Ionic liquids for the separation of gaseous hydrocarbons

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Ph.D. in physical-chemistry

Thesis start date: 11/10/2010
Thesis defense: 16th June 2014

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Summary

The goal of this project was to determine the potential of a selection of ionic liquids for the separation of ethane from ethene. This selection of ionic liquids was designed to escape the tendencies observed in the literature for the solubility of ethane and ethene in order to increase both the selectivity and absorption capacity for the unsaturated gas in ionic liquids.

To achieve this goal I designed, synthesized and characterized a selection of ionic liquids. The selected ionic liquids were based in the imidazolium cation containing a functionalization in the alkyl side chain. The chosen anions were the bis(trifluorosulfonyl)imide, $[NTf_2]$, the dicyanamide, $[DCA]$ and the methylphosphite, $[C_1HPO_3]$.
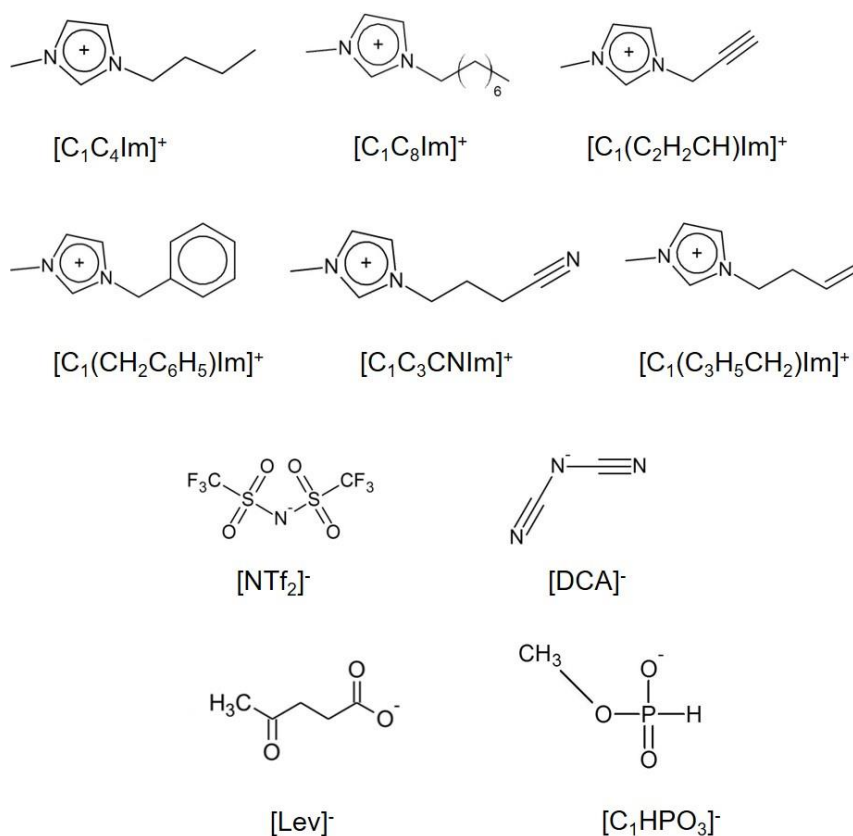
Figure 1: Cations and anions in the ionic liquids synthesized for this project

The influence on ethene absorption of the presence of three different metallic cations, lithium (I), nickel (II) and copper (II) in an ionic liquid was also studied.

Several parameters were considered for this primary evaluation, such as measurements of density, viscosity and absorption of each gas in the ionic liquids, since an ideal separation solvent should have a high absorption capacity and gas selectivity, low viscosity, high thermal stability and fast absorption kinetics for the selected gas.

The absorption of the 2 gases in the pure ionic liquids and ionic liquid + metallic salt solutions was measured in the temperature range between 303.15 K and 353.15 K and for pressures close to atmospheric. The ideal selectivity of the ionic liquid for the absorption of ethane compared to ethene was determined.

The determination of the gas solubility in function of the temperature allowed access to the thermodynamic properties of solvation of the gases in the ionic liquids, and a deeper understanding of the gas-ionic liquid interactions and the structure of the solution.

In some cases, molecular simulation results allowed the identification of the mechanisms of solvation and the preferential solvation sites for each gas in the different ionic liquids.

Problem addressed

Ethene and propene are the largest-volume organic chemical feedstock, being used as precursors to produce polymers (such as PVC, used of the majority of medical devices and sewage pipes), drugs, lubricants, anti-freeze, rubbers, solvents and fuel components.[1,2,3] These are mostly obtained from the separation of the light hydrocarbons components of naphtha, separated through cryogenic distillation.

Cryogenic distillation has been in use since the 1960's, for the ethane/ethene and propane/propene separation.[1,4] It requires large distillation towers (120-180 trays), low temperatures (-114°C) and high pressures (15-30 bar), resulting in a high capital and energy demanding process needing up to 120×10^{12} BTU/year, the equivalent of 30 months of UK electric energy demand.[5,6] This also represents 6% the industry's energy usage and around 75% of the product cost.

The high demand (236 million tons per year per annum)[2] and high purity[7] required for industrial applications of ethene and propene imply effective and reliable separation methods which are often difficult to implement. The implementation of an alternative process to cryogenic distillation with improved economic and environmental performance would represent a major advance in the sector.

The implementation of separation method based in an absorbent would also allow for the scale-down of the separation facilities and therefor the use of non-traditional sources for the capture of ethene such as waste, fermentation, microorganisms, fungus, plants, biorefineries (biomass). For example, it could be used to purify ethylene obtained from bioethanol through the Hummingbird process (BP and Technip).

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State of the art

Alternative processes for separating gaseous olefins from paraffins include ion exchanging resins[1], adsorption on high-surface-area SiO_2[2], on alumina[3], on zeolites[4] and molecular sieves[5], or on metallic organic frameworks[6], and the use of several types of membranes. [7, 8, 9]

Most of the alternatives proposed involve liquid or solid selective absorbents containing transition metals such as copper or silver, which are believed to form a complex with the unsaturated gas molecule.[7, 10-13] These alternatives have not been applied to an industrial scale due to several drawbacks linked to the synthesis, the efficacy, the reliability or the contamination of the different materials and also related to economical obstacles.[10, 11, 14]

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Key innovations

This work provided for the first time an interpretation of the difference in solubility and selectivity at the molecular level from both experimental and molecular simulation results. This knowledge has an impact in the design and development of new absorbents aiming to optimise the absorption capacity and separation selectivity of ethane/ethene and propane/propene and other gases. This work produced 1 patent for a new method for the synthesis of ionic liquids.

Relevant publications

L. Moura, M. Mishra, V. Bernales, P. Fuentealba, A. A. H. Padua, C. C. Santini and M. F. Costa Gomes, Effect of Unsaturation on the Absorption of Ethane and Ethylene in Imidazolium-Based Ionic Liquids, J. Phys. Chem. B 2013, 117, 7416-7425

L. Moura, W. Darwich, C. C. Santini and Margarida F. Costa Gomes, Imidazolium-based ionic liquids with cyano groups for the selective absorption of ethane and ethylene, Chem. Eng. J. 2015, 280, 755-762

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S. Stevanovic, A. Podgorsek, L. Moura, C. C. Santini, A. A. H. Padua and M. F. Costa Gomes, Absorption of Carbon Dioxide by Ionic Liquids with Carboxylate Anions, Int. J. of Greenh. Gas Con. 2013, 17, 78-88

This was the first collection, comparison and performance interpretation of all the published data concerning light hydrocarbon (ethane, ethene, ethyne, propane, propene, propyne) absorption and separation in ionic liquids. This "database" will serve as a guide for future research in the field.

Relevant publications

L. Moura, C. C. Santini and M. Costa Gomes, RCS book chapter 22: Gas separations using ionic liquids in Chemical process technology for a sustainable future. Editors: T. M. Letcher, J. L. Scott and D. A. Paterson

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Applications, implementations and results

Contrary to what is suggested in the literature, the solubility of unsaturated gases, such as ethene and propene is not always higher than of their saturated counterparts, ethane and propane. In fact, their solubilities range overlap.

Ethyne and propyne present the highest mole fraction solubilities, in imidazolium and/or pyrrolidinium based ionic liquids. Ethyne and propyne are followed by propane and propene with solubilities of the same order of magnitude for phosphonium based ionic liquids (larger molecular weights).

Ethane and ethene are one order of magnitude less soluble than ethyne in the same phosphonium based ionic liquids. For a low molecular weight ionic liquid such as $[C_1C_2Im][NTf_2]$ propyne is the most soluble gas, followed by ethyne and propene (3-5 times less soluble), propane and ethene (at least one order of magnitude less soluble than propyne and 3-4 times less soluble than ethyne and propene) and ethane (20 times less soluble than propyne, 4-7 times less soluble than propene and ethyne and 2 times less soluble than propane and ethene).

The tendencies observed for ethane, ethene, propane and propene 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 $P_{nmpq}^+ > N_{nmpq}^+ > C_nPyr^+ > C_nC_mPyrr^+ > C_nC_mIm^+$. In comparison, the solubility dependency in terms of the nature of the anion is much smaller, for the same gases.

The tendencies found for ethyne are the opposite. The influence of the cation size is much less important than the influence of the nature of the anion. The highest ethyne solubilities are found in ionic liquids containing anions with a Lewis base character, such as alkylphosphates, alkylphosphites and alkylsulphates. This is probably due to the presence of a relatively acidic proton in ethyne. The order of solubility of ethyne relative to anions for imidazolium and pyrrolidinium-based cations is: $C_nC_mPO_4^- > OAc^- > C_nHPO_3^- > C_nSO_4^- > TFA^- > BF_4^- > PF_6^- \approx NTf_2^-$. Ideal selectivities of 40 and 15 and mole fraction solubilities of 0.1 and 0.2 can be obtained for ethene/ethyne and propene/propyne separations, respectively.

The solubility data on ethane, ethene, ethyne and propyne (tables 1 and 2) provides a good start on a database in light hydrocarbon solubility in ILs.
This is a large amount of information and can be used sa a good basis for the development of a model that would allow the prediction of the solubility of these gases in other ionic liquids.

Table 1: Solubility of ethane, ethene, ethyne, propane, propene and propyne in several ionic liquids, expressed in Henry's law constant, K_H, the majority at 313 K

Gas

Ionic liquid	Ethane	Ethene	Ethyne	Propane	Propene	Propyne
[C₁C₂Im][NTf₂]	151-200	101-150	11-20	51-100	41-50	
[C₁(C₂H₂CH)Im][NTf₂]*	201-300	101-150				
[C₁C₄Im][NTf₂]*	101-150	101-150	11-20	51-100	21-30	
[C₁(C₃H₅CH₂)Im][NTf₂]*	101-150	101-150				
[C₁C₆Im][NTf₂]	51-100	151-200			41-50	
[C₁(CH₂C₆H₅)Im][NTf₂]*	51-100	101-150				
[C₁C₈Im][NTf₂]*	51-100	51-100				
[C₁C₁₀Im][NTf₂]	51-100					
[C₁C₃CNIm][NTf₂]*	201-300	101-150				
[(C₃CN)₂Im][NTf₂]	151-200	101-150				
[C₁C₁C₃CNIm][NTf₂]		151-200				
[C₁C₁COOC₅Im][NTf₂]	51-100					
[C₁C₁COOC₂OC₂Im][NTf₂]	51-100					
[C₁C₁COOC₂OC₂OC₄Im][NTf₂]	51-100					
[C₁C₄Im][BETI]		51-100			11-20	
[C₁C₄Im][FAP]	51-100					
[C₁C₆Im][FAP]	51-100					
[C₁C₂Im][DCA]	over 600	301-400		301-400	151-200	
[C₁C₄Im][DCA]*	301-400	201-300				
[C₁C₃CNIm][DCA]*	over 600	301-400				
[C₁C₁C₃CNIm][DCA]		301-400				
[C₁C₄Im][OAc]		151-200	0-10			
[C₁C₄Im][n-C₁₅H₃₁COO]		51-100				
[C₁C₄Im][n-C₁₇H₃₅COO]		51-100				
[C₁C₂Im][PF₆]	301-400	151-200		151-200	51-100	
[C₁C₄Im][PF₆]	301-400	151-200	11-20		51-100	
[C₁C₂Im][BF₄]			11-20			
[C₁C₄Im][BF₄]	301-400	201-300	11-20	201-300	51-100	
[C₁C₈Im][BF₄]		101-150				
[C₁C₄Im][TFA]		101-150	11-20			
[C₁C₁Im][C₁HPO₃]		301-400	0-10			0-10
[C₁C₂Im][C₁HPO₃]			0-10			
[C₁C₂Im][C₂HPO₃]		201-300	0-10		51-100	0-10
[C₁C₄Im][C₁HPO₃]*	201-300	101-150	0-10			0-10
[C₁C₄Im][C₄HPO₃]		101-150	0-10		41-50	0-10
[C₂C₄Im][C₂HPO₃]		101-150	0-10		41-50	0-10
[C₁C₁Im][(C₁)₂PO₄]		201-300	0-10			
[C₁C₂Im][(C₁)₂PO₄]			0-10			
[C₁C₂Im][(C₂)₂PO₄]						
[C₁C₄Im][(C₁)₂PO₄]		101-150	0-10			
[C₁C₄Im][(C₄)₂PO₄]						
[C₁C₁Im][C₁SO₄]			11-20			

*measurements performed in the context of this work

Solubility range

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	

Table 2: Table 3: Solubility of ethane, ethene, ethyne, propane, propene and propyne in several ionic liquids, expressed in Henry's law constant, K_H, the majority at 313 K

Gas

Ionic liquid	Ethane	Ethene	Ethyne	Propane	Propene	Propyne
$[C_1C_2Im][C_1SO_4]$			0–10			
$[C_1C_2Im][C_2SO_4]$			0–10			
$[C_1C_4Im][C_1SO_4]$		201–300	0–10			
$[C_1C_1COOC_5Im][C_8SO_4]$	51–100					
$[C_1C_2Im][CF_3SO_3]$	301–400	201–300		201–300	51–100	
$[(C_2SO_2C_2)C_1Im][CF_3SO_3]$		151–200			101–150	
$[C_1C_6Pyrr][NTf_2]$	51–100	51–100				
$[C_1C_4Pyrr][NTf_2]$	101–150	51–100	11–20			
$[C_1C_4Pyrr][FAP]$	51–100					
$[C_1C_4Pyrr][DCA]$		151–200	0–10			
$[C_1C_4Pyrr][OAc]$		101–150	0–10			
$[C_1C_4Pyrr][TFA]$		101–150	0–10			
$[C_1C_1Pyrr][C_1HPO_3]$		301–400	0–10			
$[C_1C_2Pyrr][C_2HPO_3]$		201–300	0–10			
$[C_1C_4Pyrr][C_4HPO_3]$		101–150	0–10			
$[N_{(1)444}][NTf_2]$					11–20	
$[N_{(4)111}][NTf_2]$		101–150			41–50	
$[N_{(4)113}][NTf_2]$		101–150			41–50	
$[N_{(6)111}][NTf_2]$		101–150			21–30	
$[N_{(6)113}][NTf_2]$		101–150			31–40	
$[N_{(10)111}][NTf_2]$		51–100			21–30	
$[N_{(6)222}][NTf_2]$		51–100			21–30	
$[N_{(10)113}][NTf_2]$		51–100			21–30	
$[N_{(1)888}][NTf_2]$		21–30				
$[N_{1132\text{-}OH}][NTf_2]$	151–200					
$[P_{(14)666}][NTf_2]$		11–20			0–10	
$[P_{(14)666}][Cl]$		21–30				
$[P_{(14)666}][FAP]$	0–10				0–10	
$[P_{(14)666}][DCA]$		41–50			0–10	
$[P_{(2)444}][(C_2)_2PO_4]$		51–100			11–20	
$[P_{4444}][TMPP]$	21–30	21–30		0–10		
$[P_{(14)666}][TMPP]$	11–20	11–20		0–10	0–10	
$[P_{(14)444}][DBS]$		21–30		0–10		

Solubility range

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	

For this project, a selected group of ionic liquids were used to test the influence of structural modifications in the ionic liquid on the absorption of ethane and ethene. The presence of: an increasing alkyl side-chain on the cation of the ionic liquid; unsaturations on the alkyl side-chain on the cation of the ionic liquid; cyano groups in the cation or anion of the ionic liquid or both and a phosphite based anion in the ionic liquid were tested for their influence on the density and viscosity of the ionic liquid and in the solubility of ethane and ethene. The selected ionic liquids were synthesized via a one-step or two-step synthesis path, with purities of at least 99%. The ionic liquids were characterized by proton and carbon NMR spectroscopy, high resolution mass spectroscopy, and density and viscosity measurements. Solutions of ionic liquid with metallic salts of lithium (I), nickel (II) and copper (II) were also characterized in terms of density and viscosity.

The ionic liquid with the highest density is $[C_1(C_2H_2CH)Im][NTf_2]$ and the one with the lowest is $[C_1C_4Im][DCA]$. The ionic liquid with highest viscosity is $[C_1C_4Im][Lev]$ and the one with the lowest is $[C_1C_4Im][DCA]$. The presence of unsaturations in the alkyl chain of the cation can lead to viscosities up to 2 times greater than in ionic liquids with saturated side alkyl chains.

Small changes in the structure of the ionic liquid can have large effects in the ethane and ethene solubility and ethane/ethene separation selectivity of the ionic liquid. 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 $C_1HPO_3^-$ or DCA, lead to decreases in the solubility of ethane and ethylene, when compared to a reference ionic liquid, $[C_1C_4Im][NTf_2]$. The only exception is for $[C_1(C_3H_5CH_2)Im][NTf_2]$, where ethane solubility is not greatly affected. The introduction of these groups in the ionic liquid also leads to increases in the ethene selectivity. The solubility of ethane is more affected by changes in the ionic liquid than ethene. 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 ethane and ethene solubility but the increase was larger for the saturated gas. The only exceptions are for the ionic liquid containing a double bond (where the solubility of ethane is similar and the solubility of ethene decreases 14%) and containing a benzyl group (where the solubility of both gases decreases in a similar way).

For the group of ionic liquids tested, the difference in solubility of the two gases in each ionic liquid is due to entropic factors, which means that the solubility is still controlled by non-specific interactions, in the same way as it was observed in the literature analysis. The interactions between the selected group of ionic liquids and ethene were not strong or specific enough to gain against what is lost due to entropy. This was further confirmed by observing that for the group of ionic liquids selected for this study, the ones that present higher ethene absorption capacity and lower ideal selectivity are the ones with highest molar volume and vice-versa, as can be observed in figure 2.

For the group of ionic liquids tested the one possessing the largest ethene capacity and lowest ideal selectivity corresponds to the one containing the largest alkyl chain in the cation, $[C_1C_8Im][NTf_2]$. The ionic liquid family that presents the best selectivity and smallest absorption capacity for ethene is the one containing cyano groups; $[C_1C_3CNIm][NTf_2]$, $[C_1C_4Im][DCA]$ and $[C_1C_3CNIm][DCA]$.

The influence in ethene solubility of the presence of three different metallic cations, lithium (I), nickel (II) and copper (II) in an ionic liquid was also studied. The presence of copper was found to cause a large increase in the solubility of ethene. The solubility, at 303 K, of the metallic salts in $[C_1(CH_2C_6H_5)Im][NTf_2]$ decreases with the size of the metallic cation. The addition of these metallic salts to the ionic liquid caused an increase its density of up to 2% for the salt types and concentrations studied and an increase in viscosity of 42%, 50% and 34% upon addition of the lithium, nickel and copper salts respectively and at 298 K. The addition of copper salts almost doubles the absorption capacity of ethene in the ionic liquid $[C_1(CH_2C_6H_5)Im][NTf_2]$. We observe that metallic cations such as lithium and nickel slightly affect the solubility of ethene, and not through coordination of the unsaturated gas.
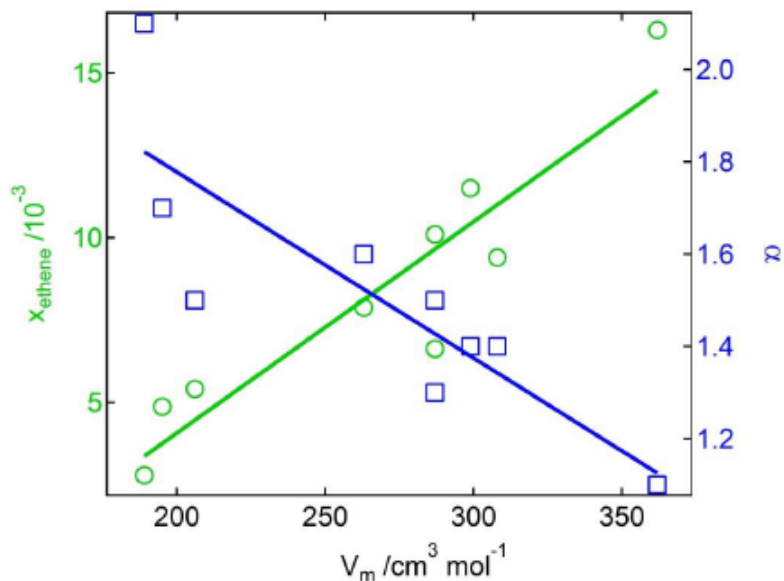
Figure 2: Molar volume of the ionic liquids, in cm³ mol⁻¹, versus the molar fraction absorption capacity of each ionic liquid for ethene and versus the ionic liquids ideal selectivities

I plan to develop ionic liquids, deep eutect solvents and other liquid absorbents containing functionalizations, anions (such as $AlCl_4^-$) or metals that could promote a specific interaction with ethene in order to obtain absorbents with higher capacity and selectivity, which are necessary in an industrial application.

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 it should be taken into account into developing an ionic liquid for separation purposes.

This work provided the basis, the knowledge and the spark to write and secure a prestigious UK Royal Academy of Engineering Research Fellowship to develop and test liquid technologies based in ionic liquids and deep eutectic solvents for gas separations under realistic conditions, with collaboration and support from Shell (UK/Netherlands) and Solvay (UK/Canada/Belgium).