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Dossier

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Gaseous Hydrocarbon Separations Using Functionalized Ionic Liquids

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Abstract — *The functionalization of the side chains on the cation or the anion of an ionic liquid is a common approach to tailor its properties for different processes including the separation of gases. In this paper, we present the current state of the art concerning the usage of ionic liquids for hydrocarbon separations. We also show how the functionalization of ionic liquids or the appropriate anion/cation combinations can contribute to the increase of the performance of the ionic liquids for the separation of gaseous hydrocarbons – either by improving the capacity of the ionic liquid to absorb a given gas or by increasing the selectivity towards a particular hydrocarbon. Original results concerning the usage of olefin-complexing metal salts of lithium (I), nickel (II) and copper (II) dissolved in ionic liquids for selectively absorbing light olefins are presented. It is observed that the absorption capacity of an imidazolium-based ionic liquid is doubled by the addition of a copper (II) salt. This result is compared with the effect of the functionalization of the ionic liquid and the advantages and difficulties of the two approaches are analyzed.*

Résumé — **Liquides ioniques fonctionnalisés pour la séparation d'hydrocarbures gazeux** — La fonctionnalisation des chaînes latérales sur le cation ou l'anion d'un liquide ionique est une approche commune pour adapter ses propriétés pour les différents processus, y compris la séparation de gaz. Dans cet article, nous présentons l'état actuel des recherches concernant l'utilisation de liquides ioniques pour les séparations d'hydrocarbures gazeux. Nous montrons comment la fonctionnalisation de liquides ioniques ou des combinaisons d'anions/cations appropriées peuvent contribuer à l'augmentation de leur performance pour la séparation des hydrocarbures gazeux – soit par l'amélioration de la capacité du liquide ionique pour absorber un gaz donné ou en augmentant la sélectivité pour un hydrocarbure particulier. Des résultats originaux concernant l'utilisation de sels métalliques de lithium (I), le nickel (II) et le cuivre (II) dissous dans des liquides ioniques pour absorber sélectivement des oléfines légères sont présentés. On constate que la capacité d'absorption d'un liquide ionique à base d'imidazolium est doublée par addition d'un sel de cuivre (II). Ce résultat est comparé avec l'effet de la fonctionnalisation du liquide ionique. Les avantages et les difficultés de ces deux approches sont analysés.*

INTRODUCTION

Separation techniques like distillation, crystallization, liquid-liquid extraction or absorption are commonly used and are based on the creation or on the addition of a new phase. They require either an energy transfer or the use of a mass-transfer agent. Changing from an energy-separating agent to a mass-separating agent can potentially reduce the process energy requirements, but the selected absorbent should be easy to recycle, have low volatility, and the solubilities of the species to separate should be significantly different. These constraints, together with the need to obey tougher environmental regulations, render the choice of the absorbent difficult.

Membranes make use of liquid or solid (frequently polymeric) barriers to separate species that present different permeability. Membranes are used in small, compact and clean units that require low energy to achieve separation, but are still difficult to scale-up. Adsorption is a surface-based process that frequently relies on a solid agent to achieve separation. The separation is achieved due to different interacting forces at the interface (originating physisorption or chemisorption processes) that selectively interacts with certain components in detriment of others from a liquid or gas mixture. The adsorbent material should have high surface area, good mechanical properties, fast adsorption kinetics and the ability to be regenerated without loss of its properties. Commonly used supports are alumina, ion exchanging resins, high-surface-area silica zeolites and molecular sieves. Electrophoresis and centrifugation are examples of separation techniques that exploit the differences in the responses of the constituents of a feed to an external force or gradient. They are especially useful and versatile for separating biochemical [1]. Cryogenic distillation is used for the separation of large volumes of hydrocarbon gases (*i.e.* ethane/ethylene or propane/propylene) and is viewed as an expensive, energy demanding process whose replacement by a more economic and environmentally friendly alternative performance would represent a major advance in the field.

1 IONIC LIQUIDS AS SEPARATING AGENTS

Ionic liquids have been suggested as new separating agents for gaseous hydrocarbon separations namely for olefin/paraffin gas separation. They can also act as absorbents or as solvents for the chemical complexation of olefins with silver or copper salts. Ionic liquids are composed uniquely of ions and have a melting point below 100°C. Many present unique properties such as negligible vapor pressure, high thermal, chemical and electrochemical stability, flame retardant effect, and high ionic conductivity. Ionic liquid are also called "designer solvents" due to the large variety of combination possibilities of cations and anions, leading to tunable physical chemical properties.
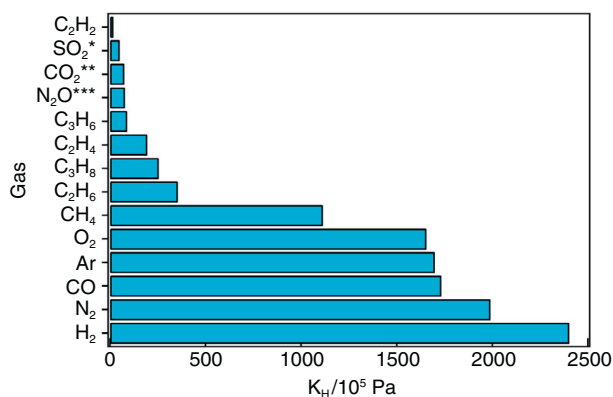

Figure 1

Henry's law constant, K_H, for several gases in ionic liquid $[C_1C_4Im][BF_4]$ at 313 K. * 293 K; ** 314 K; *** 298 K [2].

In Figure 1, are shown the Henry's law constants, K_H, of different gases in one ionic liquid – 1-butyl-3-methylimidazolium tetrafluoroborate, $[C_1C_4Im][BF_4]$ – [2]. As can be observed, the mole fraction solubility spans over more than two orders of magnitude, depending on the nature of the gas. These differences can be explored by proposing some ionic liquids as selective absorbents for gases.

Monoatomic, diatomic, non-polar or gases with low polarizability present the lowest solubilities in the ionic liquid $[C_1C_4Im][BF_4]$. Unsaturated hydrocarbons frequently present a higher solubility in ionic liquids than their saturated counterparts and so these fluids are considered promising for saturated/unsaturated hydrocarbon separation. The exact reasons for the observed trends are still poorly understood, even if they are essential for the development of new gas separation processes [3, 4].

The functionalization of the side chains or the modification of the ionic liquid anion are popular approaches to tailor its properties for particular applications such in catalysis [5], energy storage [6], capture of carbon dioxide [3] and in separation technology [7]. In this work, we have studied the possibility of using ionic liquids for the separation of light saturated and unsaturated hydrocarbons and have started by compiling the literature results on the solubility of ethane and ethylene in different ionic liquids formed by the cations and anions in Table 1. The Henry's law constants for ethane and ethylene are reported in Figure 2 [2, 8-26] and Table 2 [2, 8-26].

2 FUNCTIONALIZATION OF THE IONIC LIQUIDS

There are few examples of an experimental rational approach for the design of an ionic liquid to optimize the

TABLE 1

Abbreviation, full designation and structure of some cations of ionic liquids. $C_{n/m}$ represent alkyl chains of variable size. In the anions, R_n represents alkyl chains of variable size

Abbreviation	Full name	Structure
Cations		
$C_nC_mIm^+$	1-C_n-3-C_mImidazolium	
$C_1(C_3H_5CH_2)Im^+$	1-(buten-3-yl)-3-methylimidazolium	
$C_1(C_2H_2CH)Im^+$	1-methyl-3-(propyn-3-yl)imidazolium	
$C_1(CH_2C_6H_5)Im^+$	1-benzyl-3-methylimidazolium	
$C_1C_3CNIm^+$	1-(3-cyanopropyl)-3-methylimidazolium	
$(C_3CN)_2Im^+$	1,3-(3-cyanopropyl)Imidazolium	
$C_1(C_8H_{16}C_2H_2C_8H_{17})Im^+$	1-(Z-octadec-9-enyl)-3-methylimidazolium	
$C_nC_mPyrr^+$	C_nC_mPyrrolidinium	
C_nPyr^+	C_nPyridinium	
$P_{n\ m\ p\ q}^+$	$C_nC_mC_pC_q$Phosphonium	
Anions		
NTf_2^-	Bis(trifluoromethylsulfonyl)imide	
DCA^-	Dicyanamide	
$C_nHPO_3^-$	C_nPhosphite	
PF_6^-	Hexafluorophosphate	
$CF_3SO_3^-$	Trifluromethanesulfonate	
BF_4^-	Tetrafluoroborate	

(continued)

TABLE 1 *(continued)*

Abbreviation	Full name	Structure
TMPP$^-$	Bis(2,4,4-trimethylpentyl)phosphinate	
BETI$^-$	Bis(perfuoroethylsulfonyl)imide	
FAP$^-$	Tris(pentafluoroethyl)trifluorophosphate	
OAc$^-$	Acetate	
C$_n$CO$_2$$^-$	Carboxylate	
TFA$^-$	Trifluoroacetate	
C$_n$SO$_4$$^-$	C$_n$Sulfate	
DBS$^-$	Dodecylbenzenesulfonate	

solubility of one of the gases in the separation of ethane/ethylene or propane/propene. Moura *et al.* [27, 28] have selected several functionalized ionic liquids designed to maximize the solubility and interactions of ethylene in the ionic liquid in detriment of the solubility of ethane. The functionalizations used were the increasing alkyl side-chain on the cation of the ionic liquid ([C$_1$C$_4$Im][NTf$_2$] and [C$_1$C$_8$Im][NTf$_2$]); unsaturations on the alkyl side-chain on the cation of the ionic liquid ([C$_1$(C$_2$H$_2$CH)Im][NTf$_2$], [C$_1$(C$_3$H$_5$CH$_2$)Im][NTf$_2$] and [C$_1$(CH$_2$C$_6$H$_5$)Im][NTf$_2$]); cyano groups in the cation or anion of the ionic liquid or both ([C$_1$C$_3$CNIm][NTf$_2$], [C$_1$C$_3$CNIm][DCA] and [C$_1$C$_4$Im][DCA]) and a phosphite based anion in the ionic liquid ([C$_1$C$_4$Im][C$_1$HPO$_3$]). The authors observed that small changes in the structure of the ionic liquid can have large effects in the ethane and ethylene solubility as illustrated in Figure 2 and can significantly influence the ideal selectivity of ethylene as shown in Figure 3 [9-26, 28, 29].

Adding unsaturations in the alkyl chain of the cation of the ionic liquid, cyano groups in the alkyl chain of the cation or anion and changing the anion of the ionic liquid from an NTf$_2$$^-$ to a C$_1$HPO$_3$$^-$ or DCA, lead to decreases in the
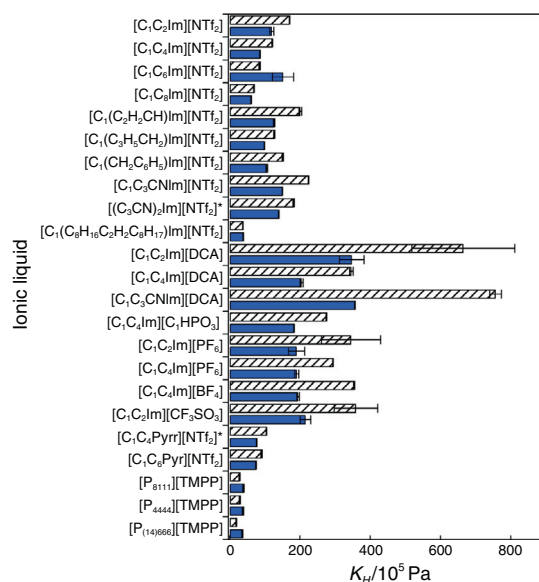

Figure 2

Henry's constant, K_H, of ethane (empty bars) and ethylene (full bars) in the ionic liquids at 313 K (* at 303 K) (Tab. 2)[2, 8-26].

TABLE 2

Ionic liquid	References
$[C_1C_2Im][NTf_2]$	[8-14]
$[C_1C_4Im][NTf_2]$	[9, 15-20]
$[C_1C_6Im][NTf_2]$*	[15, 16, 21]
$[C_1C_8Im][NTf_2]$	[10]
$[C_1(C_2H_2CH)Im][NTf_2]$	[10]
$[C_1(C_3H_5CH_2)Im][NTf_2]$	[9]
$[C_1(CH_2C_6H_5)Im][NTf_2]$	[9]
$[C_1C_3CNIm][NTf_2]$*	[10, 19, 21, 22]
$[(C_3CN)_2Im][NTf_2]$*	[19]
$[C_1(C_8H_{16}C_2H_2C_8H_{17})Im][NTf_2]$	[23]
$[C_1C_2Im][DCA]$	[12, 21]
$[C_1C_4Im][DCA]$	[10]
$[C_1C_3CNIm][DCA]$	[10]
$[C_1C_4Im][C_1HPO_3]$	[10]
$[C_1C_2Im][PF_6]$	[12]
$[C_1C_4Im][PF_6]$*	[15-17, 19-22, 24]
$[C_1C_4Im][BF_4]$	[2, 12, 21, 24]
$[C_1C_2Im][CF_3SO_3]$	[12]
$[C_1C_4Pyrr][NTf_2]$	[12, 24]
$[C_6Pyr][NTf_2]$	[24]
$[P_{8111}][TMPP]$	[25]
$[P_{4444}][TMPP]$	[25]
$[P_{(14)666}][TMPP]$	[25]

●	$[C_1C_2Im][NTf_2]$	[11-13, 15-17]
●	$[C_1(C_2H_2CH)Im][NTf_2]$	[10]
●	$[C_1C_4Im][NTf_2]$	[9, 18-22, 24]
◆	$[C_1C_8Im][NTf_2]$	[10]
▲	$[C_1(C_3H_5CH_2)Im][NTf_2]$	[9]
■	$[C_1(CH_2C_6H_5)Im][NTf_2]$	[9]
●	$[C_1C_3CNIm][NTf_2]$*	[10, 19, 21, 22]
▲	$[C_1C_3CNIm][DCA]$	[10]
▲	$[(C_3CN)_2Im][NTf_2]$*	[10]
◆	$[C_1(C_8H_{16}C_2H_2C_8H_{17})Im][NTf_2]$	[23]
■	$[C_1C_2Im][PF_6]$	[12]
▼	$[C_1C_4Im][PF_6]$*	[15-17, 19-21, 24, 28]
■	$[C_1C_4Im][C_1HPO_3]$	[10]
▲	$[C_1C_2Im][DCA]$	[12, 21]
◆	$[C_1C_4Im][DCA]$	[10]
◆	$[C_1C_4Im][BF_4]$	[12, 21, 24]
■	$[C_1C_2Im][CF_3SO_3]$	[12]
▼	$[P_{8111}][TMPP]$	[25]
■	$[P_{4444}][TMPP]$	[14]
▲	$[P_{(14)666}][TMPP]$	[26]
●	$[C_1C_4Pyrr][NTf_2]$	[12, 24]
◆	$[C_6Pyr][NTf_2]$	[29]

Figure 3

Ethane/ethylene ideal selectivity *versus* Henry's constant, K_H, of ethylene in the ionic liquids at 313 K (* at 303 K).

solubility of ethane and ethylene, when compared to a reference ionic liquid, $[C_1C_4Im][NTf_2]$ (Fig. 2). The only exception is for $[C_1(C_3H_5CH_2)Im][NTf_2]$, where ethane solubility is not greatly affected. These modifications in the ionic liquids also lead to increases in the ethane/ethylene separation selectivity (Fig. 3). The solubility of ethane is more affected by changes in the ionic liquid than that of ethylene. For example, increasing the alkyl side chain of the cation from $[C_1C_4Im][NTf_2]$ to $[C_1C_8Im][NTf_2]$ leads to an increase in both the ethane and the ethylene solubility but the increase is larger for the saturated gas. The only exceptions are for the ionic liquid containing a double bond in the alkyl side-chain of the cation (where the solubility of ethane is similar and the solubility of ethylene decreases 14%) and that
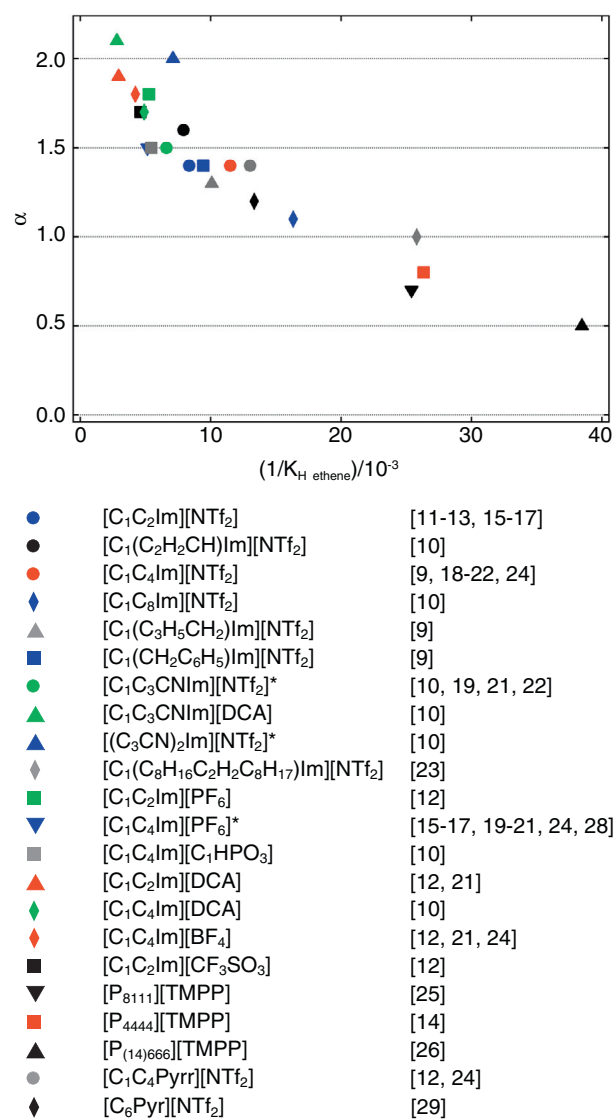
containing a benzyl group (where the solubility of both gases decreases in a similar way). The authors also found the ionic liquid with the highest separation selectivity for the ethane/ethylene reported in the literature – $[C_1C_3CNIm][DCA]$.

Green *et al.* [29] determined the solubilities of ethane and ethylene in an imidazolium based ionic liquid, with an 18 carbon long alkyl side chain, $[C_1(C_8H_{16}C_2H_2C_8H_{17})Im][NTf_2]$, designed to have increased solubility for the nonpolar species. For this ionic liquid and for ionic liquids with large nonpolar content, the solubility of ethane or propane is slightly higher than that of their unsaturated counterparts (Fig. 2; Fig. 4, [11-22, 24, 26]), in contrast to the relative
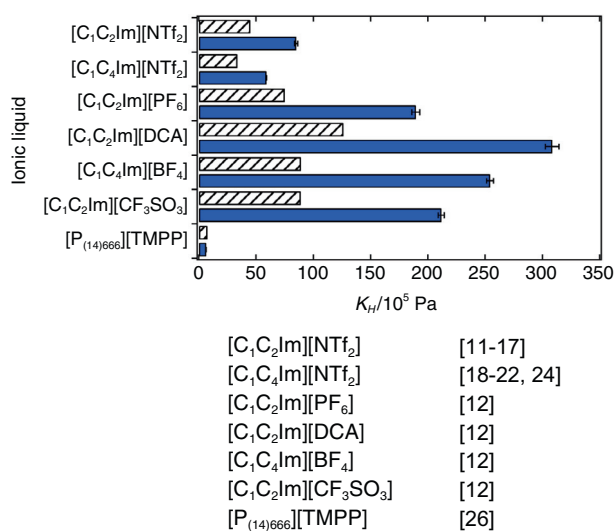
$[C_1C_2Im][NTf_2]$	[11-17]
$[C_1C_4Im][NTf_2]$	[18-22, 24]
$[C_1C_2Im][PF_6]$	[12]
$[C_1C_2Im][DCA]$	[12]
$[C_1C_4Im][BF_4]$	[12]
$[C_1C_2Im][CF_3SO_3]$	[12]
$[P_{(14)666}][TMPP]$	[26]

Figure 4

Henry's constant, K_H, of propane (empty bars) and propene (full bars) in the ionic liquids at 313 K (* at 303 K).

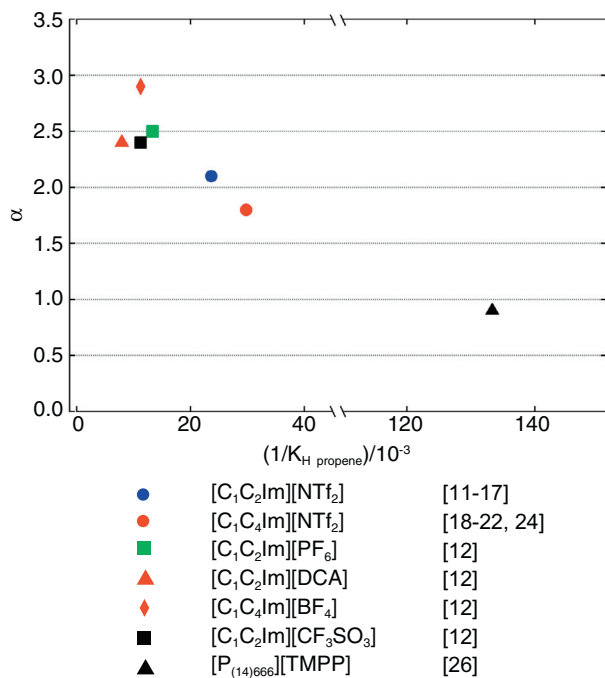|		
●	$[C_1C_2Im][NTf_2]$	[11-17]
●	$[C_1C_4Im][NTf_2]$	[18-22, 24]
■	$[C_1C_2Im][PF_6]$	[12]
▲	$[C_1C_2Im][DCA]$	[12]
◆	$[C_1C_4Im][BF_4]$	[12]
■	$[C_1C_2Im][CF_3SO_3]$	[12]
▲	$[P_{(14)666}][TMPP]$	[26]

Figure 5

Propane/propene ideal selectivity *versus* Henry's constant, K_H, of propene in the ionic liquids at 313 K (* at 303 K).

Figure 6

Upper plot: mole fraction absorption capacity for ethylene ($x_{ethylene}$) in blue and ionic liquid ideal separation selectivity for ethane/ethylene (α) in green *versus* the molar volume (V_m), in $cm^3 \cdot mol^{-1}$, of the ionic liquids. Lower plot: mole fraction absorption capacity for propylene ($x_{propylene}$) in light green and ionic liquid's ideal separation selectivity for propane/propylene (α) in blue *versus* the molar volume (V_m), in $cm^3 \cdot mol^{-1}$, of the ionic liquids. The lines represent the simple linear regression of the data. In the lower plot, the full green line corresponds to the full circles and the dotted line includes also the open circle.

– $[P_{8111}][TMPP]$ [23],
– $[P_{4444}][TMPP]$ [25],
– $[P_{(14)666}][TMPP]$ [14],

(Fig. 2) by Liu *et al.* for the separation of ethane and ethylene and for the separation of propane and propene in $[P_{(14)666}]$ $[TMPP]$ [26](Fig. 4). $[P_{(14)666}][TMPP]$ presents the lowest selectivity for the ethane/ethylene and propane/propene separation.

For both separations in the studied ionic liquids we observe that the selectivity increases with the decrease of the solubility of the unsaturated gas. (Fig. 3; Fig. 5, [11-22, 24, 26]). These results indicate that the solubility

solubilities in conventional, more polar ionic liquids. The same observation was made for phosphonium-based ionic liquids:
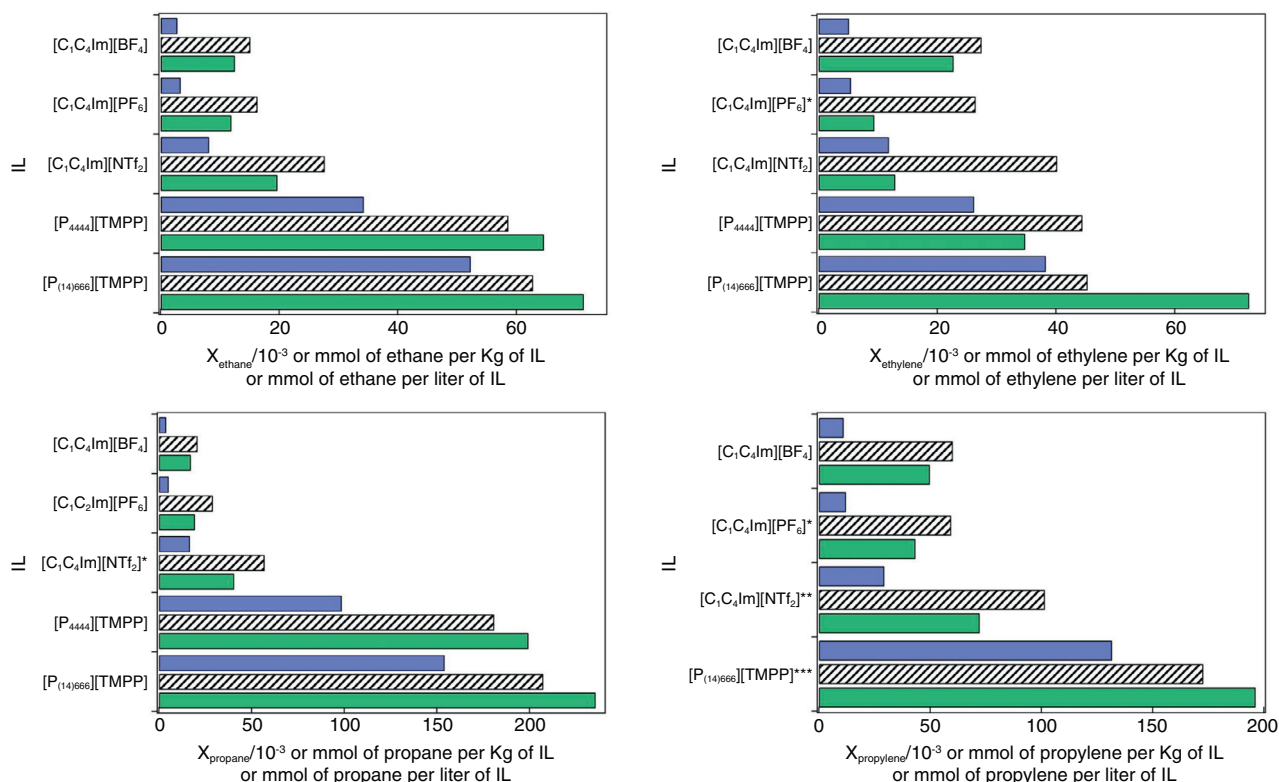
Figure 7

Upper plots: mole fraction ($\times 10^3$, blue bars), quantity of gas per mass of solvent ($\times 10^4$, patterned bars) or per volume of solvent (green bars) of ethane (on the left) and ethylene (on the right) for different ionic liquids. Lower plots: mole fraction ($\times 10^3$, blue bars), quantity of gas per mass of solvent ($\times 10^4$, patterned bars) or per volume of solvent (green bars) of propane (on the left) and propylene (on the right) for different ionic liquids. All the values refer to 1 bar partial pressure of gas and 313 K (* values at 320 K).

of ethane, ethylene, propane and propylene in the ionic liquids tested are controlled by non-specific interactions, even for ionic liquids containing side-chain functionalization designed to optimize the interactions with one of the hydrocarbons to be separated. This can be further confirmed in Figure 6 since the ionic liquids that present higher ethylene or propene absorption capacity and lower ideal selectivity are the ones with highest molar volume and *vice-versa*.

3 IONIC LIQUIDS WITH COMPLEXING AGENTS

Certain metal transition cations, such as Cu(I) or Ag(I) are able to form π-complexes with unsaturated hydrocarbons. The metal and alkene act as an electron donor and acceptor, forming a coordinative bond if the orbitals involved present the correct symmetry and if the metal possesses high electron affinity for good σ-bond accepting properties and low promotion energy for good π-backbonding [26]. This complexation reaction is used to increase the absorption capacity of the ionic liquid for unsaturated light hydrocarbons.

The influence in ethylene solubility of the presence of three different cations, lithium (I), nickel (II) and copper (II) in $[C_1(CH_2C_6H_5)Im][NTf_2]$ ionic liquid was studied by Moura [30]. The authors concluded that cations such as lithium and nickel slightly affect the solubility of ethylene. The addition of copper salts almost doubles the absorption capacity of ethylene in the ionic liquid $[C_1(CH_2C_6H_5)Im][NTf_2]$, a value compatible with the ones reported in the literature for other metallic cations [31, 32].

Sanchéz *et al.* [31] studied the absorption of ethane and ethylene in silver salt solutions with the ionic liquids:
– $[C_1C_2Im][NTf_2]$,
– $[C_1C_2Im][CF_3SO_3]$,
– $[C_1C_4Im][NO_3]$,
– $[C_0C_2Im][NO_3]$,
– $[C_1C_{2\text{-OH}}Im][NO_3]$,
– $[4\text{-butyl-}C_4Pyr][NO_3]$,
– $[N_{1112\text{-OH}}][NO_3]$,
with Ag^+ concentrations ranging from 0.45 mol.L^{-1} to 4.4 mol.L^{-1}. The results were compared to the solubility of ethane and ethylene in $[C_1C_2Im][NTf_2]$. The authors

TABLE 3

Solubility of ethane, ethylene, propane and propylene in several ionic liquids expressed in Henry's law constant, K_H, the majority at 313 K
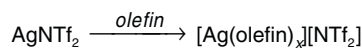
Ionic liquid	Ethane	Ethylene	Propane	Propylene
[C₁C₂Im][NTf₂]				
[C₁(C₂H₂CH)Im][NTf₂]*				
[C₁C₄Im][NTf₂]*				
[C₁(C₃H₅CH₂)Im][NTf₂]*				
[C₁C₆Im][NTf₂]				
[C₁(CH₂C₆H₅)Im][NTf₂]*				
[C₁C₈Im][NTf₂]*				
[C₁C₁₀Im][NTf₂]				
[C₁C₃CNIm][NTf₂]*				
[(C₃CN)₂Im][NTf₂]				
[C₁C₁C₃CNIm][NTf₂]				
[C₁C₁COOC₅Im][NTf₂]				
[C₁C₁COOC₂OC₂Im][NTf₂]				
[C₁C₁COOC₂OC₂OC₄Im][NTf₂]				
[C₁C₄Im][BETI]				
[C₁C₄Im][FAP]				
[C₁C₆Im][FAP]				
[C₁C₂Im][DCA]				
[C₁C₄Im][DCA]*				
[C₁C₃CNIm][DCA]*				
[C₁C₁C₃CNIm][DCA]				
[C₁C₄Im][OAc]				
[C₁C₄Im][n-C₁₅H₃₁COO]				
[C₁C₄Im][n-C₁₇H₃₅COO]				
[C₁C₂Im][PF₆]				
[C₁C₄Im][PF₆]				
[C₁C₄Im][BF₄]				
[C₁C₈Im][BF₄]				
[C₁C₄Im][TFA]				
[C₁C₁Im][C₁HPO₃]				
[C₁C₂Im][C₂HPO₃]				
[C₁C₄Im][C₁HPO₃]*				
[C₁C₄Im][C₄HPO₃]				
[C₂C₄Im][C₂HPO₃]				
[C₁C₁Im][(C₁)₂PO₄]				
[C₁C₄Im][(C₁)₂PO₄]				

Solubility range legend:

$K_H/10^{-5}$ Pa	Color
No data	
0-10	
11-20	
21-30	
31-40	
41-50	
51-100	
101-150	
151-200	
201-300	
301-400	
401-500	
501-600	
over 600	

observed that the ionic liquid-silver salt solution selectivities were always higher than for [C₁C₂Im][NTf₂], which presents an ethylene selectivity under 2, at 303 K and 1 bar. The highest selectivity was obtained for the 1.8 mol.L⁻¹ silver solution in [C₁C₂Im][CF₃SO₃⁻], with a selectivity of 100 at 1 bar and 333 K. The authors defined selectivity as the proportion between mole of ethylene and the mole of ethane at a certain pressure.

Mortaheb et al. [32] studied the effect of temperature and silver salt concentration on the absorption of ethane and ethylene in ionic liquid [C₁C₄Im][NO₃]. A maximum selectivity of 15 was obtained for 5 mol.L⁻¹ silver salt at 278 K. The authors defined selectivity as the proportion between amount of ethylene and the amount of ethane.

Faiz and Li [33] reviewed the application of ionic liquid/ metal salt composite membranes for olefin/paraffin separations. They concluded that even though the concept was successfully applied for separation, the long-term stability of the membranes is still a major issue.

A task specific ionic liquid complex salt, [Ag(olefin)ₓ] [NTf₂], formed as described in Scheme 1, provided an ideal selectivity of 40, a much larger selectivity when compared to the silver salt-[C₁C₄Im][BF₄] solution of 16, at 298 K:

$$AgNTf_2 \xrightarrow{\text{olefin}} [Ag(olefin)_x][NTf_2]$$

Scheme 1

Synthesis of ionic liquid [Ag(olefin)ₓ][NTf₂].

TABLE 4

Solubility of ethane, ethylene, propane and propylene in several ionic liquids expressed in Henry's law constant, K_H, the majority at 313 K

Solubility range legend:

$K_H/10^{-5}$ Pa	Color
No data	(white)
0-10	
11-20	
21-30	
31-40	
41-50	
51-100	
101-150	
151-200	
201-300	
301-400	
401-500	
501-600	
over 600	

This salt was also successfully used to create an adaptive self-healing propane/propene separation membrane, although the details of its long term stability were not provided [34, 35].

Ortiz *et al.* [36] studied the selective absorption of propylene from propane/propylene mixtures in [C₁C₄Im][BF₄] with, and without, silver ions, at several temperatures and pressures. They demonstrated that the propylene selectivity is less than 3 in absence of the silver salt in the ionic liquid and 8 to 16 upon addition of 0.25 mol.L⁻¹ silver salt in the ionic liquid at 298 K and between 1 and 3 bar. Higher pressures proved to lower the selectivity for the silver salt containing ionic liquid, probably due to the saturation of the silver ions. The propylene absorption capacity for the ionic liquids-silver salt solution was compared to aqueous solutions with the same silver salt concentration and it was found that the aqueous solutions presented lower propylene capacities. Although allowing the increase of the capacity and selectivity of the selected support for the unsaturated gas,

the use of metals presents drawbacks due to their cost, contamination, degradation, safety problems, limited metal salt solubility and high viscosities of the resulting liquid absorbent [26, 35, 37, 38, 39].

A detailed engineering analysis is out of the scope of the present paper but would most certainly be necessary in order to properly compare these new technologies based on the use of ionic liquids with traditional processes such as cryogenic distillation. Although costs may considerably vary with time, the current process is so expensive energetically and presents such a negative environmental impact that the detailed analysis of possible alternatives is very pertinent.

CONCLUSIONS AND PERSPECTIVES

Contrary to what is suggested in the literature, the solubility of unsaturated gases, such as ethylene and propylene in ionic liquids is not always higher than of their saturated

counterparts, ethane and propane. In fact, their solubility ranges overlap. As can be seen in Figure 7, this fact is true independently of the way the gas solubility is expressed – in mole fraction, per mass or per volume of solvent.

The tendencies observed for ethane, ethylene, propane and propylene are similar. The solubility of these gases increases with the size of the non-polar domains of the cation or anion of the ionic liquid, suggesting that the solubility of these gases in the group of ionic liquids studied is ruled by nonspecific interactions. The solubility order in terms of cations is:

$$P_{nmpq}^+ \; > \; C_nPyr^+ \; > \; C_nC_mPyrr^+ \; > \; C_nC_mIm^+$$

In comparison, the solubility dependency in terms of the nature of the anion is much smaller, for the same gases.

It would be of great interest to develop ionic liquids containing functionalizations or anions (such as $AlCl_4^-$) that could promote a specific interaction with ethylene or propylene. Another promising possibility is to develop ionic liquids containing metal ions in their structure [40]. However, the more specific are the interactions between the gas and the ionic liquid, the harder the recycling of the absorbent will be, and a balancing effect between specificity and recovery should be taken into account on the development of an ionic liquid for separation purposes.

The published solubility data on ethane, ethylene, propane and propylene (Tab. 3, 4) provides a good start on a database in light hydrocarbon solubility in ionic liquids. This information can be used as a good basis for the development of a model that would allow the prediction of the solubility of these gases in other ionic liquids.

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