universidade de aveiro

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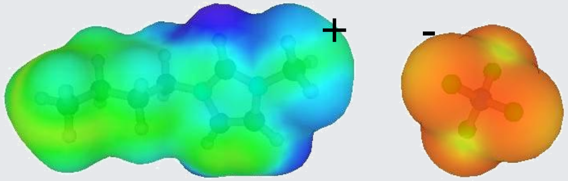
# Capture of Pollutants from Post-Combustion Streams with Ionic Liquids




Luís M. C. Pereira

luismanuel@ua.pt

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# Summary

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    1.2. Ionic Liquids
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# 1. General Introduction

## 1.1 Air Pollution

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**WHO** → ***"contamination of the indoor or outdoor environment by any chemical, physical or biological agent that modifies the Natural characteristics of the atmosphere"***

↓

**300+ substances considered air pollutants**
- **-$CO_2$**
- **-CO**
- **-$SO_2$**
- **-$NO_x$** → **NO**, **$NO_2$**
- **-$N_2O$**
- **-PM**
- **-VOCs**
- **- ...**

### $N_2O$ anthropogenic source:

**-Agriculture – 57%**
**-Chemical industry – 29%**
**-Transport – 5%**

### $NO_x$ anthropogenic sources:

**-Fossil fuel Combustion - 61% (Coal-fired electric power plants and industrial combustion)**

### Control Methods:

- **Process optimization**
- **Thermal decomposition**
- **Selective Non Catalytic Reduction (SNCR) 10-90%**
- **Selective Catalytic Reduction (SCR) 80-95%**
- **Low-$NO_x$ burner (LNB) 14-65%**
- **Over Fire Air (OVA) +10-25%**

# 1. General introduction

## 1.1 Air Pollution

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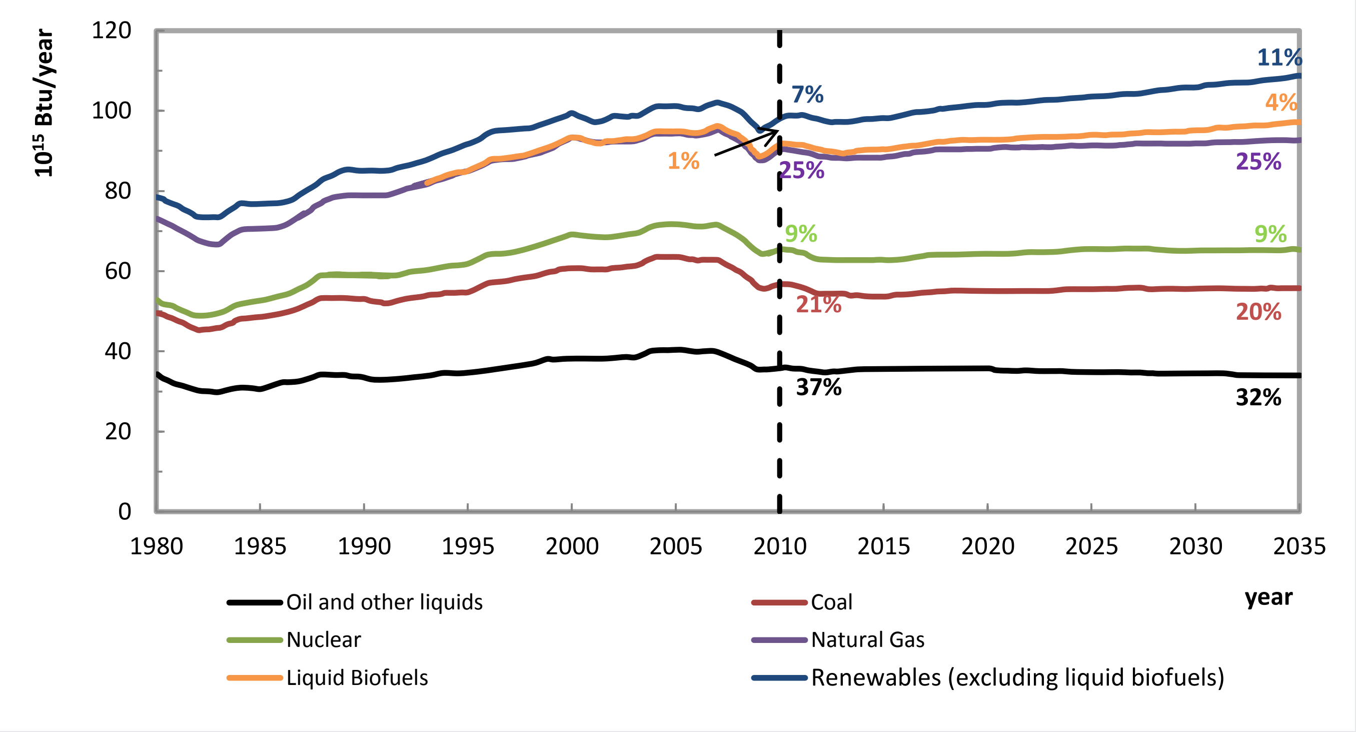
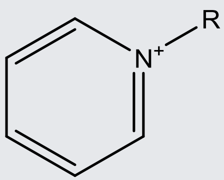
[1)] U.S Energy Information Administration. "*Annual Energy Outlook 2012*"



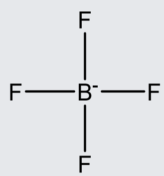

- Dependency on fossil fuels will continue
- Stricter legislation will continue appearing
- Need for better and more efficient control methods

Ionic Liquids (ILs) as capturing agents

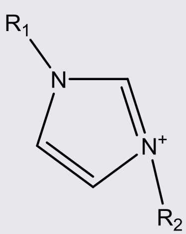
***"salts composed of large organic cations and organic or inorganic anions that cannot form an ordered crystal and thus remain liquid at or near room temperature"***



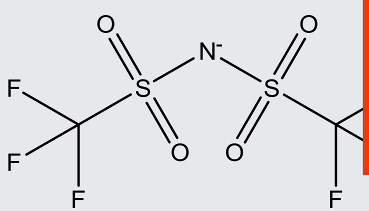

pyridinium




tetrafluoroborate




imidazolium




bis(trifluoromethylsulfonyl)imide

- ✓ physicochemical properties can be tuned
- ✓ negligible vapour pressure
- ✓ highly solvating capacity either for polar and nonpolar compounds
- ability

**$10^6$ ILs**

s for pollutants: Stationary phase or absorbent solvent

Pollutants solubility in ILs, namely for $CO_2$, $CH_4$, $H_2S$, $SO_2$, CO and $NH_3$ → good results!!

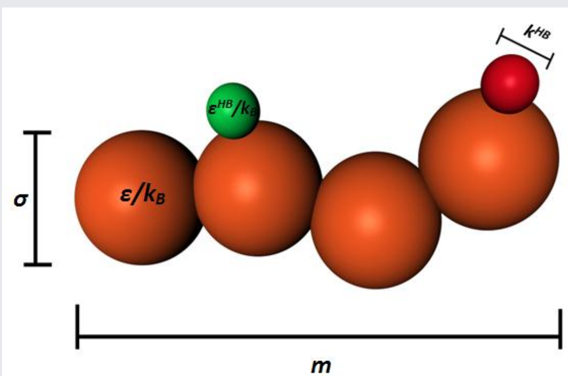
**-$NO_x$**
**-$N_2O$**

SAFT- Statistical Associating Fluid Theory

✓ Soft-SAFT EoS

[2] Vega *et al.*, J. Ind. Eng. Chem. Res., **1998**. **37**(2): p. 660-674.

$$A^{res} = A^{ref} + A^{chain} + A^{assoc} + A^{polar}$$




-Uses a LJ spherical fluid (as "soft" reference fluid)
-uses statistical mechanisms to calculate total energy of interactions (hydrogen bonding)

-ILs are well modelled by using all five molecular parameters ($m$, $\sigma$, $\varepsilon/k_B$, $\varepsilon^{HB}/k_B$ and $k^{HB}$)
-Gases by just three or five molecular parameters ($m$, $\sigma$, $\varepsilon/k_B$, $Q$ and $x_p$).

-do not require ILs' critical properties

$$\sigma_{ij} = \eta_{ij}\frac{\sigma_{ii}+\sigma_{jj}}{2}$$

$$Q = Q_{exp} \times x_p$$

$$\varepsilon_{ij} = \xi_{ij}\sqrt{\varepsilon_{ii} \times \varepsilon_{jj}}$$

# 1. General introduction

## 1.4 Scope and Objectives

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- ✓ Solubility measurement of $CO_2$, $N_2O$, $N_2$ and $CH_4$ in a Highly polar IL ($[C_2mim][CH_3OHPO_2]$)
- ✓ Soft-SAFT modelling of the measured data and extension to others Gas + IL systems
- ✓ Gas selectivies
- ✓ ILs' capturing efficiency compared to other solvents

# 2. Molecular Models

## 2.1 Molecular models for the ILs

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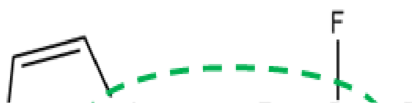
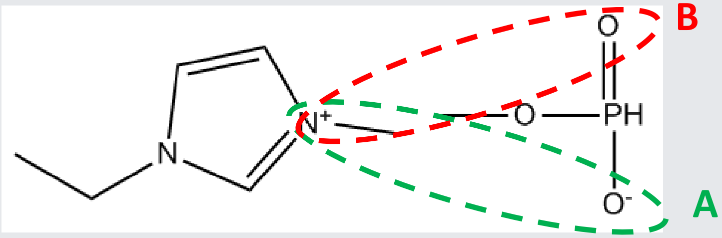
[$C_4$mim][$BF_4$]

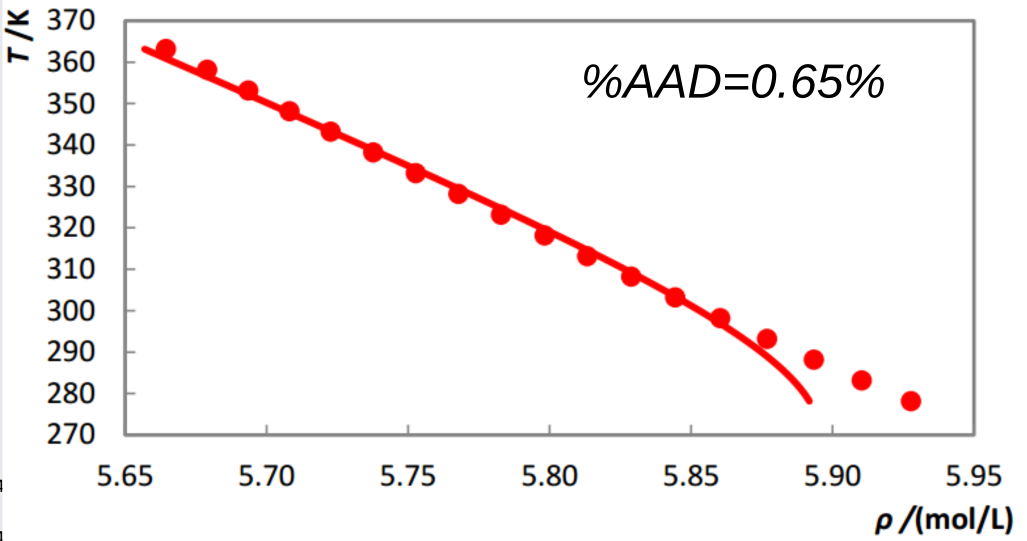



| | m | σ (Å) | $\varepsilon/k_B$ (K) | $\varepsilon^{HB}/k_B$ (K) | $k^{HB}$ (Å³) |
|---|---|---|---|---|---|
| **[$C_2$mim][$CH_3OHPO_2$]** | 5.405 | 3.686 | 414.35 | 4450 | 3950 |

[3] Vega *et al.,* J. Phys. Chem. C., **2007**. 111(43): p. 16028-16034.

[$C_2$mim][$CH_3OHPO_2$ ]




4

[4] Vega *et al.,* J. Phys. Chem. B., **2011**. 115(15): p. 4387-4398.

$T=0.7 \times \varepsilon/k_B$

[5] Johnson *et al.,* Mol. Phys., **1993**. 78(3): p. 591-618.

$T$=290.05 $K$

# 2. Molecular Models

## 2.2 Molecular models for the Gases

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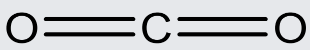


[6] Pedrosa *et al.,* Ind. Eng. Chem. Res., **2005**. 44(17): p. 7027-7037.

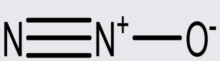
[7] Dias *et al.,* Ind. Eng. Chem. Res., **2006**. 45(7): p. 2341-2350.

| | *m* | *σ* (Å) | *ε/k<sub>B</sub>* (K) | *Q* (10^-40^ C. m²) | *x<sub>p</sub>* |
|---|---|---|---|---|---|
| $CO_2$ | 1.571 | 3.184 | 160.20 | 4.4 | ⅓ |
| $N_2$ | 1.205 | 3.384 | 89.16 | 1.2 | ½ |
| $CH_4$ | 1.000 | 3.728 | 147.20 | - | - |

**Adjusted molecular parameters for $N_2O$**

| Set | *m* | *σ* (Å) | *ε/k<sub>B</sub>* (K) | *x<sub>p</sub>* | *Q* ($10^{-40}$ C. m²) | AAD P (%) | AAD D (%) |
|---|---|---|---|---|---|---|---|
| 4 | 1.656 | 3.153 | 159.83 | ⅓ | 4.1 | 7.32 | 3.37 |

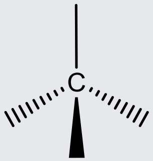
[6] Pedrosa *et al.,* Ind. Eng. Chem. Res., **2005**. 44(17): p. 7027-7037.



1st Appro
-no quadr ment

2nd Approach:
-modelled as three segments with the quadrupole moment in one of them ($x_p$ fixed to ⅓)

3rd Approach:
-modelle gments with the quadrupole nt in one of them ($x_p$ fixed t ½)



[2] Vega *et al.,* J. Ind. Eng. Chem. Res. **1998**. **37**(2): p. 660-674.

[8] Pàmies *et al.,* Ind. Eng. Chem. Res., **2001**. 40(11): p. 2532-2543.

# 3. Gas Solubilities

## 3.1 Experimental Equipment

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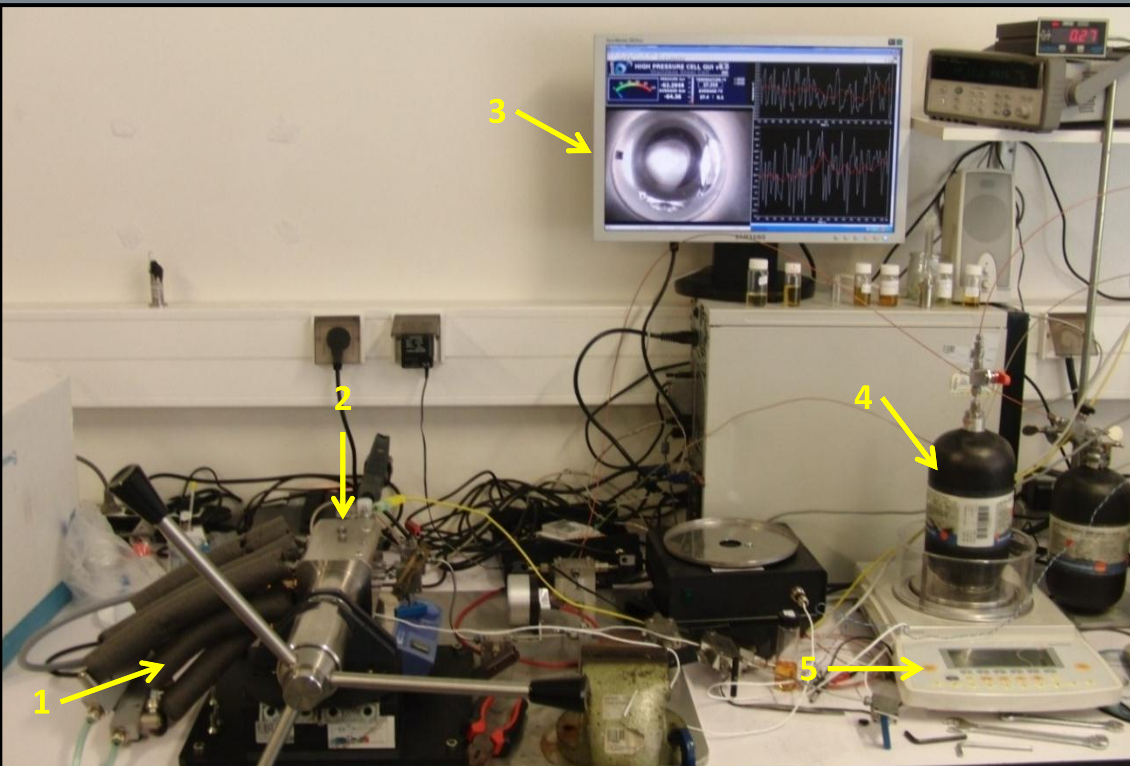


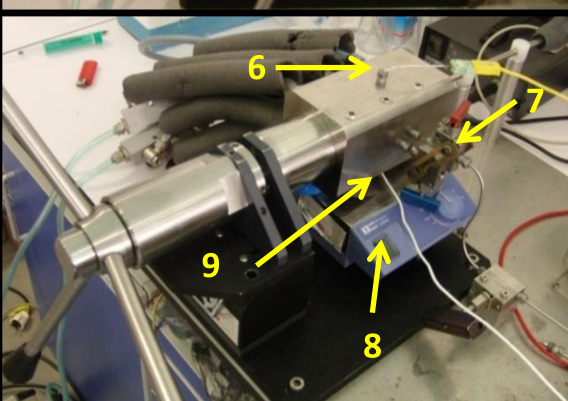


1. Thermostatized bath circulator;
2. High pressure cell;
3. Video and data acquisition;
4. Gas storage;
5. Analytical balance;
6. Temperature sensor;
7. Valves;
8. Magnetic stirrer;
9. Piezoresistive pressure transducer;
10. Gas entrance;
11. Magnetic bar;
12. Light source from an optical fiber cable;
13. Pressure probe.

0-100 MPa

293-363 K

**Solubility of $CO_2$, $N_2O$, $CH_4$ and $N_2$ in:**

- **[$C_2$mim][$CH_3OHPO_2$]**

# 3. Gases Solubilities

## 3.2 Experimental results

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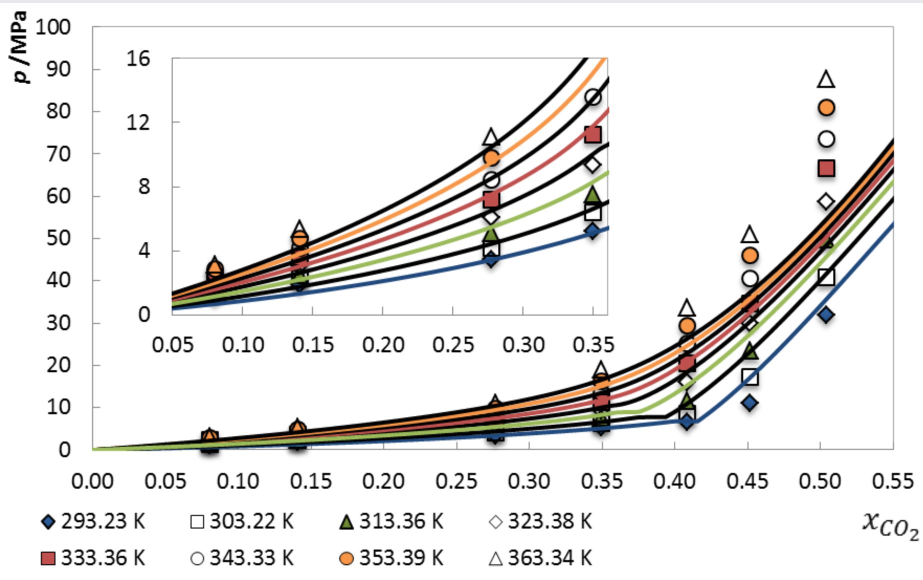
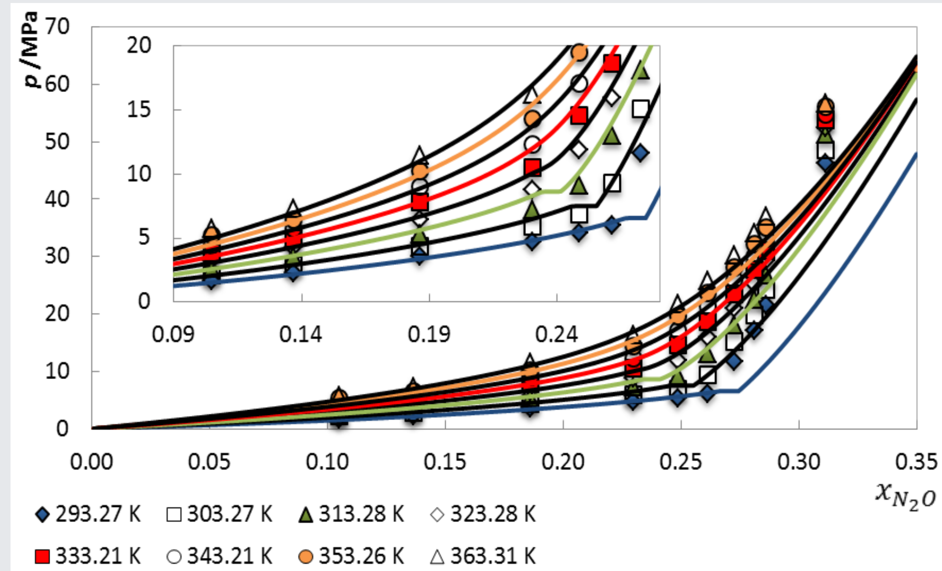
✓ $CO_2$

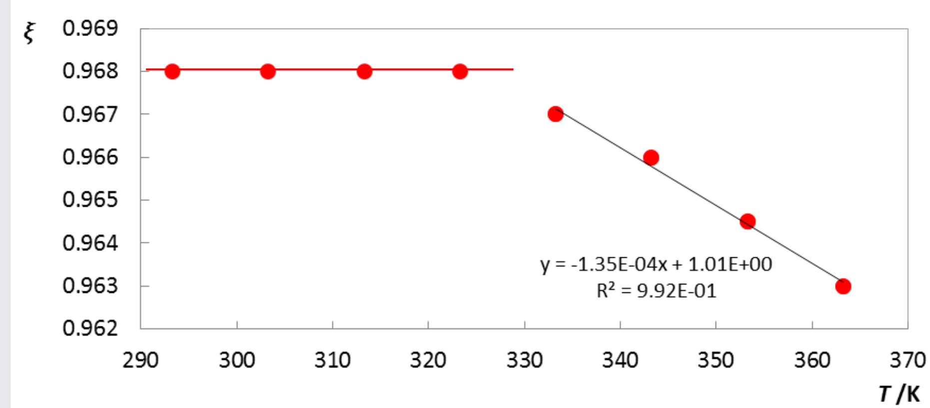



$$\xi = 1.017$$

(T independent)

✓ $N_2O$



# 3. Gases Solubilities

## 3.2 Experimental results

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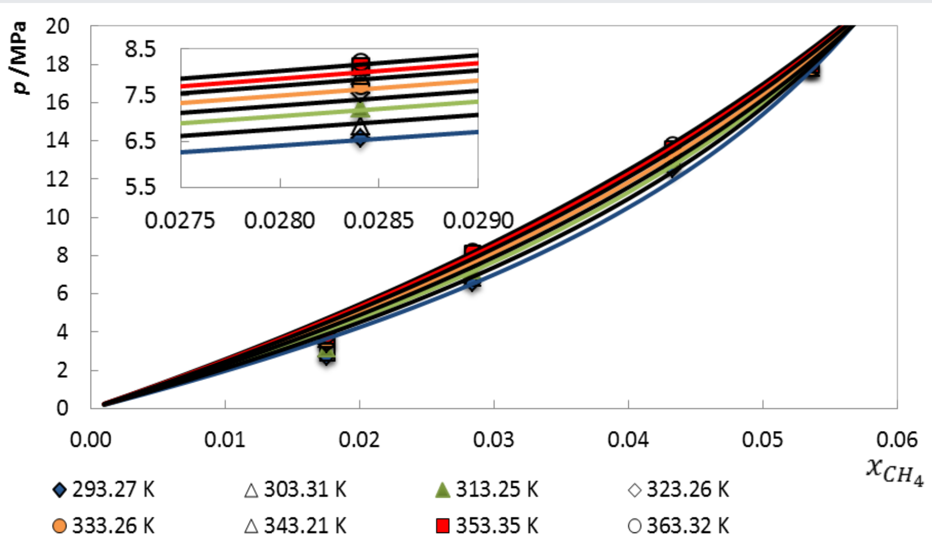
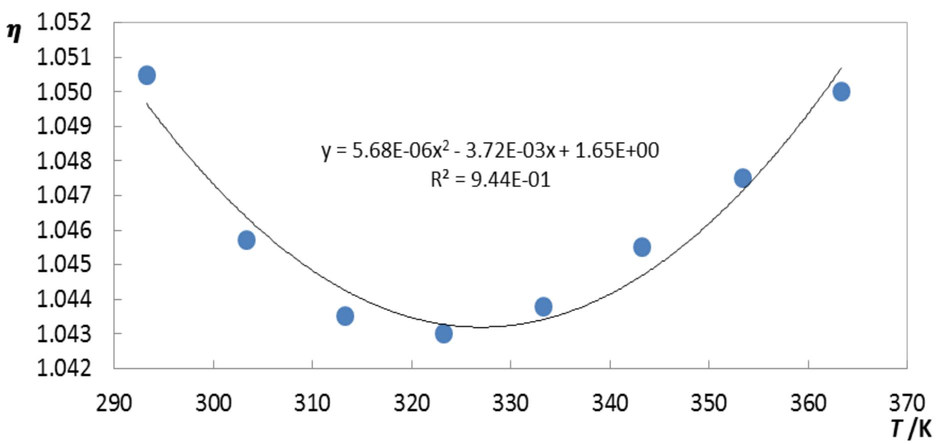
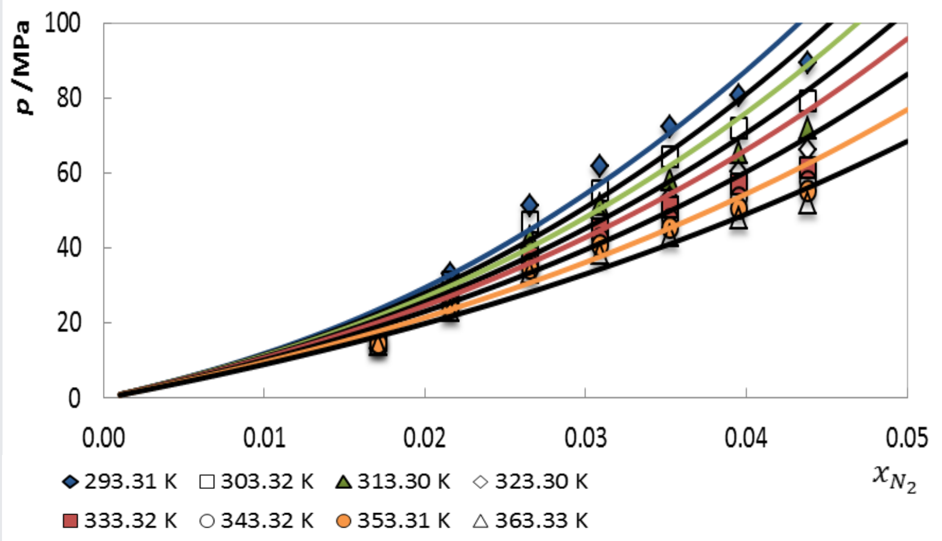
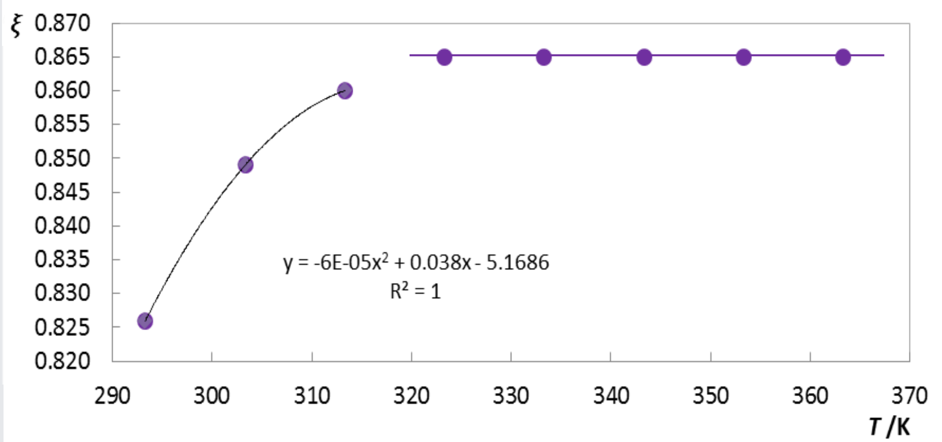
✓ $CH_4$



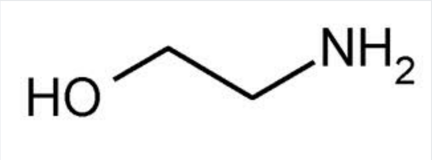

✓ $N_2$



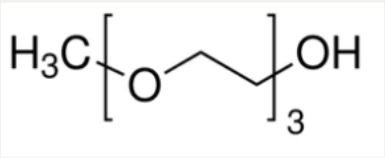



# 4. ILs' Capturing Efficiency and Selectivities

MEA - monoethanolamine




TEGMME - triethylene glycol monomethyl ether




$$S_{CO_2/N_2} = \frac{H_{N_2}}{H_{CO_2}}$$

$$S_{N_2O/N_2} = \frac{H_{N_2}}{H_{N_2O}}$$

$$S_{CO_2/N_2O} = \frac{H_{N_2O}}{H_{CO_2}}$$

| | MEA (40%) | TEGMME | $[C_2mim][CH_3OHPO_2]$ | $[C_4mim][N(CN)_2]$ | $[C_4mim][SCN]$ | $[C_4mim][BF_4]$ | $[C_4mim][Tf_2N]$ |
|---|---|---|---|---|---|---|---|
| $CO_2$ | 75.05 | 6.80 | 17.21 | 4.06 | 10.28 | 5.38 | 1.62 |
| $N_2O$ | 102.78 | 7.25 | 18.34 | 8.69 | 12.78 | 7.86 | 3.21 |
| $N_2$ | - | 52.93 | 907.41 | 462.03 | - | 178.90 | 121.60 |

# 4. ILs' Capturing Efficiency and Selectivities

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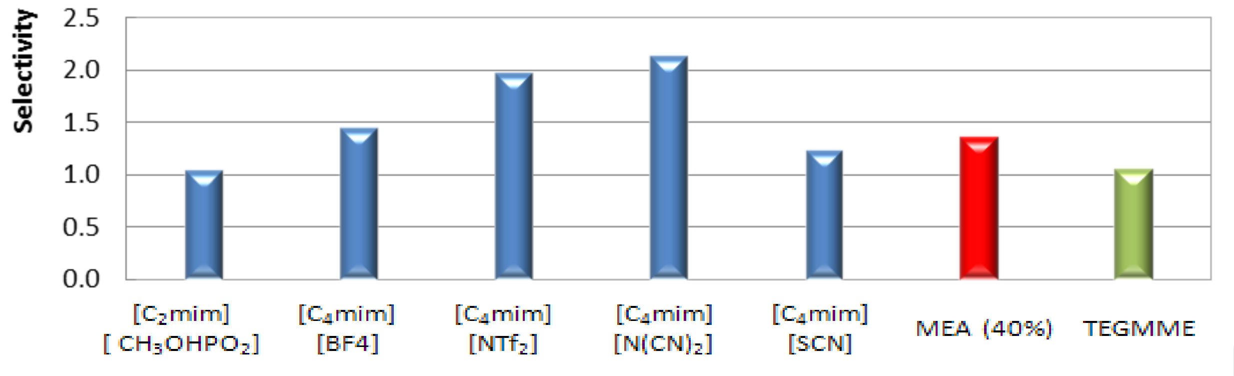
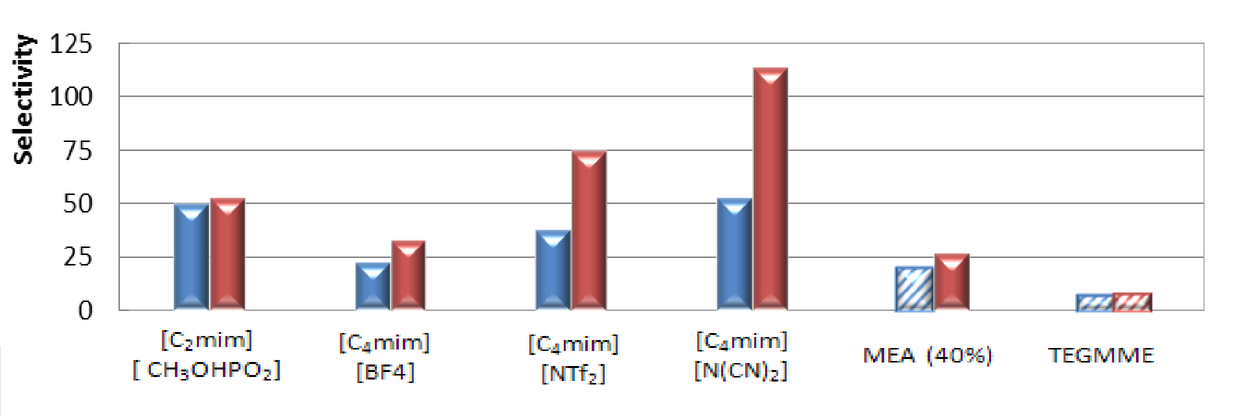
$S_{CO_2/N_2O}$




$S_{N_2O/N_2}$ ■ $S_{CO_2/N_2}$ ■



# 4. ILs' Capturing Efficiency and Selectivities

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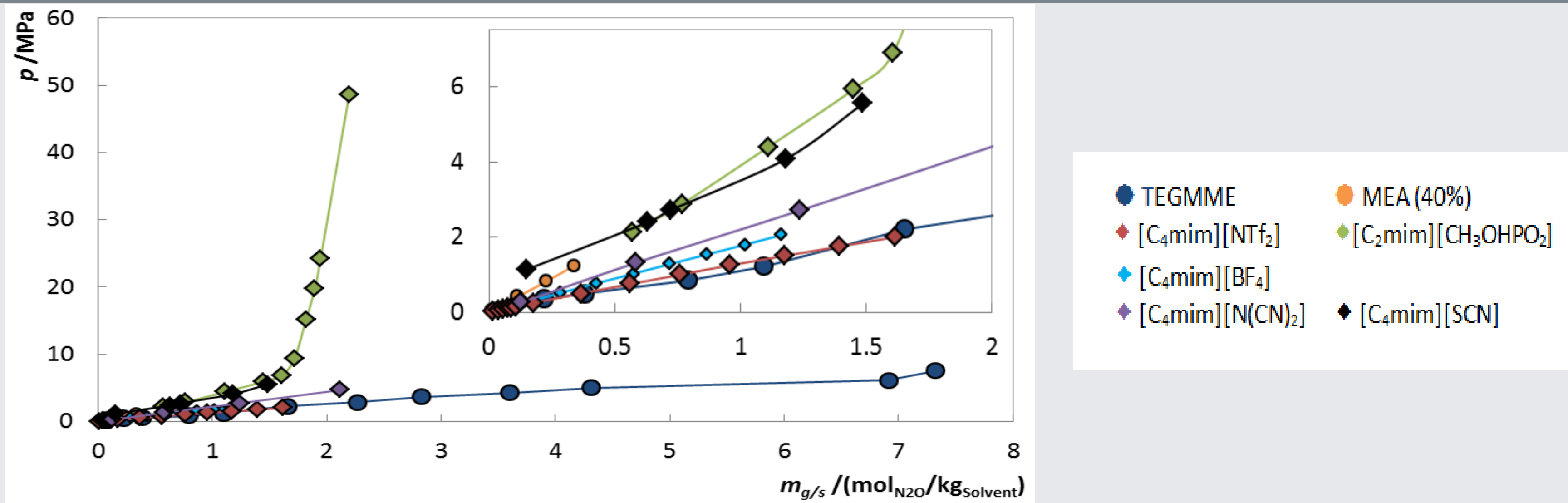


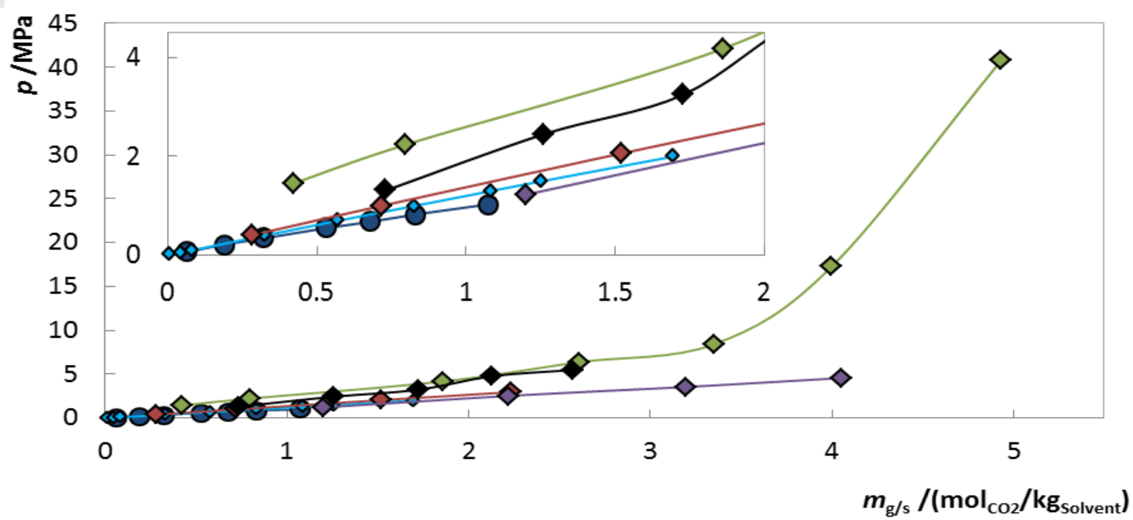


69.69 $g_{N_2O}$ and 80.43 $g_{CO_2}$ per kg of IL at 2 MPa and within the temperature range (298.10-303.31) K

# 5. Conclusions

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- ✓ $CO_2$, $CH_4$, $N_2$ and $N_2O$ solubility in [$C_2$mim][$CH_3OHPO_2$] was measured for the first time in a wide range of pressures and temperatures;
- ✓ Results showed **a similar and high solubility** of $CO_2$ and $N_2O$ in the ILs when compared to $CH_4$ and $N_2$;
- ✓ Molecular parameters were **proposed** for $N_2O$ and the ILs [$C_2$mim][$CH_3OHPO_2$], [$C_4$mim][$N(CN)_2$] and [$C_4$mim][SCN];
- ✓ Soft-SAFT EoS was able to describe/predict **pure compounds** and **binary mixtures successfully**;
- ✓ Soft-SAFT EoS can be used as a **prediction tool** for pre-selection of the better ILs to dissolve some gases;
- ✓ ILs **high selectivity** toward $CO_2$ and $N_2O$ and **high absorption capacity** make them feasible candidates to be used to capture or separate these pollutants from post-combustion streams.

# 6. Future work

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- Gases solubilities in other ILs (anion and alkyl chain effect)
- Solubility of other gases in ILs ($O_2$, $O_3$, HCl, HF, dioxins and furans)
- Extend soft-SAFT EoS to the measured systems

# Thank you
# for your attention!!