Universidade de Aveiro Departamento de Química
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Avaliação do COSMO-RS para previsão de constantes de Henry e selectividades

Evaluation of COSMO-RS for Henry constants and selectivity prediction

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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia Química, realizada sob a orientação científica do Dr. João Coutinho, Professor associado com agregação, do Departamento de Química da Universidade de Aveiro

Dedico este trabalho aos meus pais, irmã e em especial ao meu sobrinho Xavier.

"… he who seeks for methods without having a definitive problem in mind seeks for the most part in vain."

David Hilbert

o júri

presidente

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agradecimentos

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palavras-chave

Líquidos iónicos, constantes de Henry, dióxido de carbono, etano, metano, azoto, oxigénio, sulfeto de hidrogénio, solubilidade, selectividade, COSMO-RS.

resumo

Com este trabalho pretende avaliar-se um modelo predictivo, o COSMO-RS, no cálculo de constantes de Henry e selectividades. O modelo de previsão é baseado em cálculos químicos de quântica unimolecular para moléculas individuais e foi utilizado para prever solubilidades e selectividades de diferentes gases, entre os quais o dióxido de carbono (dada a sua importância actual em questões ambientais), em líquidos iónicos.

A capacidade deste modelo foi discutida com base na análise de dados experimentais recolhidos em literatura existente e é apresentada uma discussão das suas limitações.

Os líquidos iónicos são uma classe recente de solventes, designados por “solventes verdes” que possuem um vasto conjunto de propriedades interessantes, entre os quais elevada capacidade de solvatação, pressões de vapor ínfimas e a possibilidade de modelar as suas propriedades físicas uma vez que é possível “desenhar” um líquido iónico para determinada aplicação, pois existe um número quase infinito de combinações entre aniões e catiões.

key-words

Ionic liquids, Henry’s constants, carbon dioxide, ethane, methane, nitrogen, oxygen, hidrogen sulfide, solubility, selectivity, COSMO-RS.

abstract

The aim of this work is to do the evaluation of a predictive method, COSMO-RS, for prediction of Henry’s constants and selectivities. Predicitve model is based on unimolecular quantum chemical calculations for individual molecules and it was used to predict solubilities and selectivities of different gases, carbon dioxide included (due to its importance on environmental issues), in Ionic Liquids.
The ability of this model for the description of the solubility of gases in ionic liquids has been discussed based on the analysis of experimental data obtained from the open literature and it is made a discussion on the current limitations of COSMO-RS model. Ionic liquids are a novel class of compounds considered as “green solvents” which include important characteristics such as high solvation capacity, negligible vapour pressures and the possibility to “shape” the solvent for a particular application due to the great variety of cations and anions (there are virtually an infinite number of possible combinations).

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NOTATION

List of Symbols

α'	electrostatic misfit interactions coefficient
σ	polarization charge density
$\sigma_{\mathrm{acceptor}}$	polarization charge of an hydrogen bonding acceptor
σ_{donor}	polarization charge of an hydrogen bonding donor
σ_{HB}	hydrogen bonding threshold
τ_{vdW}	element-specific vdWs coefficient
τ'_{vdW}	element-specific vdWs coefficient
a_{eff}	effective contact area between two surface segments
c_{HB}	hydrogen bond strength coefficient
$p_{Xi}(\sigma)$	sigma profile of a solute *i*
$p_S(\sigma)$	sigma profile of a solvent
x_i	mole fraction of compound *i*
A_{Xi}	total surface area of molecule *Xi*
E_{misfit}	electrostatic misfit energy
E_{HB}	hydrogen bonding energy
E_{vdW}	van der Waals energy
$P'_S(\sigma)$	normalised sigma profile of a solvent
H	Henry's law constant
T	Temperature
p	Pressure

List of Abbreviations

ILs: Ionic Liquids
CCS: CO_2 Capture and Storage
SLE: Solid-Liquid Equilibria
VLE: Vapour-Liquid Equilibria
LLE: Liquid-Liquid Equilibria
EoS: Equation of State
COSMO-RS: COnductor-like Screening MOdel for Real Solvents
GCMs: Group Contribution Methods
QM: Quantum Chemical Methods
HC: Hydrocarbon
CO_2: Carbon Dioxide
O_2: Oxygen
CH_4: Methane
C_2H_6: Ethane
N_2: Nitrogen
H_2S: Hydrogen Sulfide

Cation	**Anion**	**Name**
[C_2mim]	[DCA]	*1-ethyl-3-methylimidazolium dicyanamide*
[C_2mim]	[Tf_2N]	*1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide*
[C_2mim]	[CF_3SO_3]	*1-ethyl-3-methylimidazolium trifloromethanesulfonate*
[C_2mim]	[BF_4]	*1-ethyl-3-methylimidazolium tetrafluoroborate*
[C_2mim]	[$ETSO_4$]	*1-ethyl-3-methylimidazolium ethylsulfate*
[C_3mim]	[Tf_2N]	*1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide*
[C_3mim]	[PF_6]	*1-methyl-3-propylimidazolium hexafluorophosphate*
[C_4mim]	[BF_4]	*1-butyl-3-methylimidazolium tetrafluoroborate*
[C_4mim]	[PF_6]	*1-butyl-3-methylimidazolium hexafluorophosphate*
[C_4mim]	[Tf_2N]	*1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide*
[C_4mim]	[NO_3]	*1-butyl-3-methylimidazolium nitrate*
[C_1C_4PYRR]	[Tf_2N]	*1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide*
[C_6mim]	[PF_6]	*1-butyl-3-hexylimidazolium hexafluorophosphate*
[C_6mim]	[BF_4]	*1-hexyl-3-methylimidazolium tetrafluoroborate*

[C$_6$mim]	[Tf$_2$N]	*1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide*
[C$_6$MPY]	[Tf$_2$N]	*1-n-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide*
[C$_8$mim]	[PF$_6$]	*1-methyl-3-octylimidazolium hexafluorophosphate*
[C$_8$mim]	[BF$_4$]	*1-methyl-3-octylimidazolium tetrafluoroborate*
[C$_8$mim]	[Tf$_2$N]	*1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide*
[NBUPY]	[BF$_4$]	*N-butylpyridinium tetrafluoroburate*
[C$_{10}$mim]	[Tf$_2$N]	*1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide*
[P$_{(14)666}$]	[Cl]	*trihexyl(tetradecyl)phosphonium chloride*
[P$_{(14)666}$]	[DCA]	*trihexyl(tetradecyl)phosphonium dicyanamide*
[P$_{(14)666}$]	[TF$_2$N]	*trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide*
[P$_{(14)66}$]	[Cl]	*Trihexyl(tetradecyl)phosphonium chloride*

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1. INTRODUCTION

1.1. CLIMATE CHANGE

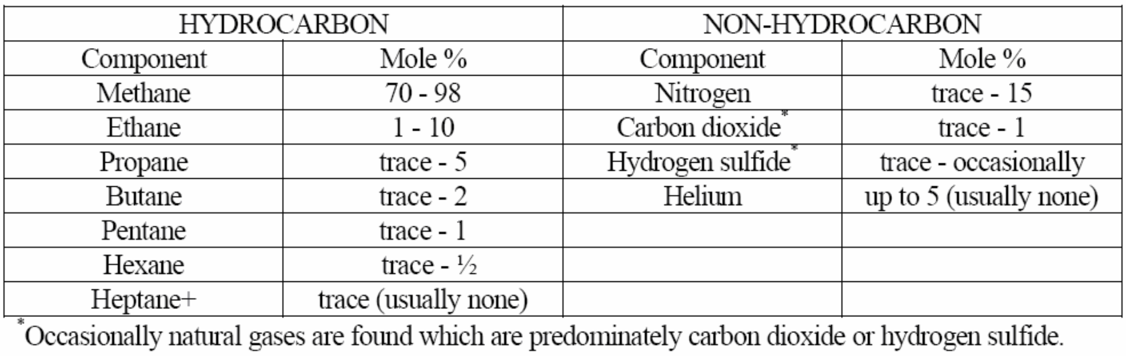
Fossil fuels will continue to be extensively used and world carbon dioxide (CO_2) gas emissions will probably still increasing during the next decades unless some stringent new policies are created. It is clear that a development as we have today is not sustainable. CO_2 is a natural, fluctuating component of the Earth's atmosphere and has been present throughout most of geological time. It is the most important anthropogenic greenhouse gas and because of the increasing accumulation in the atmosphere we have global warming effects and serious environmental problems. Over the past 200 years its concentration in the atmosphere has increased from 280 to 370 parts per million (ppm) [1] (an increase of circa 30 %) mostly since the industrial revolution due to the burning of coal, natural gas and oil.

To what extent, is not known, but the increase in CO_2 concentration in the atmosphere may lead to disastrous consequences and something must be done about it. One way to curb CO_2 emissions is by increasing energy efficiency and using alternative energy sources such as solar and wind power and nuclear energy, but policies based on these options will only partly solve the problem.

Nowadays energetic needs are accomplished by relatively inexpensive fossil fuels and switching to alternative sources will be a gradual process because nonfossil fuel energy sources are more expensive and need large areas to produce small quantities of power. For that reason it is crucial to reduce the costs of alternative energy sources. Therefore, the development of efficient methods with new technologies for capturing CO_2 from gas streams is essential.

There are already a promising number of options that can reduce CO_2 emissions designated by CO_2 capture and storage (CCS) technologies. CO_2 capture is the separation of CO_2 from emissions sources including natural gas (Table 1.1.1) [2] purification, flue gas separation.[3].

Table 1.1.1: Components of typical natural gases.



HYDROCARBON		NON-HYDROCARBON	
Component	Mole %	Component	Mole %
Methane	70 - 98	Nitrogen	trace - 15
Ethane	1 - 10	Carbon dioxide*	trace - 1
Propane	trace - 5	Hydrogen sulfide*	trace - occasionally
Butane	trace - 2	Helium	up to 5 (usually none)
Pentane	trace - 1		
Hexane	trace - ½		
Heptane+	trace (usually none)		

*Occasionally natural gases are found which are predominately carbon dioxide or hydrogen sulfide.

CO_2 CCS involves three distinct processes:

1st → capture CO_2 from the gas streams emitted during electricity production, industrial processes or fuel processing;

2nd → carry the captured CO_2 by pipeline or in tankers;

3rd → store CO_2 underground in deep saline aquifers, depleted oil and gas reservoirs.

All three processes have been in use for decades, but not with the purpose of storing the CO_2 but for using it in different applications.

Storage in deep saline aquifers has been demonstrated in one commercial-scale project, at the Sleipner site in Norway (sub-sea storage) (see Figure 1.1.1) [4]. No leakage has been detected and the behaviour of CO_2 stored has corresponded to what models had predicted.

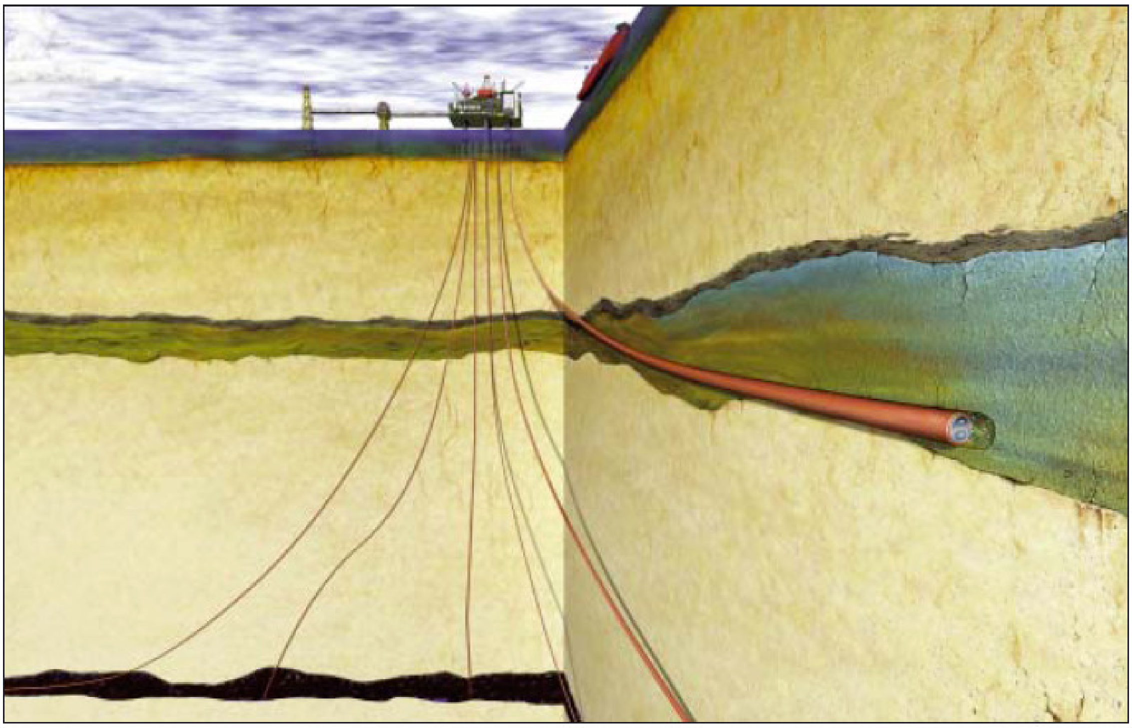


Figure 1.1.1: Injection of CO_2 into the Utsira Formation from the Sleipner A platform. (Illustration: David Fierstein.)

The underground potential is enormous but could be problematic given the unknown environmental impacts.

The CO_2 can be captured before or after combustion:

- Pre-combustion capture: convert the hydrocarbon (HC) fuel into CO_2 and Hydrogen (H_2), remove the CO_2 from the fuel gas and combust H_2. As an advantage in pre-combustion there are higher CO_2 concentration than for post-combustions capture.
- Post-combustion capture: CO_2 is captured from the flue gases (which have several contaminants) during combustion.

1.2 CO_2 CAPTURE TECHNOLOGY

The CO_2 when pressurized becomes liquid or reaches a dense state called supercritical (a state between gas and liquid). The supercritical state occurs at temperatures (T) greater than 31, 2ºC and Pressures (p) greater than 72,8 atm [5] and the density of the fluid varies with T and p. The physical properties have great influence in CCS.

New processes for CO_2 capture include membranes (to increase CO_2 concentration), air separation technologies (involving combustion in pure oxygen (O_2)), fuel cells, etc.

One of the most widely applied technologies for capturing CO_2 is chemical absorption by using amine based solvents such as a variety of alkanolamines, which are usually used in aqueous solution [6] according to the following equation (1.2.1):

$$C_nH_{2n}OHNH_2 + CO_2 + H_2O \rightarrow C_nH_{2n}OHNH_3^+ + HCO_3^- \qquad \textbf{(1.2.1)}$$

This is an effective way to capture CO_2 but there are several problems connected to those organic solvents such as loss of volatile amines and the uptake of water into the gas stream that causes intense energy consumption, costs increase and there are also some corrosion problems associated.

Because all of this it is necessary to find new types of sequestering agents with characteristics that may correct the limitations discussed above. One such example of solvents are the ionic liquids (ILs).

ILs are attractive physical solvents for CO_2 capture and gas separations because they have properties such as large CO_2 solubility, high thermal stability, extremely low vapour pressures, and may be designed to be non-toxic and biodegradable [7]. Such materials not only have the potential to capture CO_2 with minimal solvent loss in the gas stream but are expected to be environmental benign.

1.3. IONIC LIQUIDS

1.3.1 History

Though ILs were created in the early 20th century, there was not much interest in them until the 1950s. The first discovery of a room temperature IL was in 1951. Hurley and Wier developed low melting salts with chloroaluminate ions for low-temperature electroplating of aluminium [8]. At the time some of the products were unstable in the presence of air and water and this was a major limitation to their use.

By 1992 Wilkes et al. [9] developed the imidazolium based ILs that were found to be air and water stable over a wide range of temperatures.

Over the past few decades the range of available anions and cations has expanded enormously and they are expected to have a huge potential for application in different fields of chemistry and chemical engineering.

1.3.2 ILs Applications

For several industrial processes, solvents play a very important role used in many chemical reactions and separation processes. These solvents release volatile organic compounds (VOCs) and they may cause environmental and health problems due to their significant vapour pressures that increases the risk of exposure and losses. Because of this it is important to find another class of solvents that still attends the needs of industry but reduces environmental and health risks.

Ionic liquids (ILs) are a novel class of compounds that are emerging as potential replacements for conventional solvents [10] and have been the focus of intensive research in recent years [11]. They can be considered “green solvents” due to their most important characteristic as negligible vapour pressures, which makes them ideal replacements for volatile solvents. They can also be recycled and reused repeatedly.

Ionic liquids is the term used to refer to organic salts that are liquids in their pure states at ambient conditions [12]. They are usually composed by an organic cation such as imidazolium, pyridinium or pyrrolidinium, and a smaller organic or inorganic anion such as hexafluorophosphate $[PF_6]^-$, tetrafluoroborate $[BF_4]^-$ or chloride $[Cl]^-$ [13], among others, as shown in Figure 1.3.1. [13] In general, ILs have many properties that are similar to conventional organic solvents such as good solvency power. Due to the great variety of cations and anions there are virtually an infinite number of possible combinations.

Moreover it is possible to “shape” the solvent for a particular application.

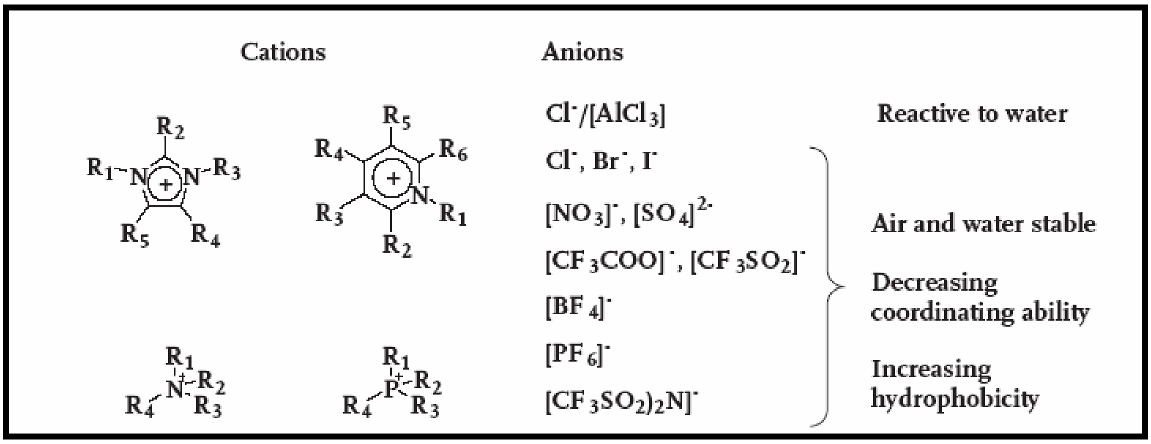


Figure 1.3.1: Examples of common cation and anion pairs used in the formation of ionic liquids, and general progression of changes in IL properties with anion type.

Researchers have shown that adjusting the structure of either the anion or the cation [14] it is possible to have large effects on many properties including densities [11], conductivities, viscosities, heat capacities, thermal decomposition, hydrophobicity, hydrogen-bonding capability and gas and liquid solubilities.

The asymmetry of the cation is believed to be the major responsible for the low melting points of ILs (below 100 ºC), while the nature of the anion is considered to be responsible for many of the physical properties of these compounds such as their miscibility with conventional solvents, density and viscosity.

The knowledge of gas solubility in the reaction media, for example, is required to properly design gas contacting equipment and to determine the intrinsic rate of catalytic reactions. Many of the reactions studied in ILs involve organic liquids or permanent or condensable gases. If a reactant gas has a low solubility in the IL, the mass transfer of the gas into the IL phase will likely be the rate-limiting factor. This limitation would require efforts to be made in order to increase the interfacial area and/or use high-pressure operations in order to reach the necessary concentration of gas in the IL. In addition, its importance in reactions and the understanding of the gas solubility process in ILs are necessary requesits for assessing the usefulness of ionic liquids in other applications.

The higher solubility of gases in ILs when compared to common solvents aroused the interest of the scientific community to this issue, as recent literature reports [15-17]. Gases such as oxygen, nitrogen, hydrogen, argon, carbon monoxide and CO_2 are among the most studied. Particular attention is given to CO_2 due to the interesting behaviour observed when this gas is used as supercritical fluid [18]. A different and interesting subject is the use of carbon dioxide like an anti-solvent in precipitations. These mentioned applications avoid the problems related with traditional separation techniques such as the loss of solvent, cross-contamination and destruction of thermo-sensible compounds [19-21].

1.4. THE COSMO-RS PREDICTIVE MODEL

Computational molecular science is an important tool for the quantitative estimation of engineering parameters such as reaction rate constants, heat capacities, phase equilibria, gas solubilities. It reduces time, resources and overall costs in the process design.

Several traditional models have been used for correlating experimental data of phase equilibria. Based on excess free Gibbs energy models, Wilson, NRTL, UNIQUAC and UNIFAC equations have been applied to correlate solid-liquid equilibria (SLE), liquid-liquid equilibria (LLE) and vapour-liquid equilibria (VLE) of systems involving Ionic Liquids (ILs) [22-24]. Local composition models have already proved being able to correlate data of ILs systems. The non-random two-liquid model (NRTL) was applied to VLE and liquid-liquid equilibria (LLE) systems [22,25,26]. A different approach was proposed by Rebelo (1999) [27] that uses a "polymer-like" G^E-model to correlate the LLE of ILs solutions, because of the similarity between the LLE phase diagrams of polymer solutions and those of IL solutions. However correlations and group contribution methods are not a good alternative due to the lack of experimental data. On the other hand, the use of equations of state (EoS) requires ILs critical parameters, which are not directly measurable and may be obtained only indirectly [28].

Predictive methods are often indispensable for chemical engineers in the design of chemical processes and plants because quite often no experimental data for certain compounds, neither from databases nor from experimental measurements, are available at a reasonable price for the mixture regarded.

COSMO-RS is a novel prediction method for thermodynamic equilibria of fluids and liquid mixtures. The complete name is "COnductor-like Screening MOdel for Real Solvents" and it was proposed by Klamt and co-workers [29-32]. It combines the electrostatic advantages and the computational efficiency of the quantum chemical dielectric continuum solvation model, COSMO, with a statistical thermodynamic approach for local interaction of surfaces, where the local deviations from dielectric behaviour as well as hydrogen-bonding are considered. COSMO-RS is a method based on unimolecular quantum chemical calculations of the individual species in the system and not of the mixture itself, and can be considered as an alternative to the structure-interpolating group-contribution methods (GCMs).

1.5. OBJECTIVES OF THIS WORK

The purpose of this work is to evaluate a predictive method, COSMO-RS, for the prediction of Henry Constants for systems of imidazolium, pyridinium and phosphonium-based ILs plus Carbon Dioxide (CO_2) and other gases like Oxygen (O_2), Methane (CH_4), Ethane (C_2H_6), Nitrogen (N_2) and Hydrogen Sulfide (H_2S).

For this purpose predicted Henry constants using the COSMO-RS are compared against experimental data obtained from the open literature. A discussion on the current limitations of the COSMO-RS model for the description of the solubility of gases in ionic liquids will be presented.

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2. COSMO-RS

2.1. THEORY

The knowledge of thermodynamic properties of solutions or mixtures of liquids is a major requirement in chemical engineering since it is essential for all kinds of separation processes such as absorption, adsorption, distillation, solubility of gases.

From a practical point of view it is expected that soon theories may have advanced to a point where predictions of chemical, physical and transport properties can be made based on purely theoretical considerations [1].

COSMO-RS is a method based on unimolecular quantum chemical calculations of the individual species in the system and not of the mixture itself and can be considered as an alternative to the structure-interpolating group-contribution methods (GCMs).

COSMO-RS and GCMs are two different approaches for the prediction of activity coefficients of molecules in the liquid phase. In GCMs (using defined groups) the interaction energy of any system can be well approximated by the sum of functional groups interaction energies. This means that a liquid is considered to be not a mixture of interacting molecules but a mixture of interacting structural groups [2]. GCMs have a very restricted applicability because it depends on the availability of group interaction parameters and especially on experimental results.

Instead, COSMO-RS instead is a method for predicting the thermodynamic properties of mixtures on the basis of unimolecular quantum chemical calculations of the individual molecules or, to be more precise, from the molecular surface as computed by quantum chemical methods (QM) [2].

The calculation procedure of COSMO-RS is separated into two steps: quantum chemical COSMO calculations for the molecular species involved and COSMO-RS statistical calculations performed within the COSMOtherm program [3,4], as shown in Figure 2.1.1

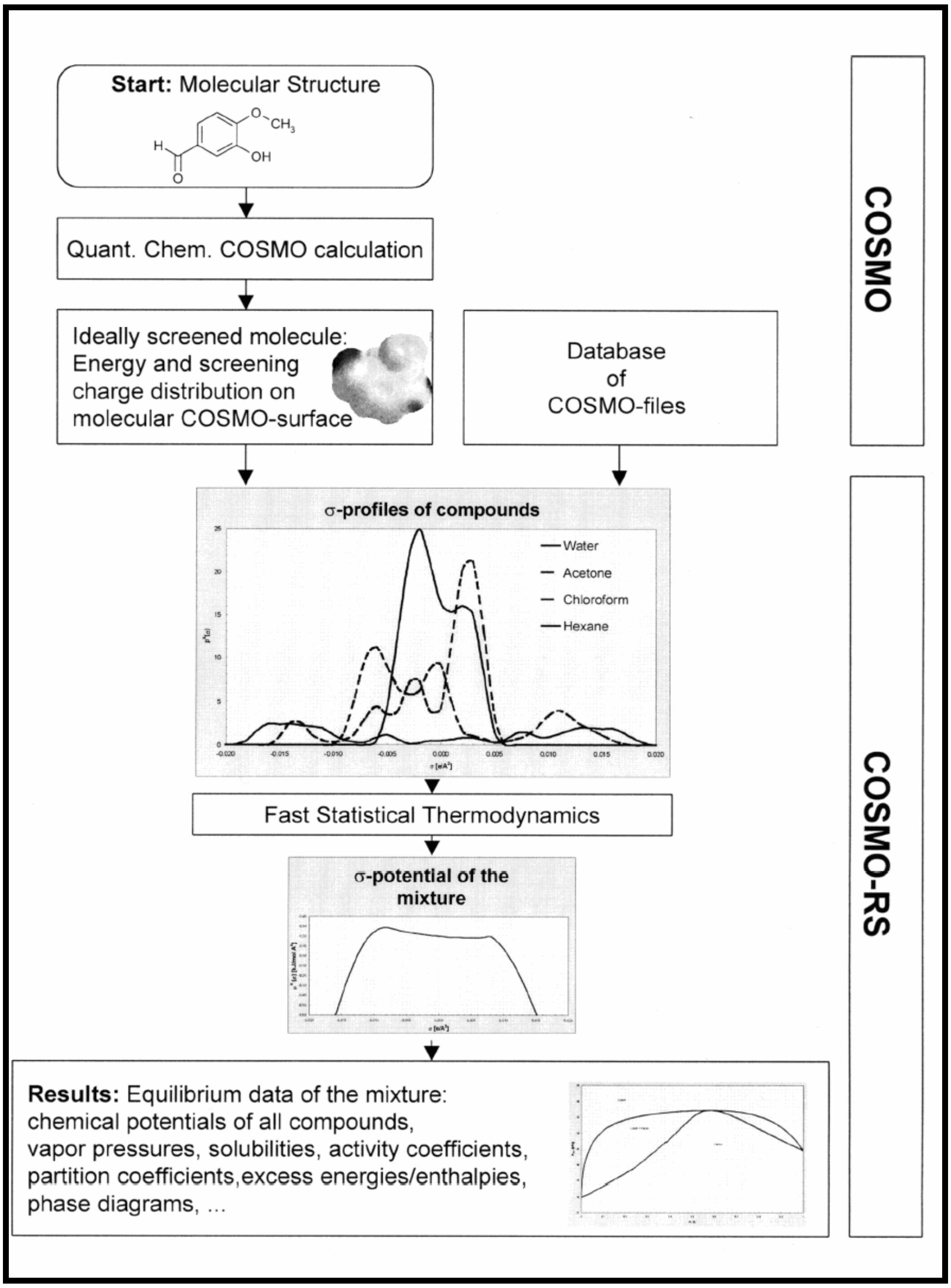

Figure 2.1.1: Flow chart of a COSMOtherm calculation of thermodynamic properties [4].

In the first step QM COSMO calculations have to be done for the molecular species involved, where the information about solvents and solutes is extracted. In these calculations, the continuum solvation model COSMO is applied in order to simulate a virtual conductor environment for the molecule. Then the solute molecule induces a polarization charge density, σ, on the interface of the molecule and the conductor. These charges act back on the solute and produce a more polarized electron density than in vacuum.

Throughout the quantum chemical self-consistency algorithm cycle, the solute molecule is converged to its energetically optimal state in a conductor with respect to electron density. The molecular geometry can be optimized using conventional methods for calculation in vacuum [5].

The calculations end up with the self-consistency state of the solute in the presence of a virtual conductor that surrounds the solute outside the cavity. These quantum chemical calculations have to be performed only once for each molecule of interest and then can be stored in a database [5].

The COSMO-RS calculation that predicts the thermodynamic properties such as chemical potentials, Henry constants, solubilities, vapour pressures, etc are done in few seconds and then can be used in the task of screening a large number of compounds from a database. It depends on a small number of 16 adjustable parameters, some of wich are physically predetermined [1] (from known properties of individual atoms) and that are not specific for functional groups or type of molecules. Moreover, it is statistical thermodynamics that enables the determination of the chemical potential of all components in the mixture and, from these, thermodynamic properties can be derived.

The deviations of the real fluids behaviour with respect to an ideal conductor are take into account, and the electrostatic energy differences and hydrogen-bonding energies are quantified as functions of the local COSMO polarization charge densities, σ and σ', of the interacting surface of the molecule divided into segments [3,4].

COSMO-RS parameters are not specific regarding functional groups or molecule types. The parameters have to be optimized only for the QM method that is to be used as a basis for the COSMO-RS calculations. Thus the resulting parameterization is completely general and can be used to predict the properties of almost any mixture. This is the main practical difference between COSMO-RS and the GCMs.

The 3D polarization density distribution on the surface of each molecule Xi is converted into a distribution function, the σ-profile, $p^{Xi}(\sigma)$, that describes the polarity of each surface segment on the overall surface of the molecule. If a mixture is considered, the σ-profile of a solvent S, $p_S(\sigma)$, is the result of adding the individual $p^{Xi}(\sigma)$ weighed by their mole fractions, xi, as expressed in 2.1.1.

$$p_S(\sigma) = \sum_{i \in S} x_i p^{X_i}(\sigma) \qquad \textbf{(2.1.1)}$$

For the statistical thermodynamics is expedient to consider a normalized ensemble and since the integral of $p^{Xi}(\sigma)$ over the entire σ-range is the total surface area A^{Xi} of a compound *Xi*, the normalized σ-profile, $p'_S(\sigma)$, of the overall system is defined as follow in 2.1.2.

$$p_S'(\sigma) = \frac{p_S(\sigma)}{A_S} = \frac{p_S(\sigma)}{\sum_{i \in S} x_i A^{X_i}} \tag{2.1.2}$$

The electrostatic misfit energy (E_{misfit}) and hydrogen-bonding (E_{HB}) are described as functions of the polarization charges of the two interacting segments, σ and σ' or $\sigma_{\mathrm{acceptor}}$ and σ_{donor}, if the segments are located in a hydrogen bond donor or acceptor atom, as described in 2.1.3. and 2.1.4. The van der Waals energy (E_{vdW}) is dependent only on the elements of the atoms involved and is described by 2.1.5.

$$E_{misfit}(\sigma, \sigma') = a_{eff} \frac{\alpha'}{2} (\sigma + \sigma')^2 \tag{2.1.3}$$

$$E_{HB} = a_{eff}\, c_{HB} \min(0; \min(0; \sigma_{donor} + \sigma_{HB}) \max(0; \sigma_{acceptor} - \sigma_{HB})) \tag{2.1.4}$$

$$E_{vdW} = a_{eff} (\tau_{vdW} + \tau'_{vdW}) \tag{2.1.5}$$

where α' is the coefficient for electrostatic misfit interactions, a_{eff} is the effective contact area between two surface segments, c_{HB} is the coefficient for hydrogen bond strength, σ_{HB} is the threshold for hydrogen bonding and τ_{vdW} and τ'_{vdW} are element-specific vdWs coefficients.

The most important descriptor used in COSMO-RS is in fact the local screening charge density, σ, which would be induced on the molecular surface if the molecule would be embedded in a virtual conductor. This descriptor can be calculated by quantum chemical programs using the continuum solvation model COSMO, and it is an extremely valuable descriptor for the local polarity of molecular surface and it is the only descriptor determining the interaction energies. Thus, the ensemble of surface pieces characterizing a liquid system *S* is described by the distribution function, $p_S(\sigma)$, that depicts the amount of surface in the ensemble having a screening charge density σ- and σ^+. Thus, the σ- profile of a single compound is derived from the quantum chemical COSMO output for that molecule, applying some local averaging algorithm which take into account that only screening charge densities averaged over an effective contact area are of physical meaning in COSMO-RS [3,4].

The COSMO calculations have been performed with the TURBOMOLE program package [6,7] using the BP density functional theory and the TZVP (triple-ζ valence polarized large basis set) using the fully optimized geometries at the same level of theory for the lower energy conformers (file BP_TZVP_C21_0105).

For the system IL + CO_2, the cation and anion of the ionic liquid are inputed as separate compounds with the same mole fraction (see Figure 2.1.2). As the result of COSMO calculation, a COSMO file is generated. This file contains all information of the respective optimized and low energy molecular or ionic structure.

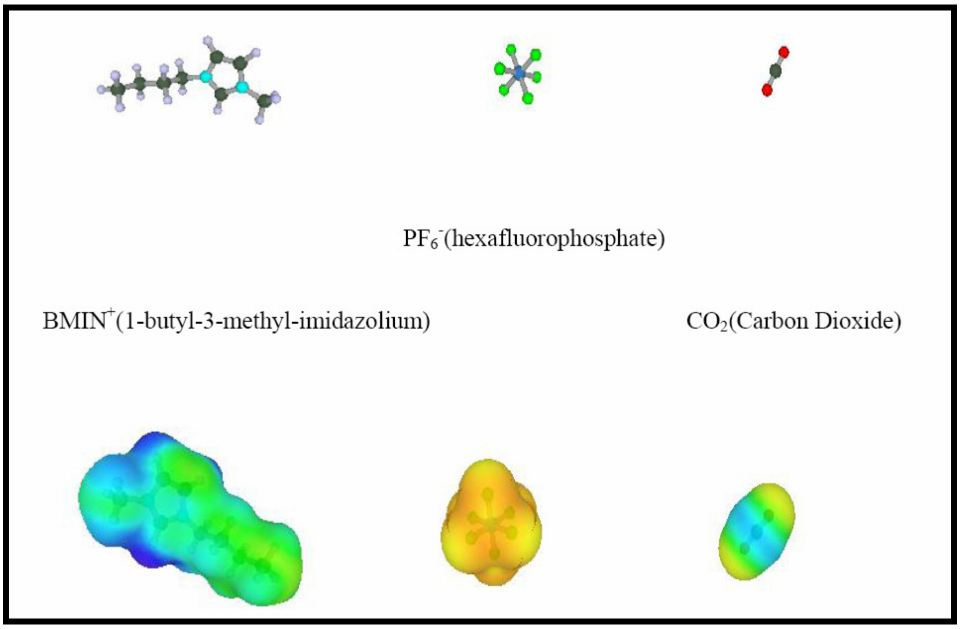

Figure 2.1.2: System IL + CO_2 used in COSMO calculations.
(COSMOtherm Version C2.1 Release 01.05).

It should be noted that COSMO-RS calculation that predict the thermodynamic property wanted, Henry constants, is done in a few seconds using COSMOtherm software (Version C2.1 Release 01.05).

2.2. CONFORMERS

The different conformations of a component may have an influence on chemical potentials and derived thermodynamic properties. The minimum energy conformation consists of the geometrically optimized minimum energy structure of the cation and of the anion. The maximum energy conformation is built analogously.

A molecule prefers to occupy the levels of the minimum potential energy and arranges its atoms accordingly. By rotation around single bonds, molecules with the same molecular formula can form geometrical isomers by arranging their atoms in different, non-equivalent positions to each other, the so-called minimum energy conformations or stable conformations. There are different energy states for the various conformers in the alkyl chains of the cations studied. Thus it is important, from a theoretical point of view, to evaluate the effect of the various conformers on the predicted systems. To study the influence of the ILs conformations on the COSMO-RS predictions, the stable conformations with the lowest and higher COSMO energies have been tested.

Some examples of the diverse energy conformations influence in the ILs [C_4mim][PF_6] and [C_4mim][BF_4] and several gases like CO_2, O_2, CH_4, C_2H_6 and N_2 are presented in Figures 2.2.1 and 2.2.2.

It should be noted that the lowest energy conformers correspond to the “conformer 0”, increasing the energy sequentially from “conformer 0” to “conformer 2”. Furthermore, just the cation several energy states were studied since the anions studied have just one optimal state, this is, just one conformer for the anion is available.

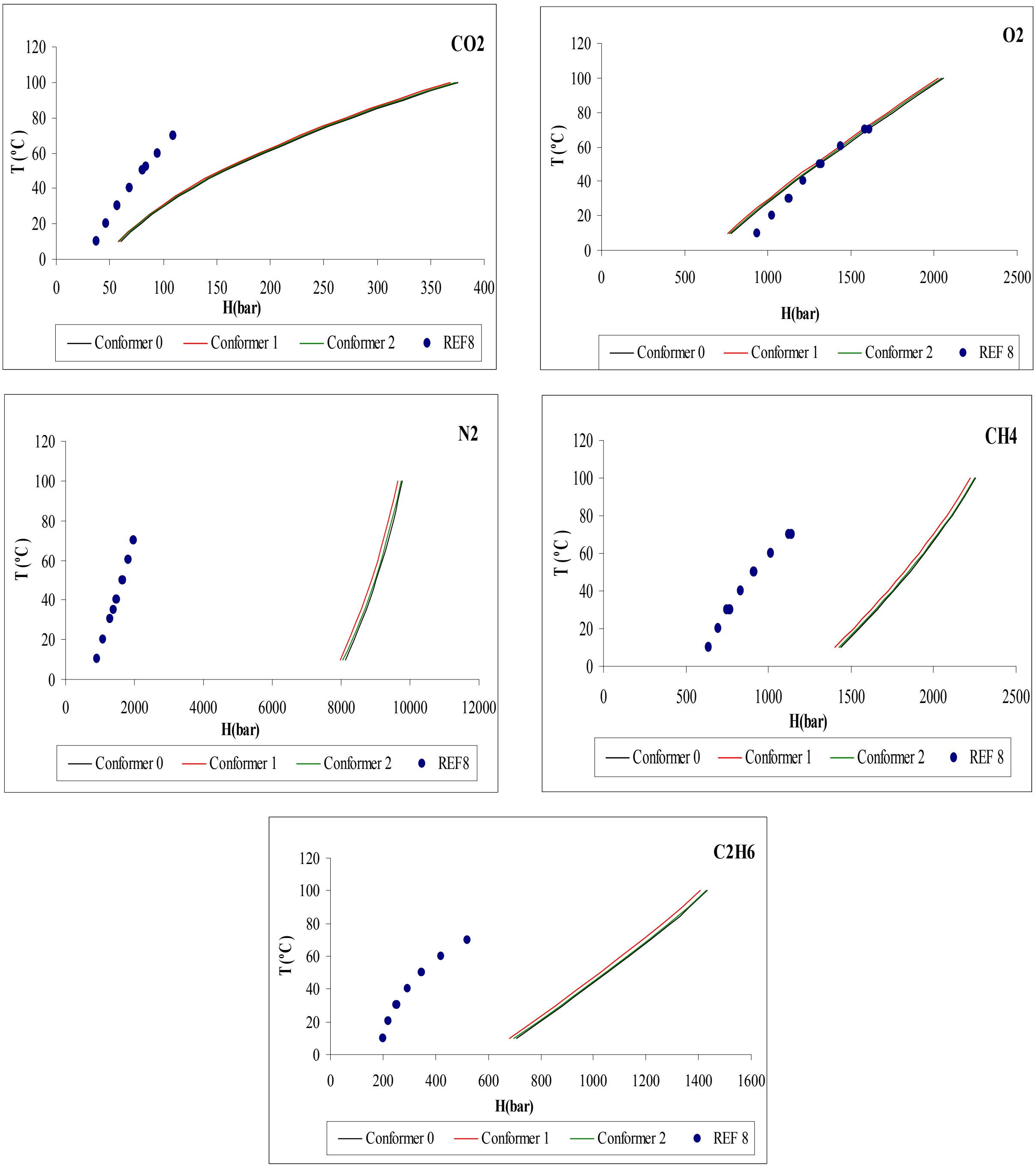

Figure 2.2.1: Henry constants values performed by COSMO-RS for three energy conformations available (conformer 0 — ; conformer 1 — ; conformer 2 —) in the IL [C_4mim][PF_6] for several gases like CO_2, O_2, N_2, CH_4 and C_2H_6 and experimental values (•)[8].

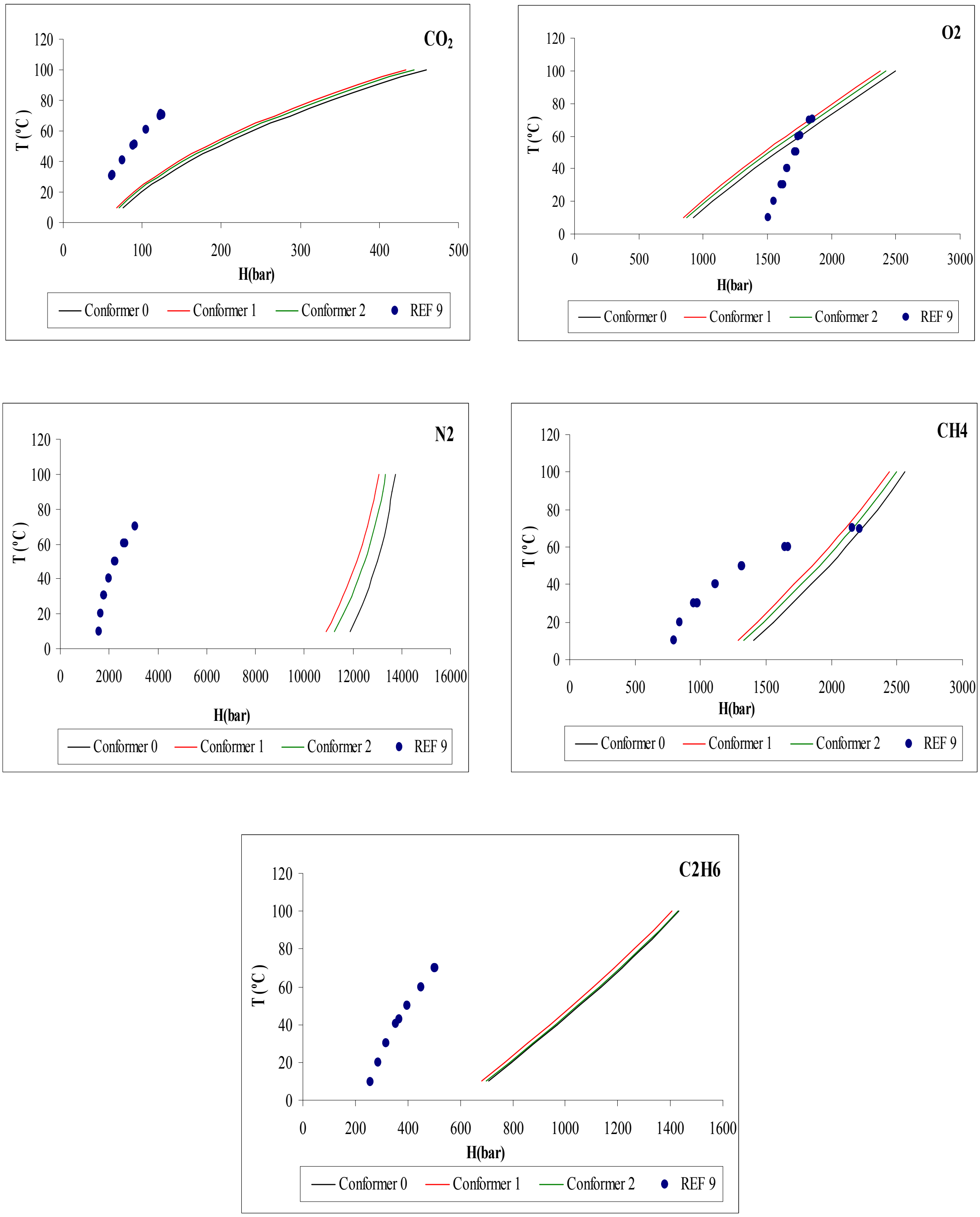

Figure 2.2.2: Henry constants values performed by COSMO-RS for three energy conformations available (conformer 0 — ; conformer 1 — ; conformer 2 —) in the IL $[C_4mim][BF_4]$ for several gases like CO_2, O_2, N_2, CH_4 and C_2H_6 and experimental values (•)[9].

When analysing Figure 2.2.1 is possible to see that conformers 1 and 2 have differences inferiors to 5 %, relatively to conformer 0. The results show that conformer 0 has higher Henry constants, *H*, followed by conformer 2 and at least conformer 1.

For the IL [C_4mim] [BF_4], in figure 2.2.2, the differences are somewhat higher than for [C_4mim][PF_6], reaching almost 15 % between them.

When analysing both figures it can be seen that there is a reduction in the *H* differences due to the conformers, for higher temperatures.

For all gases in study, Oxygen has the small difference between experimental values and those calculated with COSMO-RS. So, COSMO-RS could predict and give close values of *H* for systems IL + O_2. In the opposite way, the major deviations seem to be related to Nitrogen because it is the one that has a bigger deviation between experimental and calculated values.

For all cases studied below with COSMO-RS and in order to compare the structural influences of both the IL and the gas in the Henry's constants values, if there was more than one energy conformer to the same ionic specie, it was used the "conformer 0" in all calculations, that is the lowest energy conformer for the same ion.

2.3. COSMO-RS *vs* GCMs

The advantage of GCMs, like UNIFAC, is their degree of elaboration that resulted from the several years of development. Especially UNIFAC has been parameterized carefully for many different aspects of application using several tens of thousands of experimental data, resulting in a suite of special parameterizations, each being optimal for certain purposes and because of that it will be hard to beat the accuracy of each kind of UNIFAC in its core range of parameterization.

Another advantage of GCMs appears to be their extreme speed and their low computational requirements. If all group parameters are available, the entire calculation takes only few seconds on a personal computer. On the other hand COSMO-RS requires time-consuming quantum chemical COSMO calculations for each compound under consideration. At the moment these are accessible from a database and COSMO-RS itself is as fast as UNIFAC.

COSMO-RS is a younger method, less well developed than UNIFAC and because of that there is much less application experience with it. At the moment it is preferable for industrial users to apply a widely used GCM, if it is applicable. But COSMO-RS has a large number of methodological advantages, which makes it much more widely applicable than GCMs could ever be and this opens many new opportunities.

The greatest advantage of COSMO-RS is the fact that it is a predictive method. This causes a rather general applicability. Due to the generic functional for the interaction energies, which are based on the information from quantum chemical calculations and which does only require a few, at most, element-specific parameters, it is applicable to almost the entire organic chemistry. Thus, it can be applied to nearly any system for which no group parameters are available in GCMs. An important advantage of COSMO-RS is its ability to handle intramolecular interactions of functional groups, e.g. there are differences between primary, secondary, and tertiary hydroxy groups in alcohols, because these groups differ in the underlying quantum chemical calculations, while in GCMs each functional group has context-independent interaction parameters.

Moreover, as a result of the resolution of molecular details, COSMO-RS is able to resolve differences between isomers, which are generally identical in GCMs. The exact thermodynamics is another advantage of COSMO-RS compared to present GCMs.

Finally, COSMO-RS allows for very efficient and fast thermodynamic calculations and even for large-scale solvent screening.

2.4. REFERENCES

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3. RESULTS and DISCUSSION

The main purpose of this work is to investigate the interactions between ILs and a variety of small gaseous molecules.

Since traditional approaches to describe the properties of fluid mixtures require extensive liquid-liquid equilibria (LLE) and vapour-liquid equilibria (VLE) experimental measurements, alternative predictive methods need to be explored with more detail. Here predictions of the solubility of gases in several ILs using COSMO-RS, as mentioned on previous chapter, an approach based on unimolecular quantum chemical calculations of the individual molecules are presented.

Most of the experimental studies described in literature concerning the solubility of gases in ILs are dedicated to systems involving carbon dioxide as the solute.

The solubility of a gas in a liquid, is frequently described in terms of Henry's law constants, which is defined as,

$$H_1\,(T,p) \equiv \lim_{x_1 \to 0} \frac{f_1^L}{x_1} \approx \frac{p_1}{x_1} \qquad \textbf{(3.1)}$$

where H_1 (T,p) is the Henry's constant, x_1 is the mole fraction of gas dissolved in the liquid phase, f_1^L is the fugacity of vapour in the liquid phase and p_1 is the pressure of the gas. Equation 3.1 implies that, for gases that behave nearly ideally, the solubility is linearly related to the pressure.

In Tables 3.1 to 3.6 are reported the references to all experimental data found in the literature for the solubility of different gases such as CO_2, O_2, N_2, H_2S, CH_4 and C_2H_6 in several ILs such as [$C_n$mim][PF_6], [$C_n$mim][BF_4], [$C_n$mim][Tf_2N], among others, between 10 ºC and 130 ºC at different pressures.

For all cases studied with COSMO-RS, if there was more than one energy conformer to the same ionic specie, it was used the "conformer 0" in all calculations, that is the lowest energy conformer for the same ion. The COSMO-RS calculations were made for a pseudo-binary mixture where the cation and anion, with equal mole fractions, are treated as separate species. The results are discussed below from different points of view to evaluate the influence of the ILs and gases structural variations and its dependence with temperature and the COSMO-RS predictive capability.

3.1. NITROGEN

Table 3.1: Solubility data found in literature for the system IL ([C_4mim][BF_4] and [C_4mim][PF_6]) + gas (N_2).

GAS	*ANION*	*CATION*	*Literature Reference*
N_2	[BF_4]	[C_4mim]	7
	[PF_6]	[C_4mim]	2,3,8

There is not much experimental work done with nitrogen at the moment because it is difficult to measure its extremely low solubility in ILs (for reference 2 and 3 it has not been detected any value of solubility). In Figure 3.1 it can be seen that there is a significant difference between experimental data and COSMO-RS prediction of Henry's constant, with differences greater than one order of magnitude. Even though for [C_4mim][PF_6] COSMO-RS gives a better qualitative behaviour description than for the other IL. It is possible to observe that nitrogen is experimentally more soluble in [C_4mim][PF_6] than in [C_4mim][BF_4] and that trend is correctly described and well captured by the model predictions. The temperature dependency is also fairly well described for both ILs.

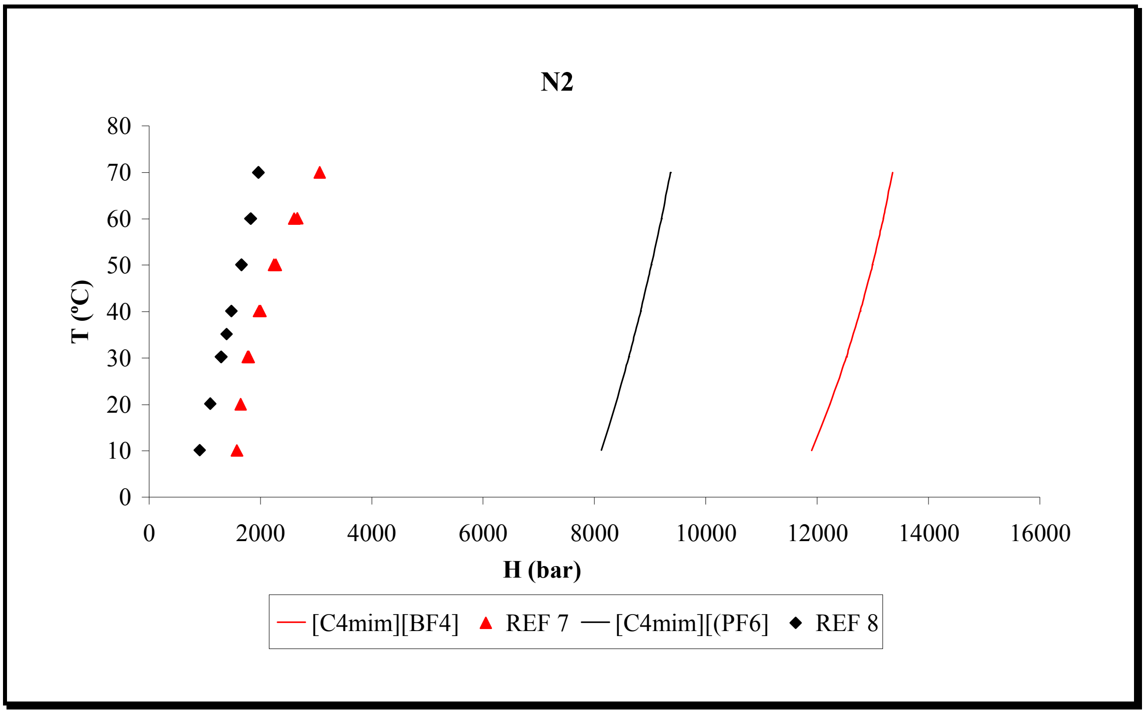

Figure 3.1: Henry's constants as function of temperature (ºC) for IL + N_2.

3.2. HYDROGEN SULFIDE

In Table 3.2 it is reported the solubility data of Hydrogen Sulfide in [C_4mim][PF_6].

Table 3.2: Solubility data found in literature for the systems IL ([C_4mim][PF_6]) + gas (H_2S).

GAS	*ANION*	*CATION*	*Literature Reference*
H_2S	[PF_6]	[C_4mim]	27

As can be seen in Figure 3.2 unlike what was observed for N_2 the COSMO-RS underpredicts the Henry constants for the H_2S. The predictions are now much closer to the experimental data for this system. Unfortunately no further data is available in the literature to compare this trend qualitative and quantitative.

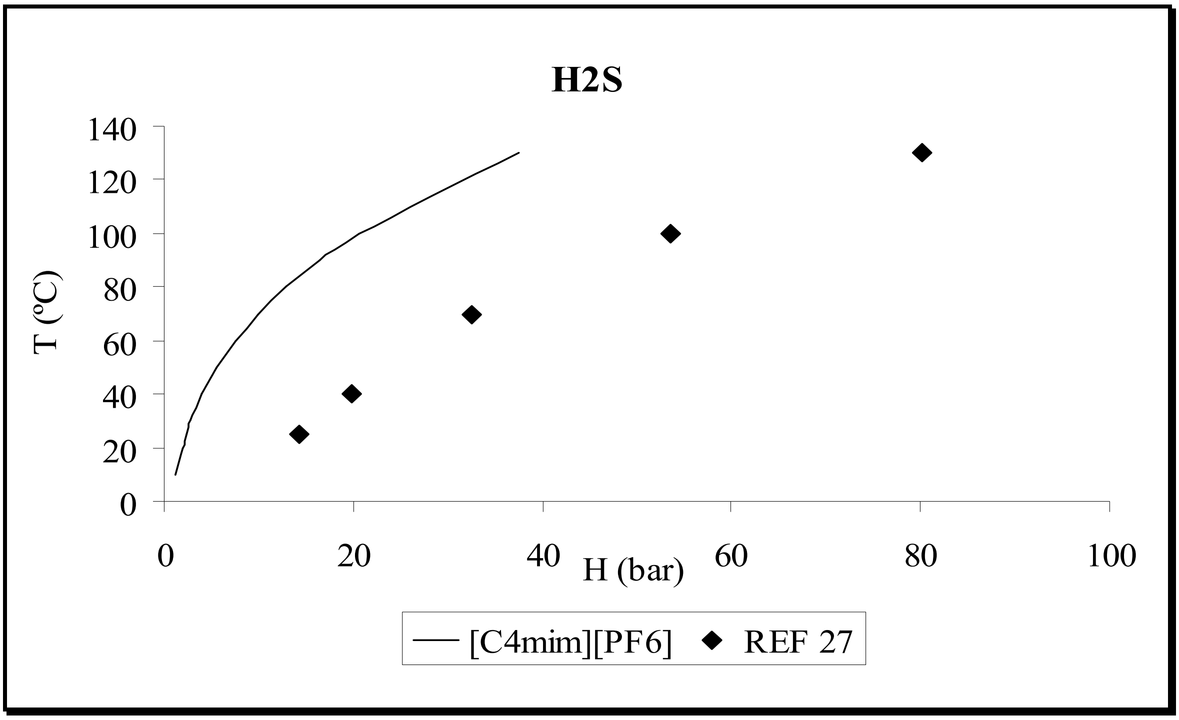

Figure 3.2: Henry's constants as function of temperature (ºC) for [C_4mim][PF_6] + H_2S.

3.3. OXYGEN

For the system IL + O_2 there are more studies and experimental data measured than for the previous gases, as can be seen in Table 3.3.

Table 3.3: Solubility data found in literature for the systems for ILs ([C_4mim][PF_6], [C_4mim][BF_4], [C_4mim][Tf_2N], [C_1C_4PYRR][Tf_2N]) + gas (O_2).

GAS	*ANION*	*CATION*	*Literature Reference*
O_2	[BF_4]	[C_4mim]	7,9
	[PF_6]	[C_4mim]	2,3,8,18
	[Tf_2N]	[C_4mim]	3
	[Tf_2N]	[C_1C_4PYRR]	3

Figure 3.3 presents a comparison with different ILs, maintaining the cation [C_4mim], while varying the anion specie ([BF_4], [PF_6] and [Tf_2N]) to all solubility data found in the literature shown in Table 3.3.

It is possible to see that experimental data are very similar for the three different ILs studied, with very small differences between them except for values found in references 2 and 3, for [C_4mim][PF_6] and also for [C_4mim][Tf_2N] in reference 3, for temperatures lower than 30ºC.

So we may say that COSMO-RS prediction of Henry's constant for Oxygen as a function of temperature in [C_4mim][PF_6] and [C_4mim][BF_4] is remarkably good. There is also a very reasonable agreement on data near 50ºC for [C_4mim][Tf_2N].

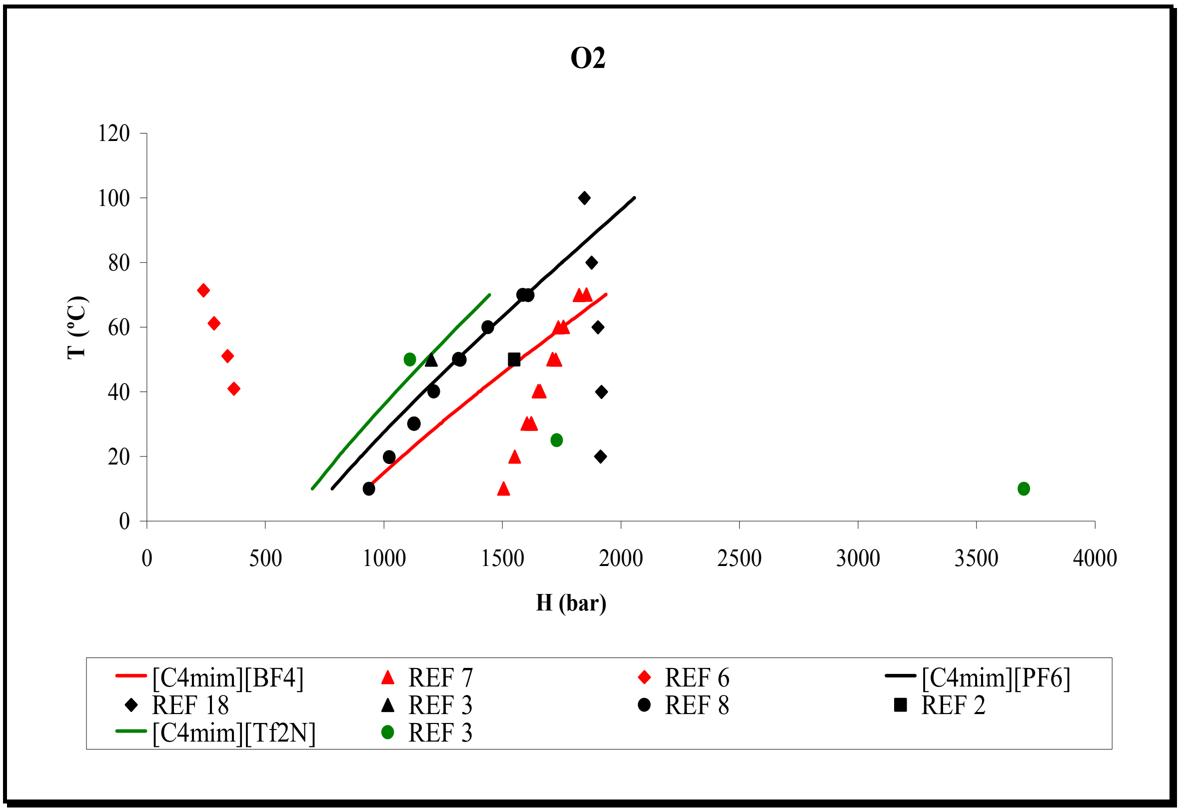

Figure 3.3: Henry's constants as function of temperature (ºC) for system: IL + O_2 ([C_4mim] cation as a constant and changing the anion).

In Figure 3.4 it is presented a comparison with two different ILs, maintaining the anion [Tf_2N], while varying the cation ([C_4mim] and [C_1C_4PYRR]) for solubility data found in the literature and shown in Table 3.3 to study the **Cation Family Influence** in Henry's constants of O_2.

It is possible to see that COSMO-RS predictions of Henry's constant for Oxygen as a function of temperature for both ILs shows a very similar behaviour and a good description of the Henry's constants at 50 ºC are achieved. However it has a temperature dependence that it is the inverse to what is experimentally observed. The experimental temperature dependence is not usual and needs further experimental confirmation.

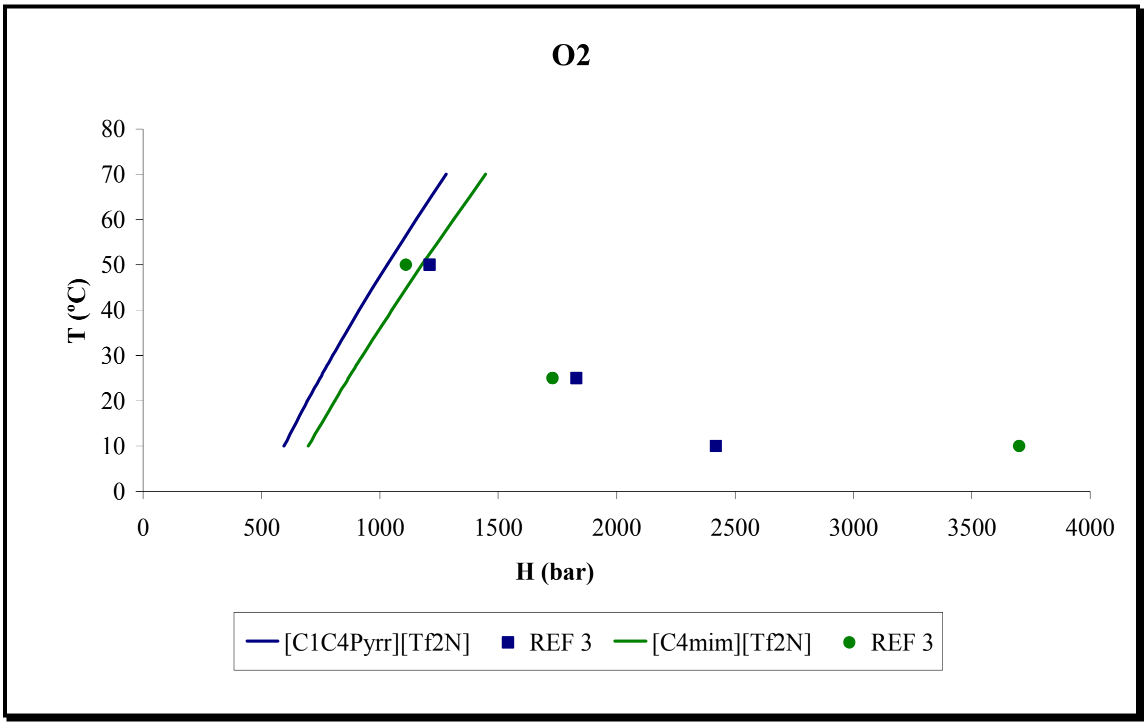

Figure 3.4: Henry's constants as function of temperature (ºC) for system: O_2 + IL (changing the cation and $[Tf_2N]$ anion as a constant).

3.4. METHANE

On Table 3.4 it is possible to see that there are a great variety of solubility data for methane with different ILs expressed as Henry's Law constants as a function of temperature.

Table 3.4: Solubility data found in literature for the systems for ILs ([C_2mim][CF_3SO_3], [C_4mim][BF_4], [C_2mim][DCA], [C_4mim][PF_6], [C_2mim][Tf_2N] and [C_6mim][Tf_2N]) + gas (CH_4).

GAS	*ANION*	*CATION*	*Literature Reference*
CH_4	[BF_4]	[C_4mim]	7
	[CF_3SO_3]	[C_2mim]	23
	[DCA]	[C_2mim]	23
	[PF_6]	[C_4mim]	2,8,24
	[Tf_2N]	[C_2mim]	23
	[Tf_2N]	[C_6mim]	23

In Figure 3.5 it is presented a comparison with three different ILs, maintaining the cation specie [C_2mim] (*1-ethyl-3-methylimidazolium*) while varying the anion specie in order to infer about the **Anion Identity Influence** (*dicyanamide, bis(trifluoromethylsulfonyl)imide* and *trifloromethanesulfonate*).

It is possible to see in this figure that COSMO-RS prediction of Henry's constants for methane in ILs as a function of temperature presents a similar behaviour for [DCA] and [CF_3SO_3]-based ILs for the temperature range considered.

For [Tf_2N] and [CF_3SO_3]-based ILs the solubilities are underpredicted but the correct trend is captured by the model. At 40ºC, COSMO-RS predictions and experimental data for [C_2mim][DCA] show a deviation inferior to 2 %. Although, for the other ILs differences are superior to 50 %.

From experimental data it is possible to see that methane is more soluble in the hydrophobic [C_2mim][Tf_2N] than in others more hydrophilic ILs.

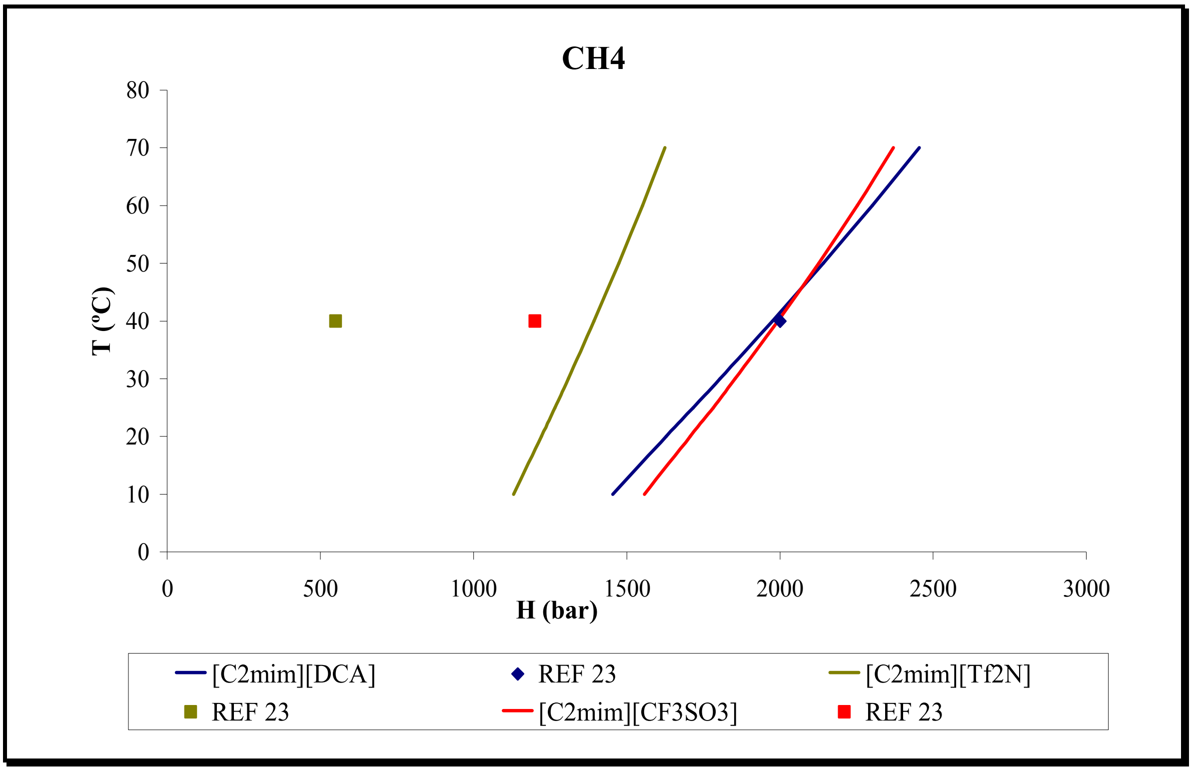

Figure 3.5: Henry's constants as function of temperature (ºC) for system: CH_4 + IL ([C_2mim] cation as a constant and changing the anion).

In Figure 3.6 there is also a comparison about the **Anion Identity Influence** and it can be seen that experimental data for the same IL may, in cases, be very different. For lower temperatures both ILs have close Henry's constants but they seem to diverge for higher temperatures. This behaviour is well captured by the model in spite of its overprediction of the Henry's constants.

At temperatures near to 70º C, experimental data and COSMO-RS predictions seems to converge for [C_4mim][BF_4]. Although, the quantitative predictions provided by COSMO-RS present considerable deviations when compared to experimental data. Nevertheless, the model correctly captures the solubility tendency with the IL polarity.

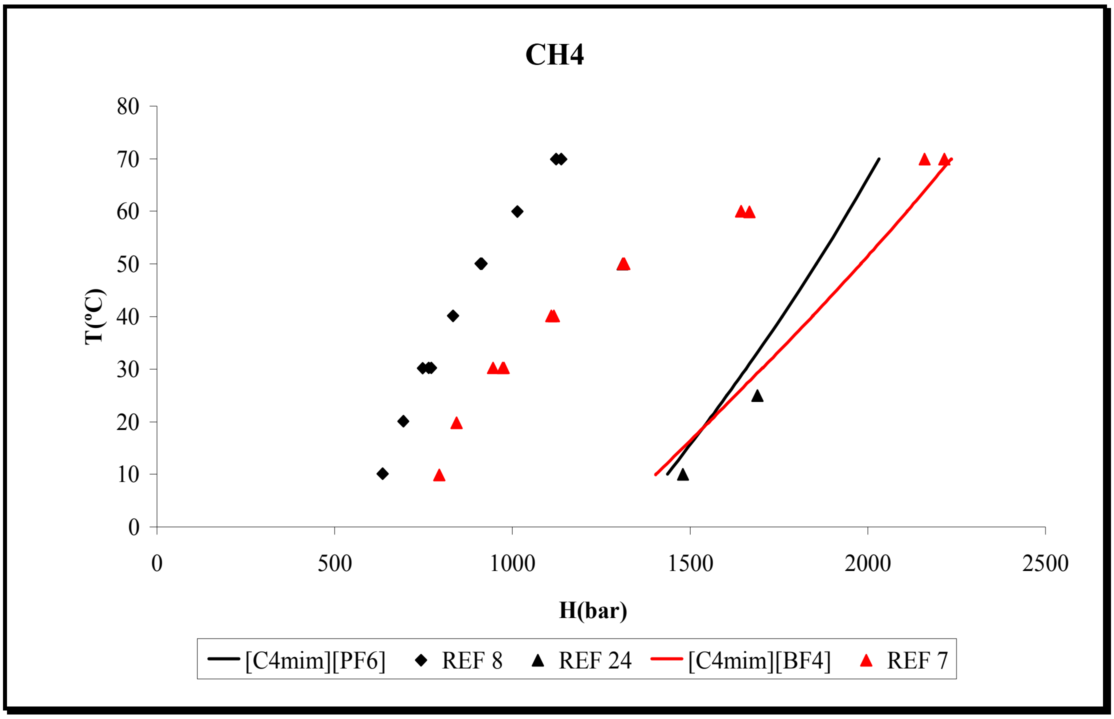

Figure 3.6: Henry's constants as function of temperature (ºC) for system: CH_4 + IL ([C_4mim] cation as a constant and changing the anion).

Figure 3.7 presents a **Cation Alkyl Chain Length Influence** study for [C_2mim][Tf_2N] and [C_6mim][Tf_2N] with methane. The COSMO-RS predictions provide a good qualitative description of Henry's constants changes along with the cation alkyl chain length increase. For this pair of ILs it is possible to see that longer alkyl chain lengths based cations provide a greater solubility for methane ([C_6mim][Tf_2N] > [C_2mim][Tf_2N]). Again it is observed that the decreased polarity favours the methane solubility and this behaviour is correctly described by the model. In addition, more experimental data at different temperature is in need.

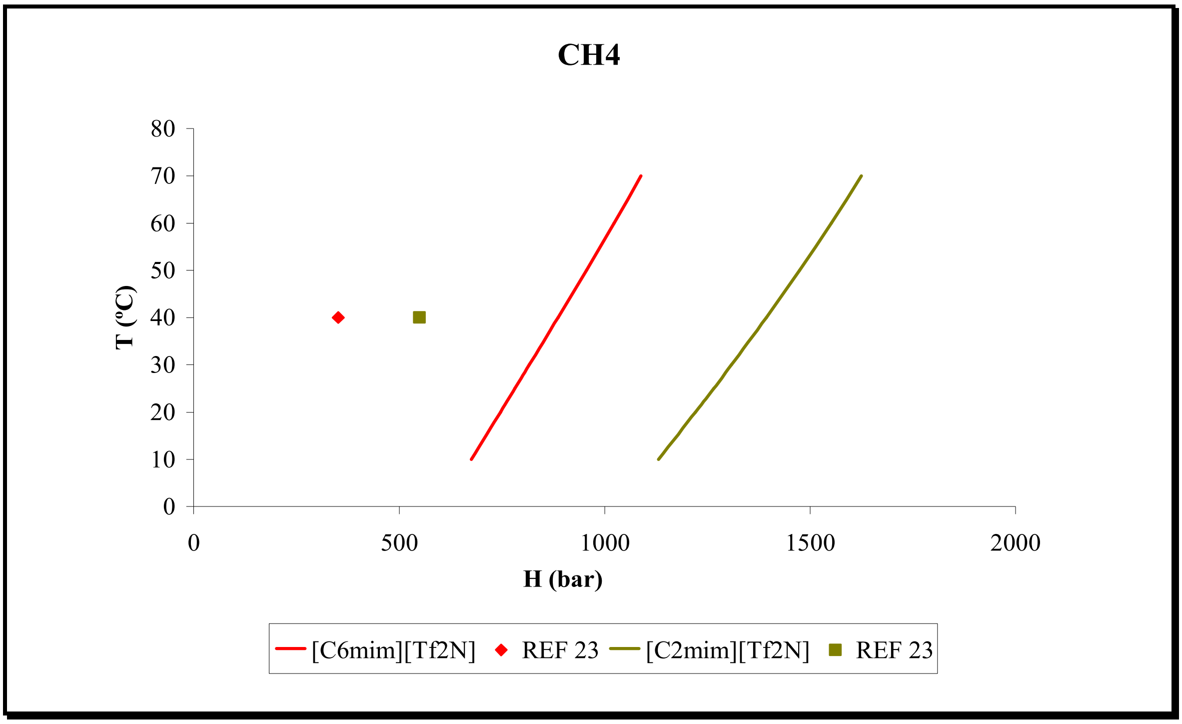

Figure 3.7: Henry's constants as function of temperature (ºC) for system: CH_4 + IL (changing the cation and $[Tf_2N]$ anion as a constant).

3.5. ETHANE

On Table 3.5 there are reported several studies of solubility data in existing literature for ethane in different ILs.

Table 3.5: Solubility data found in literature for the systems for different ILs (such as $[C_2mim][CF_3SO_3]$, $[C_4mim][BF_4]$, $[C_2mim][DCA]$, $[C_4mim][PF_6]$, $[C_2mim][Tf_2N]$, $[C_4mim][Tf_2N]$, $[C_6mim][Tf_2N]$ and $[C_1C_4PYRR][Tf_2N]$) + gas (C_2H_6).

GAS	*ANION*	*CATION*	*Literature Reference*
C_2H_6	$[BF_4]$	$[C_4mim]$	7,11
	$[CF_3SO_3]$	$[C_2mim]$	11
	[DCA]	$[C_2mim]$	11
	$[PF_6]$	$[C_4mim]$	3,8,11,24
	$[Tf_2N]$	$[C_2mim]$	11,12,26
	$[Tf_2N]$	$[C_4mim]$	3
	$[Tf_2N]$	$[C_1C_4PYRR]$	26
	$[Tf_2N]$	$[C_6mim]$	9

Figures 3.8 and 3.9 present a comparison between experimental data and COSMO-RS predictions. It is possible to see the **Anion Identity Influence** on the Henry's constants for Ethane gas solubility.

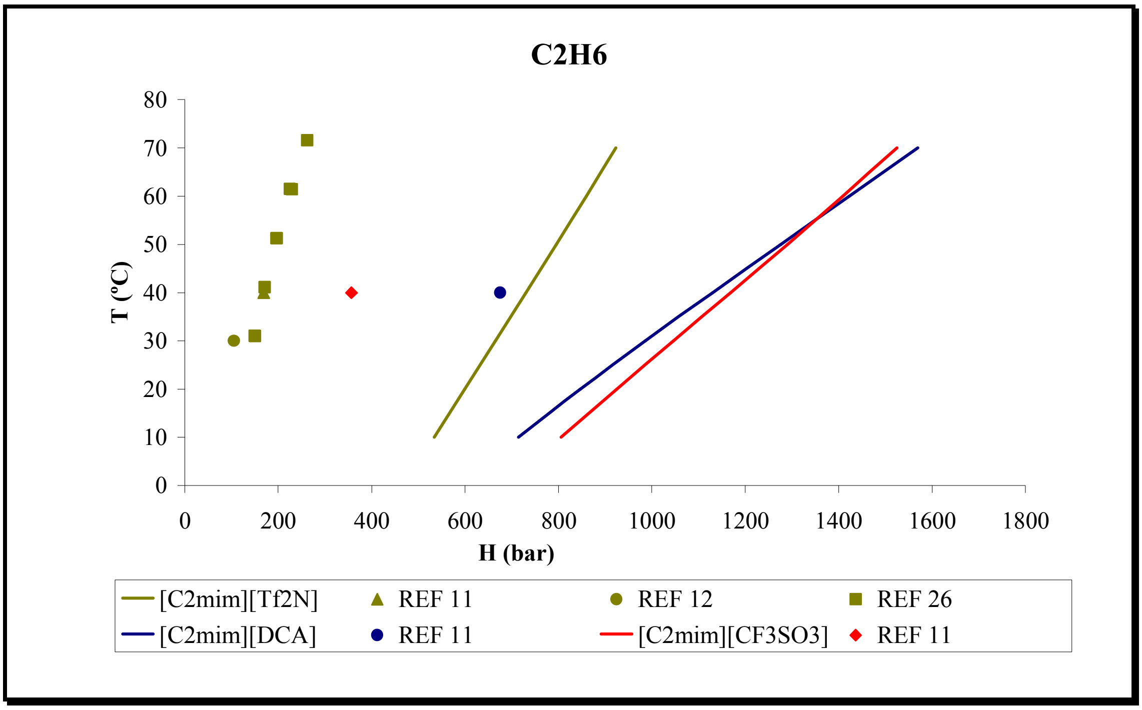

Figure 3.8: Henry's constants as function of temperature (ºC) for system: C_2H_6 + IL ($[C_2mim]$ constant and changing anion).

For these three ILs, [C$_2$mim][DCA], [C$_2$mim][Tf$_2$N] and [C$_2$mim][CF$_3$SO$_3$], the COSMO-RS predictions provide a good qualitative description of Henry's constant changes with the anion identity. The COSMO-RS prediction provides a tendency of the Henry's constant increase with the anion from [Tf$_2$N] < [DCA] < [CF$_3$SO$_3$].

In Figure 3.9 a comparison between [C$_4$mim][Tf$_2$N], [C$_4$mim][PF$_6$] and [C$_4$mim][BF$_4$] is made. For these two ILs, [C$_4$mim][PF$_6$] and [C$_4$mim][BF$_4$], COSMO-RS predictions are very similar in qualitative terms to the experimental data but they have quantitative differences to experimental data greater than 100 %. Comparing these results, ethane is more soluble in [C$_4$mim][Tf$_2$N] due to the less polar nature of the anion composing the IL. COSMO-RS predictions seem to indicate that the ethane solubility to be less dependent in [C$_4$mim][Tf$_2$N] than in the other ILs.

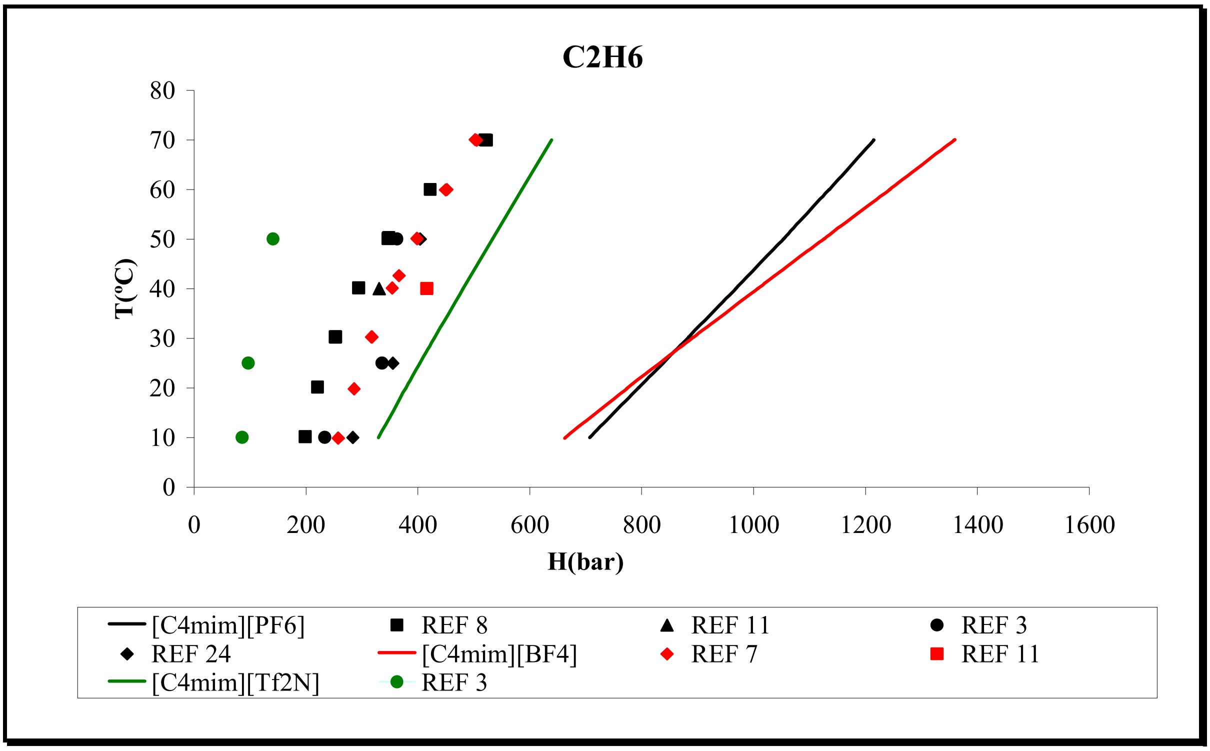

Figure 3.9: Henry's constants as function of temperature (ºC) for system: C_2H_6 + IL ([C$_4$mim] constant and changing anion).

The **Alkyl Chain Influence** presented in Figure 3.10 varies from ethyl to butyl to hexyl side alkyl chain. It should be noted that a cation chain length increase leads to an increase in the van der Waals interactions between the ILs.

The prediction by COSMO-RS calculations shows a good qualitative agreement with the experimental data available. The model adequately describes the increase in solubility with the cation alkyl chain length increase. The predictions present higher deviations from experimental data for the smaller cation alkyl chains. That maybe due to the IL molar volume increase.

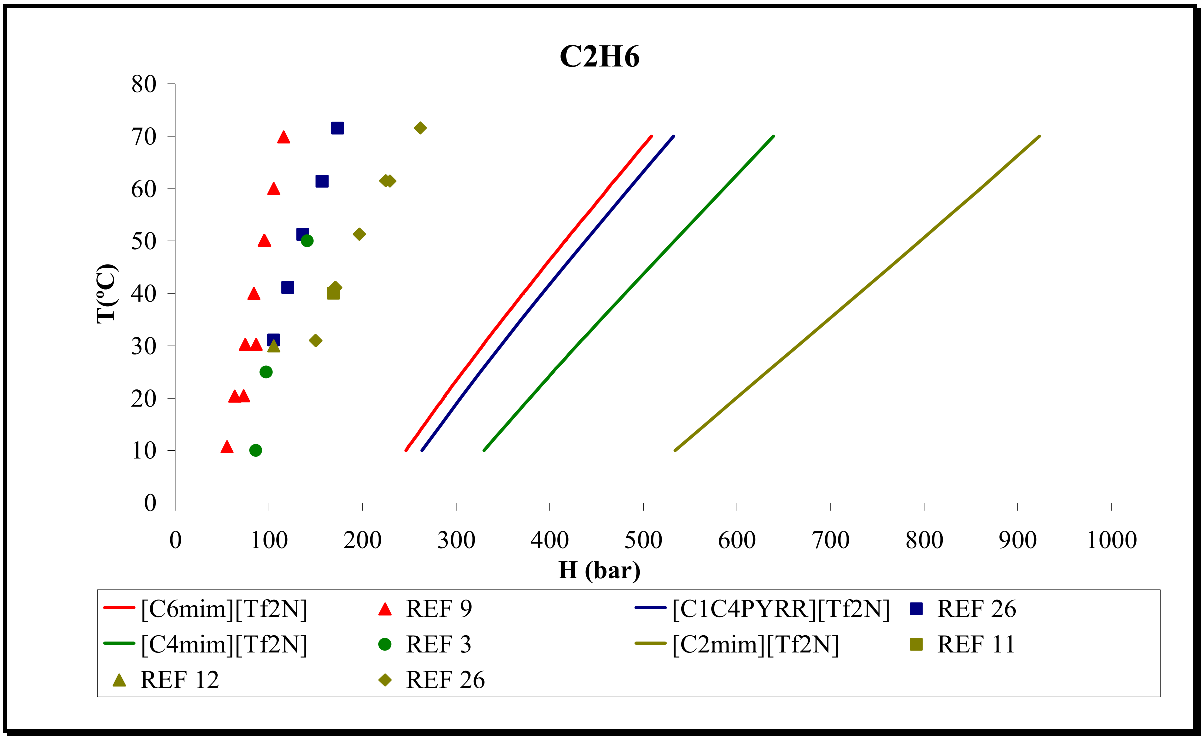

Figure 3.10: Henry's constants as function of temperature (ºC) for system: C_2H_6 + IL (changing cation and [Tf_2N] constant).

3.6. CARBON DIOXIDE

CO_2 is the most studied gas with ILs due to an increasing interest for reducing emissions and avoid global warming and also because separation of CO_2 from other gases plays a key role in a wide variety of industries, including natural gas purification.

On Table 3.6 it is summarized the enormous number of articles that report measurements of solubility CO_2 in several ILs.

Table 3.6: Solubility data found in literature for different ILs + CO_2.

GAS	*ANION*	*CATION*	*Literature Reference*
CO_2	$[BF_4]$	$[C_4mim]$	3,6,7,11,13,14,20,23
	$[BF_4]$	$[C_6mim]$	16,19,20
	$[BF_4]$	$[C_8mim]$	1,20.
	$[BF_4]$	$[C_2mim]$	16
	$[BF_4]$	[N-BUPY]	1
	$[CF_3SO_3]$	$[C_2mim]$	10,11,22,23
	[Cl]	$[P_{(14)666}]$	10,22,25
	[DCA]	$[C_2mim]$	10,11,22,23
	[DCA]	$[P_{(14)666}]$	25
	$[ETSO_4]$	$[C_2mim]$	1
	$[NO_3]$	$[C_4mim]$	1
	$[PF_6]$	$[C_3mim]$	5
	$[PF_6]$	$[C_4mim]$	1,2,3,8,10,11,13,14,16,17,22,24
	$[PF_6]$	$[C_6mim]$	16
	$[PF_6]$	$[C_8mim]$	1
	$[Tf_2N]$	$[C_3mim]$	5
	$[Tf_2N]$	$[C_1C_4PYRR]$	3
	$[Tf_2N]$	$[C_4PYRR]$	26
	$[Tf_2N]$	$[C_4mim]$	3,5,15
	$[Tf_2N]$	$[C_6mim]$	4,5,9,16,21,23
	$[Tf_2N]$	$[C_6MPY]$	4
	$[Tf_2N]$	$[C_8mim]$	5
	$[Tf_2N]$	$[C_2mim]$	10,11,12,16,22,23,26
	$[Tf_2N]$	$[C_{10}mim]$	23
	$[Tf_2N]$	$[P_{(14)666}]$	25

In Figures 3.11 to 3.13 it is shown the **Anion Identity Influence** in the solubility of CO_2 in different ILs.

In Figure3.11, ILs-based on the [C_2mim] cation with several anion species like [Tf_2N], [$ETSO_4$], [DCA], [CF_3SO_3] and [BF_4] are compared. The experimental data for the [$ETSO_4$] have a strange temperature dependency and are thus of dubious quality, requiring more experimental measurements from different authors.

From this study it is possible to see that basically there are no differences for [C_2mim][$ETSO_4$], [C_2mim][CF_3SO_3] and [C_2mim][BF_4] ILs in COSMO-RS prediction values. It is difficult to evaluate the behaviour of the experimental data since for most of these systems data at only one temperature are available but it would seem that their Henry's constants are also very close as also are those for the [DCA]-based IL for which compound the model predicts a higher Henry constant.

Carbon dioxide has a higher solubility in the less hydrophilic [C_2mim][Tf_2N] being difficult to sort the other compounds with the experimental data available in the considered temperature range.

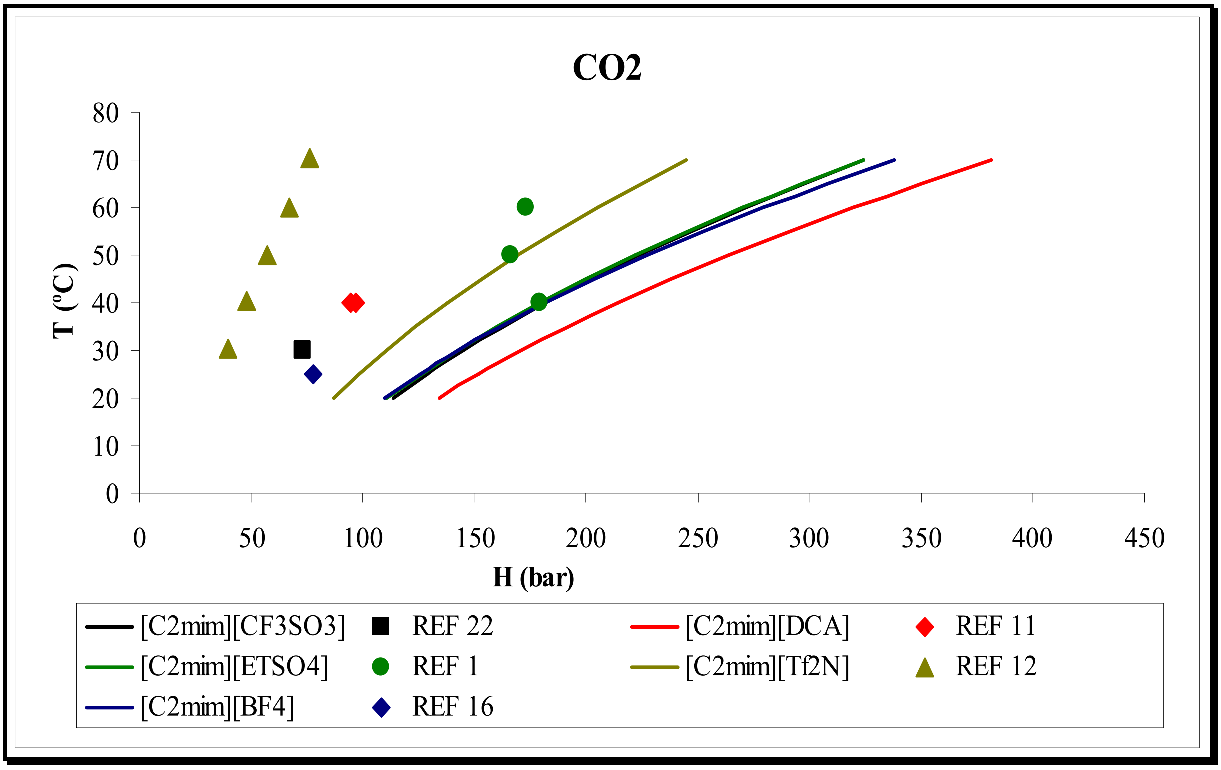

Figure 3.11: Henry's constants as function of temperature (ºC) for system: CO_2 + IL (changing anion and keep [C_2mim] constant).

The **anion influence** is analysed in Figure 3.12, where the solubility of CO_2 in $[C_4mim][BF_4]$, $[C_4mim][NO_3]$, $[C_4mim][PF_6]$ and $[C_4mim][Tf_2N]$ is shown.

Anion species as $[Tf_2N]$ and $[PF_6]$ give very similar COSMO-RS prediction values and they compose the ILs that grants higher solubility for CO_2. The less soluble is the one that has the $[NO_3]$ anion specie composing the IL. For higher temperatures it is possible to see that there is divergence in experimental data and predictive values, always with differences 50 % superior from reference literature to COSMO-RS predictions. Again a very good qualitative trend in the predicted solubilities when compared with experimental data is obtained. Nevertheless, the predicted temperature dependency of the data seems however to be over predicted.

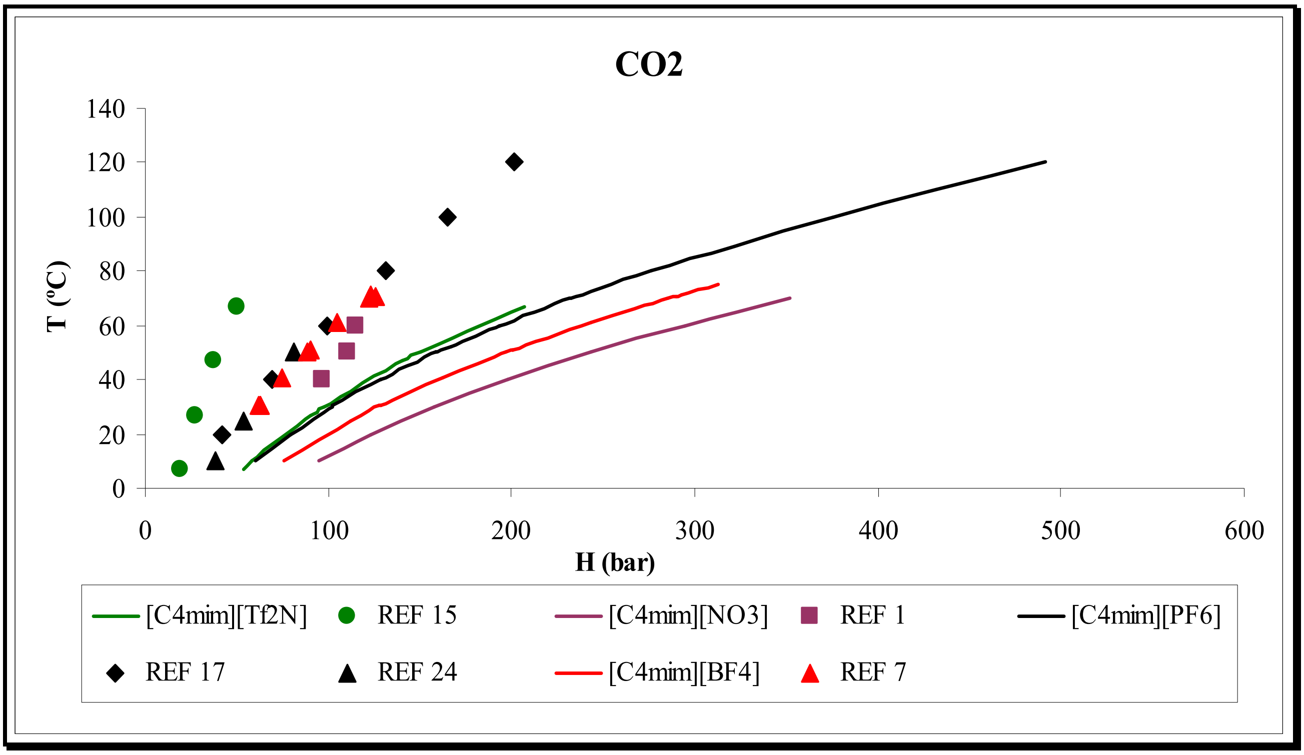

Figure 3.12: Henry's constant as function of temperature (ºC) for system: CO_2 + IL (changing anion and keep $[C_4mim]$ constant).

From the analysis of Figure 3.13 it is also possible to see the anion influence in the solubility of CO_2 in $[C_6mim][BF_4]$, $[C_6mim][PF_6]$ and $[C_6mim][Tf_2N]$.

COSMO-RS provides very similar values for the $[Tf_2N]$ and $[PF_6]$-based ILs that have the higher solubility for CO_2. The less soluble is the one that has the $[BF_4]$ anion. At temperatures near 15 ºC there is a difference superior to 150 % and for higher temperatures it is possible to see that there is a divergence between experimental data and predictive values, reaching a relative deviation of the order of 250 % from COSMO-RS to reference literature. Again the temperature dependency of the Henry constants seems to be over predicted by the model. For [C_6mim][BF_4] the difference between COSMO-RS prediction values and experimental data varies from 30 to 70 %.

Finally, analysing these three last figures it is possible to conclude that, independently of the cation nature, [Tf_2N]-based ILs give always the higher solubility for CO_2 in ILs.

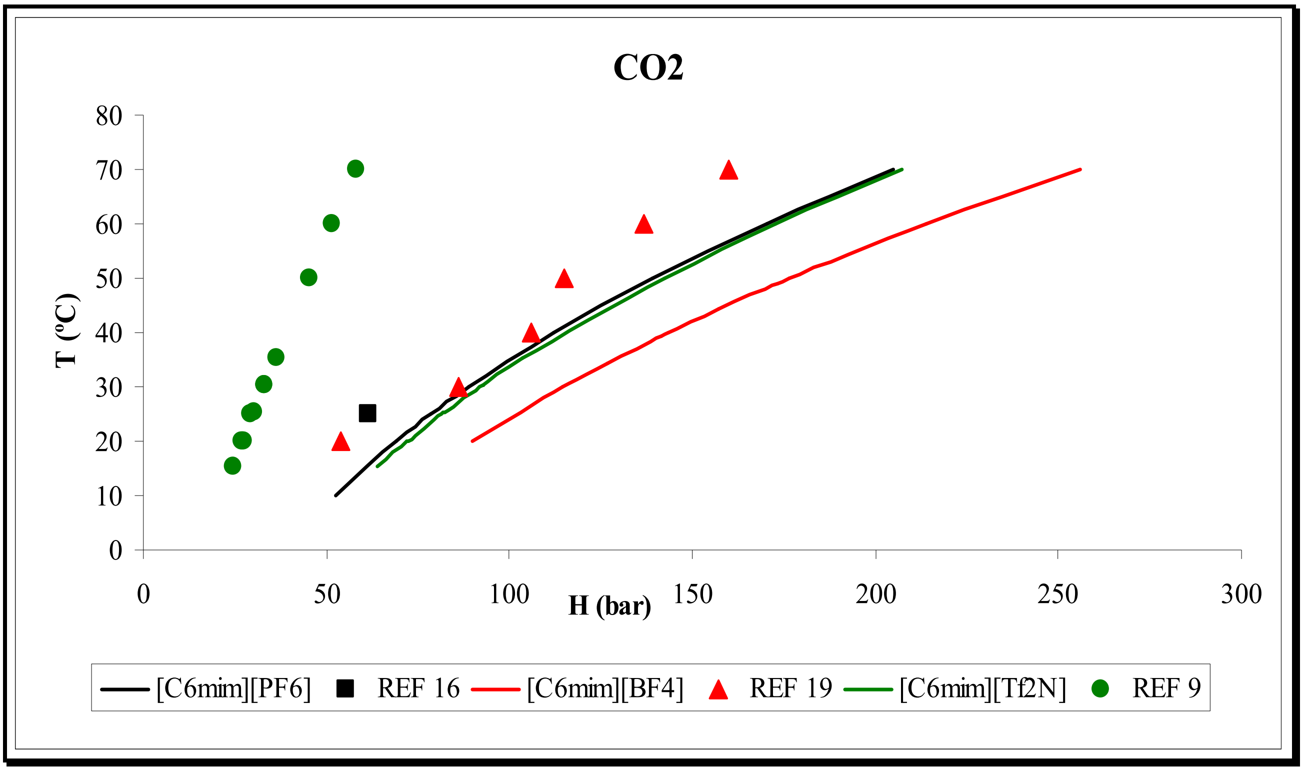

Figure 3.13: Henry's constants as function of temperature (ºC) for system: CO_2 + IL (changing anion and keep [C_6mim] constant).

The **Cation Alkyl Chain Length Influence** for the solubility of CO_2 in different ILs can be analysed in Figures 3.14 to 3.16.

In Figure 3.14 it is possible to see that COSMO-RS predictions for the relative order of solubility is: [C_2mim][BF_4] < [N-BUPY][BF_4] ≤ [C_4mim][BF_4] < [C_6mim][BF_4] < [C_8mim][BF_4]. Experimental data for some systems seems to be of dubious quality but the general trend seems to be correctly captured by the COSMO-RS predictions.

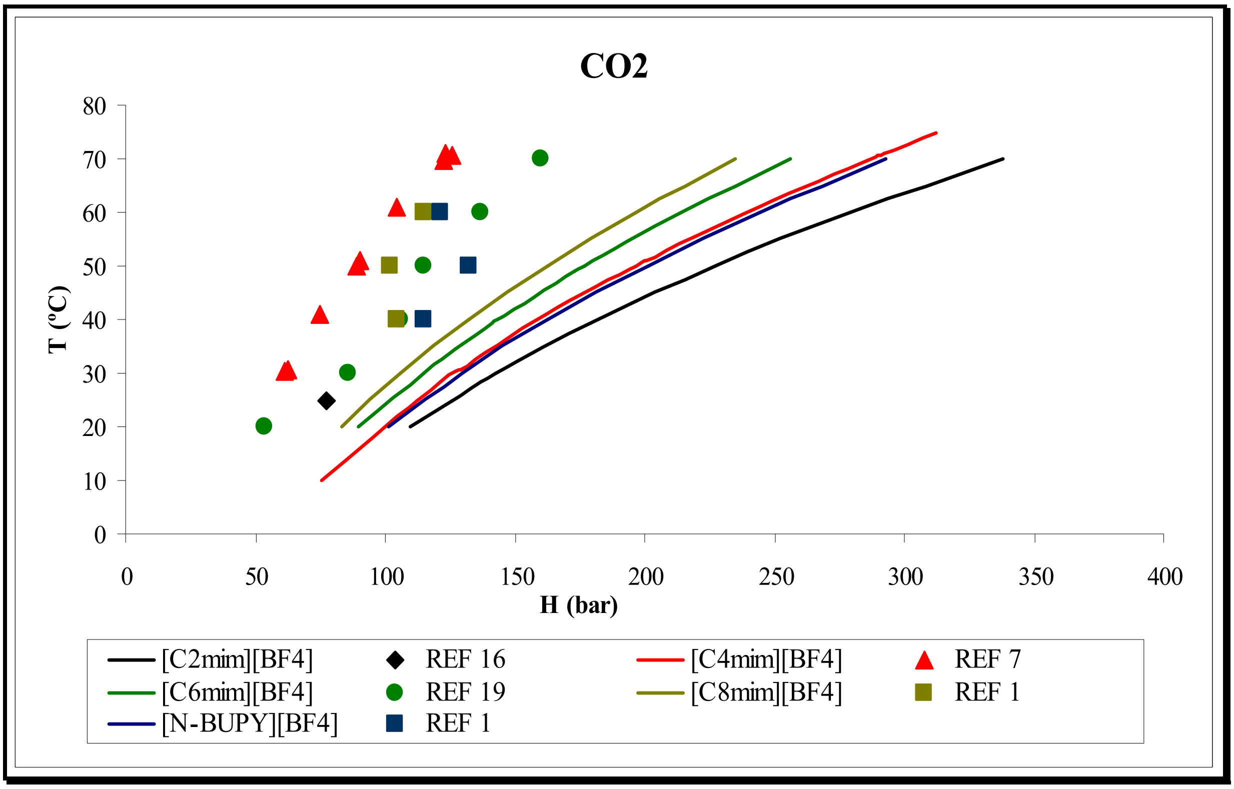

Figure 3.14: Henry's constants as function of temperature (ºC) for system: CO_2 + IL (changing cation and keeping the $[BF_4]$ constant).

The Figure 3.15 also corroborates the results obtained above. It is here possible to see that increasing the cation alkyl chain length will lead to a predicted increase in CO_2 solubility in ILs. So the relative order for solubility is: $[C_3mim][PF_6]$ < $[C_4mim][PF_6]$ < $[C_6mim][PF_6]$ < $[C_8mim][PF_6]$. Again the data quality does not allow definite conclusions on this point.

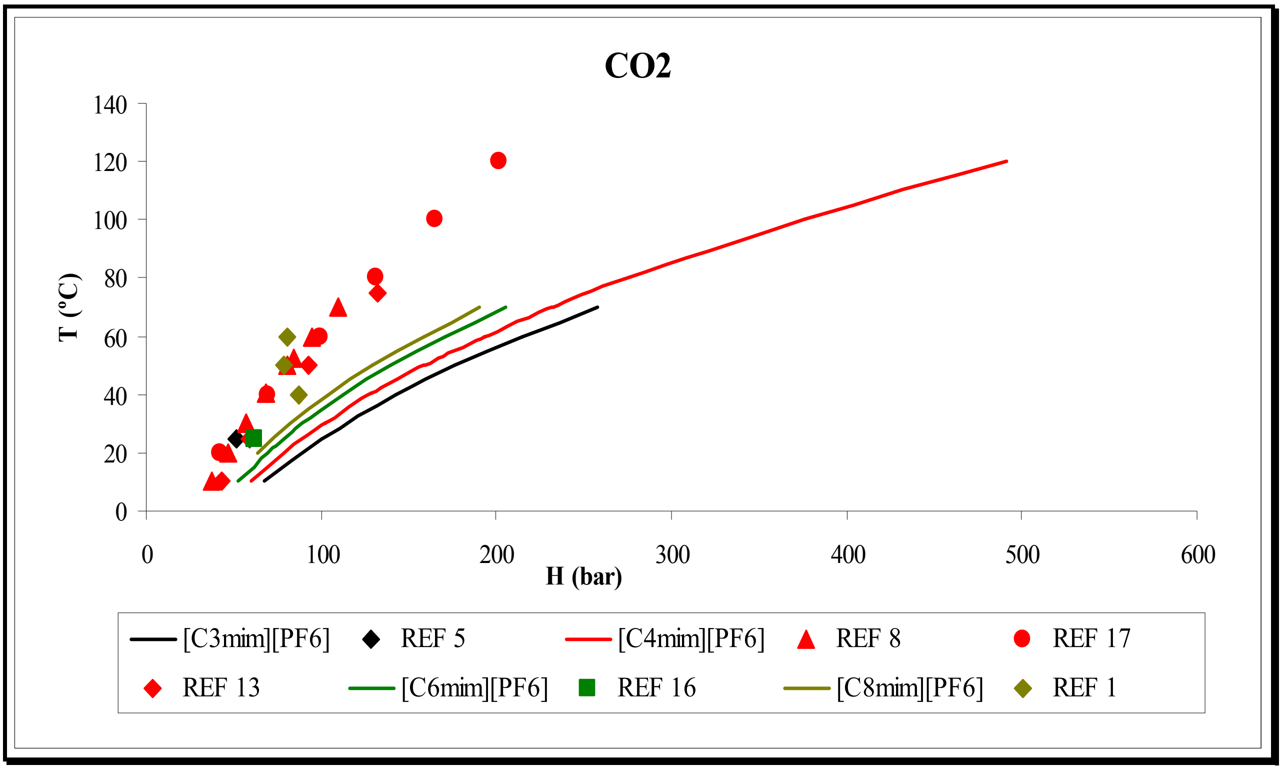

Figure 3.15: Henry's constants as function of temperature (ºC) for system: CO_2 + IL (changing cation and keeping $[PF_6]$ constant).

In Figure 3.16 it is possible to see that experimental data for all $[Tf_2N]$-based ILs studied are very similar, independently of the **alkyl chain length** of the cation.

Once more in this figure it is perceptible that solubility of CO_2 increases with increasing the cation alkyl chain length. The only special case is $[C_6MPY]$ because it is a structurally different that provides a higher solubility of the gas in the IL.

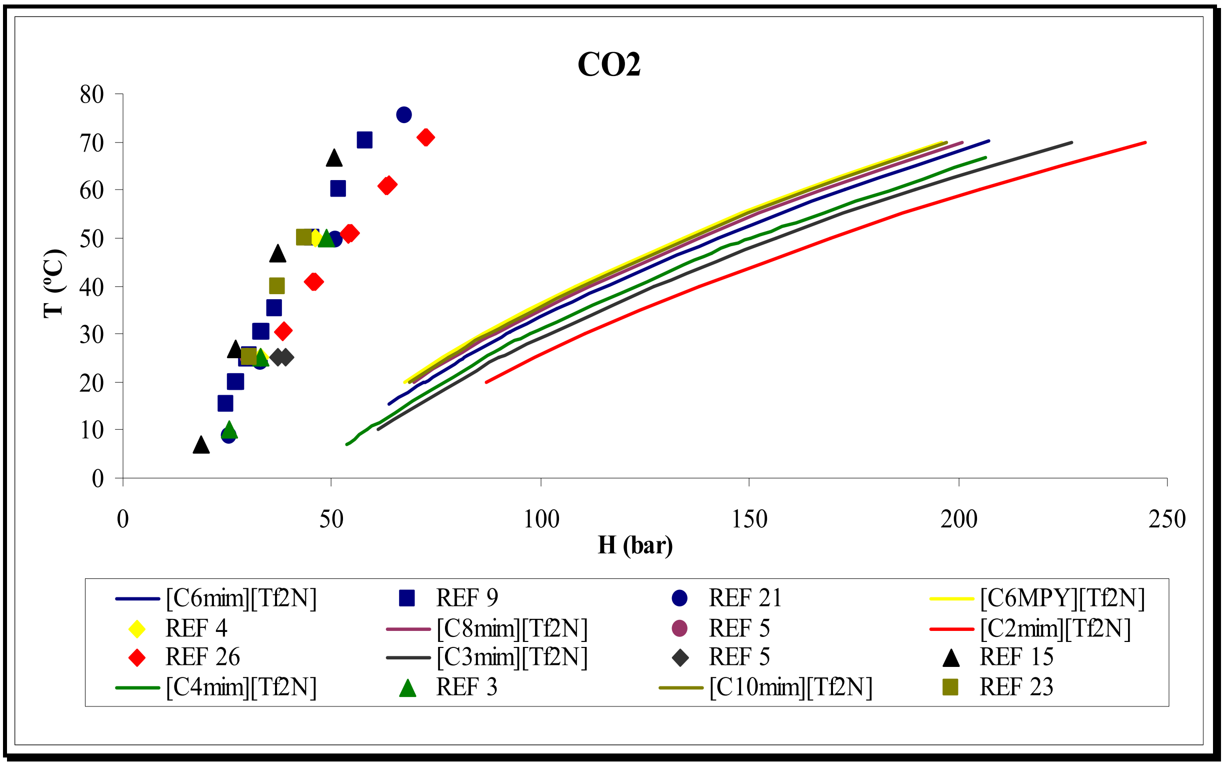

Figure 3.16: Henry's constants as function of temperature (ºC) for system: CO_2 + IL (changing cation and keeping [Tf_2N] constant).

Figure 3.17 shows the solubility prediction values for Phosphonium-Based ILs as obtained from COSMO-RS and unfortunately only one experimental value to each one. From the analysis of this figure it is possible to see that there are no substantial differences in the solubility of CO_2 by changing the anion. Experimental data differ from predictive values at around 150 %. The variations in solubility among the different ILs do not seem to be correctly described by the COSMO-RS although it is not possible to make a judgement based on just these few experimental data points.

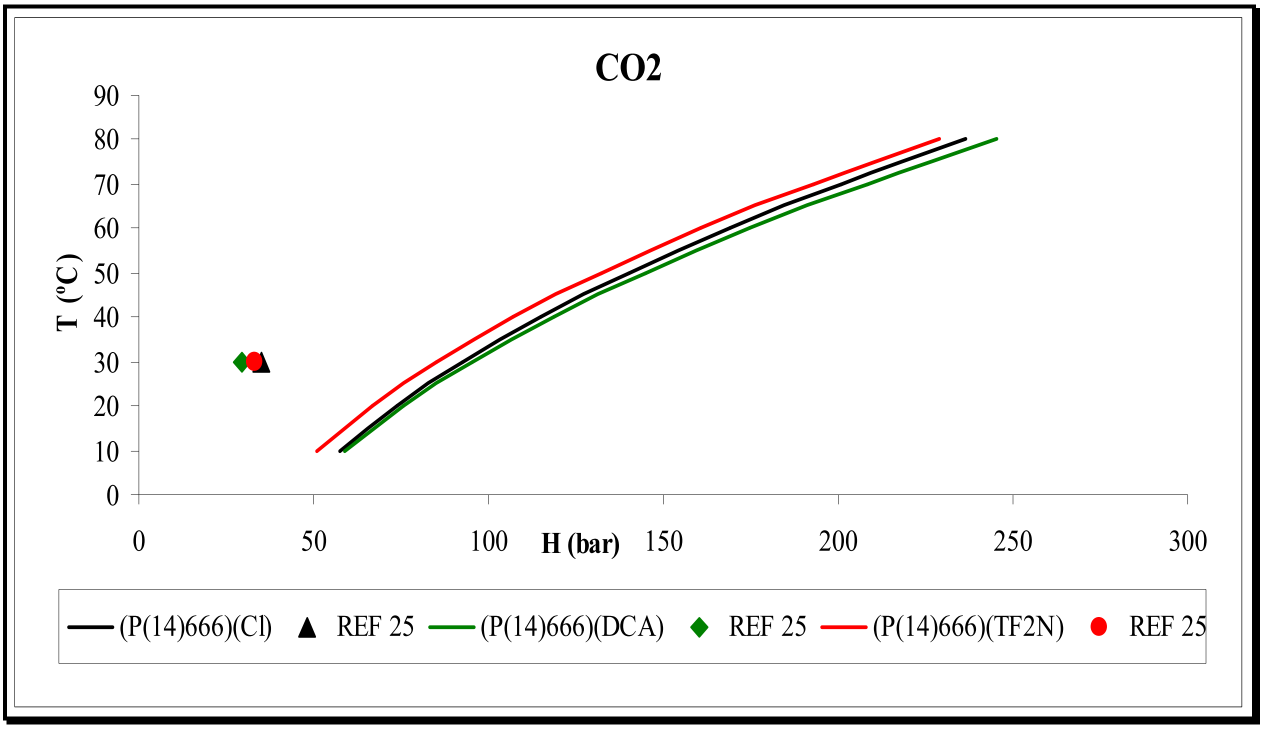

Figure 3.17: Henry's constant as function of temperature (ºC) for system: CO_2 + IL (changing anion and keeping [$P_{(14)\,666}$] constant).

3.7. CONCLUSIONS

For almost all the studied gases Henry's constants predictions given by COSMO-RS are relatively close to experimental data for the temperature range considered. Specially, the COSMO-RS predictions for methane and ethane solubilities in ILs showed to be very close to the experimental data and proved to describe well both qualitatively and quantitatively the equilibrium behaviour experimentally observed.

In addition, it was experimentally found that longer alkyl chain cations could provide a greater solubility for CH_4, C_2H_6 and CO_2 and the COSMO-RS showed to correctly describe that trend. For O_2, H_2S and N_2 it is not possible to evaluate the COSMO-RS Henry's constants predictive capability because the experimental data showed to be very scarce.

Analysing the anion influence in the experimental solubilities of CH_4, C_2H_6 and CO_2 it is possible to conclude that [Tf_2N]-based ILs present a higher solubility for these gases while [DCA]-based ILs present the lowest solubilities. In both cases the correct qualitative trend was predicted by the COSMO-RS calculation results.

The temperature dependency of the Henry constants seems to be over predicted by the model for almost all gases expect for H_2S and some experimental data found for O_2.

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4. SELECTIVITY

Given that Henry's Law constants are inversely proportional to solubility that means that a small Henry's Law constant is a sign of high gas solubility and, on the contrary, a big Henry's Law constant indicates low gas solubility. Analysing figure 4.1 [1] is possible to see that water vapour is very soluble in IL and methanol, but methane and ethane are not (they are more soluble in toluene than in other two solvents). These differences could be used for gas separations. As an example, it is possible to use [C_4mim][PF_6] (in figure 4.1 [C_4mim][PF_6] ↔ [Bmim][PF_6]) to remove H_2O and CO_2 from natural gas stream, with expected selectivities, supported on Henry's Law constants. [1] Several ILs could be capable of absorbing large quantities of gases at low temperature and then being renewed at high temperature or low pressure. [1]

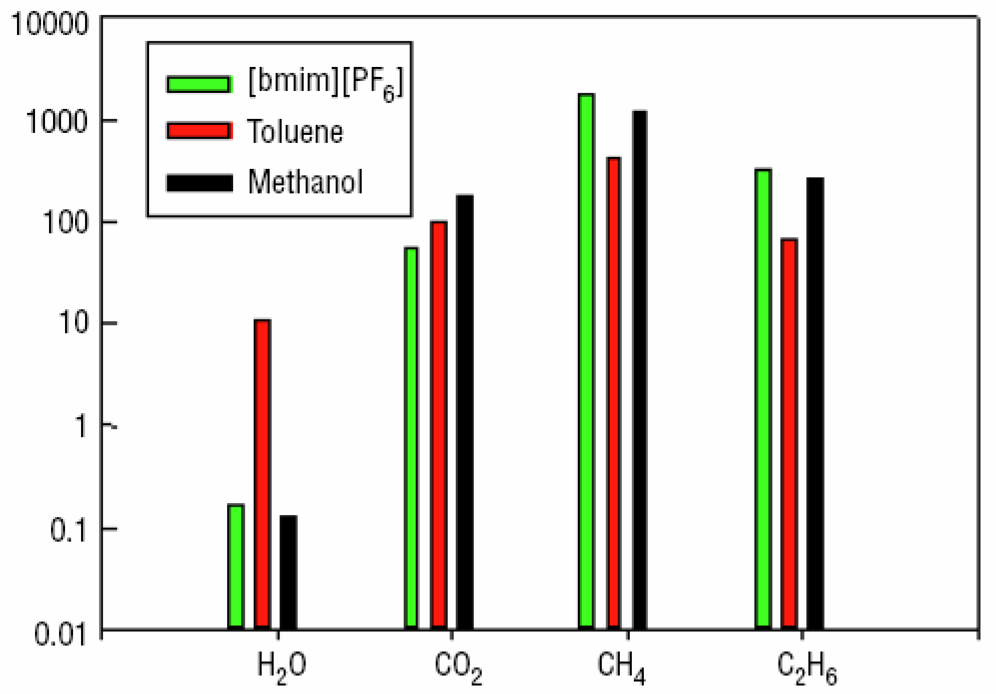

Figure 4.1: Comparison of Henry's law constants for H_2O, CO_2, CH_4 and C_2H_6 in [C_4mim][PF_6], toluene and methanol at 25°C. [1]

Table 4.1 shows solubility data found in literature used on selectivity calculations for all gases studied with different ILs.

Table 4.1: Solubility data found in literature for systems of ILs with different gases studied used in selectivity calculations.

GAS	*ANION*	*CATION*	*Literature Reference*
H_2S	[PF_6]	[C_4mim]	2
N_2	[PF_6]	[C_4mim]	3
	[BF_4]	[C_4mim]	4
O_2	[PF_6]	[C_4mim]	3
	[BF_4]	[C_4mim]	4
	[Tf_2N]	[C_4mim]	5
	[Tf_2N]	[C_1C_4PYRR]	5
CH_4	[PF_6]	[C_4mim]	3
	[BF_4]	[C_4mim]	4
	[Tf_2N]	[C_2mim]	6
C_2H_6	[PF_6]	[C_4mim]	3
	[BF_4]	[C_4mim]	4
	[Tf_2N]	[C_4mim]	5
	[Tf_2N]	[C_1C_4PYRR]	5
	[Tf_2N]	[C_2mim]	7
CO_2	[PF_6]	[C_4mim]	3
	[BF_4]	[C_4mim]	4
	[Tf_2N]	[C_4mim]	8
	[Tf_2N]	[C_1C_4PYRR]	5
	[Tf_2N]	[C_2mim]	7

From Figure 4.2 to Figure 4.5 it is presented a comparison between experimental selectivity calculations based on experimental data and selectivity predicted by COSMO-RS calculations of CO_2 with O_2, N_2, CH_4 and C_2H_6 as a function of temperature in some ILs studied. Figure 4.2 presents selectivity of Carbon Dioxide with Oxygen (based on experimental data and COSMO-RS prediction) in different ILs as a function of temperature.

In this case both experimental and predictive values of selectivity have the same trend and is possible to see that selectivity diminish with increasing temperature. This behaviour can be explained with the fact that Henry's Law constants are inversely proportional to solubility which means that a small Henry's Law constant is a sign of high gas solubility.

Selectivity predicted by COSMO-RS is lower than selectivity calculated based on experimental values. Comparing only experimental values is possible to see that [Tf_2N] anion provides bigger selectivity than the other anions presented on this study and the relative order of selectivity is: [C_4mim][PF_6] < [C_4mim][BF_4] < [C_1C_4PYRR][Tf_2N] < [C_4mim][Tf_2N].

Analysing COSMO-RS prediction values for selectivity it is possible to see that [PF_6] anion gives a bigger selectivity value although they have small differences between them (the relative order is [C_4mim][Tf_2N] < [C_1C_4PYRR][Tf_2N] < [C_4mim][BF_4] < [C_4mim][PF_6]).

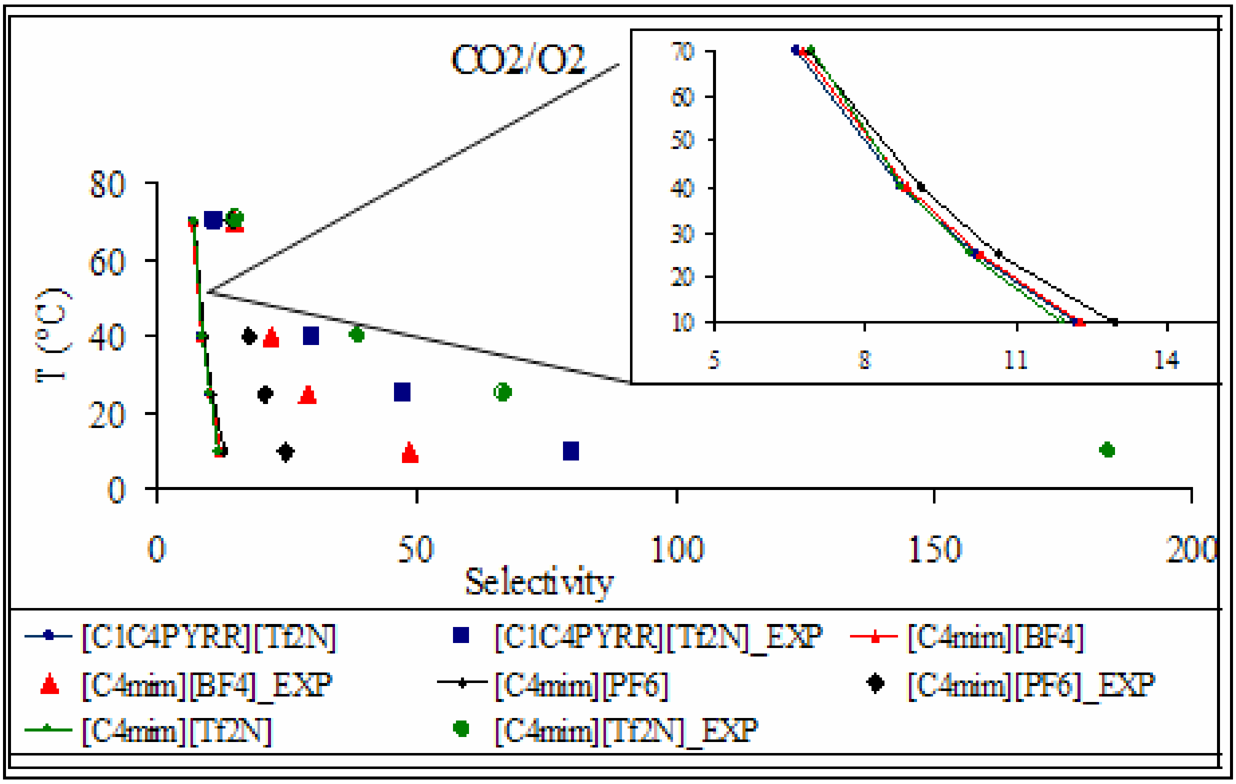

Figure 4.2: Selectivity of CO_2 with O_2 (based on experimental data and COSMO-RS prediction) in [C_1C_4pyrr][Tf_2N], [C_4mim][Tf_2N], [C_4mim][BF_4] and [C_4mim][PF_6] as a function of temperature.

Figure 4.3 presents selectivity of Carbon Dioxide with Nitrogen (based on experimental data and COSMO-RS prediction) in different IL's as a function of temperature.

For this case experimental values of selectivity are lower than the predictive values of COSMO-RS but there are few literature references with experimental values for nitrogen. In both cases they have the same tendency and it is also possible to see once again that selectivity diminish with increasing temperature.

Analysing COSMO-RS prediction values it is possible to see that both ILs have close selectivities but [C_4mim][BF_4] gives better selectivity for CO_2.

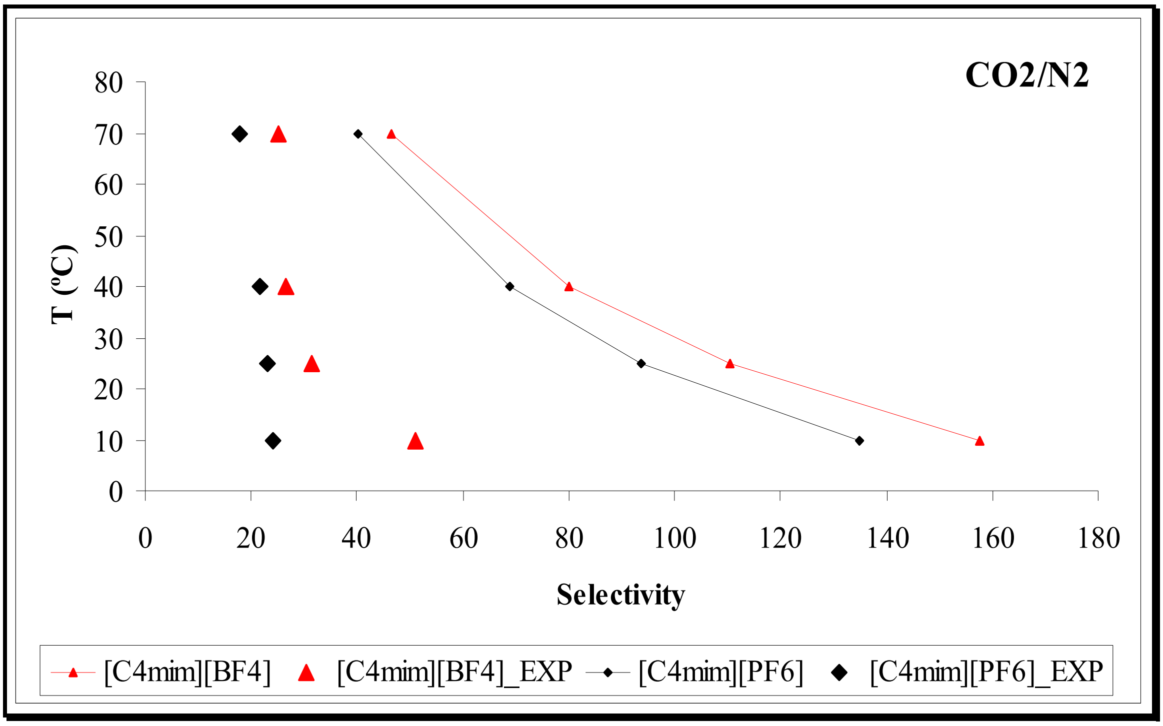

Figure 4.3: Selectivity of CO_2 with N_2 (based on experimental data and COSMO-RS prediction) in [C_4mim][BF_4] and [C_4mim][PF_6] as a function of temperature.

Figure 4.4 show selectivity of Carbon Dioxide with Methane (based on experimental data and COSMO-RS prediction) in different ILs as a function of temperature. Both experimental and predictive values of selectivity have the same trend and they are very similar.

[C_4mim][BF_4] has the same trend but for temperatures greater than 40 ºC experimental values are dubious. Given that there are few experimental values this selectivity value is included.

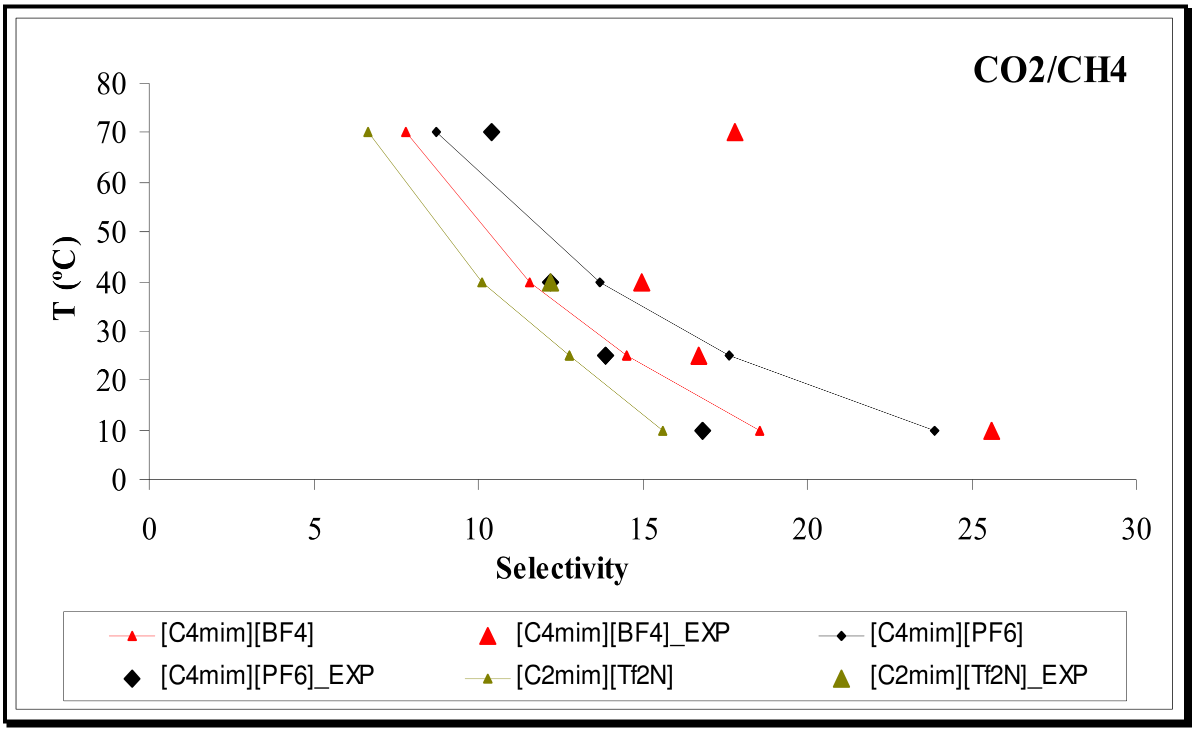

Figure 4.4: Selectivity of CO_2 with CH_4 (based on experimental data and COSMO-RS prediction) in $[C_2mim][Tf_2N]$, $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$ as a function of temperature.

Figure 4.5 presents selectivity of Carbon Dioxide with Ethane (based on experimental data and COSMO-RS prediction) in different ILs as a function of temperature.

Experimental selectivity values are lower than the one predicted by COSMO-RS. There are big similarities for both methods and once more, for these couple of gases, the same trend is observed and is possible to see that selectivity diminish with increasing temperature.

For lower temperatures, selectivity predicted is always bigger for CO_2 than for other studied gases.

From COSMO-RS is possible to see that $[PF_6]$ anion provides bigger selectivity than the other anions presented on this study and the relative order of selectivity is: $[C_1C_4PYRR][Tf_2N]$ < $[C_4mim][Tf_2N]$ < $[C_2mim][Tf_2N]$ < $[C_4mim][BF_4]$ < $[C_4mim][PF_6]$.

Analysing experimental values for selectivity it is possible to see that $[BF_4]$ anion gives a higher selectivity value although they have small differences between them (the relative order is $[C_1C_4PYRR][Tf_2N]$ < $[C_2mim][Tf_2N]$ < $[C_4mim][Tf_2N]$ < $[C_4mim][PF_6]$ < $[C_4mim][BF_4]$). For temperature range considered selectivity almost does not vary for three ILs [C_1C_4PYRR][Tf_2N], [C_2mim][Tf_2N] and [C_4mim][Tf_2N].

The anion polarity of IL has influence on selectivity prediction because from the analysis of figure 4.4 and figure 4.5 is possible to see that anion [PF_6] gives greater solubility for COSMO-RS prediction and, on the other hand greater solubility is given by anion [BF_4]. It was proven that the anion plays an important role in selectivity.

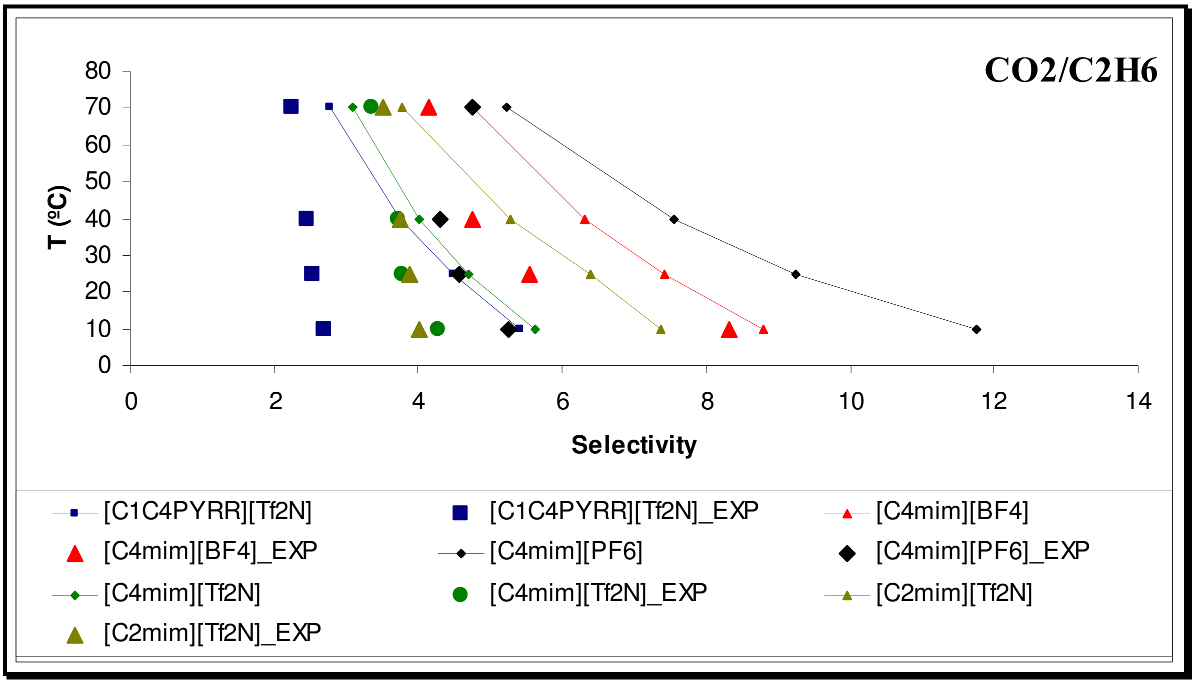

Figure 4.5: Selectivity of CO_2 with C_2H_6 (based on experimental data and COSMO-RS prediction) in [C_1C_4pyrr][Tf_2N], [C_4mim][Tf_2N], [C_4mim][BF_4], [C_4mim][PF_6] and [C_4mim][Tf_2N] as a function of temperature.

All results, from figure 4.2 to figure 4.5, show the same selectivity trend for CO_2 with O_2, N_2, CH_4 and C_2H_6 as a function of temperature in all ILs studied. Selectivity decreases with increased temperature and this behaviour was expected as shown in previous chapter.

From Figure 4.6 to Figure 4.10 it is presented a comparison between experimental selectivity calculations based on experimental data and selectivity predicted by COSMO-RS calculations of CO_2 with H_2S, O_2, N_2, CH_4 and C_2H_6 as a function of temperature for different ILs studied, as show in table 4.1.

Figure 4.6 show selectivity of all studied gases with CO_2 on [C_4mim][PF_6]. H_2S show a opposing trend from all other gases and as a result is possible to say that H_2S is more soluble in [C_4mim][PF_6] than CO_2, especially at lower temperatures. In this case experimental data differ from predictive values almost ten times more.

For Oxygen, Methane and Ethane both experimental and predictive values of selectivity presents a very good trend, as expected from previous results.

Experimental selectivity in Nitrogen differs about five times from predictive values from COSMO-RS. For this particular gas is very difficult to found experimental solubility data.

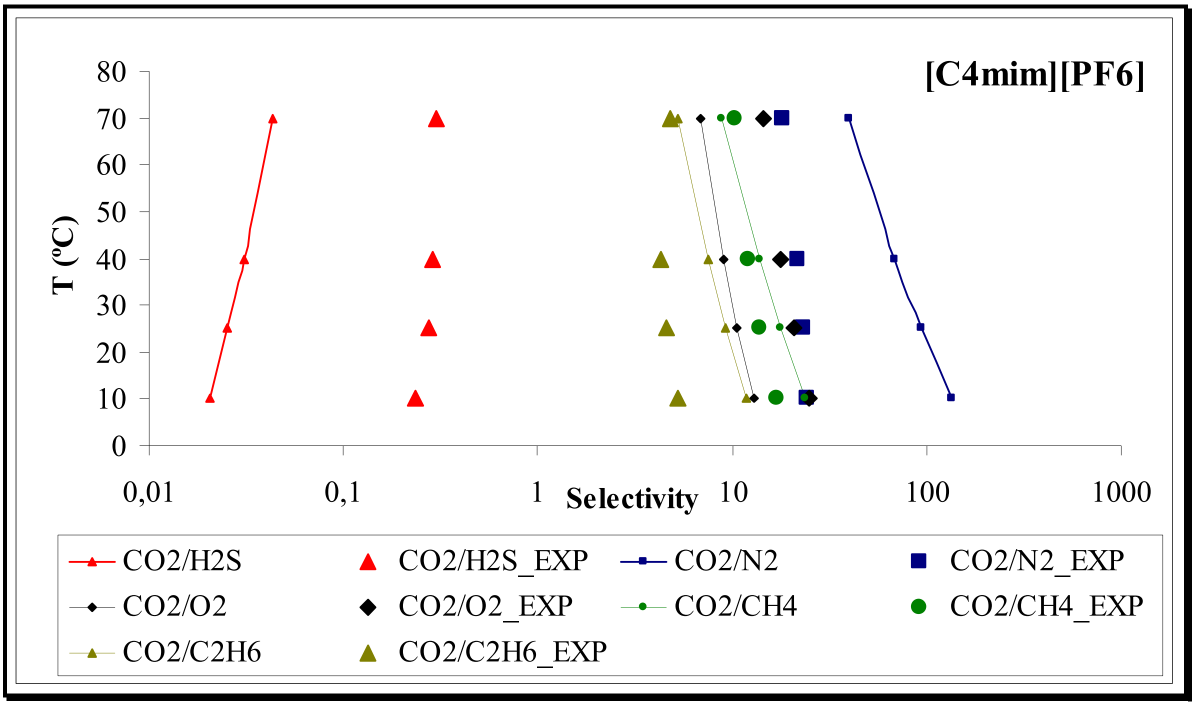

Figure 4.6: Selectivity of CO_2 with H_2S, N_2, O_2, CH_4 and C_2H_6 (based on experimental data and COSMO-RS prediction) in [C_4mim][PF_6] as a function of temperature.

Next figure presents selectivity for different gases in [C_4mim][BF_4]. Once more it is possible to see that there are a big similarity between COSMO-RS and experimental values for Methane and Ethane. All gases present the same tendency of lower selectivity for higher temperatures.

In Oxygen and Nitrogen there is an approach of selectivity values for lower temperatures. COSMO-RS predictive values for N_2 are quite different of experimental data despite the fact that the same trend is observed.

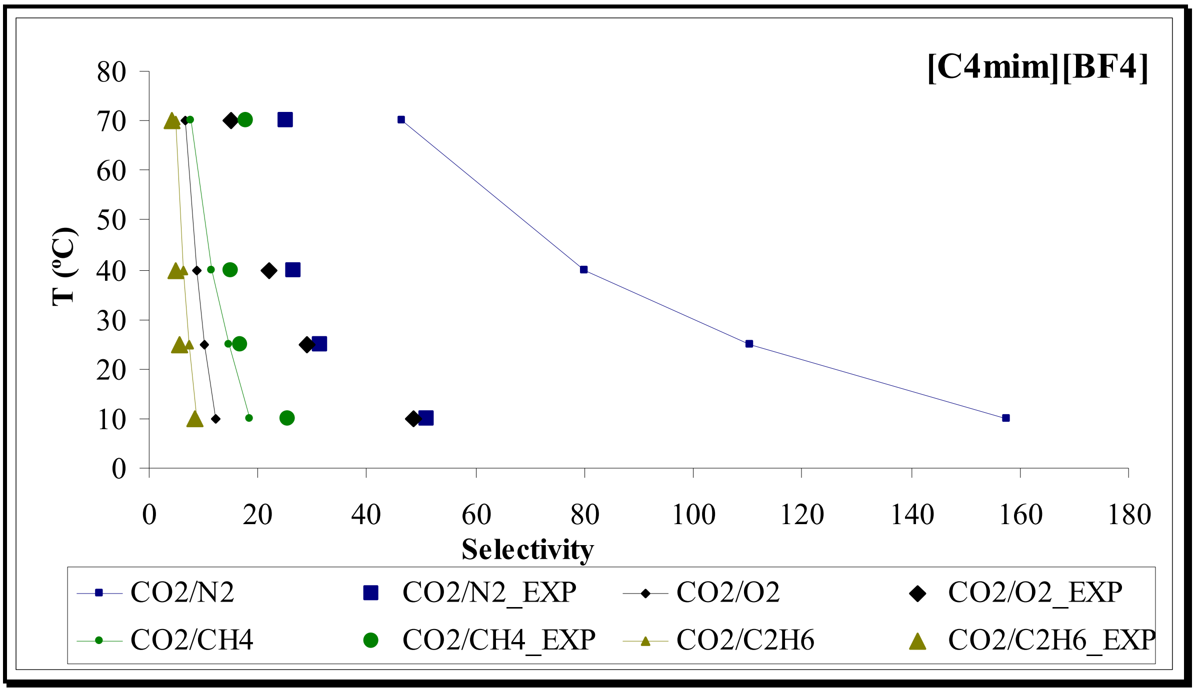

Figure 4.7: Selectivity of CO_2 with N_2, O_2, CH_4 and C_2H_6 (based on experimental data and COSMO-RS prediction) in [C_4mim][BF_4] as a function of temperature.

In figure 4.8, changing the anion it is possible to see that there are no significant differences with Ethane both in COSMO-RS predictive values and experimental values. Comparing with previous figure is possible to conclude that anion [Tf_2N] confer higher selectivity for O_2. With [C_4mim][Tf_2N] although the same trend is observed for Oxygen and Ethane experimental values differ, in Oxygen, almost ten times more than predicted values for lower temperatures.

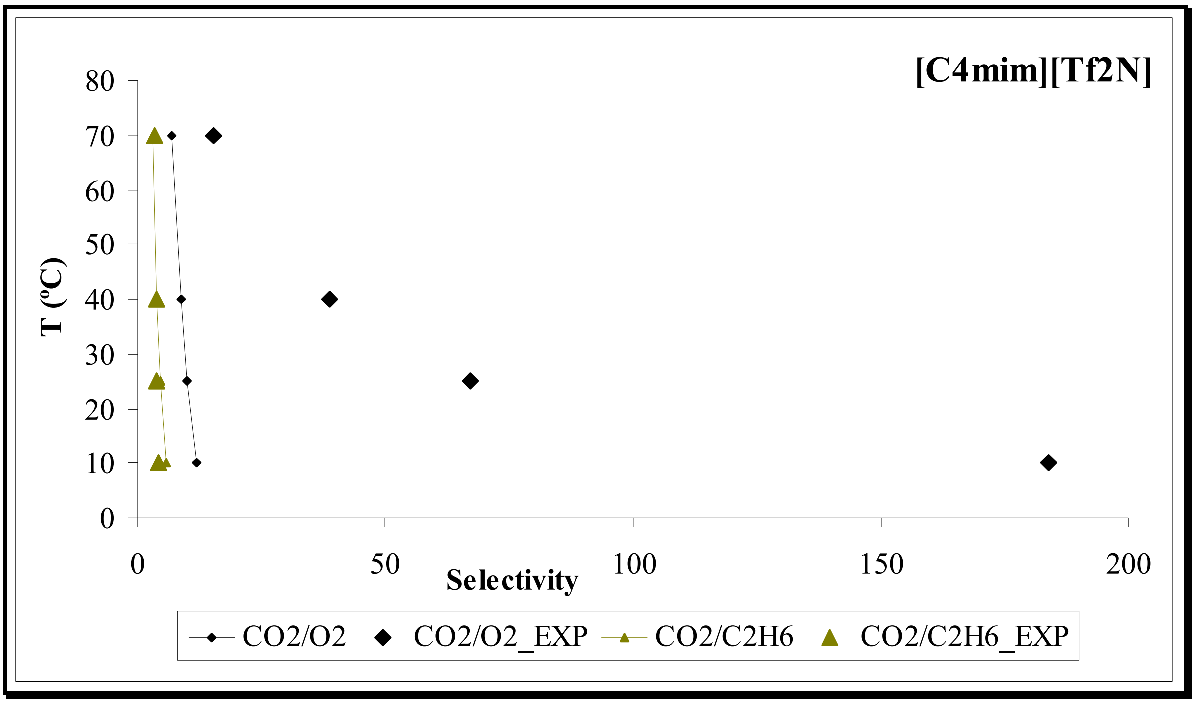

Figure 4.8: Selectivity of CO_2 with O_2 and C_2H_6 (based on experimental data and COSMO-RS prediction) in $[C_4mim][Tf_2N]$ as a function of temperature.

Next figure presents a **Cation Alkyl Chain Influence** comparing with previous one. Changing $[C_4mim]$ for $[C_1C_4PYRR]$ the same trend is observed but for lower temperatures Oxygen experimental selectivity decreases due to higher cation sphericity. COSMO-RS predictive values do not have significant differences changing cation.

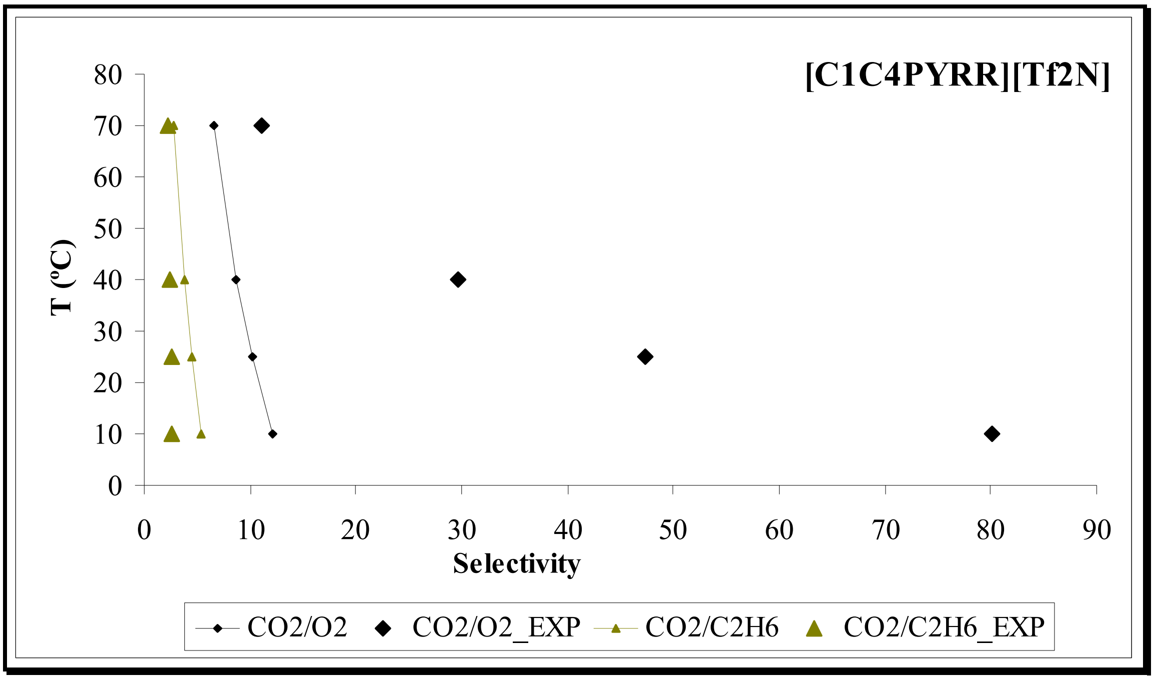

Figure 4.9: Selectivity of CO_2 with O_2 and C_2H_6 (based on experimental data and COSMO-RS prediction) in [C_1C_4PYRR][Tf_2N] as a function of temperature.

In figure 4.10 both studied hydrocarbons in [C_2mim][Tf_2N] have very low selectivities, both experimental and predictive. For higher temperatures there are a better approach of this values, as expected.

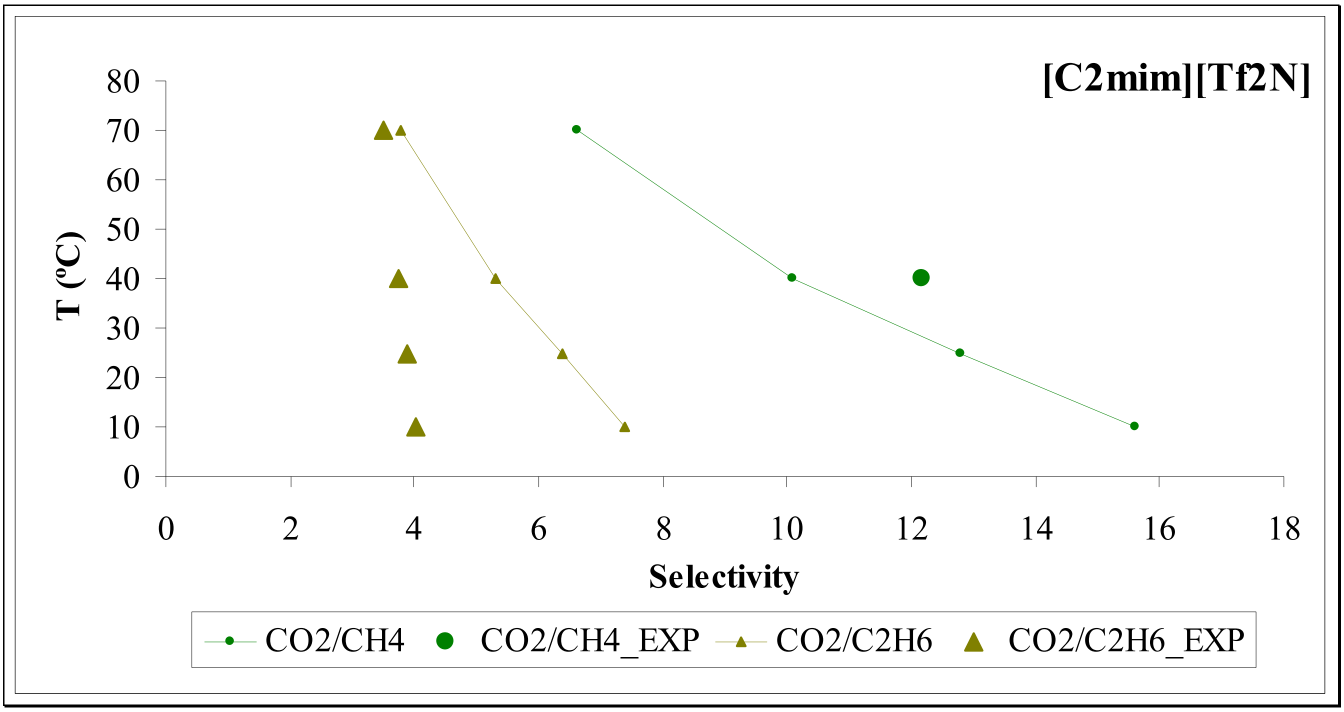

Figure 4.10: Selectivity of CO_2 with O_2 and C_2H_6 (based on experimental data and COSMO-RS prediction) in $[C_2mim][Tf_2N]$ as a function of temperature.

4.1. REFERENCES

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5. Conclusions and Future Work

In this work several attempts were carried in order to evaluate the COSMO-RS capability of predicting Henry's constants of several gases in common ILs and the IL selectivities in respect to CO_2.

COSMO-RS showed to be capable to produce acceptable predictions gases in ILs Henry's constants and CO_2 selectivities in ILs. Furthermore, COSMO-RS and its implementation in the program COSMOtherm showed to be capable of giving satisfactory *a priori* qualitative predictions of the vapour-liquid systems behaviour, which may be of considerable value for the exploration of suitable ILs for practical and specific applications prior to make extensive experimental measurements.

For almost all the studied gases Henry's constants predictions given by COSMO-RS are relatively close to experimental data for the temperature range considered. Specially, the COSMO-RS predictions for methane and ethane solubilities in ILs showed to be very close to the experimental data and proved to describe well both qualitatively and quantitatively the equilibrium behaviour experimentally observed.

In addition, it was experimentally found that longer alkyl chain cations could provide a greater solubility for CH_4, C_2H_6 and CO_2 and the COSMO-RS showed to correctly describe that trend. For O_2, H_2S and N_2 it is not possible to evaluate the COSMO-RS Henry's constants predictive capability because the experimental data showed to be very scarce.

Analysing the anion influence in the experimental solubilities of CH_4, C_2H_6 and CO_2 it is possible to conclude that [Tf_2N]-based ILs present a higher solubility for these gases while [DCA]-based ILs present the lowest solubilities. In both cases the correct qualitative trend was predicted by the COSMO-RS calculation results.

It was found that the selectivity in ILs in respect to CO_2 decreases with increasing temperature both experimentally and predicted by COSMO-RS. In what concerns the selectivities COSMO-RS particularly showed to provide best quantitative results and almost all the trends are well described.

Finally as future work and developments it would be interesting to optimize COSMO-RS internal parameters in order to achieve a better description of the experimental solubilities and selectivities for gases in ionic liquids. Furthermore, more experimental data is extremely required for a better evaluation of the COSMO-RS predictive capabilities both for Henry's constants and selectivities predictions.

Nevertheless, it should be noted that COSMO-RS, at the present, is not able to treat ions correctly at finite low ionic strength due to the long-range ion-ion interactions involved, and besides the small effects it induces they must be considered, and much more experimental and theoretical work is needed to improve such type of predictions.