



## Imidazolium-based ionic liquids with cyano groups for the selective absorption of ethane and ethylene

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### HIGHLIGHTS

- Absorption of ethane and ethylene were determined in different imidazolium ionic liquids.
- The solubility of the gases decreases with the presence of cyano or propyl groups in the cation.
- The solubility of ethane and ethylene is lower in ionic liquids with dicyanamide or phosphite anions.
- Ethane/ethylene ideal selectivity increases with the presence of cyano groups in the ionic liquid.

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### ABSTRACT

The density, viscosity and absorption of ethane and ethylene were determined experimentally, as a function of temperature and at atmospheric pressure, in different imidazolium-based ionic liquids: 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide, [C<sub>1</sub>C<sub>8</sub>Im][NTf<sub>2</sub>], 1-methyl-3-(propyl-3-yl)imidazolium bis(trifluoromethanesulfonyl)imide [C<sub>1</sub>(C<sub>2</sub>H<sub>2</sub>CH)Im][NTf<sub>2</sub>], 1-(3-cyanopropyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [C<sub>1</sub>C<sub>3</sub>CNIIm][NTf<sub>2</sub>], 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide [C<sub>1</sub>C<sub>3</sub>CNIIm][DCA], 1-butyl-3-methylimidazolium dicyanamide, [C<sub>1</sub>C<sub>4</sub>Im][DCA] and 1-butyl-3-methylimidazolium methylphosphite [C<sub>1</sub>C<sub>4</sub>Im][C<sub>1</sub>HPO<sub>3</sub>]. The densities and viscosities of the ionic liquids studied are strongly dependent on the anion and, at 313 K, follow the order: [C<sub>1</sub>(C<sub>2</sub>H<sub>2</sub>CH)Im][NTf<sub>2</sub>] > [C<sub>1</sub>C<sub>3</sub>CNIIm][NTf<sub>2</sub>] > [C<sub>1</sub>C<sub>3</sub>CNIIm][DCA] > [C<sub>1</sub>C<sub>4</sub>Im][C<sub>1</sub>HO<sub>3</sub>] > [C<sub>1</sub>C<sub>4</sub>Im][DCA] and [C<sub>1</sub>C<sub>3</sub>CNIIm][NTf<sub>2</sub>] > [C<sub>1</sub>C<sub>3</sub>CNIIm][DCA] > [C<sub>1</sub>C<sub>4</sub>Im][C<sub>1</sub>HPO<sub>3</sub>] > [C<sub>1</sub>(C<sub>2</sub>H<sub>2</sub>CH)Im][NTf<sub>2</sub>] > [C<sub>1</sub>C<sub>4</sub>Im][DCA], respectively. The differences in the molecular structures of the ionic liquids allowed the identification of the influence of increasing the alkyl side chain of the cation, of the presence of unsaturated C≡C and C≡N bonds on the alkyl side chain of the cation and finally of a phosphite based anion on the selective absorption of ethane and ethylene. The solubility of ethylene is higher than that of ethane in the ionic liquids studied and varies from 18.41 × 10<sup>-3</sup> in [C<sub>1</sub>C<sub>8</sub>Im][NTf<sub>2</sub>] at 303.17 K to 1.603 × 10<sup>-3</sup> in [C<sub>1</sub>C<sub>4</sub>Im][DCA] at 343.61 K. The introduction of the different functional groups leads to a decrease on the gas absorption compared with that of [C<sub>1</sub>C<sub>8</sub>Im][NTf<sub>2</sub>] but to an increase of the ideal separation selectivity of ethane and ethylene.

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### 1. Introduction

Ethylene and propylene have a growing global demand owed to their widespread use as precursors for the production of polymers, lubricants, rubbers, solvents and fuel components [1]. Presently, these gases are mostly obtained from the separation of the light hydrocarbons components of naphtha through cryogenic

distillation. Cryogenic distillation is one of the most costly processes in the petrochemical industry, the separation of ethylene and propylene from ethane and propane, respectively, taking up to 6% of the energy used in petrochemical industry distillation [1,2].

The search for alternative separation processes led to the investigation of ionic liquids as new separating agents for olefin/paraffin gas separation, serving as absorbents or alternatively as solvents for the chemical complexation of olefins with silver or copper salts [3,4], ion exchanging resins [2], adsorption on high surface-area

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## Nomenclature

### List of symbols

$\alpha$	ideal selectivity	$^1\text{H}$	hydrogen-1
$\rho$	density	AMVn	automated micro viscosimeter
$\Delta\rho$	density correction factor for high viscosities	$\text{C}_2\text{H}_4$	ethene
$\delta$	relative deviation	$\text{C}_2\text{H}_6$	ethane
$\eta$	dynamic viscosity	$\text{CD}_2\text{Cl}_2$	dichloromethane
$\mu$	chemical potential	$\text{C}_n\text{H}_m$	hydrocarbons
$\phi$	fugacity coefficient	DMA	density meter from Anton Paar
$\Delta_{sol}G^\infty$	Gibbs energy of solvation	$\text{H}_2$	molecular hydrogen
$\Delta_{sol}H^\infty$	enthalpy of solvation	HRMS	high resolution mass spectra
$\Delta_{sol}S^\infty$	entropy of solvation	IL(s)	ionic liquid(s)
$a$	density fitting parameter	K	degrees kelvin
$A_i$	adjustable parameters of the empirical equation of gas absorption correlation	$m$	amount of ionic liquid in grams
$b$	density fitting parameter	Mpa	megapascal
$f$	fugacity	mPa	milipascal
$k$	adjustable parameter of VFT equation	$\text{N}_2$	molecular nitrogen
$K_H$	Henry's law constant	NMR	nuclear magnetic resonance
$p^0$	standard-state pressure	$\text{O}_2$	molecular oxygen
$pVT$	pressure–volume–temperature	Pa	Pascal
$R$	gas constant	ppm	parts per million
$C$	adjustable parameter of VFT equation	$R$	gas constant
$^{13}\text{C}$	carbon-13	T	temperature
		VFT	Vogel–Fulcher–Tammann
		Z	compressibility factor

$\text{SiO}_2$  [5], on alumina [6], on zeolites [7] and molecular sieves [8], or on metallic organic frameworks [9], and the use of several types of membranes [10]. The use of absorbent agents can be less energy demanding but it is often technologically more challenging as the absorbent needs to be efficiently separated and then recycled with reasonable purity. Membrane separation processes are considered as a very promising as they allow the use of small, compact and clean units that require low energy but that are still difficult to scale-up as the active separating agents eventually become saturated and need to be regenerated, rendering the continuous running of the process very difficult.

Ionic liquids aroused interest owing to their assumed ability to selectively and efficiently absorb olefins even if the molecular reasons for this behavior are not yet well understood. In order to gain further insight on the mechanisms involved and to favor the selective absorption of gaseous alkenes, we have proposed the use of imidazolium-based ionic liquids with alkyl side-chains containing unsaturations [11]. We have observed that the introduction of double bonds or phenyl groups in the alkyl side-chains of imidazolium based ionic liquids decreases the solubility of both gases and only has a small effect in the ideal selectivity for the separation of gaseous alkane/alkene mixtures. The effect of the introduction of nitrile groups in the ionic liquids has been previously reported. Enhanced separation abilities were claimed by Mokrushin et al. [12] and Xing et al. [13] have reported that the introduction of nitrile groups in the alkyl side-chains of imidazolium-based ionic liquids contributed to an increase of the selectivity for the separation of ethylene from ethane – from 1.37 to 1.61 and then to 2.01 (introduction of two nitrile groups) – even if the solubility of ethylene significantly decreased.

In this work, the influence of the presence of functionalities such as cyano ( $-\text{C}\equiv\text{N}$ ) or propyne ( $-\text{C}\equiv\text{C}-$ ) groups in the molecular structure of imidazolium-based ionic liquids on the ethane and ethylene absorption is studied. The solubility of ethane and ethylene was measured in different ionic liquids as a function of

temperature and from its variation it was possible to calculate the thermodynamic properties of solvation, thus permitting an insight into the mechanisms involved in the solvation of the two gases.

## 2. Experimental

### 2.1. Materials

Linde Gas supplied the gases used for this study: ethane 3.5, mole fraction purity of 0.9995 (impurities are comprised of other  $\text{C}_n\text{H}_m$  at  $\leq 450$  ppm) and ethylene 2.8, mole fraction purity of 0.998 (impurities are comprised of other  $\text{C}_n\text{H}_m \leq 1800$  ppm,  $\text{O}_2 \leq 30$  and  $\text{N}_2 \leq 150$ ). All gases were used as received from the manufacturer.

1-Methylimidazole (>99%) (Aldrich), chlorobutane, benzyl chloride and 4-chloro-1-butene (>99%, Aldrich) and 3-chloro-1-propene (>99%, Aldrich) were distilled prior to use. Bis(trifluoromethanesulfonyl)imide lithium salt (Solvionic) was used without further purification.

The ionic liquids used in this work, 1-methyl-3-(propyn-3-yl)imidazolium bis(trifluoromethanesulfonyl)imide [ $\text{C}_1(\text{C}_2\text{H}_2\text{CH})\text{Im}$ ][NTf<sub>2</sub>], 1-(3-cyanopropyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [ $\text{C}_1\text{C}_3\text{CNIm}$ ][NTf<sub>2</sub>], 1-(3-cyanopropyl)-3-methylimidazoliumdicyanamide [ $\text{C}_1\text{C}_3\text{CNIm}$ ][DCA] and 1-butyl-3-methylimidazolium methylphosphite [ $\text{C}_1\text{C}_4\text{Im}$ ][ $\text{C}_1\text{HPO}_3$ ] were synthesized as previously reported and as described in the [Supplementary Information](#). [14–17] The ionic liquid 1-butyl-3-methylimidazolium dicyanamide [ $\text{C}_1\text{C}_4\text{Im}$ ][DCA] was obtained from Solvionic with a purify of 98% and 1-methyl-3-octyl-imidazolium bis(trifluoromethanesulfonyl)imide [ $\text{C}_1\text{C}_8\text{Im}$ ][NTf<sub>2</sub>] was kindly provided by laboratory QUILL (Queen's University Ionic Liquid Laboratory), Belfast, Northern Ireland, UK with a purity higher than 99%. Their structures are represented in [Fig. 1](#).

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