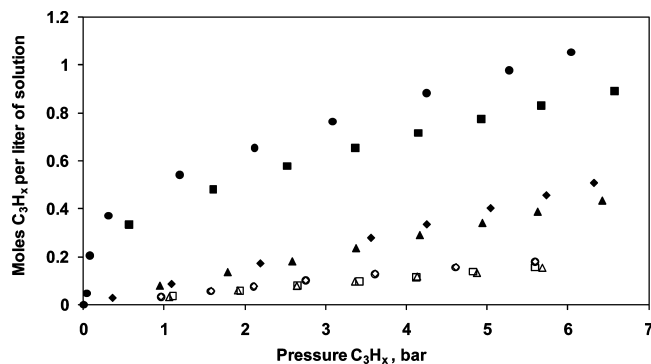


Figure 2. Solubility of propylene and propane in Ag^+ -RTILs mixtures and silver-free ionic liquids at 298 K. The symbols refer to the following solvents, silver salt concentrations, and gases. Ag^+ -BmpyBF₄ 0.25 M: (○) C_3H_8 and (●) C_3H_6 . Ag^+ -BmimBF₄ 0.25 M: (□) C_3H_8 and (■) C_3H_6 . BmpyBF₄: (◇) C_3H_8 and (◆) C_3H_6 . BmimBF₄: (△) C_3H_8 and (▲) C_3H_6 .

the Henry's constants found in the present work for absorption of propane and propylene in BmimBF₄ medium and the values reported previously by Camper *et al.*¹⁸ at 313 K obtained from a single experimental data point.

The behavior of both solvents is very similar, being the ratio of the physical solubilities at 298 K of 2.48 for the silver-free BmimBF₄ and 2.37 for BmpyBF₄.

4.2. Solubility in Ag^+ -RTILs. To improve the capacity and selectivity of absorption for propylene, a complexation agent (Ag^+) has been added to the ionic liquids and the effects on the total propylene absorption of the silver ion concentration and temperature have been analyzed.

Experimental results show that both ionic liquids containing silver ions ($[\text{AgBF}_4] = 0.25 \text{ M}$) have much higher capacity for propylene than propane at 298 K, as clearly shown in Figure 2. The Ag^+ -BmpyBF₄ [0.25 M] system presents a slightly higher propylene absorption capacity than Ag^+ -BmimBF₄ [0.25 M] solution. Propane showed similar solubility in the silver-free ionic liquid and in the AgBF_4 solution; therefore, a salting out effect was not observed. Because the presence of the salt did not decrease the solubility of propane, it has been assumed that the physical solubility of the propylene also has a similar value in the silver solution and in the silver-free ionic liquid.

Figure 3 presents the solubility of propylene in reactive Ag^+ -BmimBF₄ and Ag^+ -BmpyBF₄ media at 298 K as a function of pressure and silver tetrafluoroborate concentration. The data show the positive influence of both the gas pressure and silver concentration on the solubility of propylene. The amount of propylene absorbed by the solvents containing Ag^+ at 0.1 M is approximately twice more than that in the standard ionic liquids, for a propylene pressure of 2 bar. The absorption of C_3H_6 increases linearly with the silver ion concentration as shown in Figure 4, obtaining values up to 12 times higher when a concentration 1 M of the metallic cation, Ag^+ , is used.

The molar selectivity toward propylene is calculated from the individual gas absorption data according to eq 12.

$$\text{selectivity} = \frac{(C_{\text{C}_3\text{H}_6}^T / C_{\text{C}_3\text{H}_8}^T)}{(P_{\text{C}_3\text{H}_6} / P_{\text{C}_3\text{H}_8})} \quad (12)$$

Selectivity values calculated from the data of individual gas absorption in BmpyBF₄ at different silver ion concentration and 298 K are plotted in Figure 5. Selectivity reached the highest value at the lowest gas partial pressure because the physical solubility contribution was dominated by the amount absorbed due to the chemical complexation-reactions. When the silver

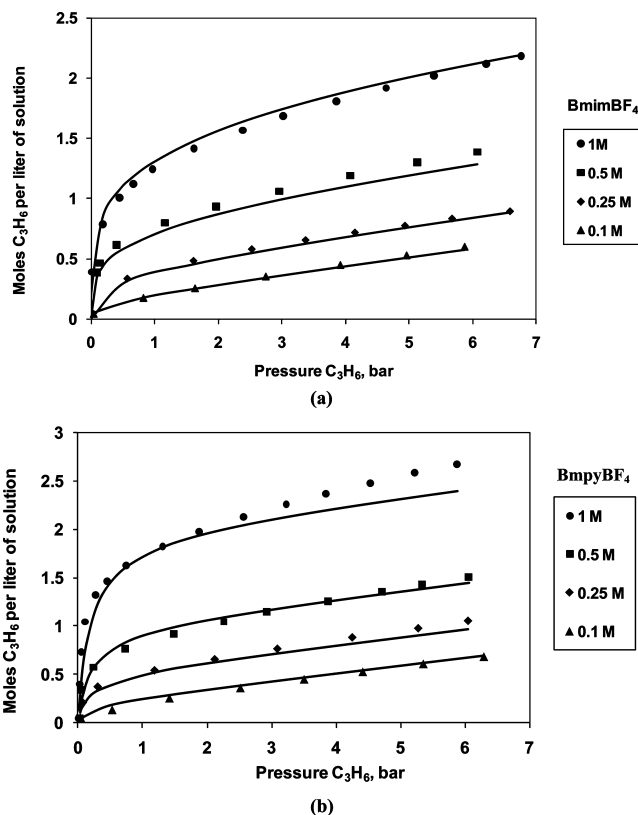


Figure 3. Equilibrium isotherms of propylene in (a) AgBF_4 -BMImBF₄; (b) AgBF_4 -B4MPyrBF₄ at $T = 298 \text{ K}$: (symbols) experimental; (lines) calculated.

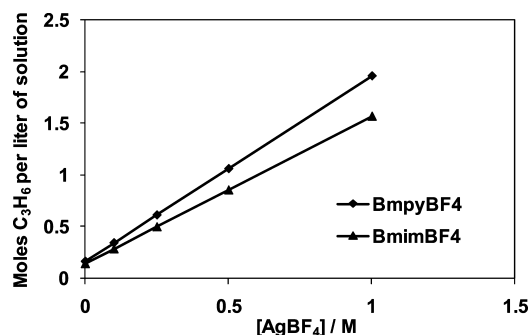


Figure 4. Propylene solubility as a function of the silver salt concentration at 2 bar of pressure and 298 K in RTILs.

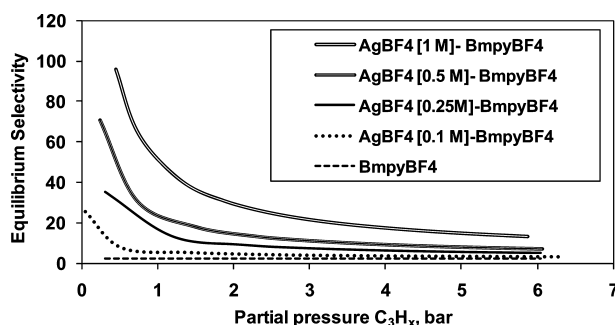


Figure 5. Equilibrium selectivity for propylene/propane mixtures at different silver ion concentrations and 298 K using BmpyBF₄ as solvents.

sites were becoming saturated the selectivity started to level out. Larger amounts of Ag^+ ions allow higher propylene/propane selectivity for the same pressure as expected. For an industrial application with the real mixed stream, feed gas pressure and

Table 2. C₃H₆/C₃H₈ Selectivity in Ag⁺–BmimBF₄ and Ag⁺–BmpyBF₄ Reactive Systems at 298 K at Various Pressures and Silver Ion Concentrations

P (bar)	selectivity									
	BmimBF ₄					BmpyBF ₄				
	IL	0.1 M	0.25 M	0.5 M	1 M	IL	0.1 M	0.25 M	0.5 M	1 M
0.5	2.5	10.1	21.5	40.5	78.4	2.4	10.6	23.0	43.7	103.4
1	2.5	6.9	13.5	24.5	46.6	2.4	7.2	14.4	26.4	61.3
2	2.5	5.0	8.8	15.2	27.9	2.4	5.0	8.9	15.5	34.9
4	2.5	3.9	6.1	9.6	16.8	2.4	3.7	5.8	9.3	19.7

silver ion concentration in the absorption solution will be critical parameters in order to reach the best compromise between propylene absorption capacity and selectivity. Table 2 collects the C₃H₆/C₃H₈ selectivity in both RTILs studied at 298 K at various pressures and silver ion concentrations. Slightly higher selectivities are obtained for the reactive system Ag⁺–BmpyBF₄ than for Ag⁺–BmimBF₄. Galán et al.¹¹ reported C₂H₄/C₂H₆ selectivities for various IL containing silver salts at different temperatures, which are of the same order. Thus, selectivities calculated in this work are considerably higher than the values reported by Cho et al.⁷ working with AgNO₃ aqueous media at 298 K, pointing to the higher efficiency of the RTILs in the separation process.

The propylene absorption capacity and propylene/propane selectivity in Ag⁺–BmpyBF₄ are slightly higher than in the reactive system Ag⁺–BmimBF₄. These results are in good agreement with the results reported by Meindersma et al.²⁶ who found that the ionic liquid BmpyBF₄ was the best solvent for aromatic/aliphatic separation from the ionic liquids investigated containing imidazolium and pyridinium cations. However, BmpyBF₄ is more viscous and can induce more gas diffusion limitations. Depending on the contactor selected to achieve the separation, the reactive Ag⁺–RTIL medium will be more suitable. Thus, using a membrane contactor the Ag⁺–BmpyBF₄ system will present higher mass transfer limitations than Ag⁺–BmimBF₄, although it could be more appropriate when using SILMs due to their higher surface tension.^{20,27}

In a previous work, Ortiz et al.¹² reported the temperature effect in the propylene absorption process using Ag⁺–BmimBF₄ [0.25 M] as reactive solvent, obtaining the equilibrium constants ($K_{\text{Eq},1}(T)$ and $K_{\text{Eq},2}(T)$) and enthalpies of complexation ($\Delta H_{\text{r},1}$, $\Delta H_{\text{r},2}$) by fitting the experimental data to the mathematical model developed. In this work, it has been validated for different concentrations of silver salt (between 0.1 and 1 M), using the obtained equilibrium constants, as shown in Figure 3a, with a standard deviation between simulated and experimental values of $\sigma_w = 1.5\%$.

Next, the experimental data of propylene absorption in the Ag⁺–BmpyBF₄ reactive system were fitted to the mathematical model and the equilibrium parameters were calculated employing the equation-oriented simulation software Aspen Custom Modeler. Table 3 presents the values of enthalpies of complexation and equilibrium constants at different temperatures for both reactive Ag⁺–RTILs media. From the behavior of the propylene solubility shown in Figure 6, which increases with decreasing temperature, it can be concluded that the absorption of propylene is an exothermic process. The obtained values for the equilibrium constants for the primary and secondary complexation reactions in both media suggest that the formation of the secondary complex species in the Ag⁺–BmpyBF₄ is more favorable than in the Ag⁺–BmimBF₄ reactive medium under similar operative conditions.

4.3. Mixed Gas Solubility in Ag⁺–RTILs. To examine the absorption equilibrium of an olefin/paraffin gas mixture in the

Table 3. Enthalpies of Complexation and Equilibrium Constants for Different Temperatures

temp (K)	BmimBF ₄		BmpyBF ₄	
	$\Delta H_{\text{r},1}$ (kJ mol ^{−1})	$\Delta H_{\text{r},2}$ (kJ mol ^{−1})	$\Delta H_{\text{r},1}$ (kJ mol ^{−1})	$\Delta H_{\text{r},2}$ (kJ mol ^{−1})
	−11.0 ± 2.5	−38.7 ± 7.8	−21.3 ± 4.2	−51.6 ± 9.1
	BmimBF ₄		BmpyBF ₄	
	$K_{\text{Eq},1}$ (L mol ^{−1})	$K_{\text{Eq},2}$ (L mol ^{−1})	$K_{\text{Eq},1}$ (L mol ^{−1})	$K_{\text{Eq},2}$ (L mol ^{−1})
278	337.0 ± 129.8	18.2 ± 1.7		
288	285.8 ± 110.1	10.2 ± 0.9	223.6 ± 101.0	54.3 ± 17.2
298	245.1 ± 94.4	5.9 ± 0.5	165.8 ± 74.9	26.3 ± 8.4
308	212.2 ± 81.8	3.6 ± 0.3	125.4 ± 56.7	7.6 ± 2.4
318	185.5 ± 71.5	2.2 ± 0.2		

Ag⁺–BmimBF₄ [0.25 M] at 298 K, autoclave experiments were carried out with different initial feed composition between 50% and 80% molar of propylene. These experiments were performed following the same procedure described for the experiments with pure gas, except that after the system reached equilibrium, the stirrer was turned off and a gas sample was withdrawn for GC analysis. GC analysis yielded the composition of the gas phase in the autoclave, and since the total pressure was known, the partial pressure of each gas was determined. The mass balance allowed straightforward calculation of the number of moles of each gas dissolved in the liquid phase. The resulting equilibrium data are shown in Figure 7 along with the calculated value from the mathematical model developed previously.

Because of the higher chemical affinity and the influence of the chemical reaction with silver ions, the solution absorbed considerably more propylene than propane. From the comparison with the calculated data for pure gas, it was observed that the propylene absorption in the mixture was almost identical to the pure gas absorption. The propane gas seemed to show considerably lower solubility when propylene was present compared to the pure gas. A possible explanation of this effect for the propane equilibrium values is that the high concentration of absorbed propylene created an unfavorable environment for the physically dissolved propane. Thus, higher values of selectivity are reached.

4.4. Regeneration Conditions and Thermal Stability. Regeneration of the Ag⁺–RTIL reactive solvent and desorption was possible by dissociating the olefins from the olefin/metal salt complexes using a combination of increased temperature and lower pressure. Complete propylene desorption was carried out at 313 K of temperature, 800 rpm stirred speed, and a decrease of the pressure to 20 mbar. The liquid was continuously stirred until the presence of bubbles in the liquid was no longer observed. This took about 180 min.

RTIL-based mixtures with AgBF₄ silver salt studied were stable, and the absorption loads achieved after the regeneration of the solvent were similar to that obtained with the fresh solvent. The liquid mixture was used for more than 12 absorption and regeneration cycles without observable losses in the solvent efficiency. The gas absorption results were repeatable (maximum differences of 3%) after several absorption and regeneration cycles. On the other hand, the enthalpy of complexation in Ag⁺–RTILs is lower than that of the silver aqueous solutions; therefore, the regeneration of the ionic liquid solvents requires a lower energy demand.^{7,11}

To evaluate the thermal stability of the reactive Ag⁺–RTILs mixtures, a degradability test was carried out in a vacuum rotary evaporator, with the temperature being increased by intervals of 10 K from 293 K for 180 min and 20 mbar of pressure.

For the reactive system Ag⁺–BmimBF₄ with silver salt concentrations of 0.1 and 0.25 M the solvent was degraded after

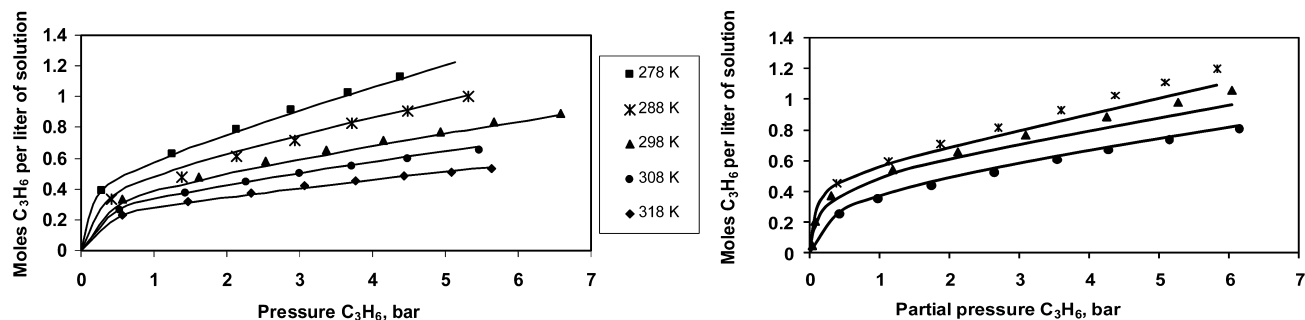


Figure 6. Equilibrium isotherms of propylene in (a) AgBF_4 [0.25 M]– BmimBF_4 and (b) AgBF_4 [0.25 M]– BmpyBF_4 : (symbols) experimental; (lines) calculated.

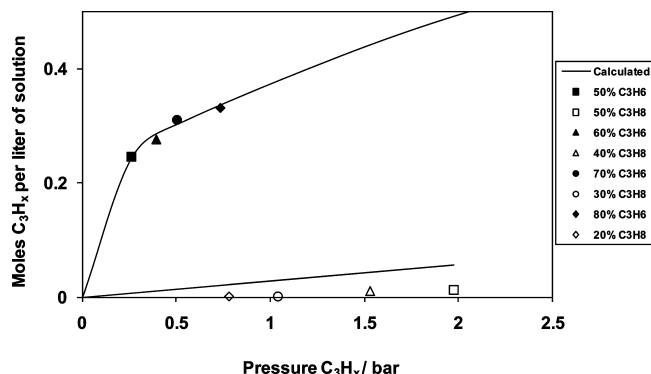


Figure 7. Equilibrium isotherms of propylene/propane mixtures in AgBF_4 [0.25 M]– BmimBF_4 at $T = 298$ K at different initial feed composition: (symbols) experimental; (lines) calculated.

having reached 343 and 333 K, respectively, the liquid turned dark and metallic silver was deposited at the glass surface, which is in good agreement with the results observed by Kim et al.²⁸ for the tests performed with a silver polymer electrolyte membrane.

5. Conclusions

Design of suitable Ag^+ –RTILs mixtures as reaction media in the separation of propylene/propane mixtures improves the efficiency for propylene absorption because the silver cation becomes chemically more active in forming silver–olefin complexes. For both ionic liquids studied (BmimBF_4 and BmpyBF_4), the solubility of propylene increases with pressure and linearly with the silver ion concentration in the range studied. The highest selectivities were achieved for the maximum silver ion concentration and for the lowest gas partial pressures where the physical effects are overlapped by the chemical complexation reactions.

The reactive system Ag^+ – BmpyBF_4 exhibits slightly higher values of propylene absorption capacity and propylene/propane separation selectivity than the Ag^+ – BmimBF_4 medium. However, it is more viscous and therefore it can induce stronger diffusion limitations of the gas in the absorption medium. The choice of absorbent does not depend solely on the absorption capacity, but selectivity, kinetics, stability, price, and regenerative potential and facility should also be considered.

A simple mathematical model based on the formation of organometallic complexes with different stoichiometry has been developed and validated for different concentrations of silver salt (between 0.1 and 1 M) and for a mixed gas stream of propylene/propane in order to describe the total propylene absorption in the reaction media under study.

Silver salt (AgBF_4) dissolved in a suitable RTILs forms stable reactive media which are able to reach a complete regeneration at 313 K, 800 rpm, and 20 mbar vacuum for 3 h. The reactive Ag^+ – BmimBF_4 medium was thermally stable up to 343 K at 0.1 M and up to 333 K at 0.25 M of silver salt concentrations; at those temperatures the silver ions started to become reduced into metallic silver.

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Nomenclature

- C = concentration (mol L^{-1})
 H = Henry's law constants (mol (L bar)^{-1})
 ΔH_r = enthalpy of reaction (kJ mol^{-1})
 ΔH_{sol} = standard solvation enthalpy (kJ mol^{-1})
 $[i]$ = molar concentration component i (mol L^{-1})
 K_{Eq} = complexation equilibrium constant (L mol^{-1})
 P = pressure (bar)
 R = universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
 T = temperature (K)
Greek Letters
 σ_w = standard weight deviation, dimensionless
Superscripts/Subscript
1, 2 = reaction identification
Eq = equilibrium
 i = component identification
 r = reaction
sol = solvation
 T = total

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