Ionic liquids for the separation of gaseous hydrocarbons

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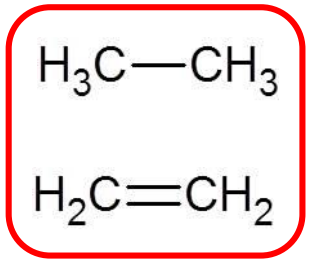
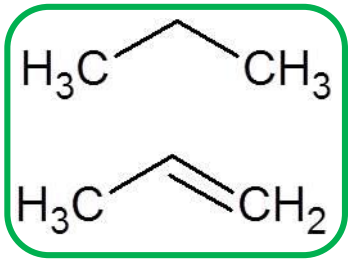
Summary

- Economic context
  - Ionic liquids as separation agents
- State of the art: Ionic liquids for hydrocarbon separation
- Choice of ionic liquids
- Ethane and ethylene solubility in ionic liquids
- Conclusions
- Perspectives and future work

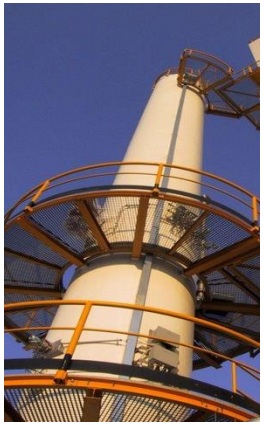
Economic context





Hydrocarbon gas

Cryogenic distillation



High energy

AIM

Ionic liquids

Low energy

30 months of UK electric energy demand

Chemical Market Resources
ICIS 2013 Data for 2012
Technip March 2014
Petrochemicals Europe

Oil & Gas Journal
Chemical Market Resources
Natural Gas Impact on Resin, Capital & Coste, February 2013

Impact

Ethylene use and capture

Crop growth

Fruit and vegetable ripening agent

Less pollutant/energy impact

Smaller scale applications

Non-traditional/sustainable sources

Biorefineries / recycling

Knowledge of separation technology

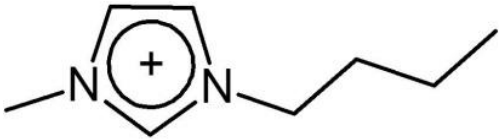
Job creation

Ionic liquids

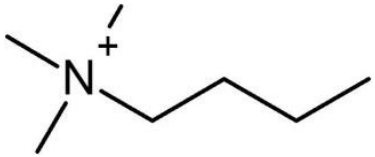
Molten salts having a T_m below 100°C

- Negligible vapour pressure
- Designer solvents

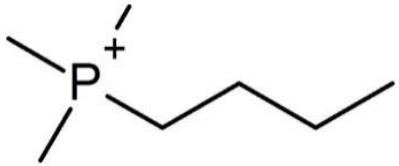
Cations



Imidazolium
$[C_nC_mIm]^+$

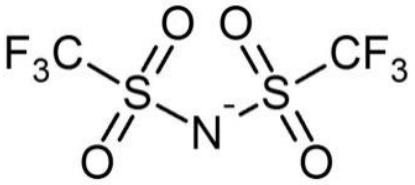


Ammonium
$[C_nC_mC_pC_qN]^+$

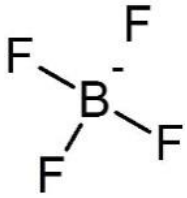


Phosphonium
$[C_nC_mC_pC_qP]^+$

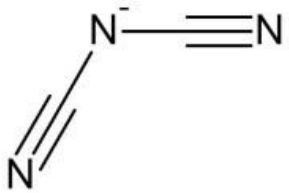
Anions



Bistriflamide
$[NTf_2]^-$



Tetrafluoroborate
$[BF_4]^-$



Dicyanamide
$[DCA]^-$

Wasserscheid, P. and Welton, T. Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2002

Ionic liquids as separating agents

- Transport and storage of AsH_3, PH_3, and BF_3 by Air Products
- Capture of CO_2 by ION Engineering
- **Hycapure™ -** Mercury removal from natural gas
  - 99.997% mercury removal
  - Commercial operation (30 m^3) since 2011

PETRONAS

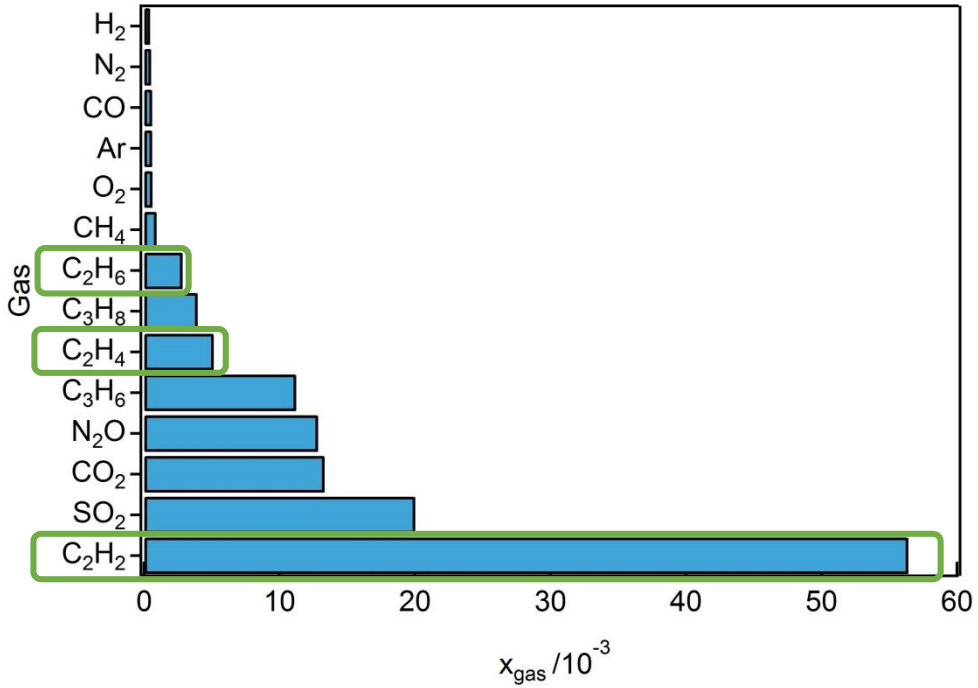
QUILL

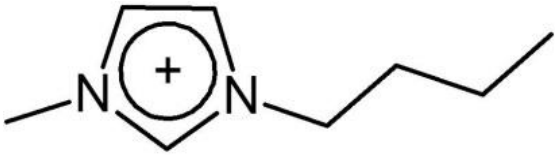
BASF website
Dalton Trans., 2015, 44, 8617

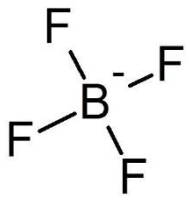
Ionic liquids as separating agents

At 313 K and 1 bar

ILs solubilize gases



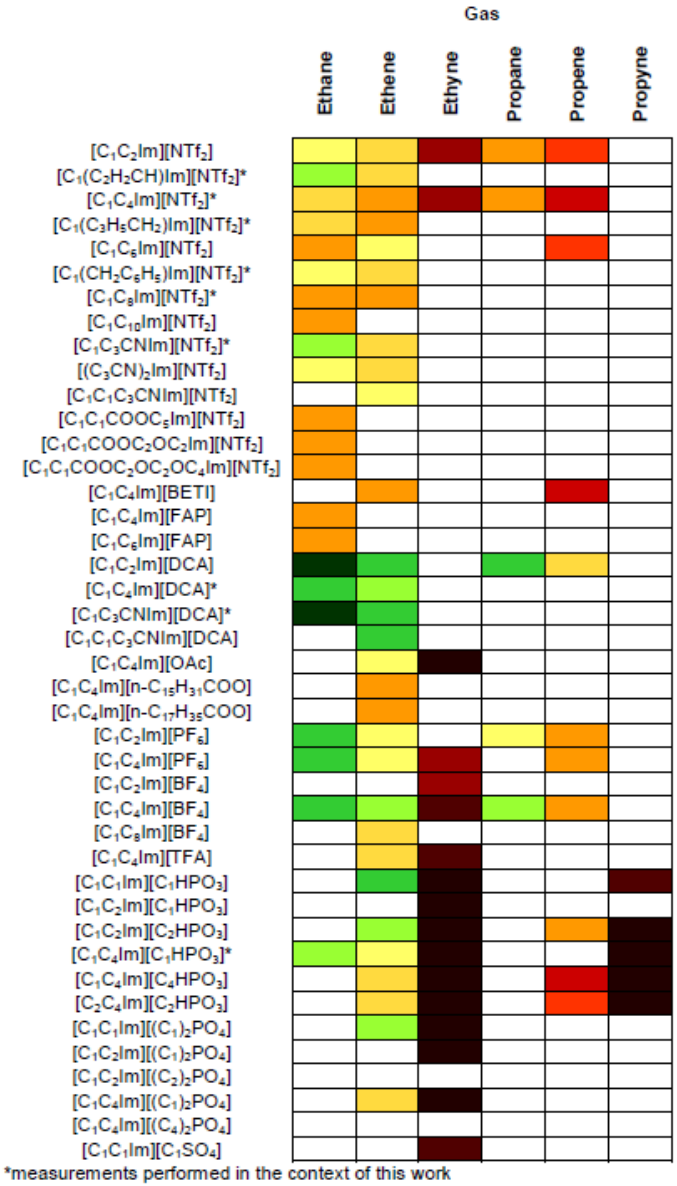




- Are unsaturated hydrocarbons always more soluble than saturated ones?
- No systematic studies
- Focus in ethane/ethylene separation

Anthony et al., J. Phys. Chem. B 2005
Jacquemin et al., J. Chem. Thermodyn. 2006
Anderson, Dixon and Brennecke, Acc. Chem. Res. 2007

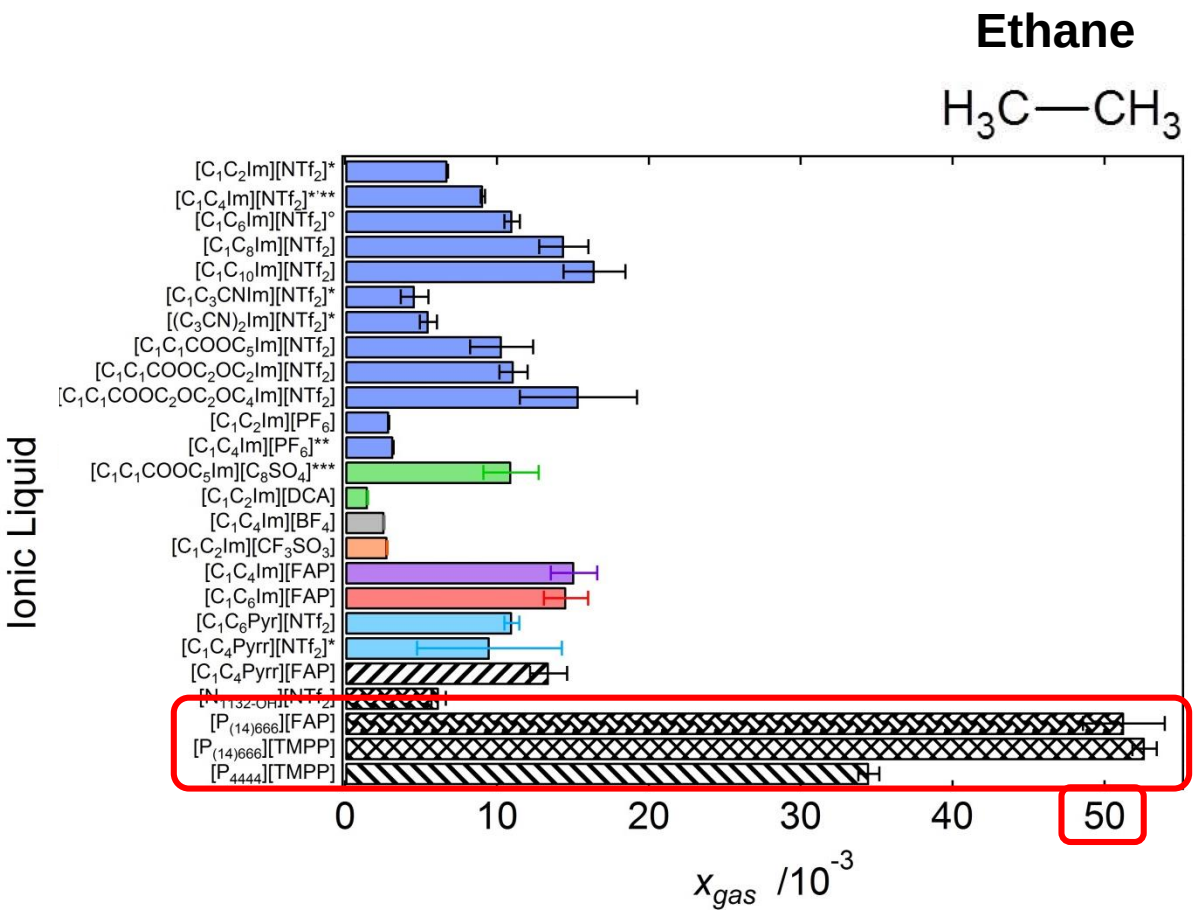
Ionic liquids in hydrocarbon separation



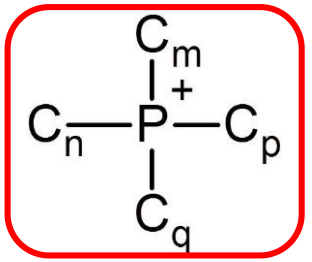
Building of a database

Moura, Santini, Costa Gomes, Gas separations using ionic liquids in Chemical Process technology for a sustainable future, RCS book

Ionic liquids in hydrocarbon separation



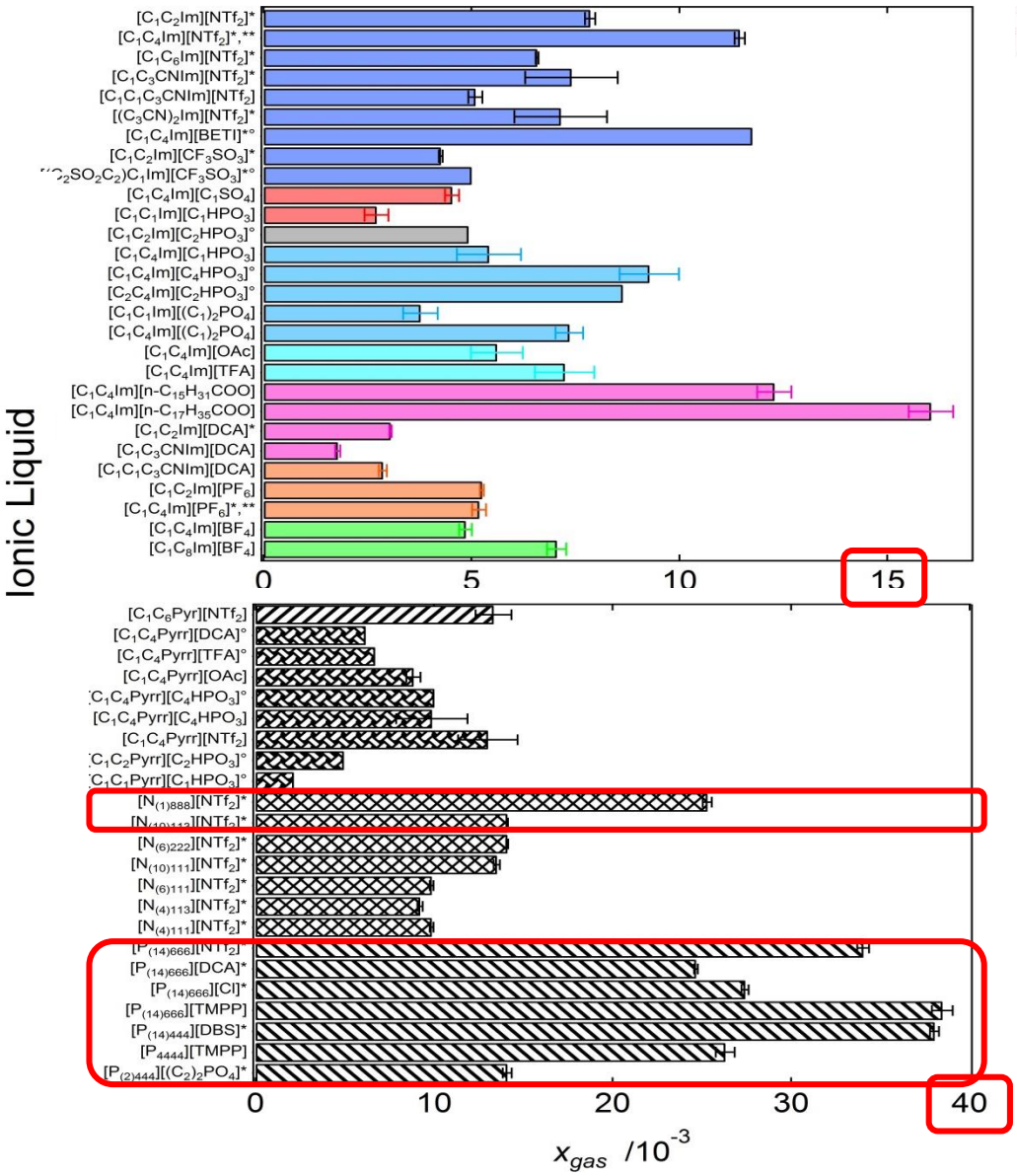
Highest solubilities



- Little effect of anion

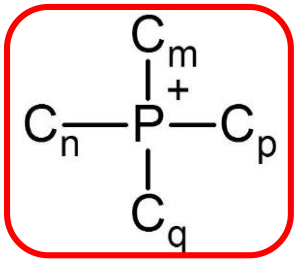
Moura, Santini, Costa Gomes, Gas separations using ionic liquids in Chemical Process technology for a sustainable future, RCS book

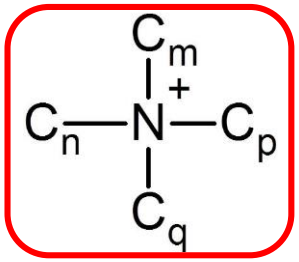
Ionic liquids in hydrocarbon separation



$H_2C{=}CH_2$ **Ethylene**

Highest solubilities





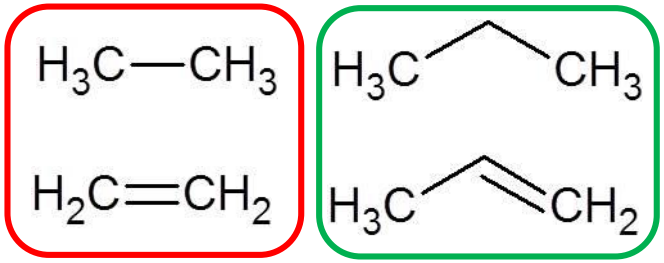
- Little effect of anion

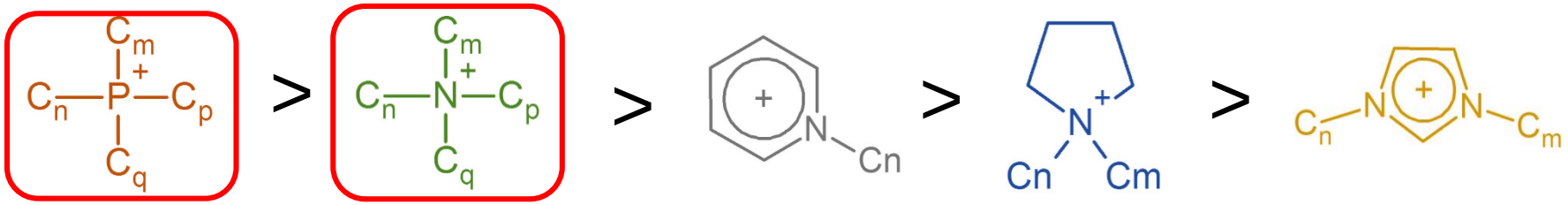
Moura, Santini, Costa Gomes, Gas separations using ionic liquids in Chemical Process technology for a sustainable future, RCS book

Ionic liquids in hydrocarbon separation

In summary

For ethane, ethylene, propane and propene



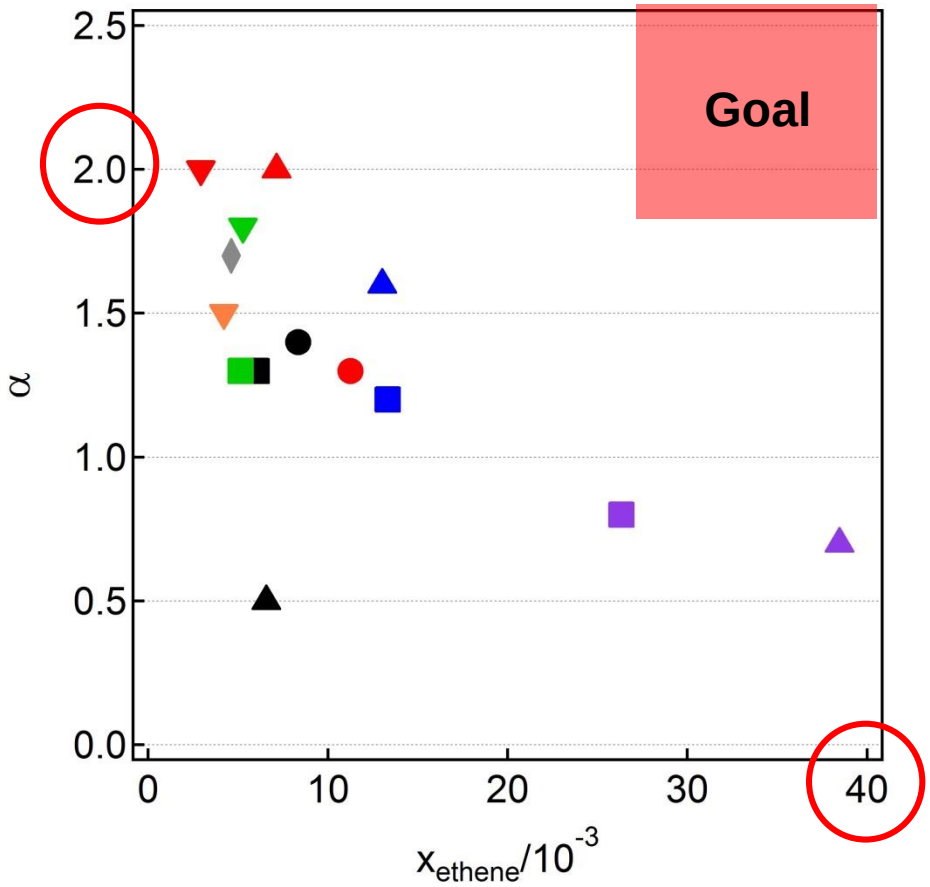


- Cations with large non-polar domains
- Little influence of the anion

Ethane/ethylene separation

Ethane $H_3C—CH_3$

Ethylene $H_2C=CH_2$



Ideal selectivity

$$\alpha = \frac{x_{C_2H_4}}{x_{C_2H_6}}$$

Mole fraction

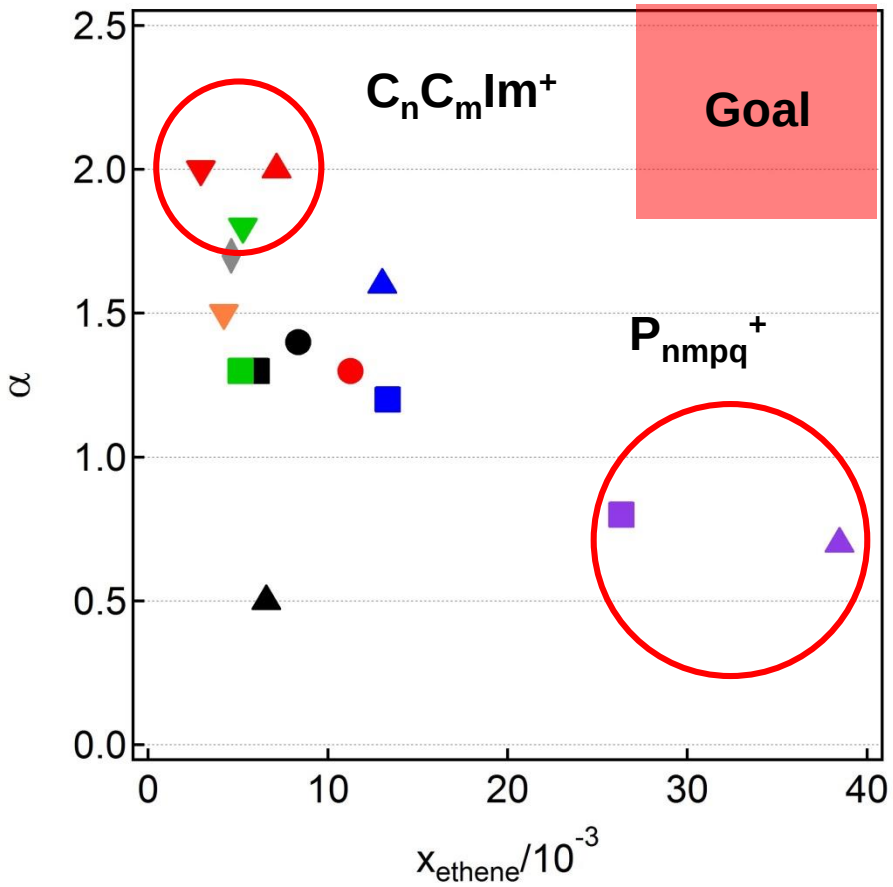
$$x_2 = \frac{n_2^{liq}}{\left(n_1^{liq} + n_2^{liq}\right)}$$

Single gas solubility experiments

Ethane/ethylene separation

Ethane $H_3C—CH_3$

Ethylene $H_2C=CH_2$



Strategy

~~**Phosphonium, $[P_{nmpq}]^+$**~~

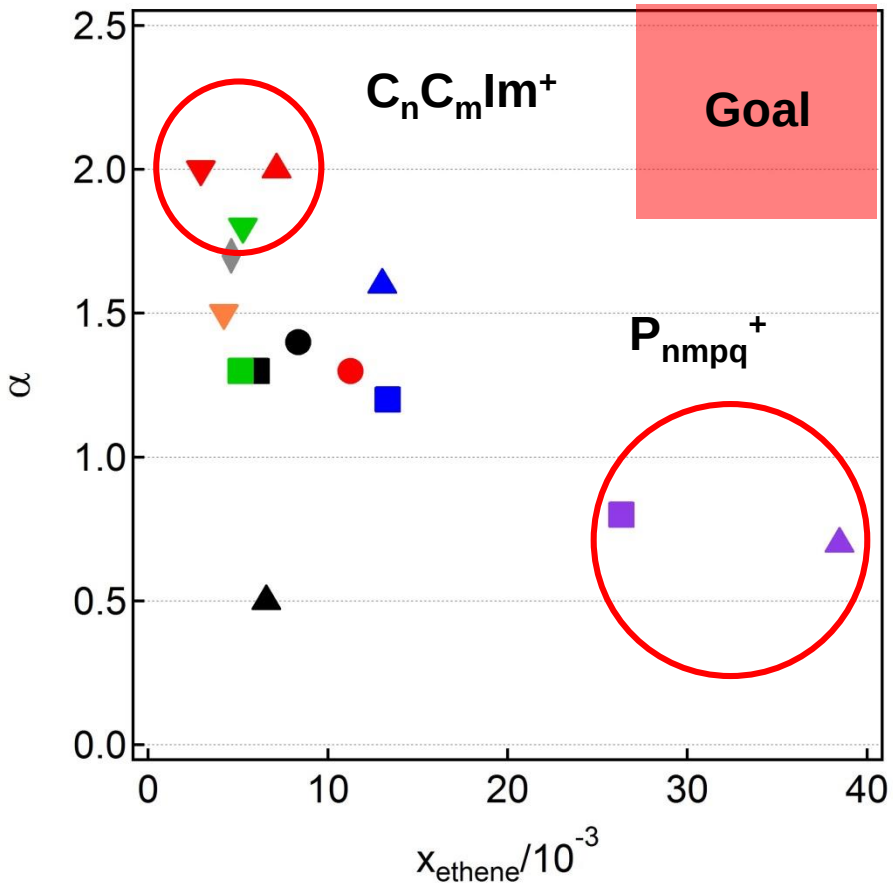
- High ethylene and ethane absorption
- Not specific
- Very viscous or solid

Wasserscheid *et al. Chem. Eng. Technol.* 2010

Ethane/ethylene separation

Ethane $H_3C—CH_3$

Ethylene $H_2C=CH_2$



Strategy

Imidazolium, $[C_nC_mIm]^+$

- Higher selectivity
- Easy functionalization, know-how

$[NTf_2]^-$

- High ethane and ethylene solubility
- Low viscosity, easy to purify, known properties

Dicyanamide, $[DCA]^-$

- Low viscosity, presence of cyano groups leads interesting propane/propene selectivity

Wasserscheid *et al. Chem. Eng. Technol.* 2010

Choice of ionic liquids

How to increase the ionic liquid-ethylene interactions?

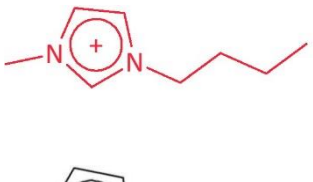
π-interactions types

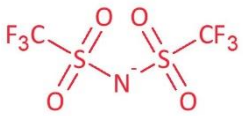
- π-π (aromatic or non-aromatic)
- π-cation
- Anion-π
- Polar-π
- Metal-π

Wasserscheid *et al. Chem. Eng. Technol.* 2010

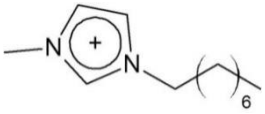
Choice of ionic liquids

1. Influence of the length of the alkyl side chain of the cation (NTf_2 anion)



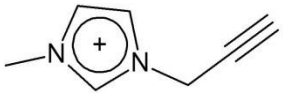


[C_1C_4Im][NTf_2]

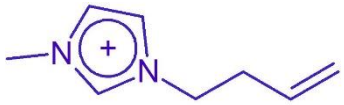


[C_1C_8Im][NTf_2]

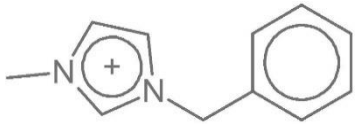
2. Influence of unsaturations in the alkyl side chain of the cation (NTf_2 anion)



[$C_1(C_2H_2CH)Im$][NTf_2]

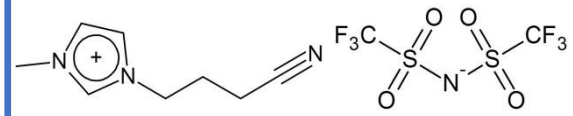


[$C_1(C_3H_5CH_2)Im$][NTf_2]

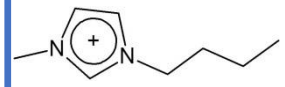


[$C_1(CH_2C_6H_5)Im$][NTf_2]

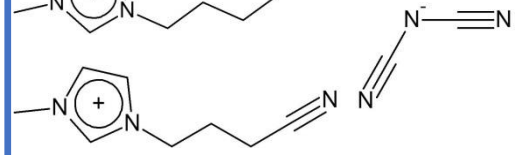
3. Influence of cyano groups



[C_1C_3CNIm][NTf_2]



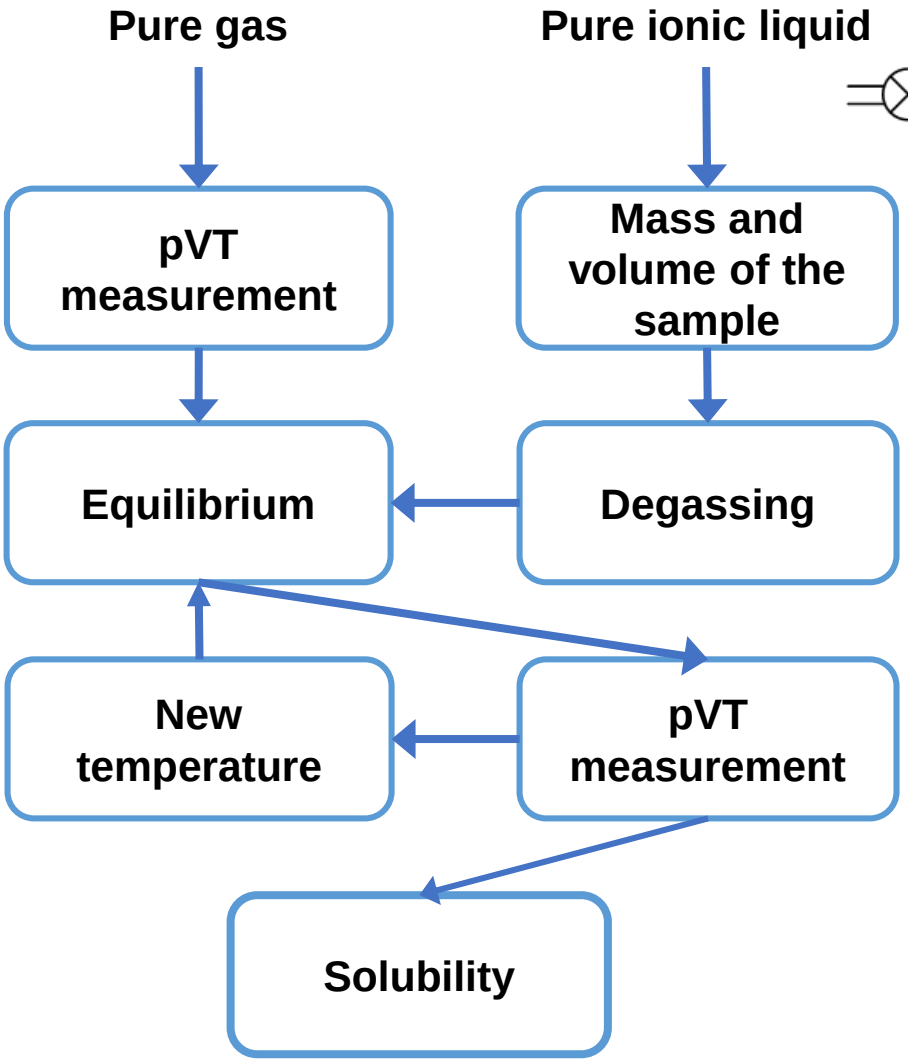
[C_1C_4Im][DCA]

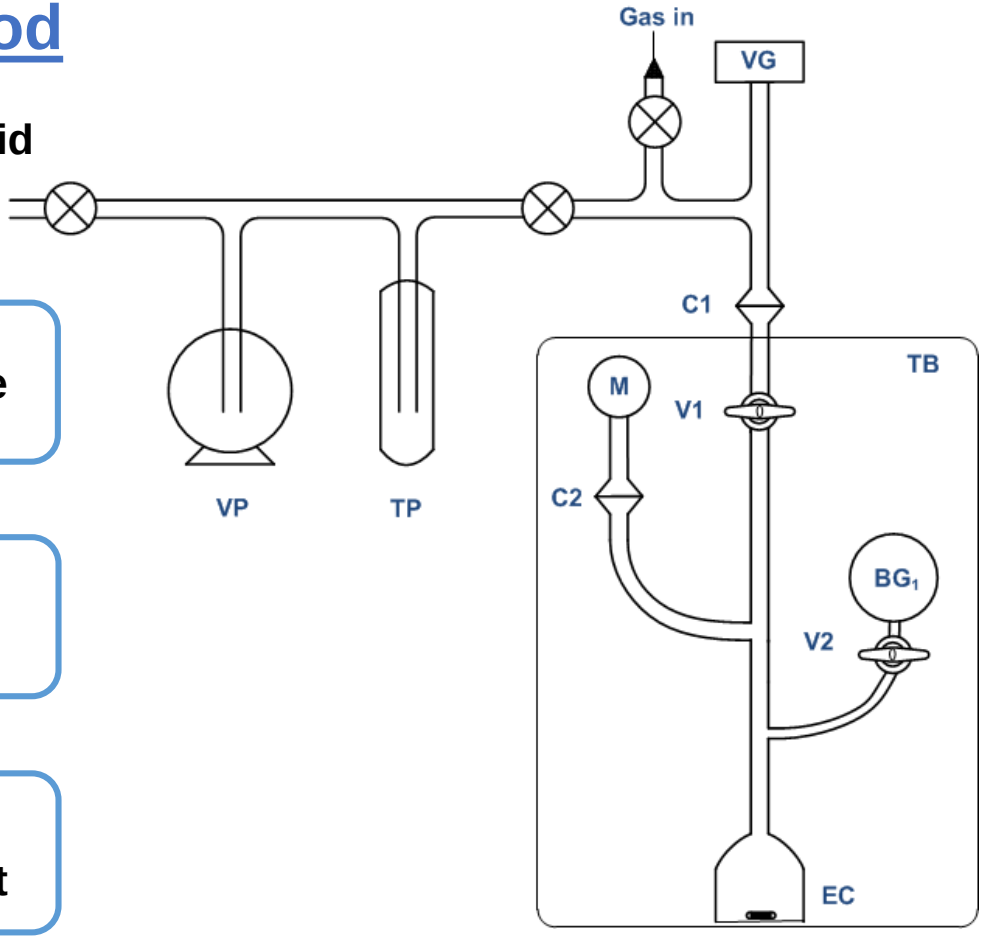


[C_1C_3CNIm][DCA]

Solubility measurements

Isochoric saturation method





- Accurate and precise measurements
- 1 liquid-gas pair – 1 month

Solubility measurements

1. Amount of gas in the ionic liquid

$$n_2^{liq} = \frac{p_{ini} V_{VG}}{\left[Z_2(p_{ini}, T_{ini}) RT_{ini}\right]} - \frac{p_{eq}\left(V_{tot} - V_{liq}\right)}{\left[Z_2(p_{eq}, T_{eq}) RT_{eq}\right]}$$

$$Z = 1 + \frac{pB}{RT}$$

Initial amount of gas Amount of free gas

2. Mole fraction

$$x_2 = \frac{n_2^{liq}}{\left(n_1^{liq} + n_2^{liq}\right)}$$

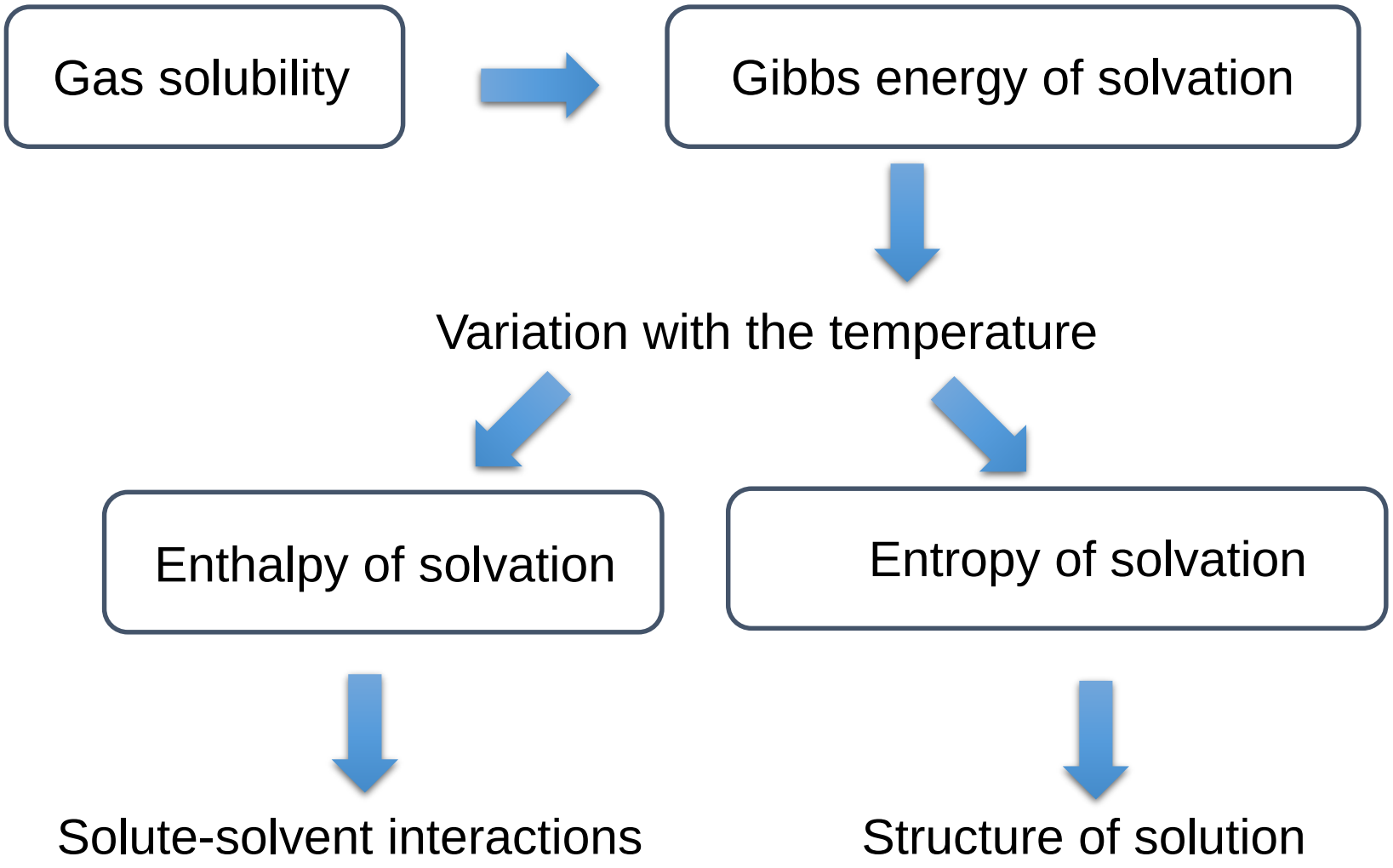
3. Henry's law constant

$$K_H \equiv \lim_{x_2 \to 0} \frac{f_2(p, T, x_2)}{x_2} \cong \frac{\phi_2(p_{eq}, T_{eq}) p_{eq}}{x_2}$$

$$\phi = e^{Bp/RT}$$

Solubility measurements

Thermodynamic properties of solvation



Solubility measurements

Thermodynamic properties of solvation

x_2

$$\Delta_{solv}G^{\infty} = RT\ln\left(\frac{K_H}{p^0}\right)$$

Variation with the temperature

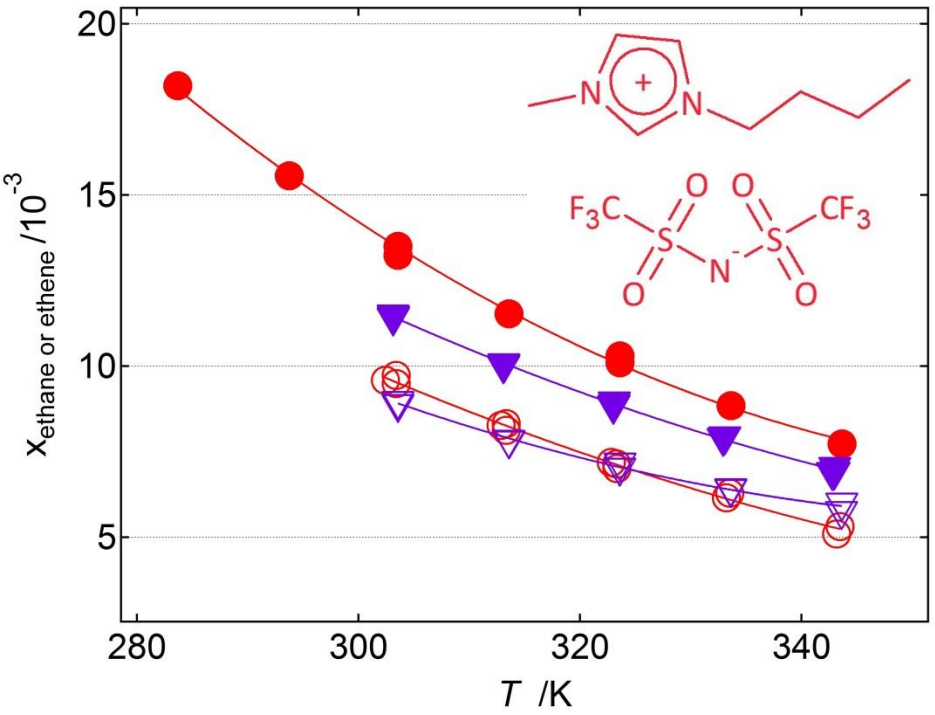
$$\Delta_{solv}H^{\infty} = RT^2\frac{\partial}{\partial T}\left[\ln\frac{K_H}{p^0}\right]$$

$$\Delta_{solv}S^{\infty} = \frac{\Delta_{solv}H^{\infty} - \Delta_{solv}G^{\infty}}{T}$$

Solute-solvent interactions

Structure of solution

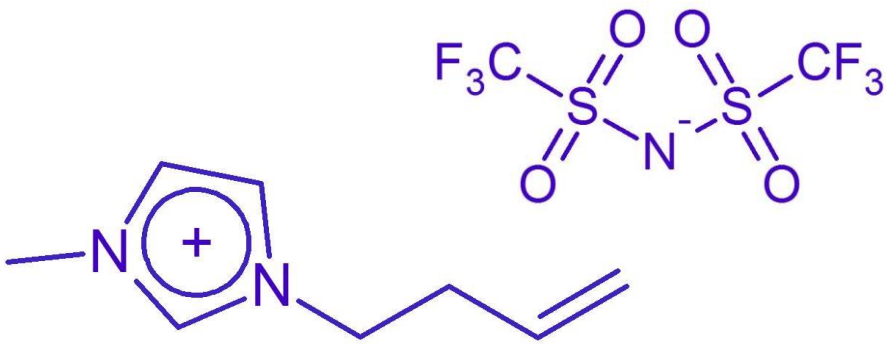
Gas solubility in ionic liquids



$$\Delta G = \Delta H - T\Delta S$$

	$\frac{\Delta_{solv}H}{kJmol^{-1}}$	$\frac{-T\Delta_{solv}S}{kJmol^{-1}}$
○ C_2H_6	-13.0 ± 0.1	26.3 ± 0.8
● C_2H_4	-11.9 ± 0.1	24.2 ± 0.7
▽ C_2H_6	-9 ± 1	22 ± 1
▼ C_2H_4	-11 ± 1	24 ± 2

$$\alpha = \frac{x_{C_2H_4}}{x_{C_2H_6}} = 1.3$$



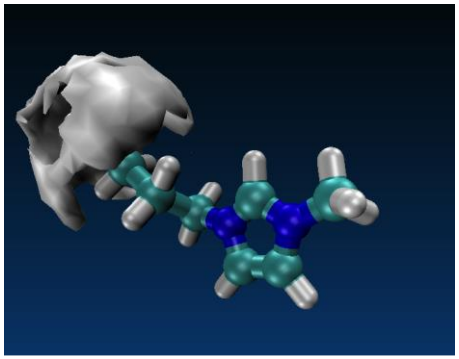
- More favorable enthalpy of solvation justifies the higher solubility of ethene

Moura *et al.* J. Phys. Chem. B 2013

Gas solubility in ionic liquids

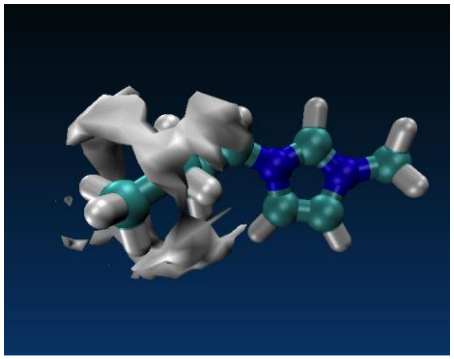
Ethane

$H_3C—CH_3$



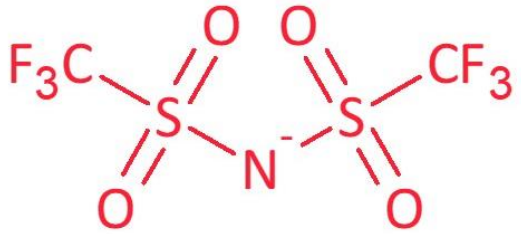
Ethylene

$H_2C=CH_2$



- Ethane and ethylene close to alkyl chain of the cation
- Ethylene closer of the aromatic ring
- Ethylene more mobile due to the competition for multiple solvation sites

- Solvation entropy more favorable for ethylene



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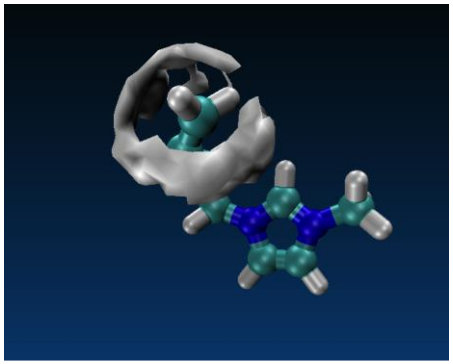
Gas solubility in ionic liquids

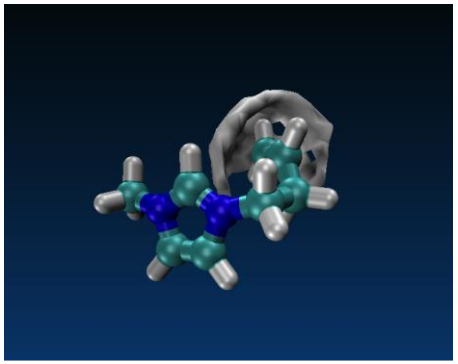
Ethane

$H_3C—CH_3$



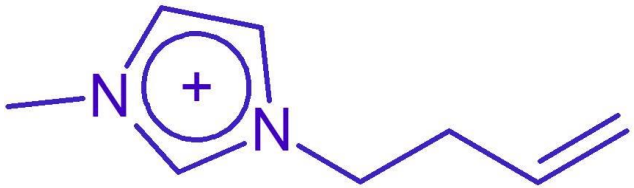
Ethylene

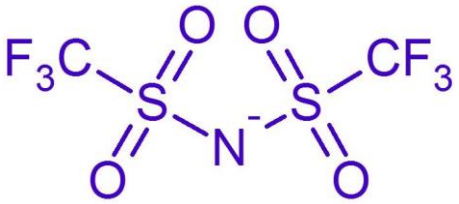
$H_2C=CH_2$



- Ethane surrounds the unsaturation
- Ethylene is found in the extremity of the alkyl chain

- Solvation enthalpy more favorable for ethylene





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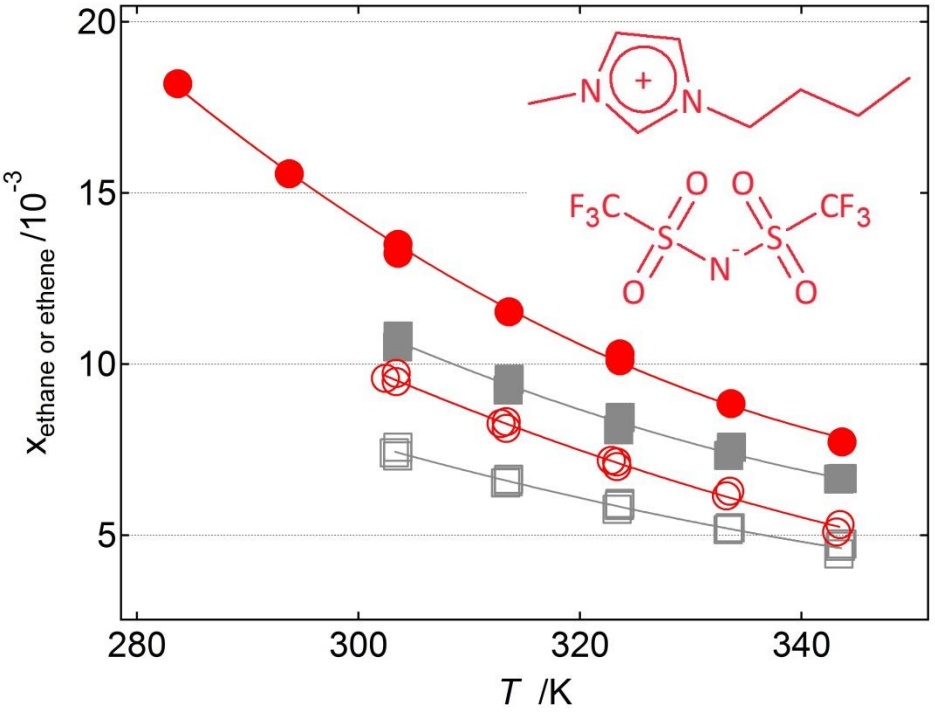
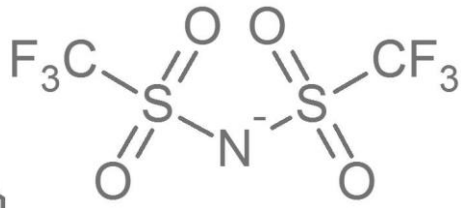
Gas solubility in ionic liquids

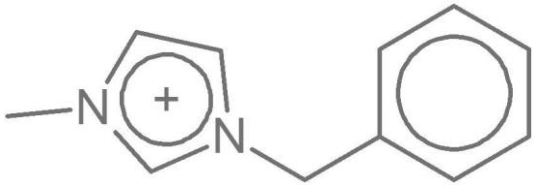


$$\Delta G = \Delta H - T\Delta S$$

	$\frac{\Delta_{solv}H}{kJmol^{-1}}$	$\frac{-T\Delta_{solv}S}{kJmol^{-1}}$
○ C_2H_6	-13.0 ± 0.1	26.3 ± 0.8
● C_2H_4	-11.9 ± 0.1	24.2 ± 0.7
□ C_2H_6	-10 ± 1	24 ± 2
■ C_2H_4	-10 ± 1	23 ± 1

$$\alpha = \frac{x_{C_2H_4}}{x_{C_2H_6}} = 1.4$$





- More favorable entropy of solvation justifies the higher solubility of ethylene

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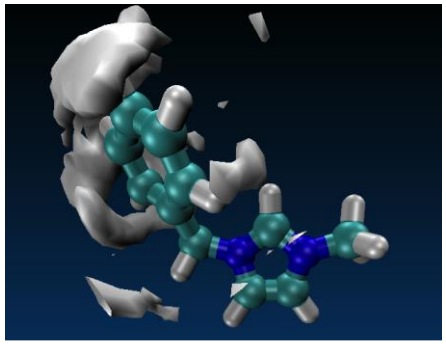
Gas solubility in ionic liquids

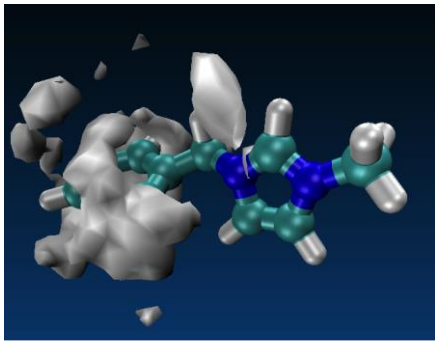
Ethane

$H_3C—CH_3$



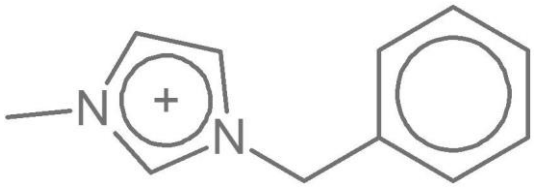
Ethylene

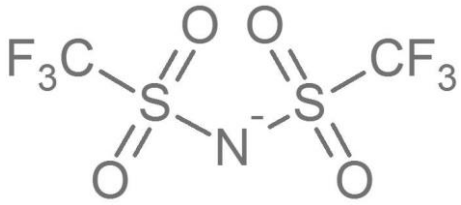
$H_2C=CH_2$



- Ethane is found close to the equatorial H of the benzyl group
- Ethylene is found planar to the aromatic ring, probably an indication of an interaction

- Solvation entropy more favorable for ethylene, it blocks the cation-anion interaction sites





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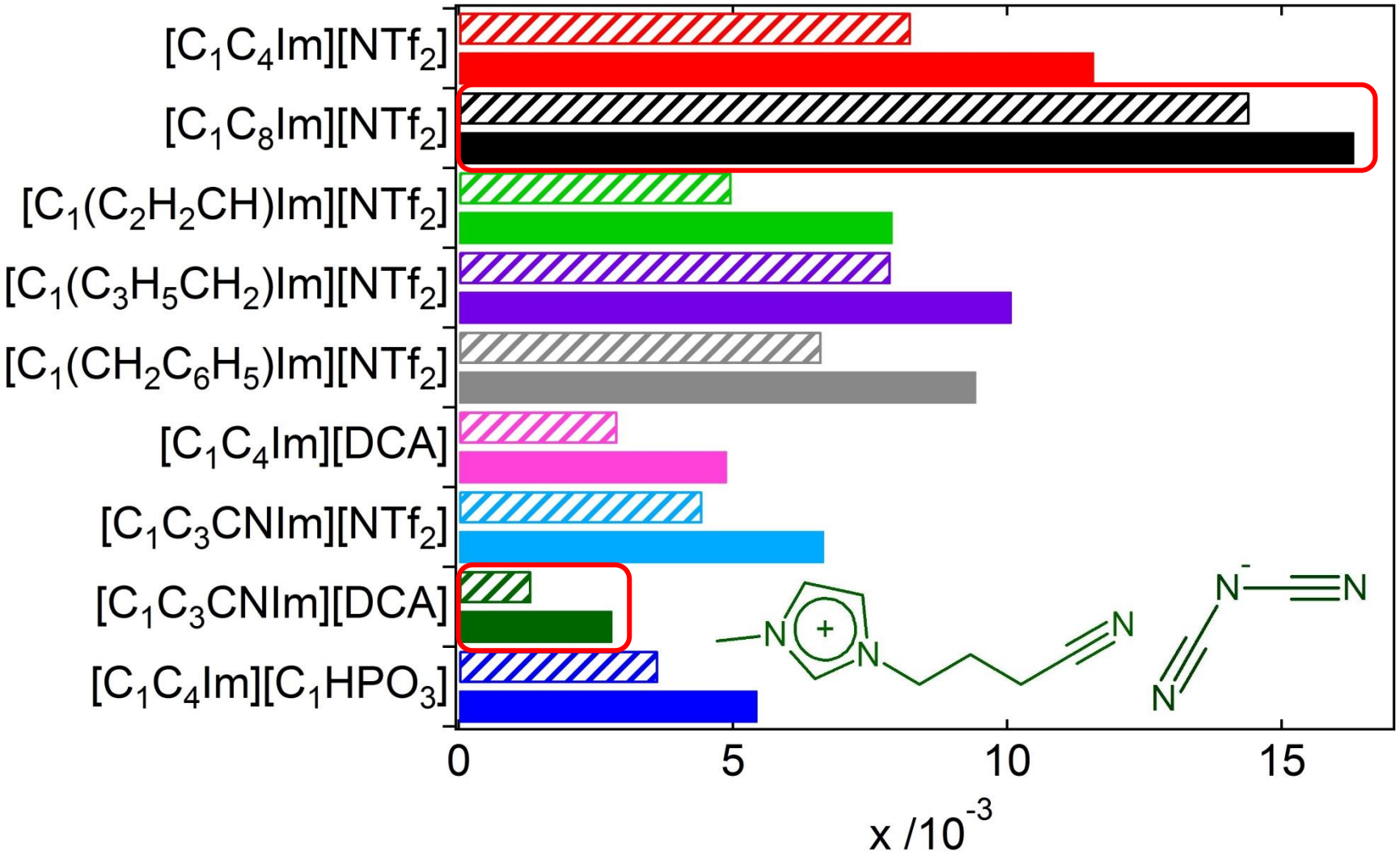
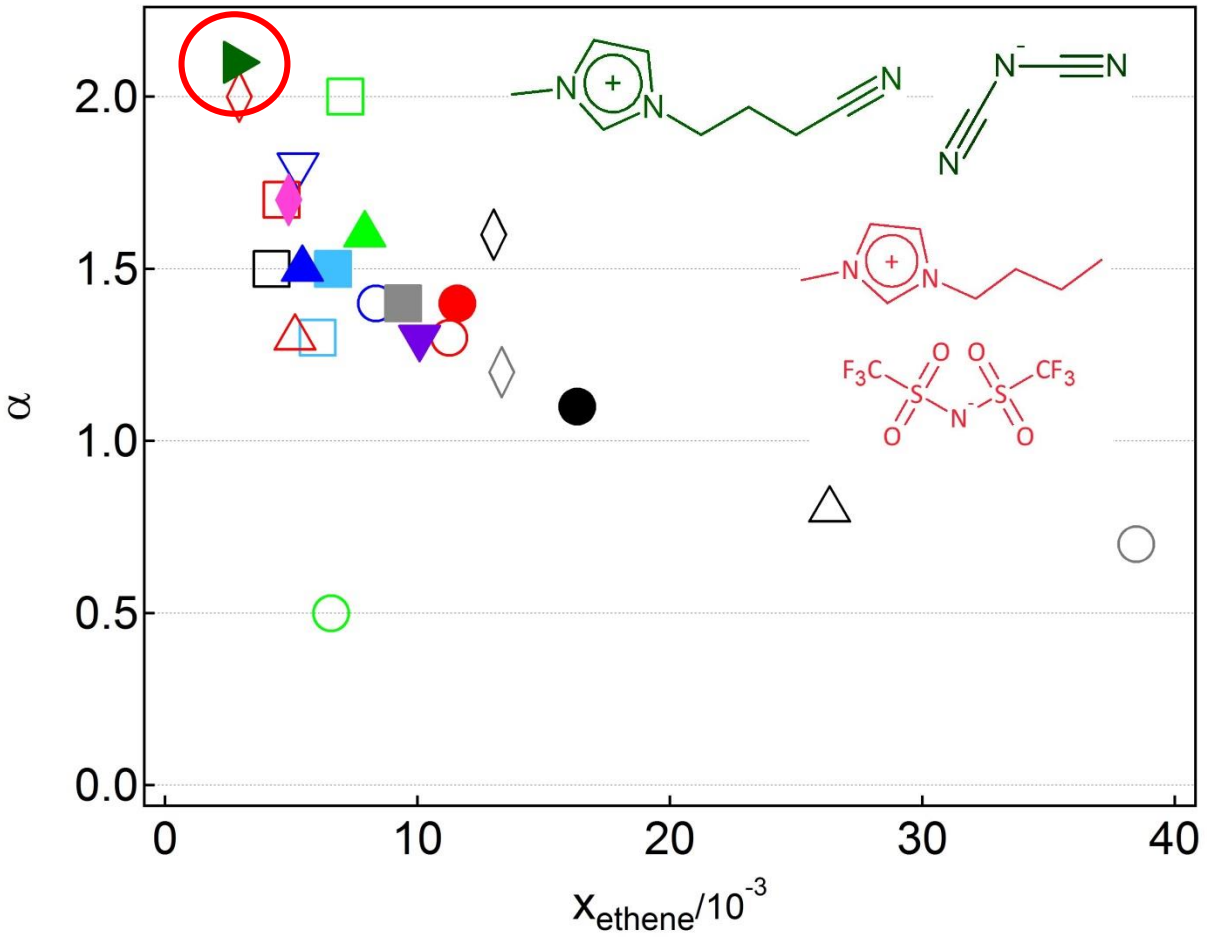
Gas solubility in ionic liquids



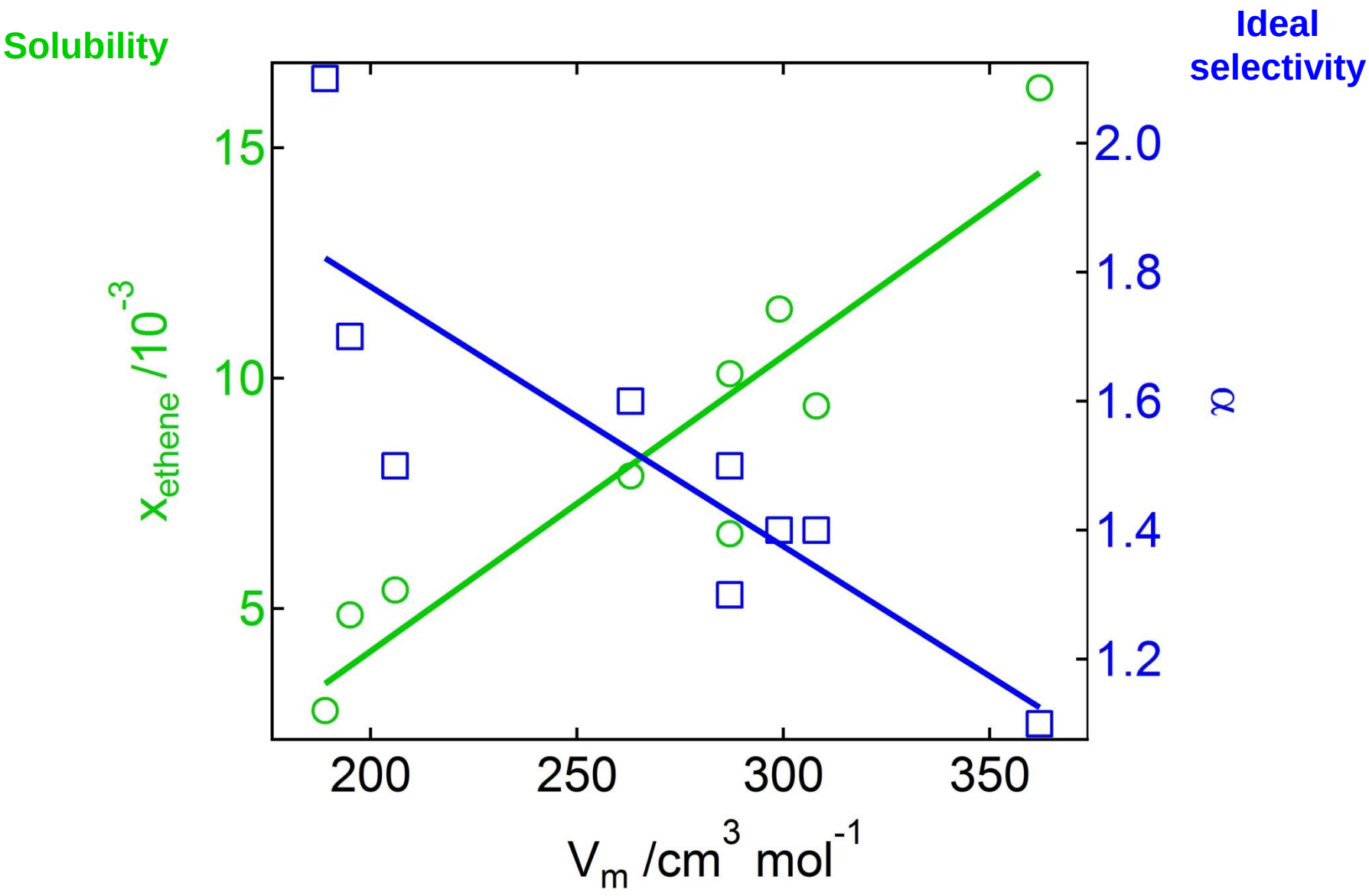
At 313 K and 1 bar

Performance



- ○-$[C_1C_2Im][NTf_2]$
- ▲-$[C_1(C_2H_2CH)Im][NTf_2]$
- ●/○-$[C_1C_4Im][NTf_2]$
- ○-$[C_1C_6Im][NTf_2]$
- ●-$[C_1C_8Im][NTf_2]$
- ▼-$[C_1(C_3H_5CH_2)Im][NTf_2]$
- ■-$[C_1(CH_2C_6H_5)Im][NTf_2]$
- ■/□-$[C_1C_3CNIm][NTf_2]$
- ▶-$[C_1C_3CNIm][DCA]$
- □-$[(C_3CN)_2Im][NTf_2]$
- ▽-$[C_1C_2Im][PF_6]$
- △-$[C_1C_4Im][PF_6]$
- ▲-$[C_1C_4Im][C_1HPO_3]$
- ◊-$[C_1C_2Im][DCA]$
- ♦-$[C_1C_4Im][DCA]$
- □-$[C_1C_4Im][BF_4]$
- □-$[C_1C_2Im][CF_3SO_3]$
- △-$[P_{4444}][TMPP]$
- ○-$[P_{(14)666}][TMPP]$
- ◊-$[C_1C_4Pyrr][NTf_2]$
- ◊-$[C_1C_6Pyr][NTf_2]$

Solubility vs selectivity



Conclusions

- We chose to study the **ethane/ethylene separation:**
  - Higher economical interest
  - Technologically more challenging
- Contrary to what is stated in the literature, ethylene is **not always** more soluble than ethane, the solubility ranges **overlap**
- Effects in **ethane/ethylene** and **propane/propene** separation should be **similar**

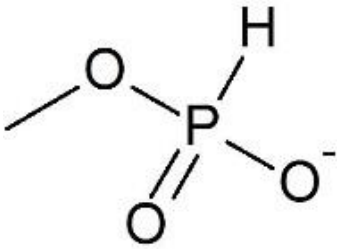
Conclusions

- Ethane/ethylene separation in selected ionic liquids
  - Complex effects – **interplay** between gas-solute **interaction** and **structure of the solution**
  - π-π and π-cation interactions are not specific enough to gain against what is lost in entropy
- **Non specific interactions** control the solubility in the **carefully chosen** ionic liquids

Perspectives

2 options

More specific interactions

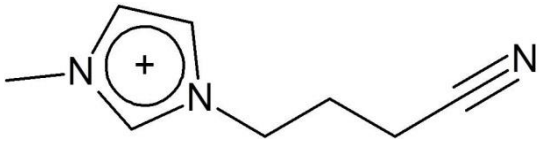


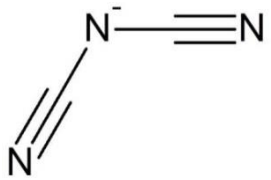
Li^{+} Ni^{2+}

Cu^{2+}

Pay higher price for recycling

Less specific interactions





Several cycles and pay low price for recycling

Interdisciplinary work is necessary to achieve a balance

Future work

5-year engineering fellowship

ROYAL ACADEMY OF ENGINEERING

- Start my research group
- Chemisorbent materials for olefin separation
- Rapid measurement of gas liquid equilibria in industrial conditions (mixed gases, T, p)
- Spectroscopic and chromatographic sensors

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Dr Sophie Fourmentin

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Dr Panagiotis Manesiotis

Dr Gosia Swadzba-Kwasny