CO_2 /CH_4 Separation with Ionic Liquids

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   - Non ideality of CO_2 /protic ionic liquid systems

3. Conclusions

1. Introduction

Environmental Issues- Climate Change

- Increasing atmospheric concentration of several greenhouse gases (GHGs), caused by human activities

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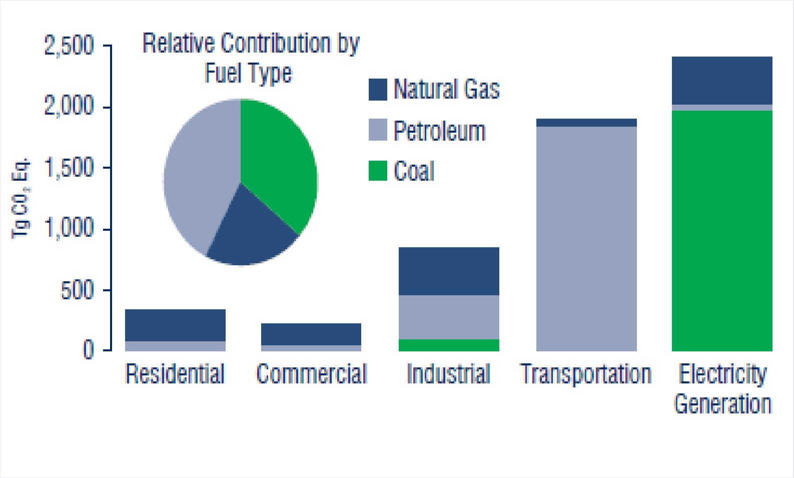
CO_2 accounts for about 80 % of the enhanced global warming effect

Main sources of CO_2



CO_2 emissions must be reduced

1. Introduction
CO_2 Mitigation

CO_2 mitigation Options

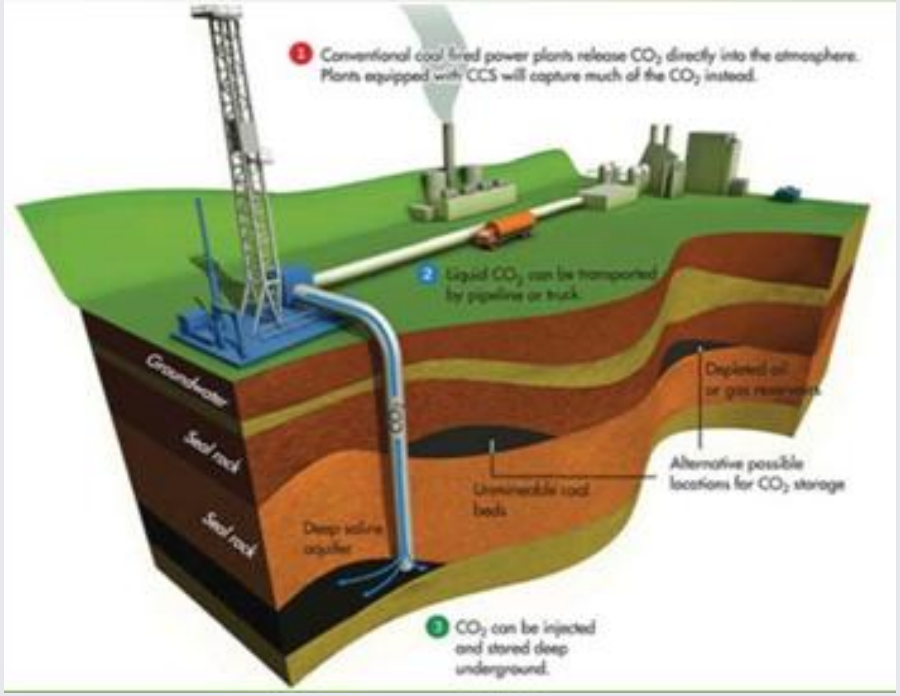
Strategies to prevent CO_2 emission

- Energy efficiency improvements
- Less carbon intensive fuels
- Nuclear power
- Renewable energy sources
- Enhancement of biological sinks

Techniques aiming at the sequestration of CO_2 (CCS)

CCS consists of :

1. Capturing CO_2 from industrial or power plants;
2. Compressing and transporting it;
3. Storing it in geological formations by injecting it into suitable, permanent sites underground.



1. Introduction

Why separate CO_2 from CH_4 ?

The separation of CO_2 from CH_4 is an important process in many industrial areas :

- Natural gas processing
- Biogas purification
- Enhanced oil recovery
- Flue gas treatment

Natural gas: →

- Less polluting than oil and coal
- Used in more efficient plants

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Primary energy source in the near future

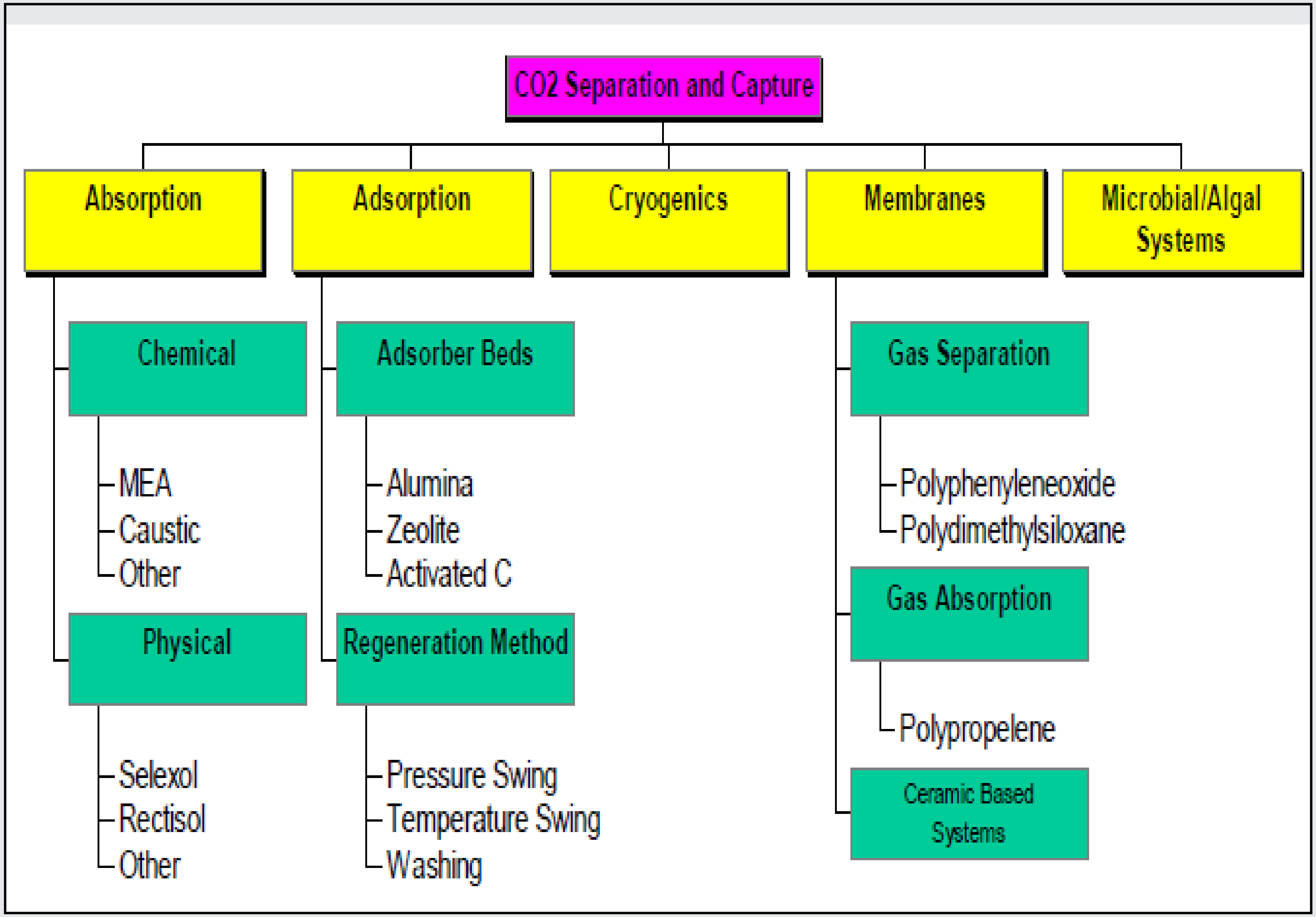
- Novel transport technologies
- The remarkable reserves found
- The lower overall costs
- The environmental sustainability

➢ **CO_2 content in natural gas varies from 4 to 50% and must be reduced to 2–5%**

- Carbon dioxide reduces the heating value
- Takes up volume in the pipeline
- Causes corrosion in pipes and process equipment (acidic gas)
- Atmospheric pollution from the combustion of natural gas

1. Introduction

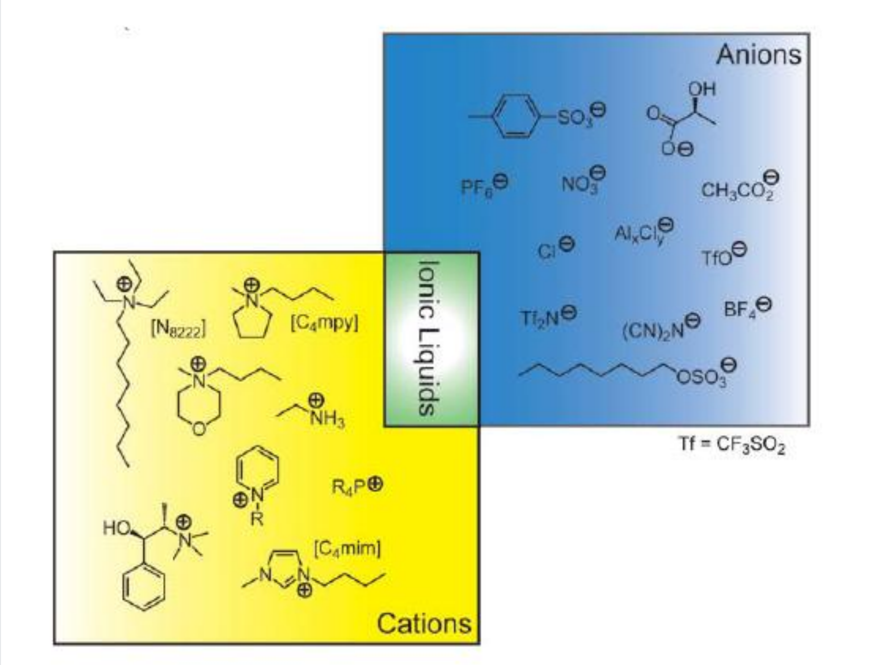
Gas treating Technologies



1. Introduction

Ionic Liquids

- Consist entirely of ionic species
- Fluid at room temperature
- Cation is generally a bulk organic structure with low symmetry
- Anion is mostly inorganic

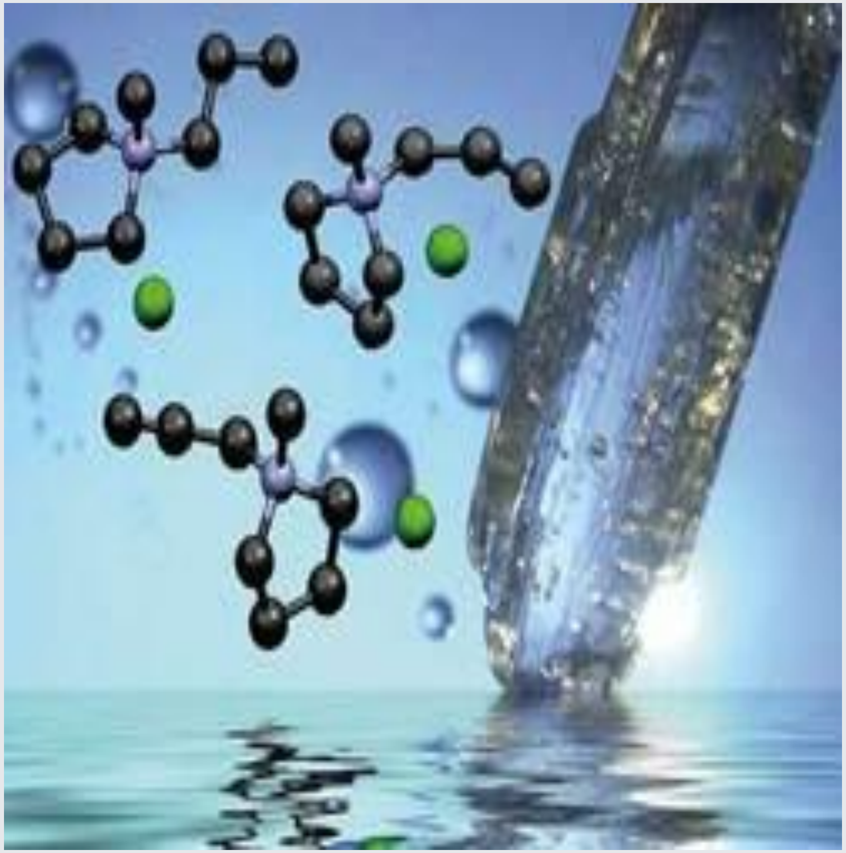


- Choices of cations and anions are numerous
- They can be used in gas separation processes as solvents, replacing the traditional solvents.

1. Introduction

Ionic Liquids – General Properties

- Present a low melting point (<100ºC), remaining liquid at Room temperature
- Very wide temperature range in the liquid state
- Non flammable
- Non explosive
- Good electrical conductivities
- Low vapor pressure
- Thermally stable
- Large electrochemical stability window
- They can be designed to posses a particular set of properties (easily modified structure)



Designer Solvents

1. Introduction

- The major drawbacks of the traditional gas absorption separation processes are mainly caused by the nature of the solvent, and the type of interactions given between the solute and the solvent.

Ionic Liquids have been proposed as promising candidates for CO_2 absorption and separation.

- To design and optimize processes using ILs, it is essential that we understand the important factors that determine CO_2 solubility.

- As it is possible to design many potential ILs, the study of them will allow us to discover the key properties in making CO_2 -philic ILs.

2. Results and Discussion

Correlation of solubility with IL surface tension

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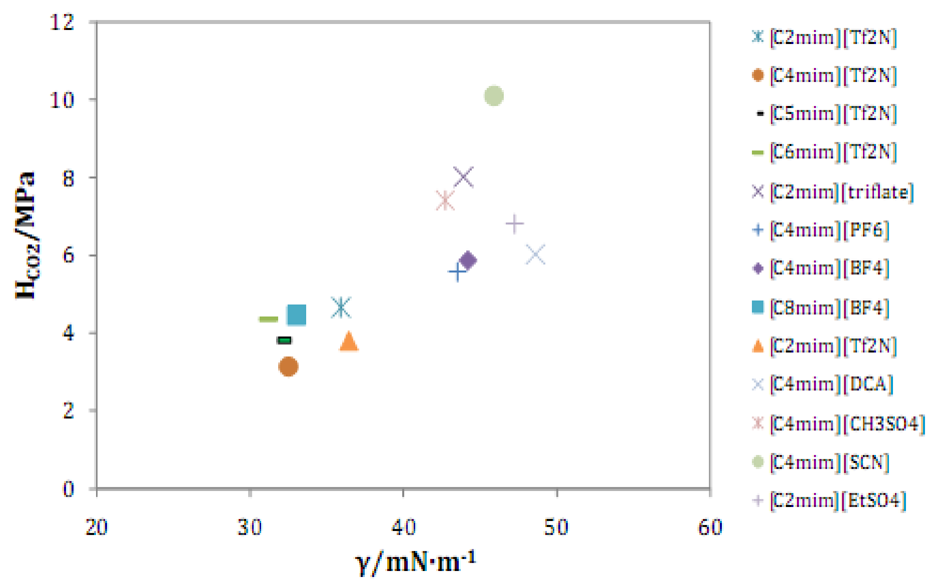
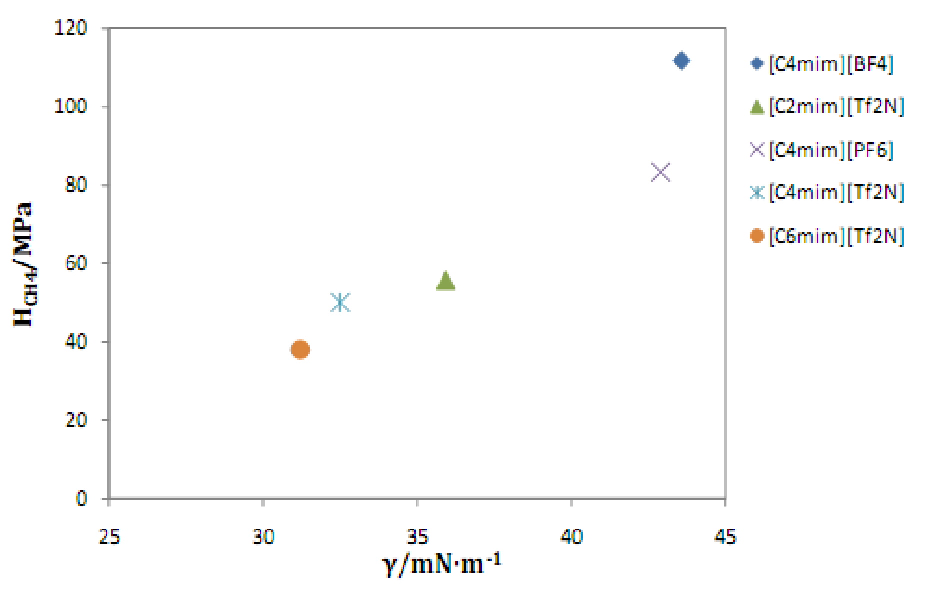




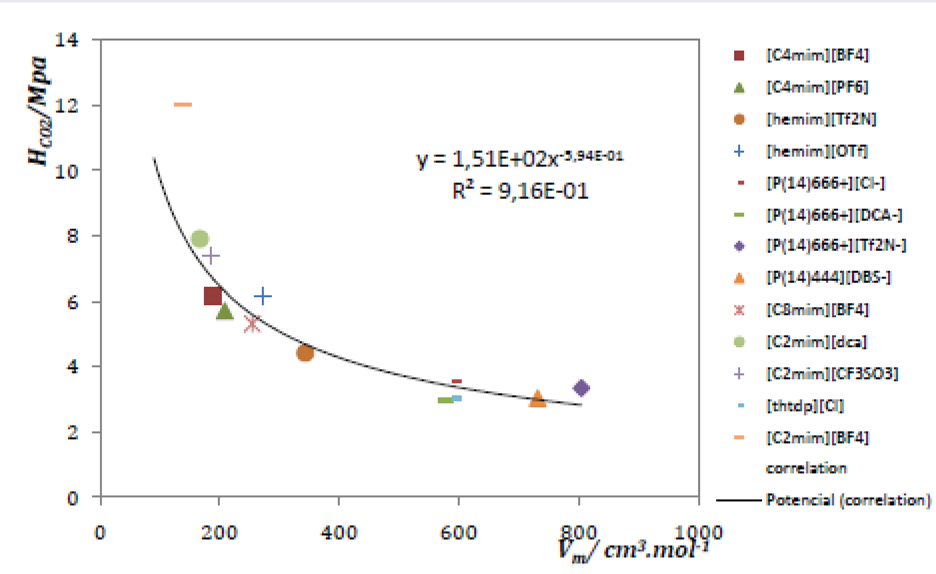
In general there is a relation between the solubility and the surface tension of the solvent.

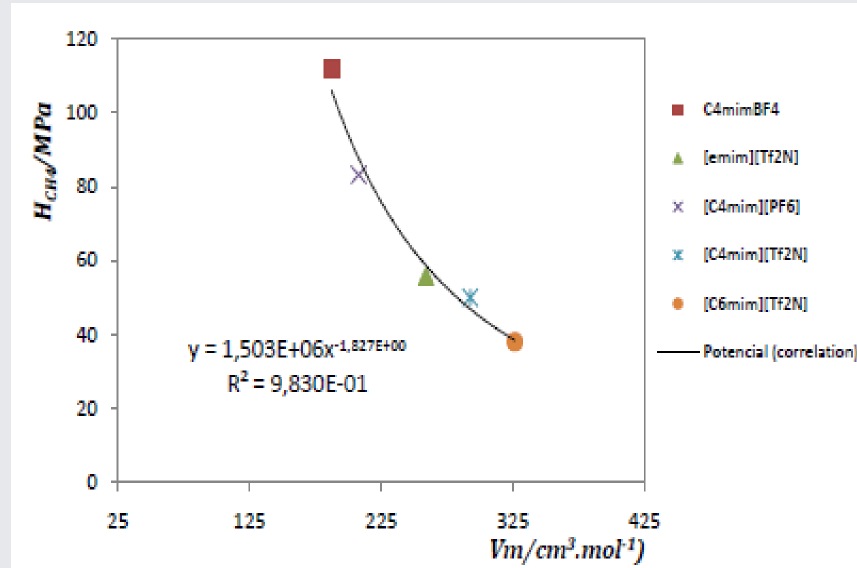
The solubility of CO_2 and CH_4 in ionic liquids decreases as the surface tension increases.

High scatter of the data is observed → No correlation can be obtained

2. Results and Discussion

Correlation of the solubility with IL molar volume





- The solubility of both gases is dependent on IL molar volume

With an increase in the molar volume of the solvent, the gas solubility increases

- For very large molar volumes, an increase of this thermodynamic property has no longer a significant effect on solubility

- The relation can be expressed by a potential equation

$$H_{CO_2} = 0.0241 \times Vm^{-0.670}$$

$$H_{CH_4} = 1.5036 \times 10^{6} \times Vm^{-1.827}$$

2. Results and Discussion

Non ideality of CO_2/non-volatile solvent systems

- **Understanding of the molecular mechanism that dominates the CO_2 sorption**

  - Design and operation of processes
  - Design of enhanced solvents for CO_2

VLE data was collected for systems of CO_2 with Ionic Liquids, alcohols, alkanes, fatty acids and fatty acid esters → compared with those on an ideal solution

Ideal solution described by Raoult's law that is defined as

$$y_{CO_2} \cdot p = \gamma_{CO_2} \cdot x_{CO_2} \cdot p^{\sigma}_{CO_2}$$

ideal solution: $\gamma = 1$

Solvents are non-volatile → Vapor phase is pure CO_2

$$y_{co_2} = 1$$

$$p = x_{CO_2} \cdot p^{\sigma}_{CO_2}$$

2. Results and Discussion

Flory-Huggins model

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- Deviations to ideality of a given mixture can be quantified estimating its excess Gibbs Energy

$$G^{E} = \underbrace{G^{E,\mathrm{Res}}}_{\text{Contribution due to the interactions}} + \underbrace{G^{E,Comb}}_{\text{Contribution due to the differences in size and shape}}$$

- The non ideality can be described in terms of the activity coefficient, γ

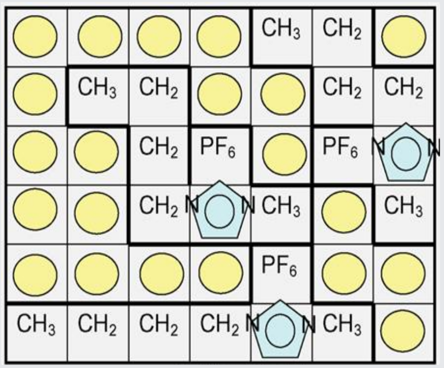
$$p = x_{CO_2} \cdot \gamma_{CO_2} \cdot p^{\sigma}_{CO_2}$$

$$\ln\left(\frac{\delta n_T G^E}{\delta n_i}\right)_{T,P,nj:i\neq j} = RT\ln(\gamma_i)$$

2. Results and Discussion

Flory-Huggins model

The fluid structure of the IL can be approximated by a solid-like structure



Flory Huggins Model

Contribution to
non ideality caused
by entropic effects

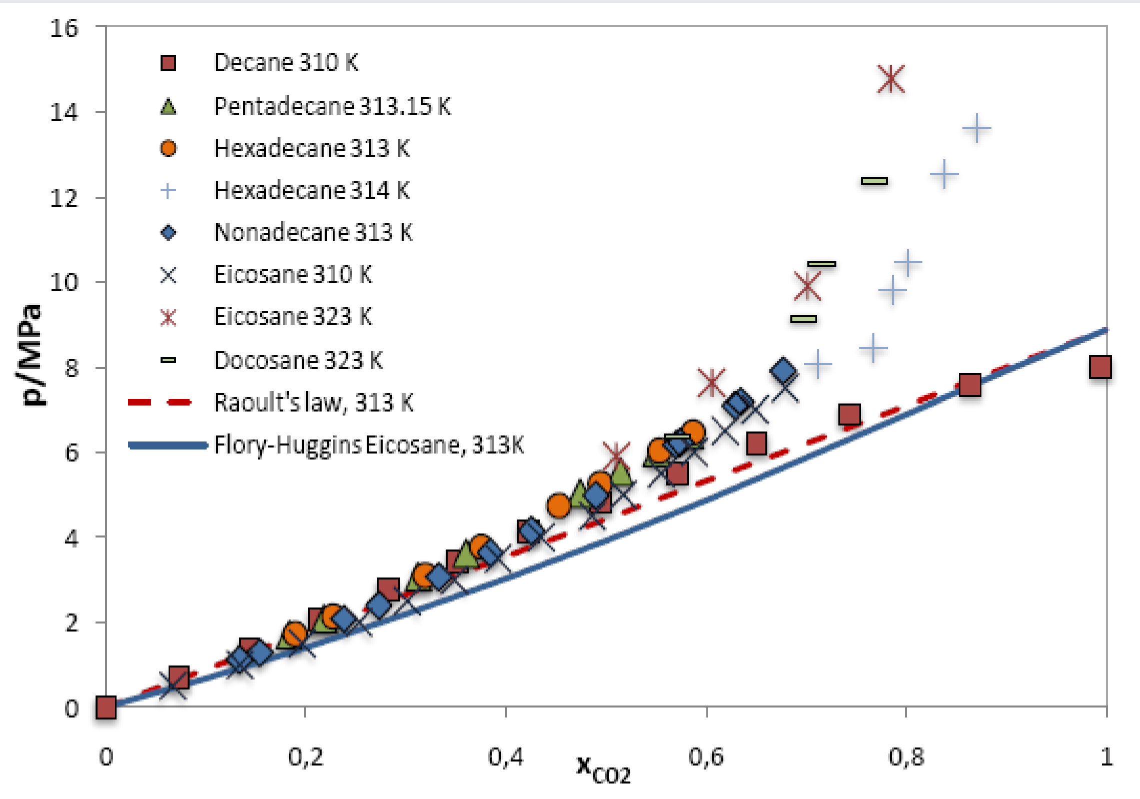
$$\ln\left(\gamma_{CO_2}^{Comb}\right) = \ln\left(\frac{\varphi_{CO_2}}{x_{CO_2}}\right) + \left(1 - \frac{\varphi_{CO_2}}{x_{CO_2}}\right)$$

$$\varphi_{CO_2} = \frac{x_{CO_2}.V_{CO_2}}{x_{CO_2}.V_{CO_2} + x_{solvente}.V_{solvente}}$$

Modified Raoult's Law: $$p = x_{CO_2}.\exp\left(\ln\frac{\varphi_{CO_2}}{x_{CO_2}} + \left(1 - \frac{\varphi_{CO_2}}{x_{CO_2}}\right)\right).p_{CO_2}^{\sigma}$$

2. Results and Discussion

Non ideality of CO_2/Alkane systems



The Flory-Huggins model predicts negative deviations to ideality

⇩

The VLE data has near ideal behavior

⇩

There is an effect of positive deviations from the residual part

⇩

CO_2-alkane interactions must be weaker than the alkane-alkane interactions

⇩

Solute – solvent interactions don't energetically compensate the interactions that are destroyed upon mixing

2. Results and Discussion

Non ideality of CO_2/Alcohol systems

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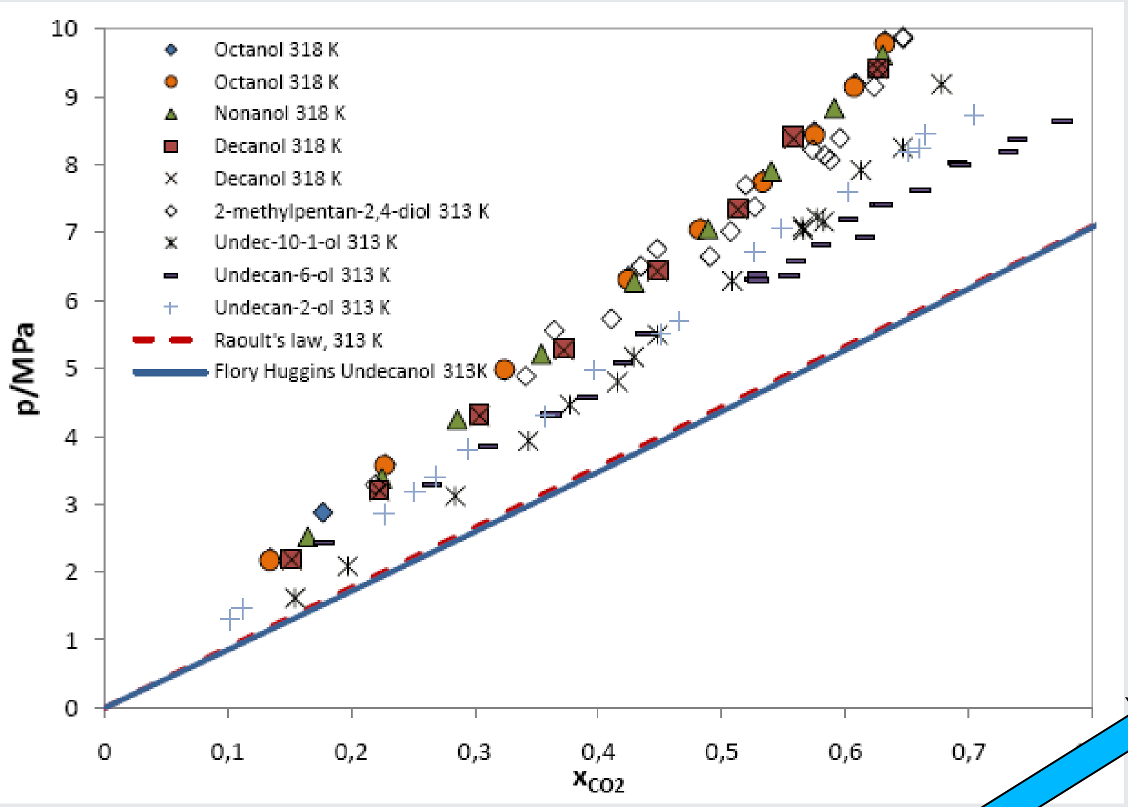

VLE data is placed above the ideality line

Positive deviations to ideality

Intermolecular forces between molecules of CO_2 and alcohol are less important than they are between alcohol-alcohol molecules

Strong solute-solvent interactions are not enough to guarantee enhanced solubility

Strong CO_2-OH interactions observed spectroscopically

2. Results and Discussion

Non-ideality of CO_2/Fatty acid esters and CO_2/IL systems

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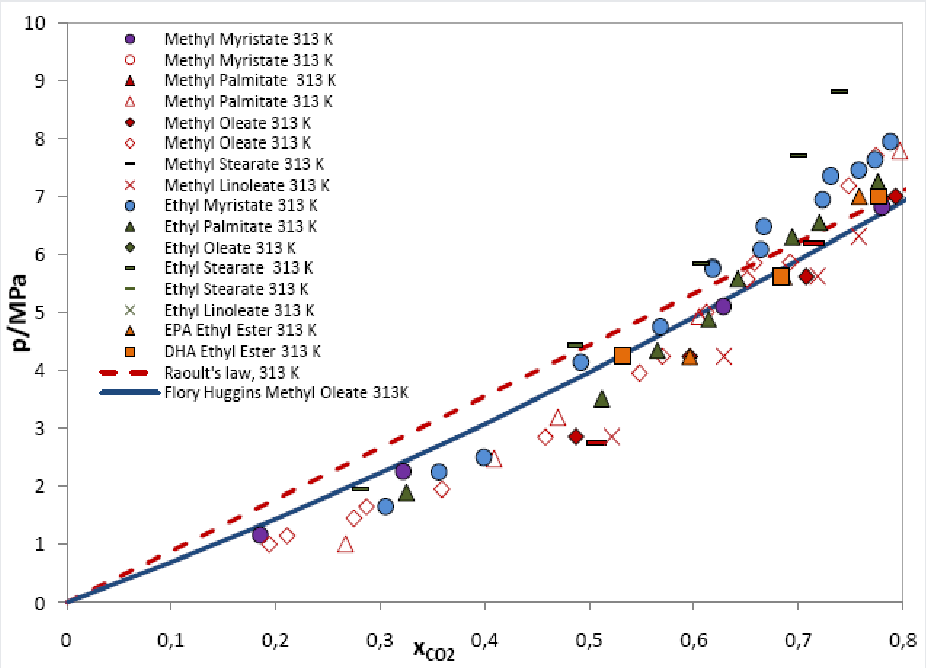
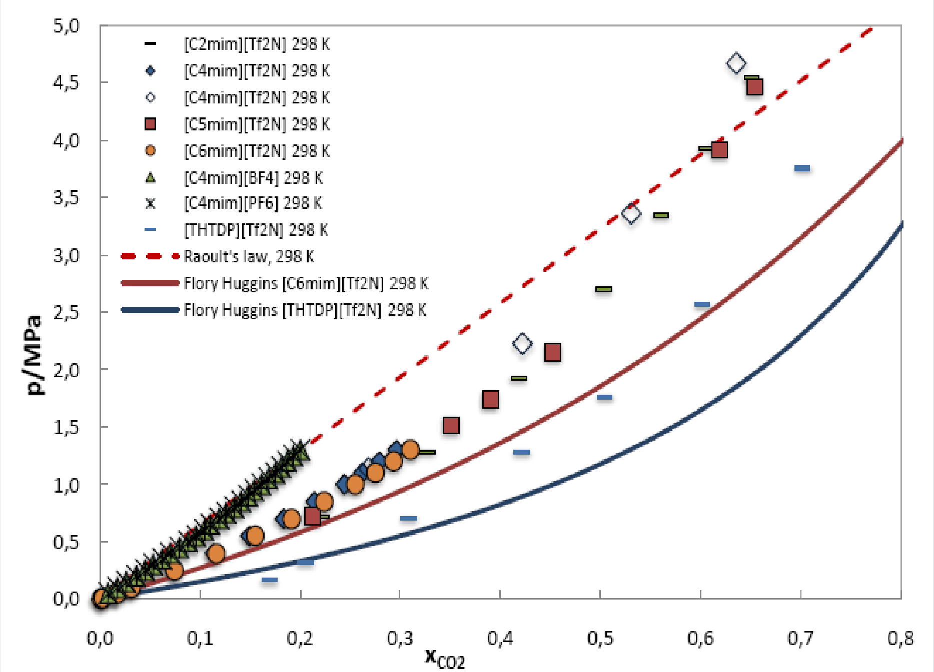




Large negative deviations to the ideal behavior

The residual contribution for the non ideality is negative

CO_2-carbonyl interactions are energetically favorable when compared with the carbonyl-carbonyl interactions established between the ester molecules

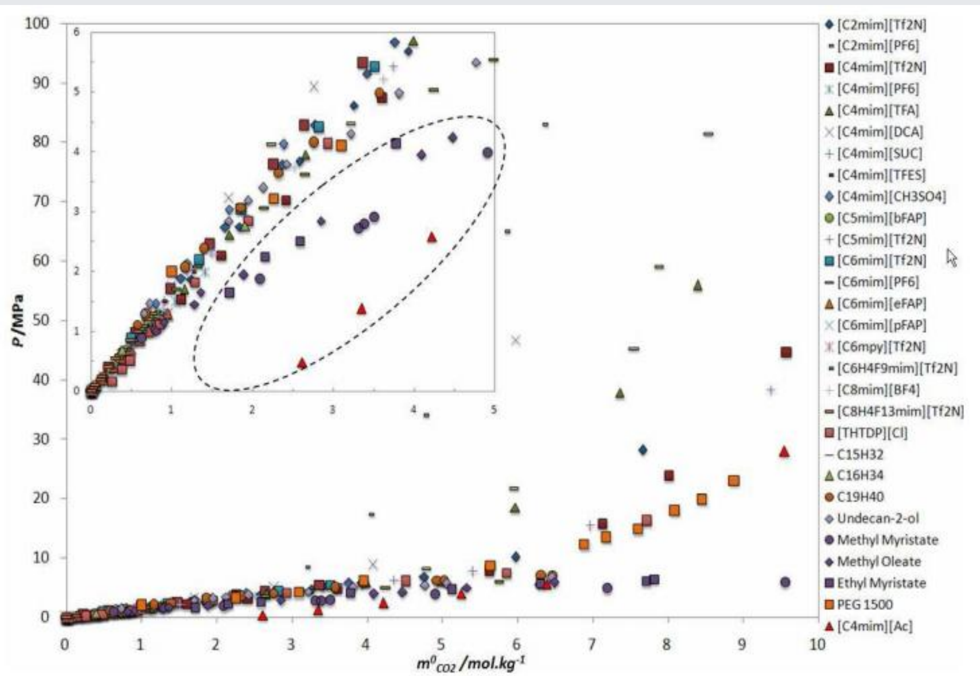
Deviations are intermediate between the ideal behavior and the predicted by the Flory-Huggins model

Combinatorial term of the Gibbs free energy is larger than the residual

Solubility of CO_2 in ILs is controlled by entropic effects

2. Results and Discussion

$$P = H_i . m_i^0$$



Carvalho,P. J. and Coutinho,J.A.P, On the Nonideality of CO_2 Solutions ion Ionic Liquids and other low volatile solvents . The Journal of Physical Chemistry Letters,2010(4),p.774-780

Solubility of CO_2 in non volatile solvents expressed in molality follows the same behavior

CO_2 solubility is solvent independent

A linear relation was adjusted to the p-m diagram at different temperatures and from the slope the Henry’s law constant was taken

converted to mole fraction basis (H_1)

2. Results and Discussion

Relation of the molar volume to molecular weight

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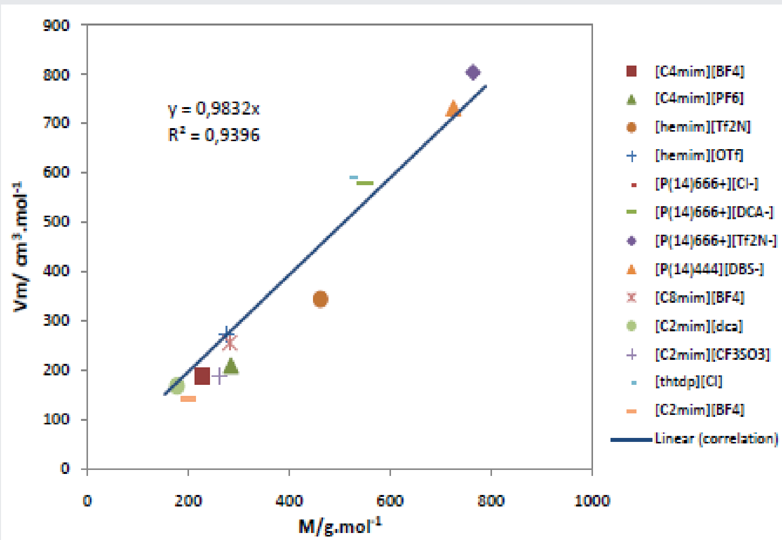
IL molar volume can be related to IL molecular weight by a linear regression



$$Vm = 0.9832 \times Mr$$

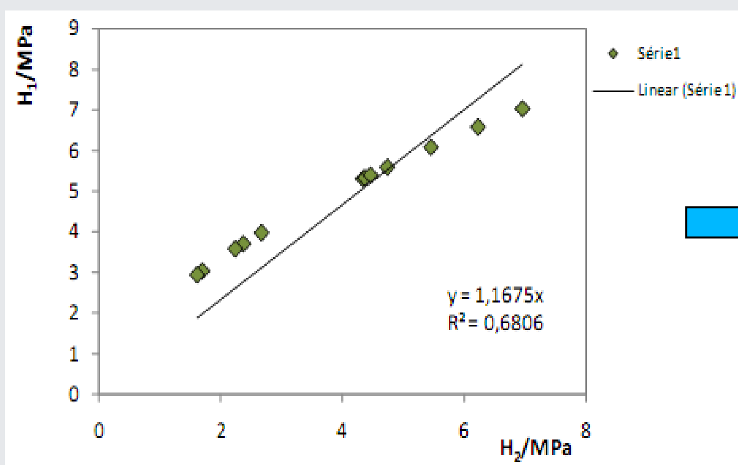
$$+$$

$$H_{CO_2} = 0.0241 \times Vm^{-0.670}$$

$$H_{CO_2} = 0.0241 \times (0.9832 \times M_r)^{-0.670}$$

Relation of the CO_2 solubility with IL molecular weight

Henry's law constants obtained in both ways at 303 K



The prediction of CO_2 solubility in IL based on IL molecular weight seems to be a good approximation

2. Results and Discussion

Solubility dependence with temperature

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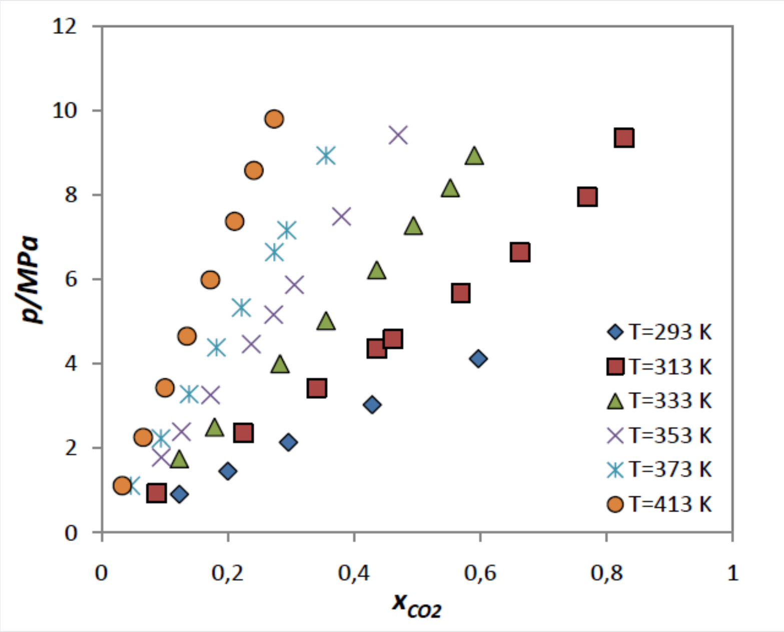
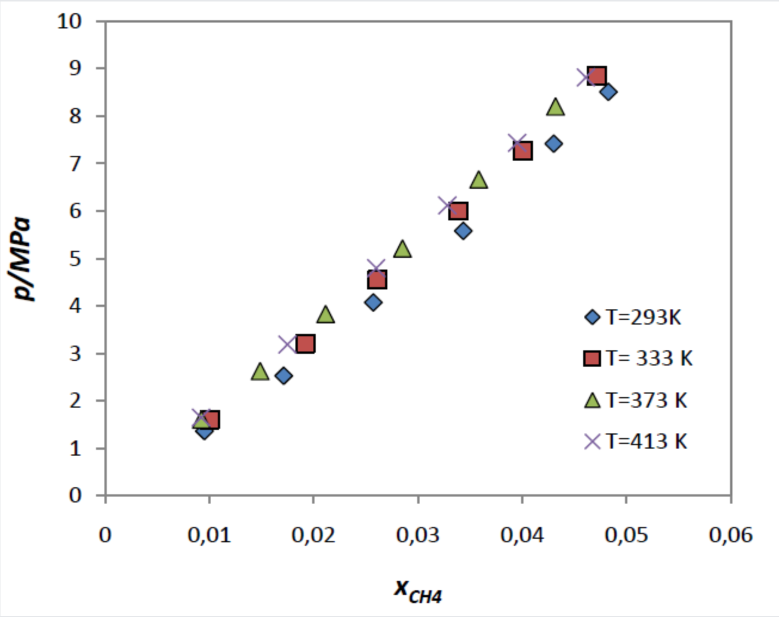
- CO_2 and CH_4 solubility in the ionic liquid [C4mim][CH3SO4]





The isotherms are well separated

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CO_2 solubility seems to be strongly temperature dependent

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As the temperature increases, the solubility becomes lower

The isotherms practically overlap each other

↓

Low temperature dependence of CH_4 solubility

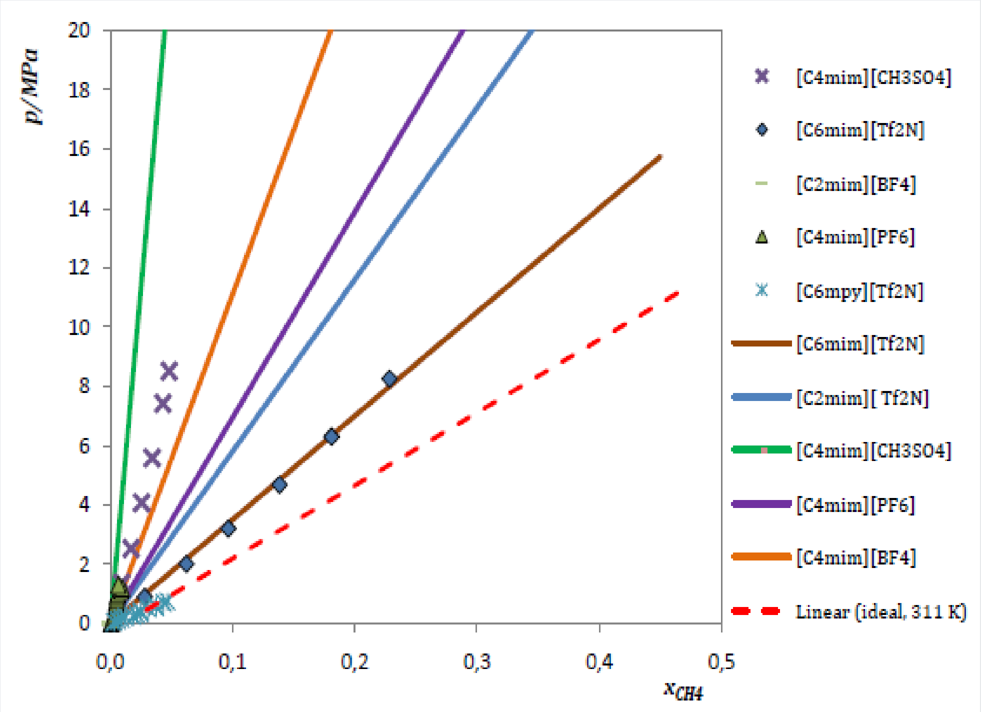
↓

The solubility remains almost the same for different temperatures

2. Results and Discussion

Deviations to ideality of CH_4 Solubility in ILs

- VLE data for CH_4/IL systems are compared to the ideal behavior that is assumed to be given by the CH_4/Hexane system.



VLE data lies above the ideal line

Strong positive deviations to ideality

CH_4-IL interactions are non favorable and much weaker than the IL-IL ones.

- The solubility increases as the chain length on the imidazolium ring of the cation increases in the order [C2mim] <[C6mim]

- The pyridinium cations present a higher solubility of CH_4 relatively to the imidazolium cations

- The solubility increases for the same cation in the order [PF6]< [BF4]< [CH3SO4]

2. Results and Discussion

CO_2/CH_4 Selectivity

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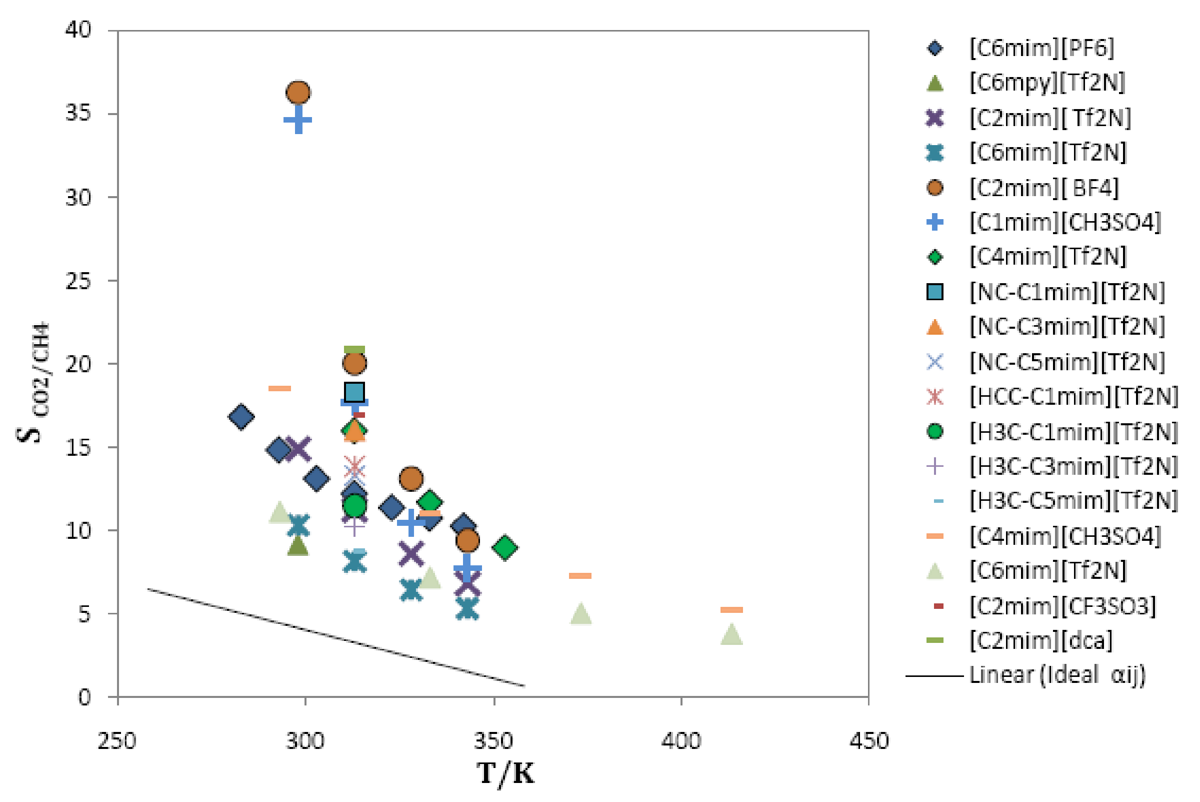
$$S_{CO_2/CH_4} = \frac{H_{CH_4}}{H_{CO_2}}$$

- From a CH_4/CO_2 mixture the component CO_2 is absorbed preferentially

- For all systems the selectivity is greater than the ideal and decreases as the temperature increases

- The largest selectivities were observed at a temperature of 298K and for the ionic liquid [C1mim][CH3SO4] and [C2mim][BF4].



2. Results and Discussion

CO_2/CH_4 Selectivity dependence with IL molar volume

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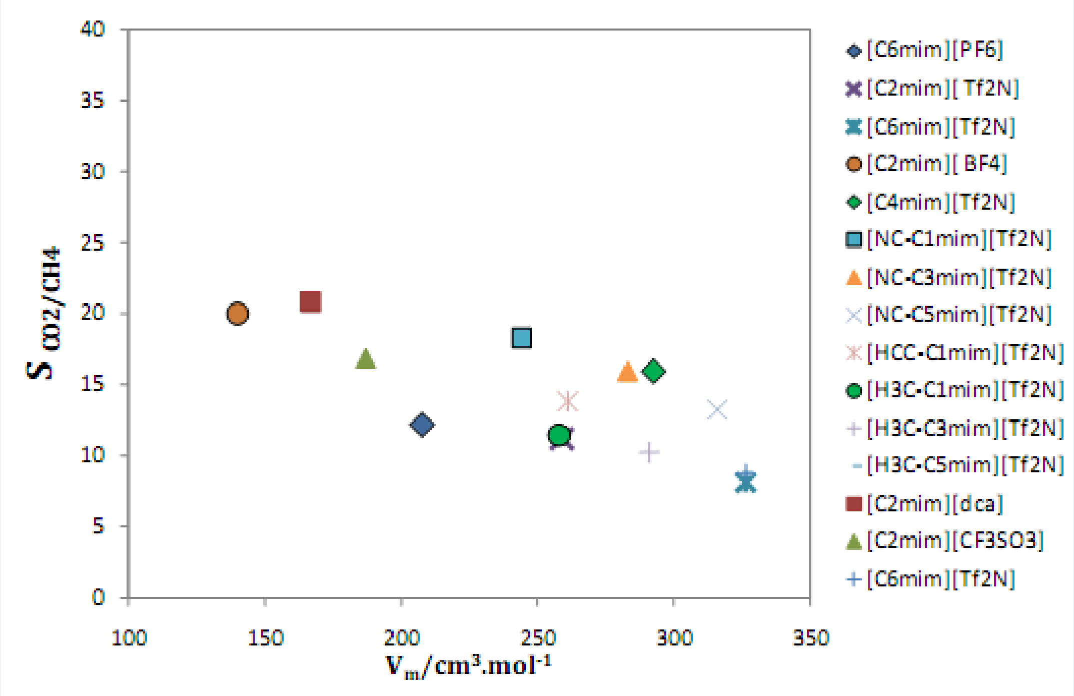
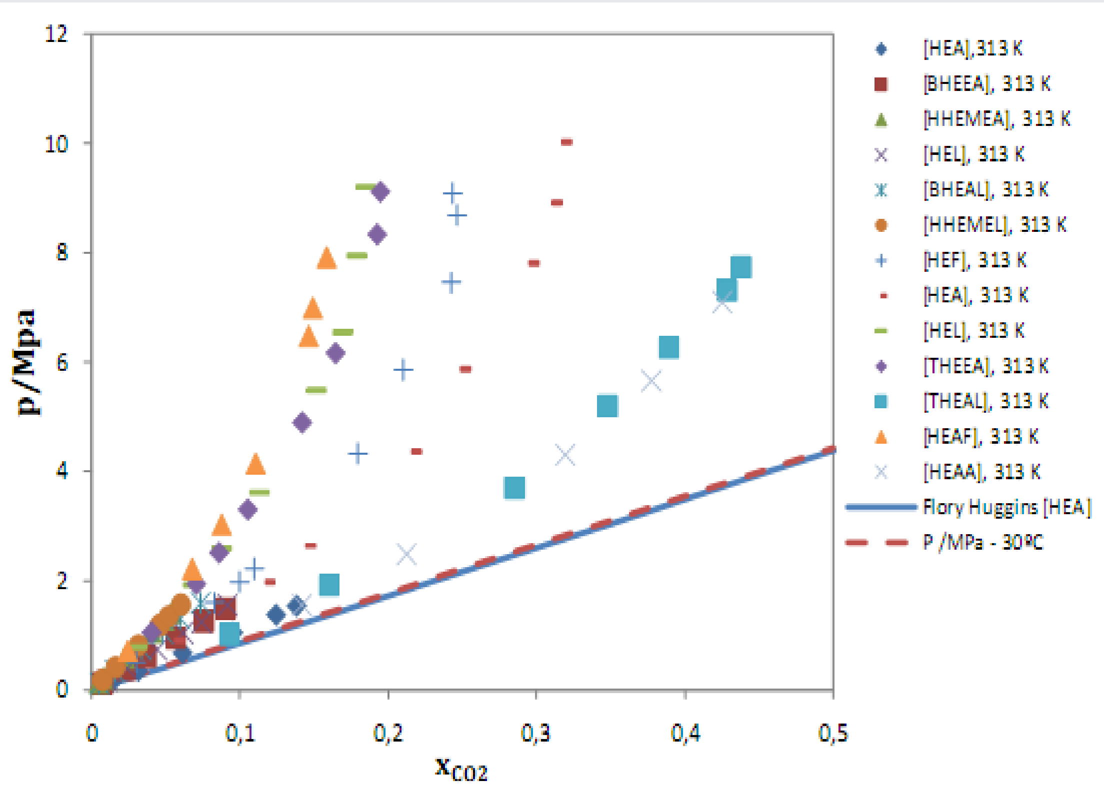


- The selectivity decreases with the ionic liquid molar volume
- Low molar volume ionic liquids are ideal for the separation of a CO_2 from CH_4
- The data available is however very limited and a define conclusion can only be achieved when more solubility data becomes available.

2. Results and Discussion

Non ideality of CO_2/Protic ionic liquids systems



Solubility data from literature lie always above the ideal behavior line

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Large positive deviations to ideality

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A CO_2-protic IL interaction is less favorable than a IL-IL one

↓

Formation of the EDA complex is not favorable.

This family of ionic liquids is not a viable option for CO_2 capture when compared with the other ionic liquids studied.

3. Conclusions

- In general it can be concluded that the solubility of CO_2 in non volatile solvents depends on the combination of the different interactions involved, namely the solute-solute, solvent-solvent and solute-solvent.

- The favorable interactions between CO_2 and the solvent are not the exclusively factor that influences the solubility.

- CH_4-IL interactions are much weaker than the IL-IL ones, since the CH_4-IL systems have strong positive deviations to ideality.

- The solubility of CH_4 becomes influenced by the alkyl chain length in the cation, representing higher solubility for longer chain lengths on the imidazolium ring.

- The greater the polarity of ILs the higher the deviation to ideality in the CH_4-IL systems.

- Prefered solubility of CO_2 in ILs compared to that of CH_4.

3. Conclusions

- Based on the selectivity the most adequate solvents are [C1mim][CH3SO4] and [C2mim][BF4].

- As the IL surface tension increases the solubility decreases

- An increase in the molar volume implies an increase in the gas solubility, but as the molar volume become very large the effect becomes insignificant.

- Solubility data of CO_2 in ILs can be obtained knowing a parameter as simple as the molar mass of the solvent.

- Selectivity decreases with the ionic liquid molar volume and thus low molar volume ionic liquids are ideal for the separation of CO_2 from CH_4

- Protic ionic liquids are not favorable as solvents for CO_2

Thank you for your Attention!