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**Seleção de solventes para destilação extrativa de
etanol**

**Selection of solvents for extractive distillation of
ethanol**



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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 Manuel da Costa e Araújo Pereira Coutinho, Professor Associado com Agregação do Departamento de Química da Universidade de Aveiro.

*“Para ser grande, sê inteiro: nada
Teu exagera ou exclui.
Sê todo em cada coisa. Põe quanto és
No mínimo que fazes.
Assim em cada lago a lua toda
Brilha, porque alta vive.”*

(Fernando Pessoa)

O júri

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Palavras-chave

Etanol; Equilíbrio Líquido-Vapor; Líquidos Iônicos; COSMOS RS;

Resumo

Os biocombustíveis têm sido alvo de grandes estudos nos últimos anos devido à escassez do petróleo.

O bioetanol é dos biocombustíveis mais produzidos no mundo, contudo o seu processo de purificação torna-se dispendioso na medida em que este só pode ser usado em misturas com combustíveis fósseis se tiver cerca de 99.5% de pureza. Tem-se vindo a estudar alternativas aos solventes usados na destilação extrativa de etanol, de forma a minimizar os custos de operação.

Os líquidos iónicos são vistos como uma solução para muitos dos problemas na indústria química num futuro próximo, devido às suas propriedades invulgares. O objetivo desta dissertação é estudar o equilíbrio líquido vapor de sistemas de líquido iónico-etanol ou água. Para o efeito medimos dois sistemas experimentais num ebuliómetro: cloreto de 1-butil-3-metilimidazólio e cloreto de colina com etanol a três pressões. Usou-se depois o modelo COSMO RS para efectuar a modelação dos dados. Discutem-se os vários factores que influenciam o comportamento dos sistemas.

Keywords

Ethanol; Vapor-Liquid Equilibrium; Ionic liquids; COSMO RS;

Abstract

Biofuels have been an important subject of study, mainly because of petroleum scarcity.

Bioethanol is the most used biofuel as alternative to petrol, but the purification cost is high and in order to use bioethanol mixed with hydrocarbons, it needs to be 99.5 % pure. Alternatives for solvents to be used in ethanol's extractive distillation are being investigated.

The ionic liquids are seen as a solution to many of the problems in the chemical industry in the near future, due to their excellent properties.

The purpose of this dissertation is to study the behavior of different ionic liquid – ethanol or water systems. This has been achieved through the study of two systems by ebulliometry: 1-butyl-3-methylimidazolium chloride and choline chloride at three different pressures. Finally using COSMO RS, the modeling of the experimental data was made. Are also discussed several factors that influence the behavior of those systems.

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Nomenclature

Ionic Liquids

Abbreviation	Ionic Liquid
[C ₁ mim][Cl]	1,3-Methylimidazolium Chloride
[C ₂ mim][Cl]	1-Ethyl-3-methylimidazolium Chloride
[C ₄ mim][Cl]	1-Butyl-3-methylimidazolium Chloride
[C ₆ mim][Cl]	1-Hexyl-3-methylimidazolium Chloride
[C ₈ mim][Cl]	1-Octyl-3-methylimidazolium Chloride
[C ₄ mim][MSO ₄]	1-Butyl-3-methylimidazolium Methylsulfate
[C ₄ mim][BF ₄]	1-Butyl-3-methylimidazolium Tetrafluoroborate
[C ₄ mim][HSO ₄]	1-Butyl-3-methylimidazolium Hydrogensulfate
[C ₄ mim][Ac]	1-Butyl-3-methylimidazolium Acetate
[C ₁ mim][DMP]	1,3-Methylimidazolium Dimethylphosphate
[C ₁ mim][ESO ₄]	1,3-Methylimidazolium Ethylsulfate
[C ₂ mim][ESO ₄]	1-Ethyl-3-methylimidazolium Ethylsulfate
[C ₄ mim][ESO ₄]	1-Butyl-3-methylimidazolium Ethylsulfate
[C ₆ mim][ESO ₄]	1-Hexyl-3-methylimidazolium Ethylsulfate
[C ₇ mim][ESO ₄]	1-Heptyl-3-methylimidazolium Ethylsulfate
[C ₁₀ mim][ESO ₄]	1-Decyl-3-methylimidazolium Ethylsulfate
[C ₁₂ mim][ESO ₄]	1-Dodecyl-3-methylimidazolium Ethylsulfate
[C ₂ mpy][ESO ₄]	1-Ethyl-3-methylpyridinium Ethylsulfate
[Choline][Cl]	Choline Chloride

Greek Symbols

α	Relative Volatility
γ	Activity Coefficient

Symbols

x	Molar fraction of the liquid phase
y	Molar fraction of the vapor phase
P	System Pressure
P^{σ}	Saturation Pressure

Symbols below the line

i, j	Pure component index
--------	----------------------

Symbols above the line

∞	Infinite
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1 Historical Introduction

Energy is a determinant factor that influences and limits our lives and the technological progress of our society. Petroleum, the most powerful and plentiful source of energy consists on a complex mixture of unsaturated hydrocarbons, that occurs in the result of organic remains deposition on the bottom of lakes and seas, which are undergoing chemical changes over millions of years¹.

The petroleum era began about 150 years ago and easily available energy has supported major advances in agriculture, industry, transportation and indeed many diverse activities overvalued by human beings. Now world petroleum and natural gas supplies have peaked and their supplies will slowly decline over the next 50 years until depletion².

Small amounts of petroleum and natural gas will remain underground but their extraction will be energetically and economically not viable. Although people are still comfortable with the security provided by fossil energy, especially petroleum and natural gas, they appear to be slow to recognize the energy crisis in the world. Oil, natural gas, coal and nuclear power provide more than 88% of world energy needs and the other 12% is provided by various renewable energy sources^{1,3}.

Renewable energy technologies already exist, but more research is needed to improve their efficiency, costs and consequently their wide acceptance and applicability. During the last decade, biofuels have emerged as an alternative to petroleum-based energy sources for some applications.

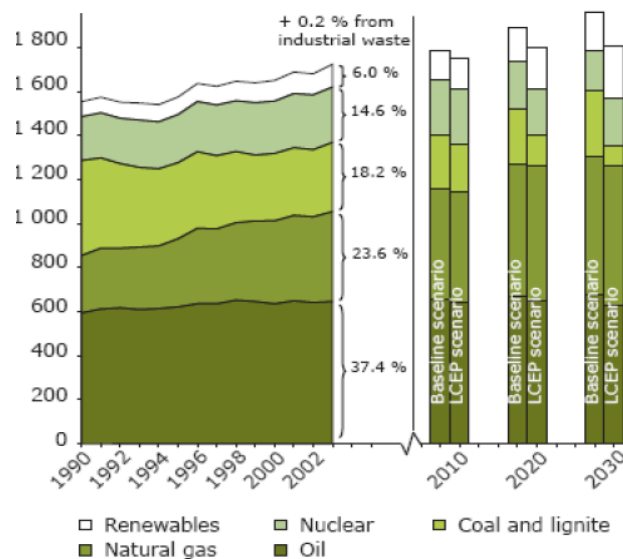


Figure 1-Consumption of fuel, natural gas, coal and lignite, nuclear and renewable energy on Europe

2 Biofuels

Biofuels are a wide range of fuels derived from biomass, which are gaining increased public and scientific attention, driven by factors such as petroleum price spikes, the need for increased energy security, and concern over greenhouse gas emissions from fossil fuels⁴.

In a political-economic point of view, the biggest advantage of its use is to make countries less dependent on petroleum sources and its variations prices and availability⁵.

Aiming at reducing the European countries dependency towards petroleum, the European Union (EU) has policies to implement renewable sources on the already available energy sources, through the Directive 2003/30/EC which aims that "member states should ensure that is placed on their markets a minimum proportion of renewable biofuels" (Figure 2)⁵.

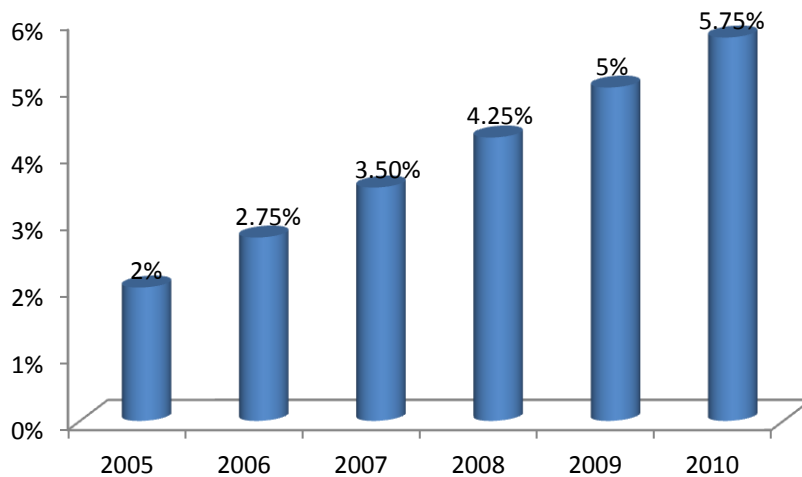


Figure 2- Minimum percentage of biofuel incorporation [3]

In Portugal, the strategy for the introduction of biofuels on the market is based primarily on their blend in conventional fuels, within limits that allow their use in vehicles without requiring additional modifications to the country vehicles fleet.

Biofuels can be classified in two different categories: first and second generation fuels.

It is referred as first generation fuels, fuels that have been derived from sources like starch, sugar, animal fats and vegetable oil, such as ETBE, biodiesel and bioethanol and first generation feedstocks are characterized by the fact that only parts of the plants are used for biofuel production. These types of fuels are obtained using conventional techniques of production and they offer the greatest short-term potentials of biofuels today. Although they differ in properties, technical requirements, economical aspects and potential, they contribute to guarantee long-term mobility when comparing environmental and social costs with conventional fuels^{1, 6}.

In other hand, second generation biofuels are not yet commercially available because their conversion technologies still need some improvement. BTL fuels and ethanol from lignocelluloses are examples of this type of fuels. Some sources define second generation fuels as biomass-to-liquid technologies, which are intended to use lignocellulosic biomass. They have been developed to overtake first generation biofuels important manufacture limitations. And unlike those, second generation feedstock types can provide the opportunity to use almost the entire plant and not only some parts of it^{1, 6}.

Currently the most used biofuels are biodiesel and bioethanol.

3 Bioethanol

Bioethanol is a fuel that has different origins, such as biomass or petrochemical processes and its molecular formula is C_2H_6O .

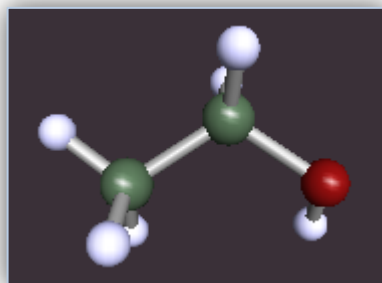


Figure 3– Molecular structure of Ethanol [5]

Also known as ethyl alcohol, it is a flammable and colorless chemical compound, every so often represented as “EtOH” or as C₂H₅OH. In Table 1 are shown the most important properties of ethanol.

Table 1 - Properties of Ethanol [2]

Properties of Ethanol		
Density	0.789	g.cm ⁻³
Melting Point	-114.3	°C
Boiling Point	78.40	°C
Viscosity	1.200	cP @ 20 °C
Solid State	Liquid	
Solubility in water	Miscible	

It can be produced from any biological feedstock that contains appreciable amounts of sugar or materials that can be converted into sugars such as starch or cellulose.⁷ Two examples of feedstock for ethanol production are sugar beets and sugar cane which contain high percentages of sugar. Corn, wheat, barley, rye and other cereals are typical feedstock's containing starch in their kernels. A large variety of feedstock is available for producing ethanol from biomass that contains large amounts of cellulose and hemicellulose³.

Sugars can be easily fermented and starch can be converted into sugar and then into ethanol. Cellulose and hemicellulose can be converted to sugar, though with more difficulty than conversion of starch.

Ethanol is considered a clean source of energy not only by the significant amount of heat released in combustion, but also because it has an oxygen atom, about 35% of its mass is composed with oxygen. Thus, when blend with conventional fuel, the combustion is cleaner, helping to reduce polluting emissions and it is used as an octane enhancer. Ethanol seems to be one of the most realistic options for setting up a truly global bioenergy trade, at least within the present decade. Use of ethanol fuel is growing rapidly as it has a considerable potential for substituting oil in the transportation sector, given the right conditions. To be mixed with fossil fuels, the ethanol must be further processed in order to remove the water contained, requiring additional fossil energy inputs to achieve 99.5% of pure alcohol⁶.

It is also expected to exhibit an exponential growth provided by the tax incentives in order to reduce atmospheric pollution.

3.1- Ethanol Vs Petrol

While bioethanol is one of the major biomass energy commodities, most of it is commercialized for alcoholic beverages, for solvent purposes and industrial applications. There is a need to maximize some of the many favorable properties of ethanol in order to achieve better results in biofuels market. Table 2 shows a comparison between bioethanol and fossil fuel properties.

Table 2- Comparison of Petrol and Bioethanol properties [2]

Parameter		Petrol	Bioethanol
Density	kg/L	0.72-0.78	0.79
Viscosity	mm ² .s ⁻¹	0.6	1.5
Latent Heat of Vaporization	kJ/kg	330-400	842-930
Flash Point	°C	< 21	< 21
Calorific Value	kJ/L	32.18	22.35
Octane Number	RON	92	>100
Ignition Temperature	°C	220	420

The octane number measure the resistance of a fuel to self-ignition and detonation. It is determined by comparing, under standard conditions, the intensity of the detonation between the fuel and two reference fuels, such as iso-octane, which resists detonation, and heptane, which detonates readily. The value of octane number is the percentage by volume of iso-octane in the iso-octane-heptane mixture that matches the fuel being tested in a standard test engine and it influences the anti-detonation property of the fuel. The ability of detonation describes an uncontrolled combustion which puts heavy mechanical and thermal loads on the engine. So, a higher octane number stands for an anti-detonation fuel which permits the engine a more efficient use of the energy provided from the combustion heat.

Ethanol is well known as an excellent anti-detonation additive and as an improver of the octane when blended with petrol, because of that its octane number is higher than conventional fuels.

Table 2 also shows that, the calorific value of ethanol and petrol are different. Due to this difference, the energy yield of ethanol is one third lower than petrol. The energy of petrol is 32.5 MJ/L and 21.2 MJ/L for ethanol. For a better explanation, one liter of ethanol only replaces 0.65 liters of petrol.

Another and important fuel property is its volatility. To perform a correct combustion, the fuel needs to be perfectly mixed with air. Although petrol has a higher calorific number, ethanol has a higher vapor pressure and, consequently, ethanol vaporizes more readily than conventional fuel and the resultant combustion is superior when it is utilized ethanol or blends composed with ethanol and petrol.

Ethanol is thus, and regardless of the production process, an exceedingly good alternative to petrol use.

3.2- Extraction processes of Ethanol

According to the literature, in 1994 the world production capacity for synthetic ethanol was about 2.6 million of tons per year and the major producer was USA. The production of ethanol by fermentation from agricultural products was just about 4 300 000 tons per year in the same country. Nowadays, it is produced about 12.9 million tons per year of bioethanol and the major producer country is Brazil, followed by India and then USA.

Formerly, ethanol was manufactured from ethylene by two ways: indirect hydration by addition of sulfuric acid and subsequent saponification of the sulfuric acid ester; and direct catalyst hydration. In the first method of production, the selectivity of ethanol is about 86% and in the second one is around 97%.

In order to produce ethanol from biomass, basically there are three different processes: corn-to ethanol, basic lignocellulosic biomass to-ethanol and integrated lignocellulosic biomass to-ethanol.⁸

In the corn to-ethanol biorefinery, there are two major processes: the dry-grind and the wet mill. The first is a conventional method to obtain ethanol and consists of

grinding, cooking, liquefaction, saccharification of the starch to sugars with enzymes, fermentation of the sugars to ethanol followed by distillation and dehydration processes.⁸⁻⁹

The wet mill process consists on a pre-processing prior to fermentation to ethanol and it can produce high-value co-products such as fibers, germ and gluten. Consequently, it is a more expensive and energy intensive process.⁸

The lignocellulosic biomass to- ethanol process can be a more promising and effective alternative. Processes of this type have a great potential as a net fossil fuel displacement because they contribute positively to a better environment, because of the diminished greenhouse emissions.⁸

An integrated lignocellulosic biomass to-ethanol process is a new concept based on the existing pulp mills. It is possible to obtain fuel at the same time as chemicals. In this process, the short fiber of cellulose is converted into ethanol and the long fiber into materials for paper production or materials such as bio-composites. All the feedstocks components are used to produce value-added multiple co-products, including energy, as the concept of biorefinery.⁸⁻⁹

In spite of all the advantages, these last processes are still not available in the industry due to existing technical, economic and commercial barriers.

Although, ethanol is an exceedingly good fuel alternative, the separation of an aqueous mixture of ethanol /water is often mentioned as a problem for the adoption of ethanol fuel. It presents an azeotrope at $x_{ethanol} \approx 0.894$ which difficult the obtainment of high purity alcohol, as shown in figure 4.

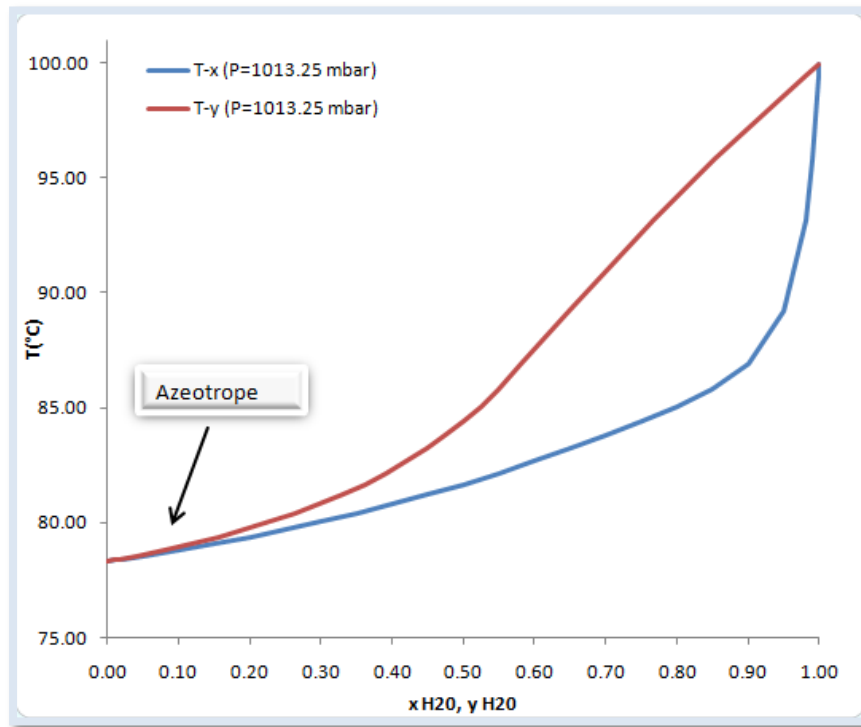


Figure 4 - Phase diagram of Ethanol-Water System

So in order to solve this dilemma, the need to discover a viable alternatives to distillation is the mainly issue.

4 Distillation

Distillation is a separation process based in vapor-liquid equilibrium of mixtures.⁸ It separates two or more liquid components based on the principle of relative volatility or boiling points. The greater the difference between their volatilities, the easier is the separation using distillation¹⁰. This process involves production of vapor by boiling the liquid mixture and removal of the vapor by condensation as shown in Figure 5. The vapor is rich in light components and the liquid is rich in heavy components.

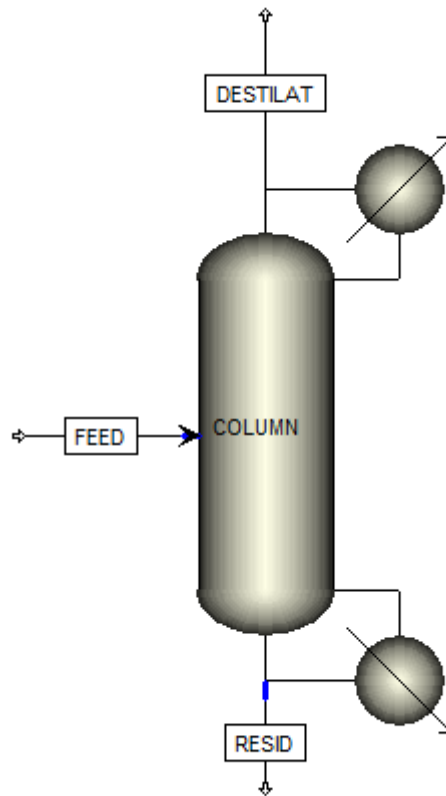


Figure 5 - Distillation Column

Often a part of the condensate is flowed back to the still and is mixed with the outgoing vapor. To enhance mass transfer, there are devices called plates, trays or packing which role is to bring the vapor and the liquid phases into contact. The greater the difference of the relative volatility, the bigger number of plates is needed.¹¹

Distillation is the mainly process utilized for alcohols recovery, due to its high percentage of alcohol product in the final stream, about 99% ends up in the alcohol product stream.

In spite of all its advantages, distillation cannot perform a complete separation in azeotropic mixtures. For the ethanol-water separation it requires additional steps like molecular sieve adsorption or changes of the process parameters in order to reach product dryness.¹² To obtain a 99.5% pure ethanol, it is necessary to overtake the azeotrope of ethanol-water system. In general, for the solutions containing around 10 to 85% of ethanol, distillation is a very effective process obtaining approximately 92.4% ethanol in the product stream. While for mixtures with 85 to near 95.6% alcohol

containing, this process becomes more expensive and requiring high reflux ratios, just as additional equipments.^{8, 12} Although, the azeotrope can be eliminated by lowering the operation pressure to a vacuum condition, the alcohol is usually dehydrated to achieve anhydrous ethanol by employing azeotropic distillation, extractive distillation, liquid-liquid extraction, adsorption, and some more complex separation methods.¹³

4.1- Azeotropic Distillation

Azeotropic distillation involves adding a third volatile component, in order to form a ternary azeotrope mixture. It affects the relative volatility of the two components to be separated and alters the separation factor in the distillation. The third component is usually called entrainer and the most commonly used for the ethanol-water separation are benzene, toluene and cyclohexane.¹¹

In this process, ethanol exits from the bottom, while water vapor and small amounts of ethanol exit at the top. Then, it enters on a decanter and splits into two phases, the organic phase composed by ethanol-entrainer and the aqueous phase constituted by water-entrainer. The first is refluxed back into the first column and the latter is processed in the entrainer recovery column.⁸

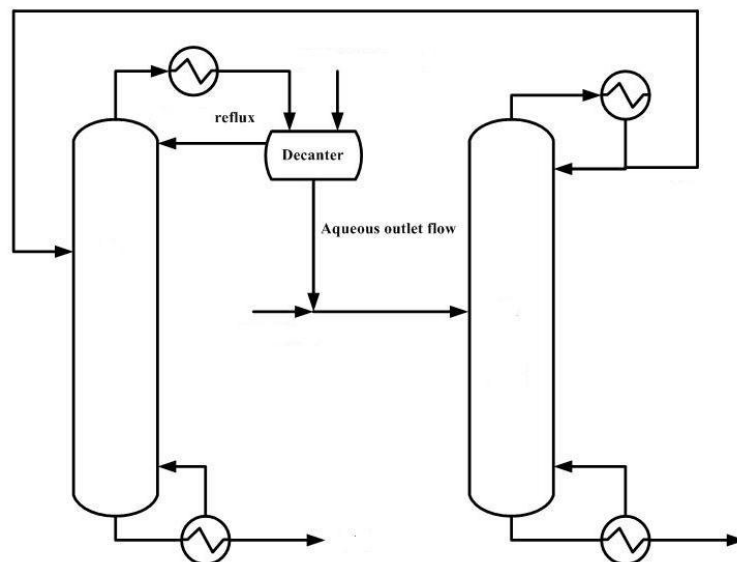


Figure 6 - Azeotropic distillation process diagram

Consequently, the system has the disadvantage of high energy requirement and large capital cost. Not mentioning the health and safety concerns about the entrainer. For ethanol production, this method is the less used.

4.2-Extractive Distillation

Extractive distillation requires for an extractive agent, the extractant. It can be a liquid solvent, or a dissolved salt, a mixture of liquid solvent and dissolved salt, hyperbranched polymers and ionic liquids. Just like azeotropic distillation, extractive distillation adds a third component in order to increase the relative volatility of the components to be separated, it uses a selective high boiling solvent to alter the separation factor (Figure 7).

Ethanol's extractive distillation is commonly carried using as a liquid solvent, ethylene glycol and under specific operating conditions it can be competitive with azeotropic distillation¹⁴.

The purpose of the utilization of a dissolved salt is to enhance the relative volatility, but also because the salt dissolves into the liquid, which is denominated as "salt-effect". The most studied salts are potassium acetate, sodium acetate and calcium chloride. In literature, it is possible to find some studies about the comparison of extractive distillation with dissolved salts and conventional liquid extractants, it concludes that the former is more efficient for ethanol-water separation. When it is used both liquid solvent and dissolved salt, the extraction is also more efficient if used only a liquid solvent.^{8, 13}

Hyperbranched polymers and ionic liquids are novel separating agents used in extractive distillation. Hyperbranched polymers are highly branched macromolecules with a large number of functional groups. They can be manufactured by one step reactions, an economical advantage, and possess a remarkable selectivity and capacity, low viscosity and thermal stability.^{8, 13}

Polymers like poli(glycerol) are used as entrainers in the ethanol-water system enhancing the separation process efficiency and selectivity, by braking the azeotropic

point. Despite some advantages, the obtained results are similar to conventional entrainers.^{8,13}

On the other hand, extractive distillation with ionic liquids has the advantage of high separation ability, easy operation and no contamination of the distillate due to their non-volatility¹⁰. It only requires one distillation column, which represents lower energy consumption. However, ionic liquids containing halogen anions are expensive and less stable.¹⁵

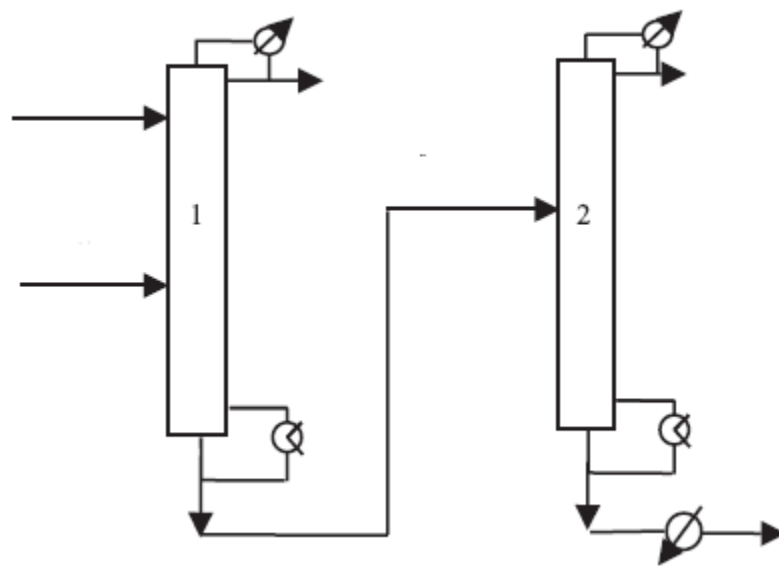


Figure 7 - Extractive distillation process diagram

5 Ionic Liquids

5.1 Properties

Ionic liquids (IL) are salts with a melting point below 100 °C, composed entirely of ionic species. The cation is a poorly coordinating, bulky organic component and the anion can be organic or inorganic, which difficults the formation of crystal lattice.^{16 15}

They have been classified as process chemicals and as performance chemicals, but also as environmental friendly and as green solvents with a wide range of potential applications. Ionic liquids have been broadly studied (Figure 6).¹⁷

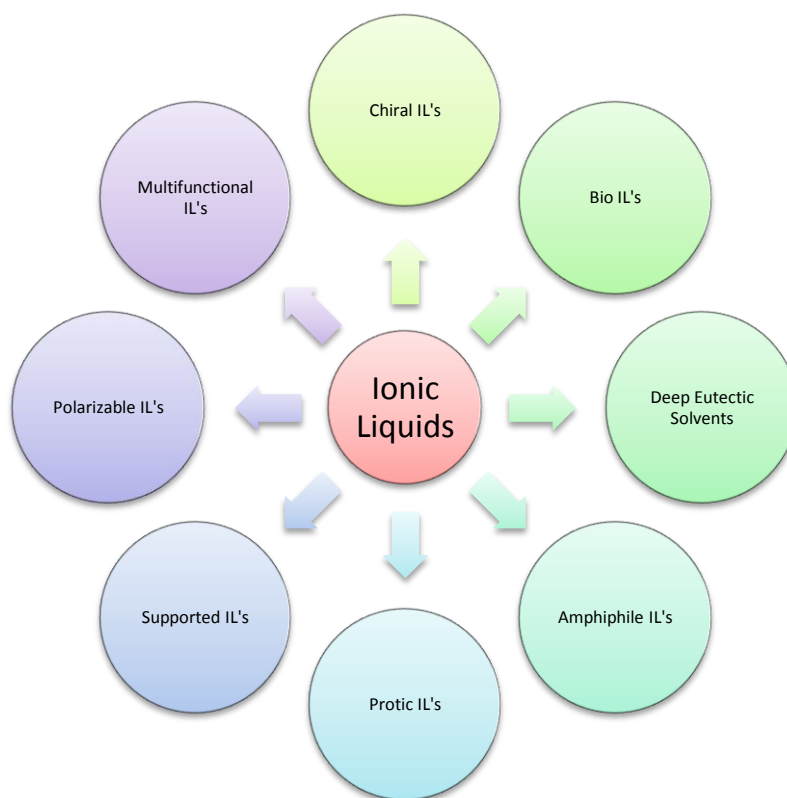


Figure 8 - Evolution of Ionic Liquids [12]

Ionic liquids tend to have very appealing solvent properties and may be miscible with both water and organic solvents¹⁸. At room temperature, they are generally in the liquid state and their vapor pressure is negligible, which allows for recovery and reuse, not mentioning economic benefits, such as extremely low solvent loss¹⁹. At normal

process operating conditions, they do not evaporate, raising some interest in the use of ionic liquids as industrial solvents to replace volatile organic compounds (VOC) and thus eliminate a source of air pollution.^{16, 20}

A large variety of ionic liquids can be created, essentially by changing the anion, cation and/or anion substituent's (Figure 7). This ability makes possible to “tune” the ionic liquid in order to be applied as necessary, for example to separate selected alcohols from water. The types of IL's available have been extended to include new generations with more specific and targeted properties²¹.

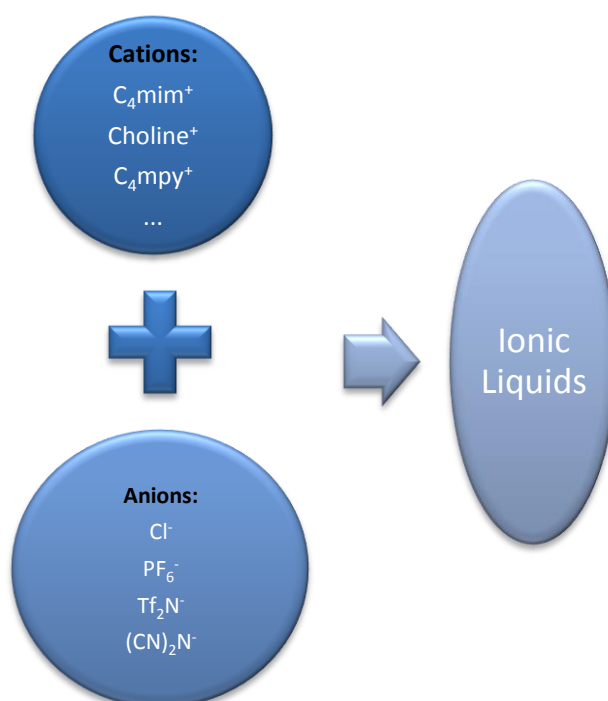


Figure 9 - Representative cations and anions of Ionic Liquids

They also are non-flammable and chemically stable. Ionic liquids can be applicable as solvents in organic synthesis, homogeneous and biphasic transfer catalysts and in electrochemistry.^{16, 20}

The presence of water in the ionic liquid phase can severely influence physical properties such as densities, viscosities and surface tensions⁹. The viscosity has strong temperature dependence allowing for fast phase separation at elevated temperatures, for example.²²

5.2 Applications

Ionic liquids can be applicable in different areas such as in Extraction, Distillation, Adsorption, Gas storage, Engineering fluids and Membrane technology²³. Energy Storage also attempts to use them to produce electrochemical double layer capacitors (ECDL), batteries, fuel cells and mobile energy.^{24 25} Surfactant technology is using IL's to produce surfactants, lubricants, antistatic, anti corrosion and dispersions.²⁵

Probably ionic liquids most important application is as solvents in organic and inorganic synthesis, homogeneous and biphasic transfer catalysis.^{24 25}

6 Modeling

The knowledge of the phase behavior of mixtures is important for different applications, especially for the simulation and optimization of separation processes, where the phase equilibrium of the system must be known. The most used thermodynamic models to describe such behavior are free energy models such as NRTL, UNIQUAC and UNIFAC. These models have the advantage of being able to describe polar, nonpolar and associative systems. However, NRTL and UNIQUAC don't have the ability to predict new systems and are restricted to low pressures.^{26 27 28} Since no UNIFAC parameters are available for ionic liquids in this work COSMO RS is used as predictive model to describe the experimental data here reported.

6.1 COSMO RS

The COSMO RS is a method proposed by Klamt and his coworkers used to predict a wide range of properties in complex liquid mixtures such as partial vapor pressures, activities, solubilities of gases, liquids and solids, partition in arbitrary phases, and phase behavior such as Vapor-Liquid Equilibrium (VLE) and Liquid-Liquid Equilibrium (LLE).²⁹

One of its most important advantages is the fact that, in the prediction of thermodynamic data, it is completely independent of any experimental data of the regarded compounds and any group interaction parameters. Unlike group contribution methods, such as UNIFAC or UNIQUAC, or other activity coefficient models, as Margules, Wilson or NRTL, COSMO RS does not consider the division of molecules into fragments losing any information about intramolecular interactions. It is based on unimolecular quantum calculations of the individual molecules and uses a very small number of adjustable parameters.^{29 30}

The calculation process of COSMO RS considers basically two major stages. The quantum chemical COSMO calculations for the molecular species involved, where the information about both solvents and solutes is extracted and COSMO RS statistical thermodynamic calculations performed in the COSMOtherm software.³¹

COSMO theory describes the interactions in a fluid as local contact interactions of molecular surfaces. In order to quantify the released energy, it analyses the values of two screening charge densities (σ and σ'), which form a molecular contact. Electrostatic misfit energy and hydrogen bonds are the most important contributions to the interaction energy, described as functions of the polarization charges of the two interacting segments, if the segments belongs to hydrogen bond donor or acceptor atom.^{29 30}

Cosmo output provides the total energy of a molecule in its conductor environment and the 3D polarization density distribution on the surface of each molecule X_i . Then this output data is converted into a distribution function, the σ -profile, $p^{X_i}(\sigma)$, which describes the polarity of each surface segment on the overall surface of the molecule and quantifies the interactions of pairwise interacting surface segments. The σ -profile of a solvent S, $p_S(\sigma)$, results of the adding the individual $p^{X_i}(\sigma)$ weighing by their mole fraction, x_i . Since it is convenient to consider a normalized ensemble and the integral of the σ -profile, $p^{X_i}(\sigma)$ is the total surface area A^{X_i} of a compound X_i , the normalized σ -profile of a solvent, $p'_S(\sigma)$, is defined in Equation 1^{30 32}:

$$p'_S(\sigma) = \frac{p_S(\sigma)}{A_S} = \frac{p_S(\sigma)}{\sum_{\epsilon S} \chi_i A^{X_i}} \quad \text{(Equation 1)}$$

The most important descriptor used in COSMO-RS is in fact σ , which would be induced on the molecular surface if the molecule would be in a virtual conductor environment. It can be calculated by quantum chemical calculations using the COSMO, and it is an extremely valuable for the local polarity of molecular surface. This descriptor is the only descriptor determining the interaction energies.³²

Cosmo RS has the potential to study ionic liquids thermodynamic behavior.

7 Motivation

This work aims to provide a comparative analysis of how the two thermodynamic models presented above can describe the phase equilibria of the binary systems: ionic liquids + ethanol.

Ethanol's purification is a very expensive process and some alternatives have been studied. Ionic liquid binary systems are an exceedingly good alternative, not because ionic liquids are environmental friendly, but because they are less costly.

In the first section, it is reported a study of two ionic liquid + ethanol systems. the experimental data is also compared with literature data from ionic liquid + water systems, so as to verify the adequacy of the experimental method adopted.

A comparison between the data obtained experimentally on the ebulliometer and the prediction of COSMO RS model is made.

In a second part several systems were studied to evaluate COSMO RS predictive ability. The importance of different cations and anions, the chain length were analyzed and the ideality deviations of ionic liquid + ethanol and ionic liquid + water were calculated. Finally, the selectivity of those systems is calculated and analyzed.

Experimental

1 Chemicals

It was used pure ethanol with 94.7 μg of water content and its molecular weight is $46.07\text{g}\cdot\text{mol}^{-1}$. The Absolute Ethanol PA was acquired at Panreac with 99.5% of purity.

The ionic liquids used are 1-butyl-3-methylimidazolium chloride and choline chloride. The choline chloride was acquired at Sigma-Aldrich with purity superior to 99%. The 1-butyl-3-methylimidazolium chloride was acquired at IoLiTec with purity superior to 98%. Their molecular weights are $174.67\text{g}\cdot\text{mol}^{-1}$ and $139.62\text{g}\cdot\text{mol}^{-1}$, respectively.

2 Equipments

2.1 Refractometer

The refractometer is an optical instrument used to measure the refractive index of a translucent substance.

The speed of light in a vacuum is always constant, but when light moves through any other medium it travels more slowly since it is constantly being absorbed and reemitted by the atoms in the material. The ratio of the speed of light in a vacuum to the speed of the light in another substance is defined as the refraction index for the substance, Equation 2.

$$\text{Refractive index } (n) = \frac{\text{Speed of light in vacuum}}{\text{Speed of light in substance}} \quad \text{(Equation 2)}$$

The correlation between light's speed in two dissimilar media, v_A and v_B , the angles of incidence (θ_A) and refraction (θ_B) and the refractive indexes of the two medium (n_A and n_B) is shown in Equation 3:

$$\frac{v_A}{v_B} = \frac{\sin \theta_A}{\sin \theta_B} = \frac{n_B}{n_A} \quad \text{(Equation 3)}$$

Thus, it is not necessary to measure the speed of light in a sample in order to determine its index of refraction. Instead, by measuring the angle of refraction, and knowing the refraction index of the layer that is in contact with the sample, it is possible to determine it accurately. Almost all refractometers utilize this principle, but may differ in their optical design.

In the Abbe refractometer the liquid sample is inserted between an illuminated prism and a refracting one. The refracting prim is made of glass with a high refractive index and the refractometer is designed to be used with samples having a refractive index smaller than that.

Since the density of a liquid usually decreases with temperature, the speed of light in a liquid will normally increase as the temperatures increases. Consequently, the refraction index will be superior as the temperature raises for a liquid. To achieve a good performance, many refractometers are equipped with a thermometer and a reservoir of circulating water to maintain a given temperature. Most of the refractive index measurements reported in the literature are determined at 20 or 25 °C.



Figure 10 - Abbe Refractometer

2.2 Ebulliometer

The ebulliometer is designed to correctly measure the boiling point of liquids by measuring the temperature of the vapor-liquid equilibrium either isobarically or isothermally.

The equipment used to execute the experimental procedure operates at constant pressure and in order to achieve a better performance was subjected to several changes and it can be seen in Figure 10.

Primarily, the ebulliometer consists in a boiling chamber, a sampling point that allowed operating in isolation, without external disturbances, and a condenser with water circulation. The system pressure was achieved using a pump connected directly to the vacuum line.

In the final version of the ebulliometer, the pressure is measured by a pressure sensor Heated Capacitance Manometer 728A Baratron MKS, placed near the sample cell, with an accuracy of 0.50%. The temperature measurement is made using a Pt100 sounder with an associated error of 0.05K, immersed directly in the sample as shown in Figure 10.



Figure 11 - Ebulliometer

3 Experimental Procedure

First of all, prepare an ethanol-ionic liquid solution richer in the most volatile component (ethanol).

Consequently, add this solution to the boiling chamber of the ebulliometer along with a magnetic stirrer.

Assemble the ebulliometer and turn on the agitation, the heating plate and the thermostatic bath. Set the pressure on the right value.

When the system is in equilibrium, the temperature does not fluctuate much with time. Remove a sample of the mixture with a syringe.

Maintaining the same sample, alter the pressure and repeat the previous step.

Repeat the last two steps of the procedure to all different pressure values.

After measuring all the data, add pure ionic liquid or a more concentrated solution in the boiling chamber so as to concentrate the solution on the ebulliometer.

Reproduce the previous steps for more concentrated solutions.

Read the refractive index of the samples in the Abbe refractometer at 30°C.

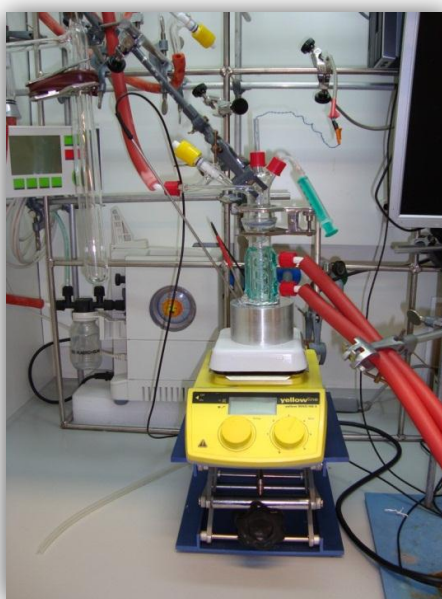


Figure 12 - Laboratory Assembly

Results and Discussion

The number of ionic liquids available commercially is today more than 1000. It is possible to synthesize more than 10^9 according to several sources. The optimization of the IL to be used for a particular purpose cannot be carried by trial and error. A predictive model such as COSMO-RS can be useful as a scanning tool to identify the best characteristics of an ionic liquid. For that purpose we started by carrying a study to evaluate the ability of COSMO-RS to predict these systems. A database was compiled from the literature and is reported in Table 3 where are presented the references of all experimental data that we were able to find in for the VLE of different ionic liquids with ethanol and their temperature and pressure ranges.

Table 3 - Database for the experimental data obtained in literature

Ionic Liquid	Pressure	T/K	Reference
[C ₄ mim][Cl]	101.3 kPa	351.44-412.6	³³
[C ₆ mim][Cl]	101.3 kPa	351.44-416.78	³⁴
[C ₄ mim][MSO ₄]	101.3 kPa	351.44-373.70	³⁵
[C ₄ mim][BF ₄]	860-7600 Pa	283.15-293.15	
[C ₄ mim][HSO ₄]	650-7870 Pa	283.15-298.15	³⁶
[C ₄ mim][Ac]	450-7870 Pa	283.15-298.16	
[C ₁ mim][DMP]	7.853-73.376 kPa	298.62-359.57	³⁷
[C ₂ mim][ESO ₄]	101.3 kPa	351.44-402.88	³⁸
[C ₂ mpy][ESO ₄]	101.3 kPa	351.44-385.52	³⁹

Based on this information, we decided to study the influence of several important factors such as the temperature, the anion and the cation of the ionic liquids using COSMO RS as a predictive model.

1 The COSMO RS prediction model for ionic liquid systems

1.1 Temperature influence

The COSMO RS has shown to be an effective method to predict the VLE of the systems measured in this work. To evaluate its ability to describe other similar system it was made a comparison between the COSMO RS predictions and published data in the literature. The results are shown in Figure 13.

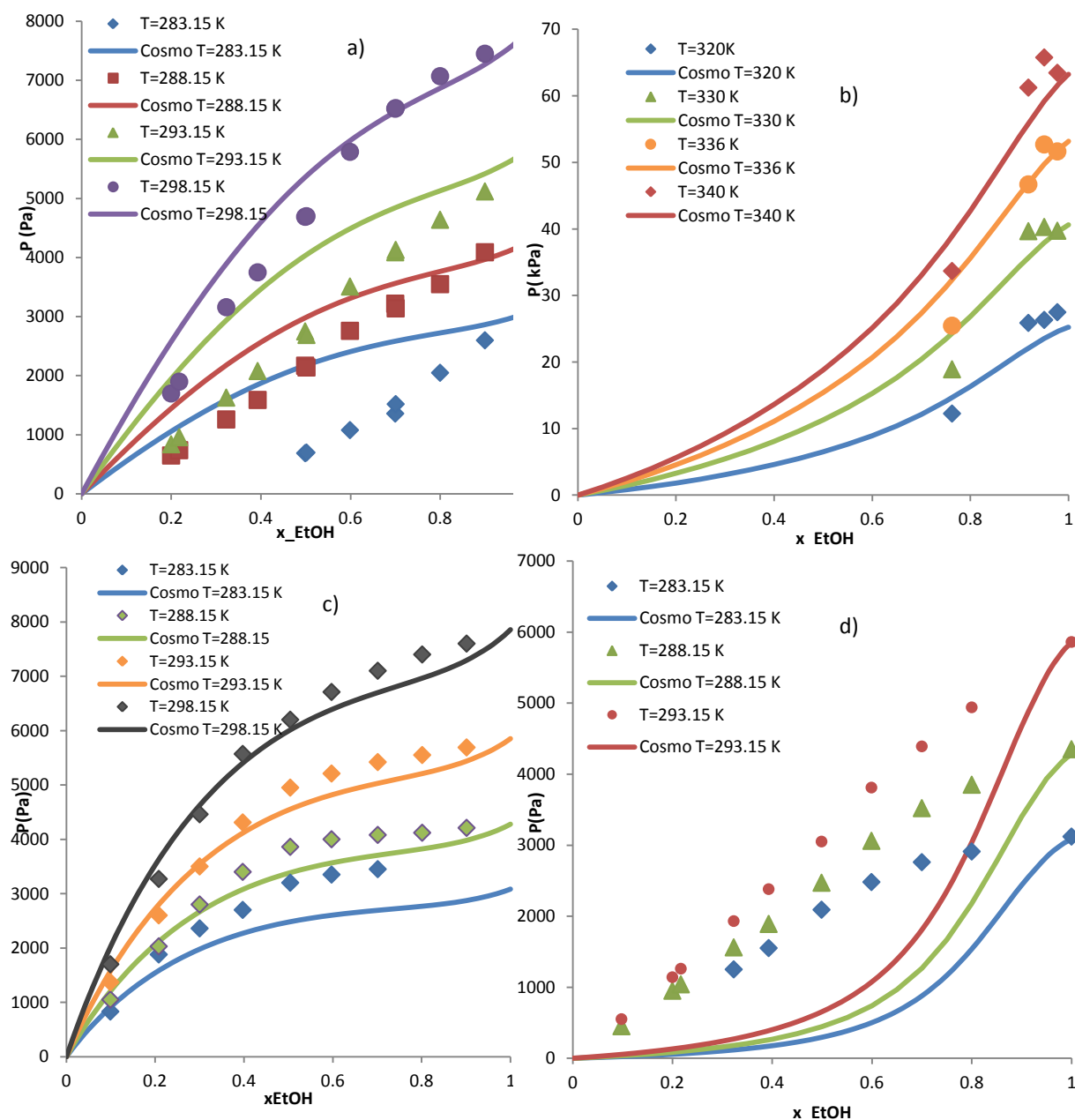


Figure 13 -Representation PTx of ionic liquid systems: a) [C4mim][HSO4]+ EtOH; b) [C1mim][DMP]+EtOH; c) [C4mim][BF4]+EtOH; d) [C4mim][Ac]+EtOH

As result of the analysis of Figure 13, it appears that COSMO RS is a good model to predict the experimental VLE data. It is also notable that the COSMO RS is especially sensitive both to changes in the ionic liquid family as the variation of the substituent group.

Another important fact that can be observed in Figure 13: a) and c) is that as the temperature increases the prediction made by COSMO RS are in better agreement with the experimental data.

1.2 Anion and Cation influence

So as to explore COSMO RS predictive properties, it was made a study to evaluate the influence of both cation and anion in the ionic liquids behavior. Primarily, it was studied the influence of the cation chain length and then the capacity to effect VLE behavior by different anions in the ionic liquid.

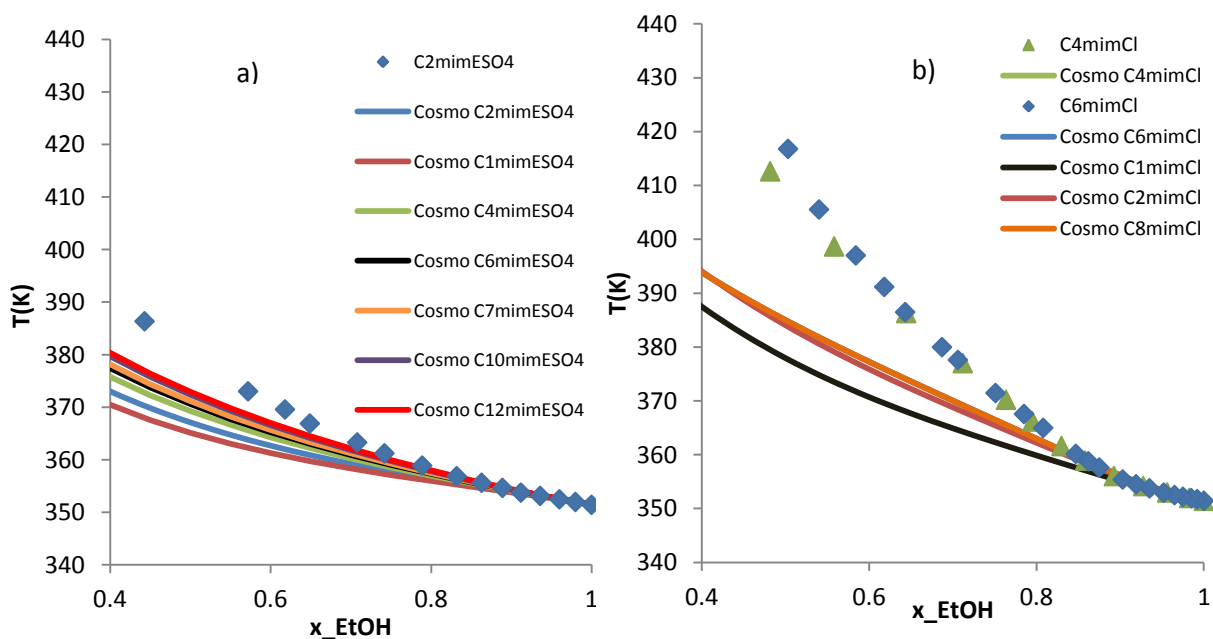


Figure 14-Representation of PTx systems of ionic liquids: a) $[Cnmim][ESO4]+EtOH$; b) $[Cnmim][Cl]+EtOH$

As represented in Figure 14, the chain length of the ionic liquid anion does not influence significantly the results obtained by COSMO RS. In the first case, the variation of the parameter n in $[C_n\text{mim}][\text{ESO}_4]$ does not change the VLE behavior of the ionic liquid. For the $[C_n\text{mim}][\text{Cl}]+\text{EtOH}$ system, the COSMO RS only describes the experimental data correctly at high ethanol concentrations. Some other cases that were studied are presented on Appendix B.

The influence of the cation adds great changes to the systems thermodynamic behavior. So as to understand which cations are good choices as entrainers in ethanol's separation, we chose 1-butyl-3-methylimidazolium cation to study the effect of several anions.

Figure 15 shows the predictions of COSMO RS for a wide range of anions at constant pressure of 0.1 MPa.

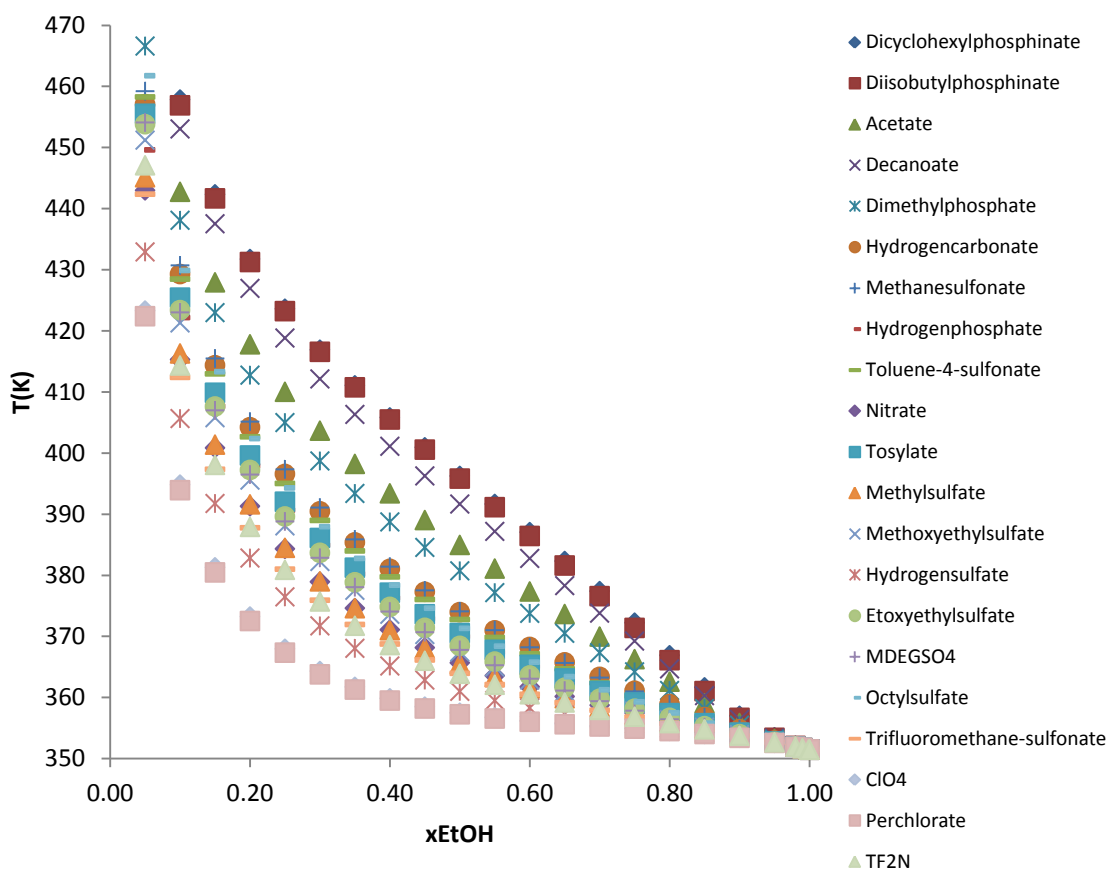


Figure 15 - Representation of PTx diagram for $[C_2\text{mim}][\text{anion}]+\text{EtOH}$ system at 1 atm.

Although ionic liquids with anions such as dicyclohexylphosphinate and diisobutylphosphinate present the best results, they are not easily available as acetate, chloride, tetrafluoroborate among others.

1.3 Activity Coefficients at Infinite Dilution

The ethanol/ionic liquid relative volatility is defined as the ratio of the distribution coefficients of ethanol and the ionic liquid (Equation 4).

$$\alpha_{AB} = \frac{\gamma^{\infty,ethanol}}{\gamma^{\infty,water}} \quad \text{(Equation 4)}$$

The entrainer must be selected according to its volatility, selectivity, ease of separation from the bottom and top products and cost. The most easily assessed is selectivity by determining the effect on the relative volatility of the two key components adding a solvent.

So as to study more correctly the influence of those the structure of the ionic liquid on the activity coefficient at infinite dilution several systems were evaluated by COSMO RS. Two major groups of systems studied were divided accordingly to Table 4.

Table 4 - Representation of the different study cases evaluated on COSMO RS

Anion	Cation
1st Case	
Different anions	[C ₂ mim] ⁺
2nd Case	
[Cl] ⁻	Oxygenated cations

Table 5 shows the anions and the cations accordingly with the numeration used in Figures 16 to 22.

Table 5 - Anions and Cations

Number	Anion
1	Dicyclohexylphosphinate
2	Diisobutylphosphinate
3	Acetate
4	Decanoate
5	Hydrogencarbonate
6	Methanesulfonate
7	Hydrogenphosphate
8	Toluene-4-Sulfate
9	Nitrate
10	Tosylate
11	Methylsulfate
12	Methoxyethylsulfate
13	Hydrogensulfate
14	Etoxyethylsulfate
15	MDEGSO ₄
16	Octylsulfate
17	Trifluoromethane-sulfonate
18	ClO ₄
19	Perchlorate
20	TF ₂ N
21	Chloride
Number	Cation
22	Choline
23	Ethyl-2-hydroxyethyltrimethylammonium
24	Hexyl-3-hydroxyethyltrimethylammonium
25	O-ethyl-N,N,N,N-tetramethylisouronium
26	O-methyl-N,N,N,N-tetramethylisouronium
27	Bis-1-hexyl-oxymethyl-3-methyl-imidazolium Cl
28	1-hexyl-oxymethyl-3-methyl-imidazolium Cl

1.3.1 1st Case: Effect of the anion

It has been shown that the anion influences the VLE behavior of ionic liquid+ ethanol systems. To evaluate this effect an analysis was made to study different anions on ionic liquid+ ethanol and ionic liquid + water systems. The activity coefficients were calculated by COSMO RS and the results are shown in Figure 16.

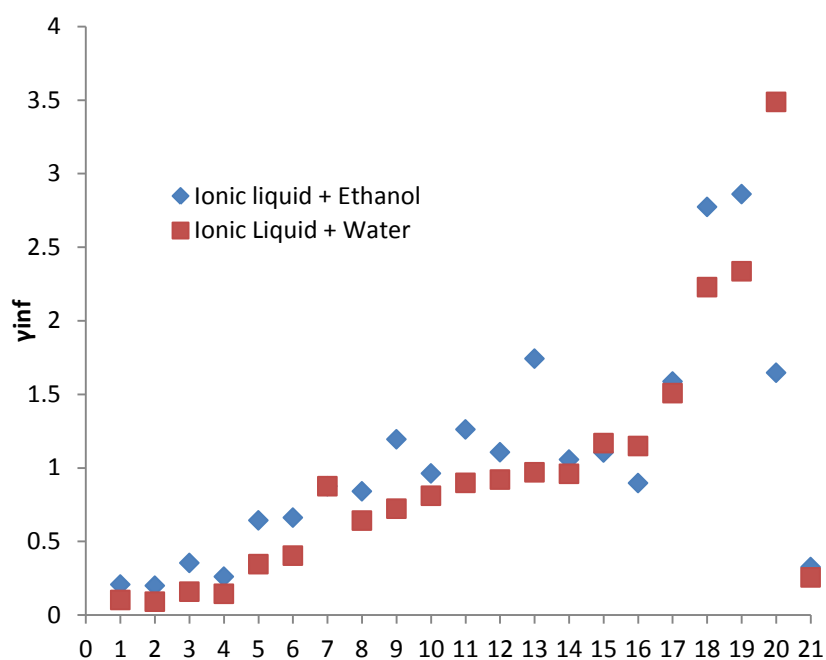


Figure 16-Representation of the activity coefficients at infinite dilution for several anions (The list of the anions is presented in Appendix C).

This coefficient represents the maximum of nonideality that a mixture can have. Figure 16 shows that there are several anions with activity coefficient at infinite dilution inferior to one and others that are superior to one.

Figure 17 exhibits the selectivity for the studied anions. According to the results, the acetate (3) anion has the most significant ability in enhancing the relative volatility. Dicyclohexylphosphinate (1), diisobutylphosphinate (2) have the ability to enhance the relative volatility also, followed by decanoate (4), hydrogencarbonate (5) and hydrogensulfate (13).

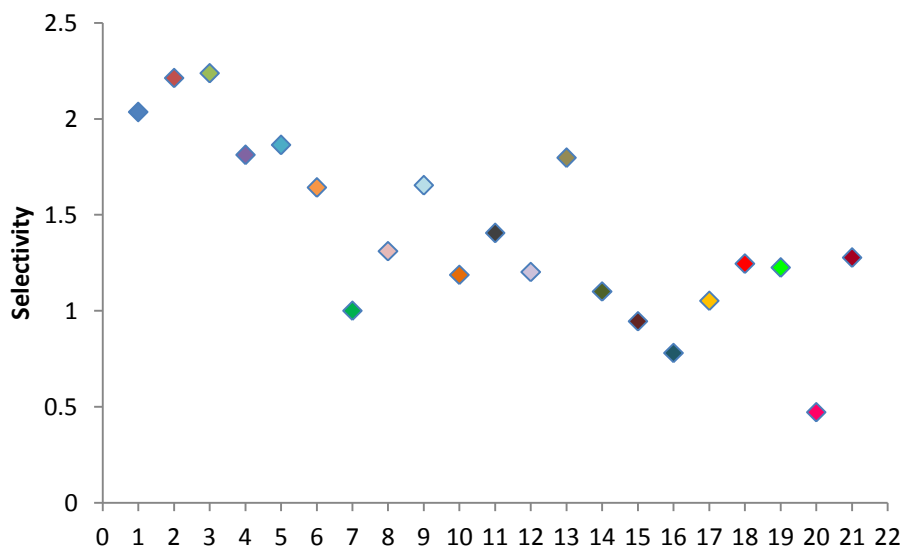


Figure 17-Selectivity for several anions (The list of the anions is presented in Table 6).

2.3.2 2nd Case: Effect of the cation

Choosing chloride as the anion, it was tested in COSMO RS, two oxygenated Imidazolium cations, bis-1-hexyl-oxymethyl-3-methyl-imidazolium and 1-hexyl-oxymethyl-3-methyl-imidazolium and several oxygenated cations as choline chloride, ethyl-2-hydroxyethyl-dimethylammonium chloride, hexyl-2-hydroxyethyl-dimethylammonium chloride, O-ethyl-N,N,N,N-tetramethylisouronium chloride and O-methyl-N,N,N,N-tetramethylisouronium chloride. The infinite dilution activity coefficients are presented in Figure 18.

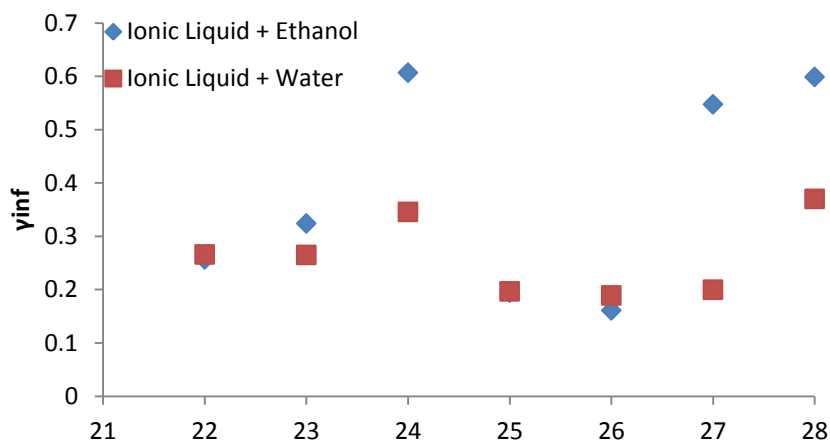


Figure 18- Representation of the activity coefficients at infinite dilution for several anions (The list of the cations is presented in Appendix C).

All values of γ^{∞} are inferior to one, which means that their interactions with ethanol and water are favourable.

Using oxygenated cations and chloride as the anion, the selectivity for both systems is presented in Figure 19.

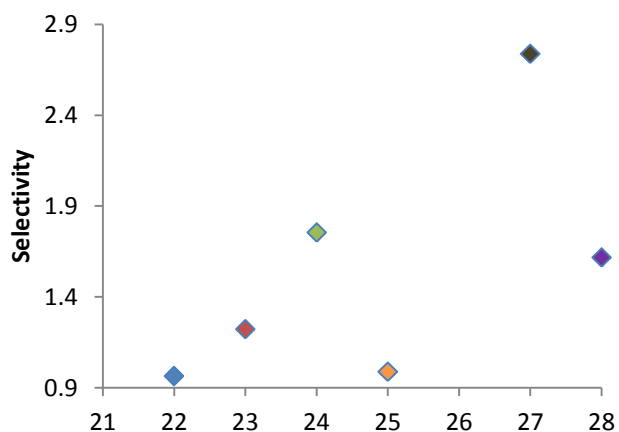


Figure 19- Selectivity for several cations (The list of the cations is presented in Table 5).

As already discussed, ionic liquid systems that have a high selectivity are the best option to the extractive distillation of ethanol. As the results show, bis-1-hexyl-oxymethyl-3-methyl-imidazolium (27) is a better option as an entrainer, because it has the higher selectivity value followed by Hexyl-3-hydroxyethyl-dimethylammonium (24).

2 Experimental Results for [C₄mim][Cl]+EtOH and [Choline][Cl]+EtOH Systems

Accordingly with the results obtained in the previous section, we decided to study the [C₄mim][Cl]+EtOH system to validate the ebulliometer and the [Choline][Cl]+EtOH as a new system. The structure of the ionic liquids studied is presented in Figure 20 below.



Figure 20 - Ionic Liquids structural formula: a) 1-Butyl-3-Methylimidazolium Chloride; b) Choline Chloride

These systems were chosen because both have a chloride anion, the [C₄mim][Cl] has a short alkyl chain as cation, and the choline chloride a small oxygenated cation.

The experimental data was obtained at three different pressure values (1000 mbar, 700 mbar and 500 mbar) to study the influence of this parameter on the boiling temperature of ionic liquid mixtures.

From Equation 5 it is possible to calculate the activity coefficient of ethanol in mixtures of ionic liquids + ethanol to study the interactions between both species and compare it with results of COSMO model.

$$y_i P = x_i \gamma_i P_i^\sigma \quad (\text{Equation 5})$$

Figure 21 shows the prediction made by COSMO for the system $[C_4mim][Cl]+EtOH$ and the experimental data obtained from the ebulliometer.

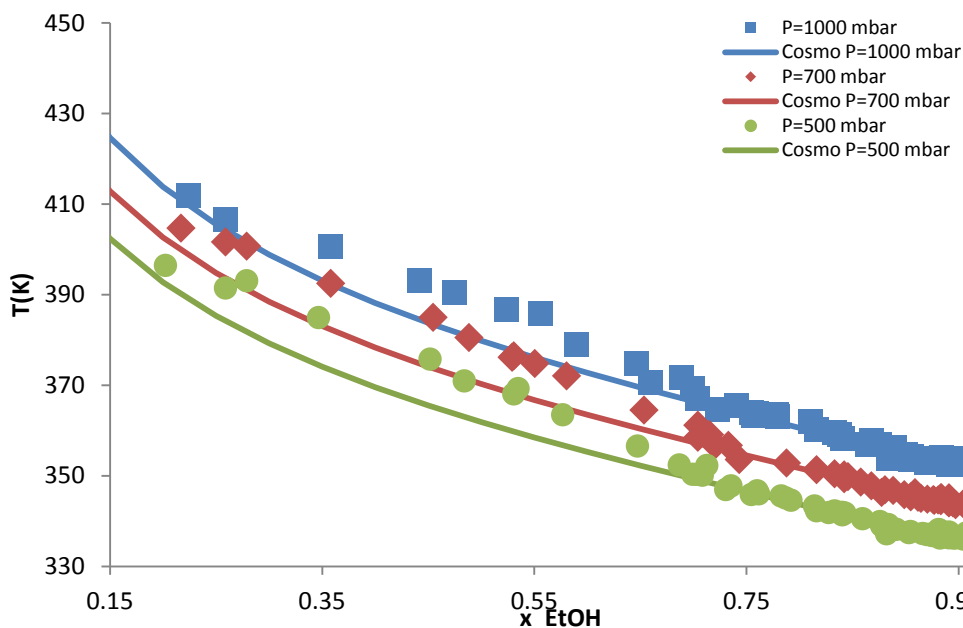


Figure 21 - PTx diagram for the system $[C_4mim][Cl]+EtOH$ (Experimental data Vs Cosmo Rs prediction)

As the alcohol percentage increases the less concentrated in ionic liquid is the mixture on the ebulliometer and a lower temperature value is needed to establish the vapour-liquid equilibrium.

For $[Choline][Cl]+EtOH$ it was also possible to obtain a good prediction of the system behavior by COSMO RS (Figure 22).

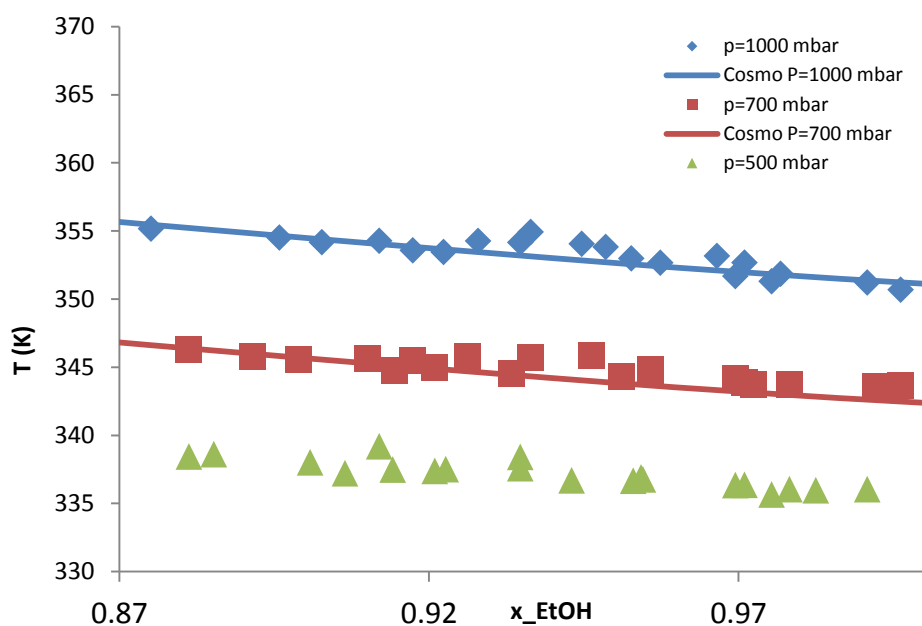


Figure 22 - PTx diagram for the system [Choline][Cl]+EtOH (Experimental data Vs Cosmo Rs prediction)

It was not possible to obtain from the COSMO RS, the data for P= 500 mbar due to an unrecognized error. Once more, as the content of alcohol increases, the more diluted the mixture is in ionic liquid and the lower the temperature value is needed to establish the vapour-liquid equilibrium.

In comparison between the two different systems, choline chloride is less soluble in ethanol than 1-butyl-3-methylimidazolium chloride and the boiling temperatures are higher on [C₄mim][Cl]+ EtOH system.

It can be explained by the structural formula of the ionic liquids (Figure 20). The 1-butyl-3-methylimidazolium cation consists of a five numbered ring with two nitrogen and three carbon atoms, with ethyl and methyl groups substituted at the two nitrogen atoms. On the other side, choline chloride is a quaternary ammonium salt with a N,N,N-trimethylethanolammonium cation with a linear structure.

Conclusions

The main objective of this thesis is to evaluate ionic liquids as potential solvents for the extractive distillation of ethanol.

Two ionic liquid + ethanol systems were studied: 1-butyl-3-methylimidazolium chloride and choline chloride. Their VLE was measured in an ebulliometer and this data, along with data from the literature was used to evaluate the predictive ability of the COSMO RS model. COSMO RS describe adequately the experimental data.

By applying the COSMO-RS model to other literature data it was found that it is a good predictive model capable of describing the VLE data available in the literature and thus to be used as a tool in the selection of ionic liquids as entrainers for extractive distillation.

Due to the very large number of potential ionic liquids their experimental selection is difficult and time consuming. For investigating the influence of ionic liquids on the separation of ethanol-water, the selectivities based on the infinite dilution activity coefficients were estimated.

It was found that ionic liquids with cations with shorter alkyl chains have a higher affinity for ethanol than cations with longer alkyl chain. The presence of oxygen in cations, especially in small cations, contributes to increase the affinity between ethanol and the IL. Regarding the anions, oxygen anions such as the acetate have better affinity with the ethanol.

Concerning the selectivity, anions such as dicyclohexylphosphinate (1), diisobutylphosphinate (2), acetate (3), decanoate (4), etoxyethylsulfate (14) and chloride (21) are good choices for the extractive distillation with ionic liquids. However, the acetate (3) anion has the most significant ability in enhancing the relative volatility. Dicyclohexylphosphinate (1), diisobutylphosphinate (2) have the ability to enhance the relative volatility either, followed by decanoate (4), hydrogencarbonate (5) and hydrogensulfate (13). Bis-1-hexyl-oxymethyl-3-methyl-imidazolium cation (27) is a better option as an entrainer, because it has the higher selectivity value followed by Hexyl-3-hydroxyethyldimethylammonium (24).

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Appendix A

Calibration curves

1 [C₄mim][Cl] + EtOH system

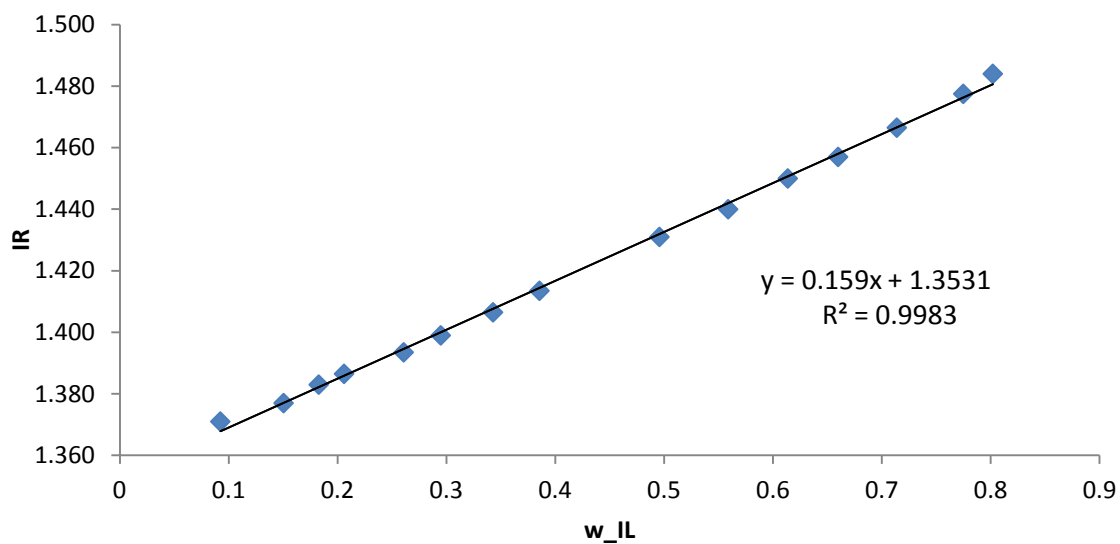


Figure 1 - Calibration curve for the system [C₄mim][Cl]+EtOH

2 [Choline][Cl] + EtOH system

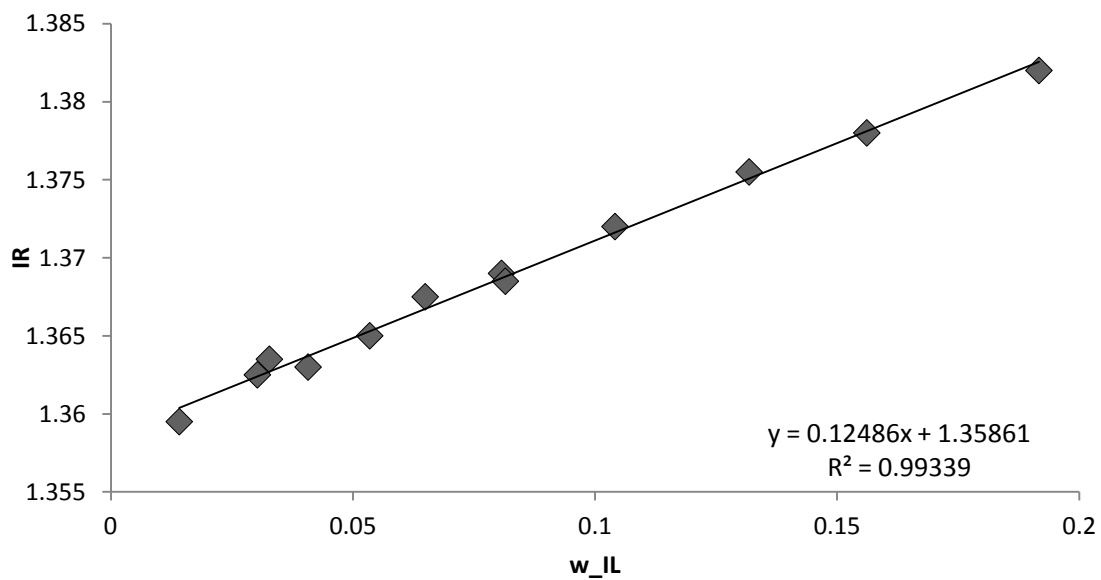


Figure 2 - Calibration curve for the system [Choline][Cl]+EtOH

Appendix B

The COSMO RS prediction model for ionic liquid systems

1 [C_nmim][MSO₄] + EtOH system

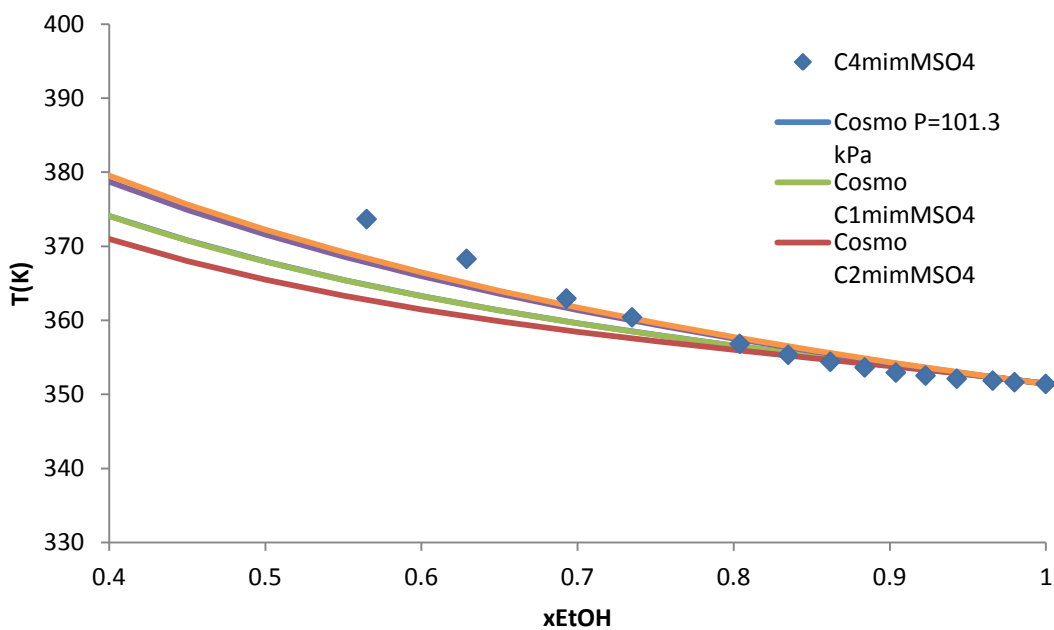


Figure 3 - Representation of PTx diagram for [C_nmim][MSO₄]+ EtOH system

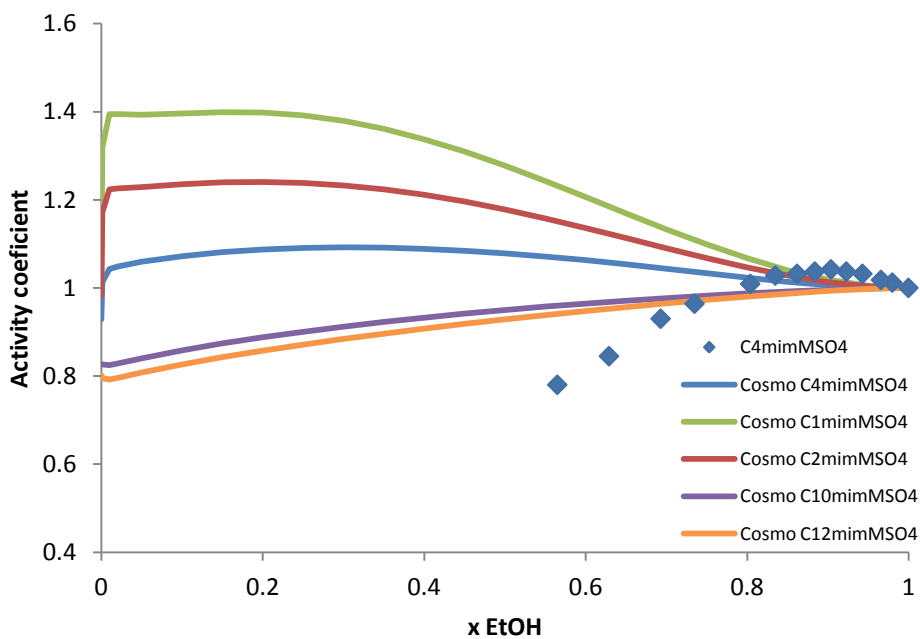


Figure 4- Representation of γ_x diagrams for [C_nmim][MSO₄]+ EtOH system

2 [C₂mpy][ESO₄] + EtOH system

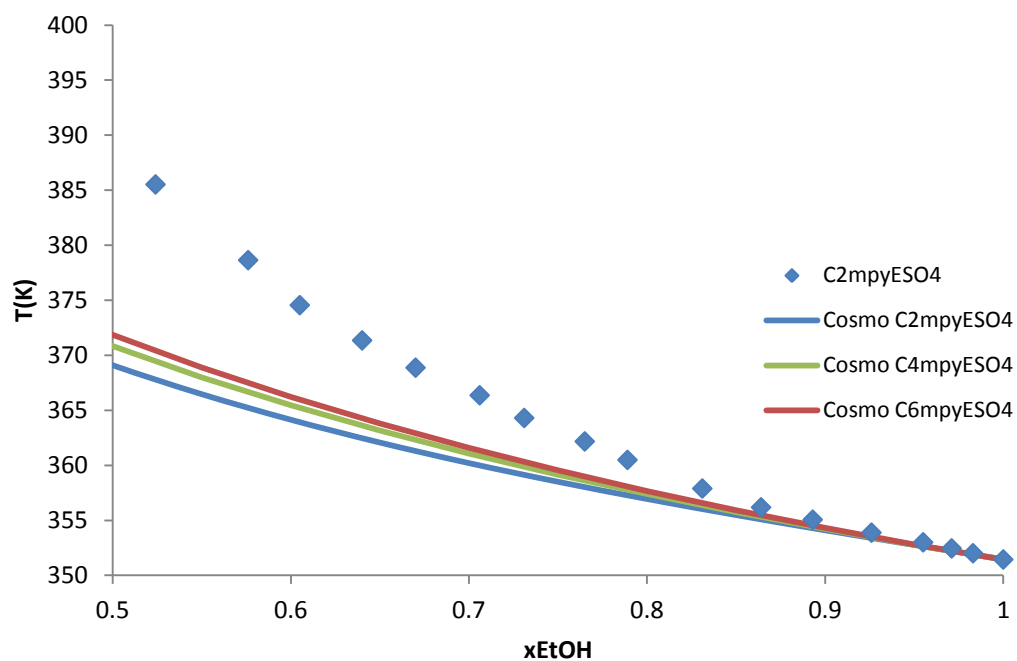


Figure 5- Representation of PTx diagram for [C_nmpy][ESO₄]+ EtOH system

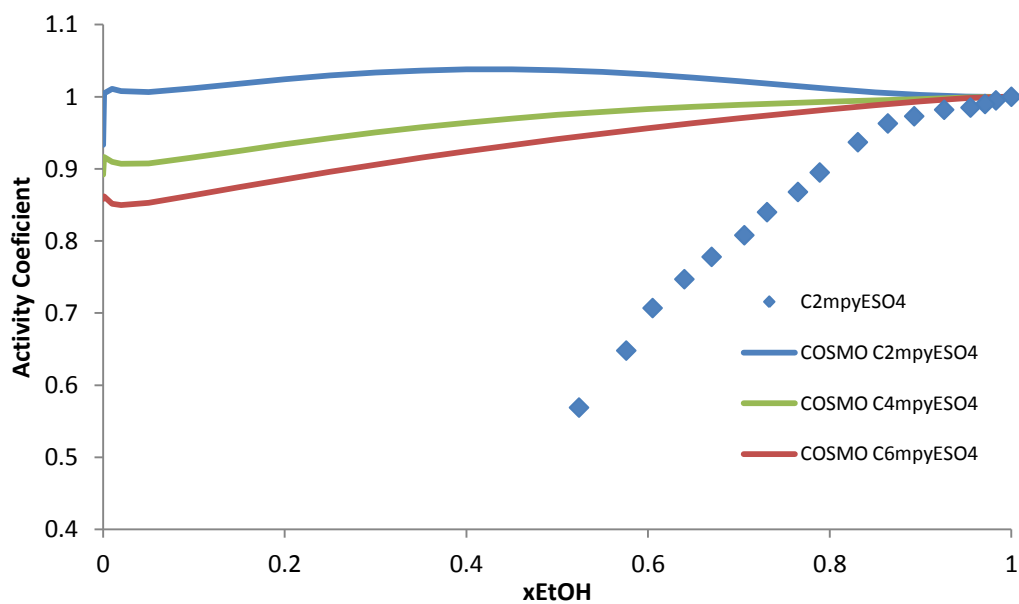


Figure 6 - Representation of γ_x diagrams for [C_nmpy][ESO₄]+ EtOH system

2 [C₂mim][anion] + EtOH system

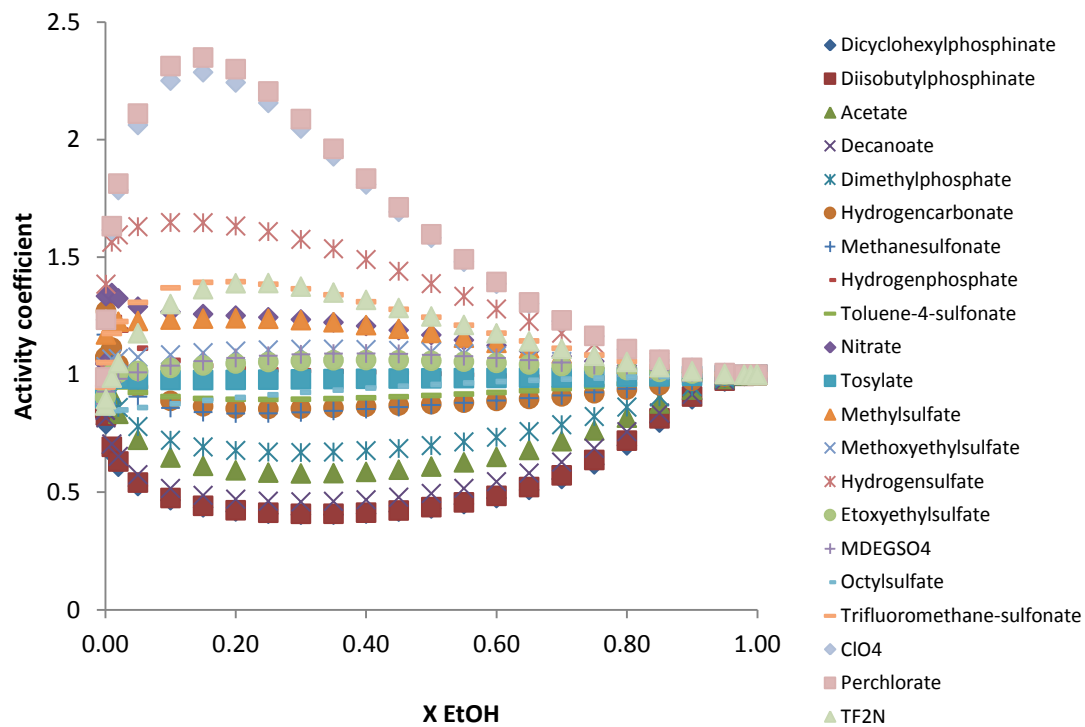


Figure 7- Representation of γ_x diagrams for [C₂mim][anion]+ EtOH system

3 [Cation][Cl] + EtOH system

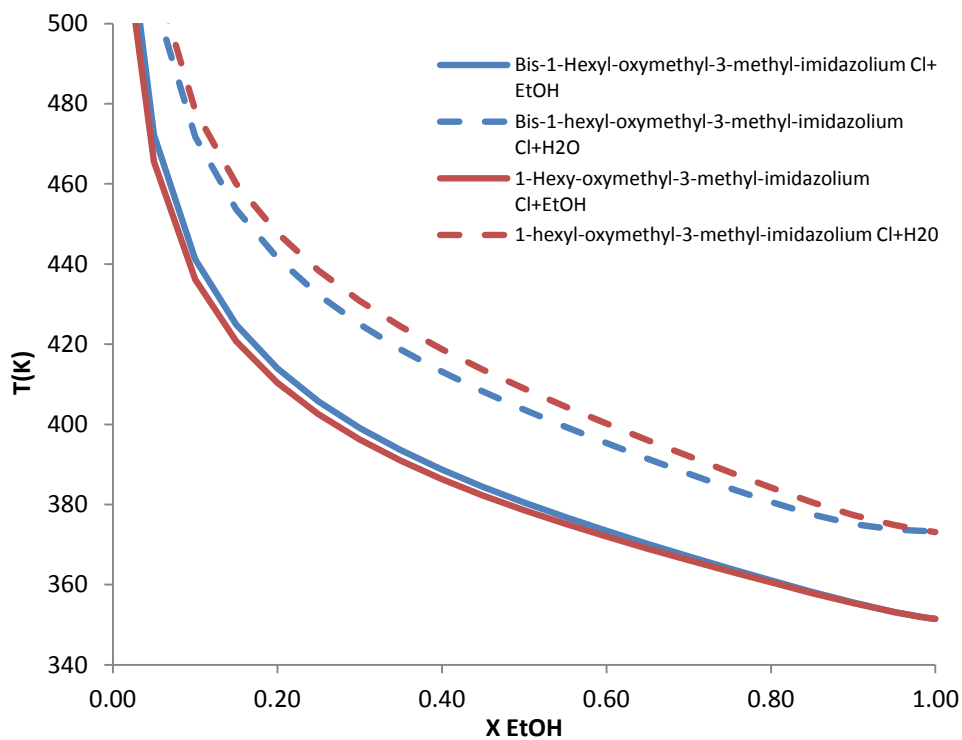


Figure 8 - Representation of PTx diagram for [Cation][Cl]+ EtOH system

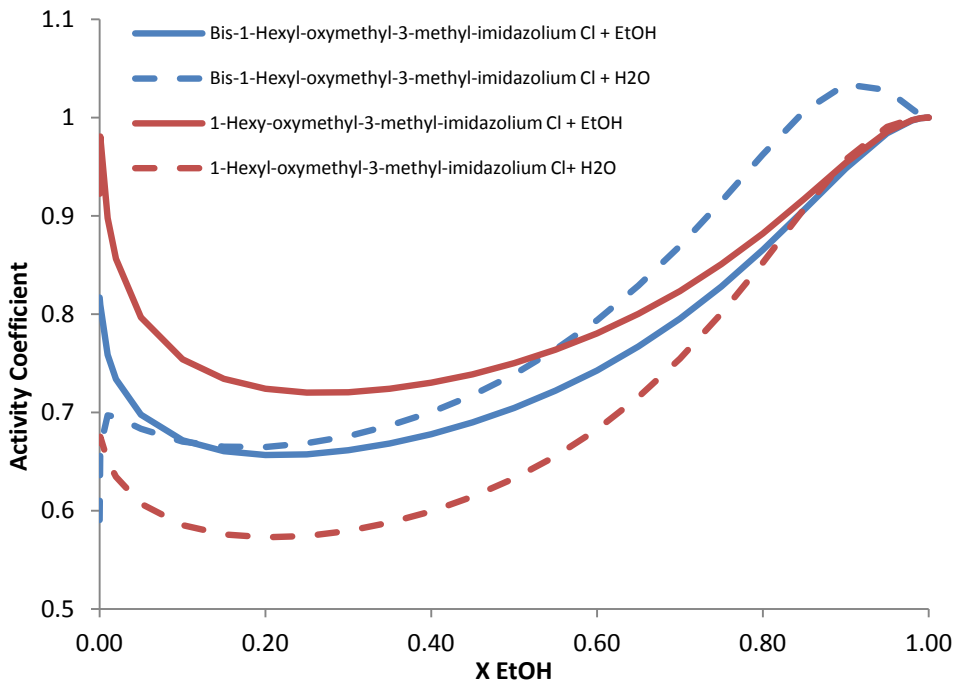
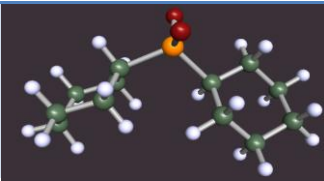
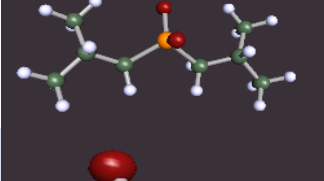
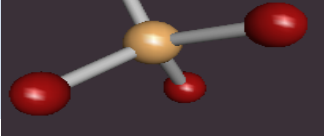
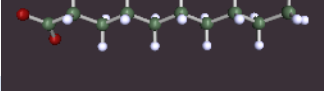
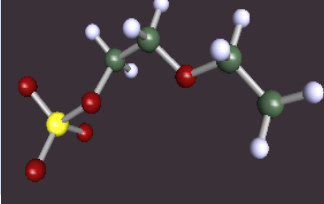
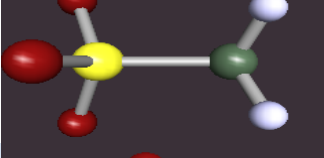
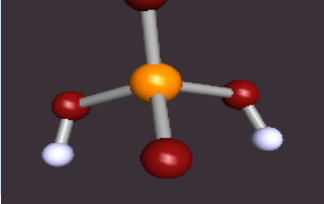
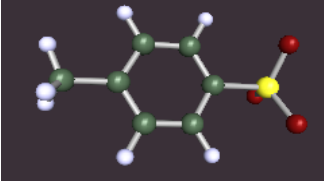
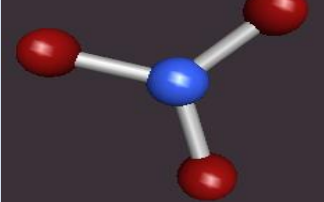


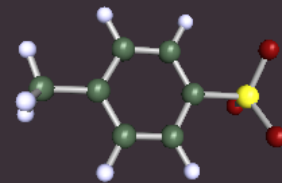
Figure 9 - Representation of yx diagrams for [Cation][Cl]+ EtOH system

Appendix C

Table 1 - Anions and Cations and COSMO geometry ¹

Number	Anion	
1	Dicyclohexylphosphinate	
2	Diisobutylphosphinate	
3	Acetate	
4	Decanoate	
5	Hydrogencarbonate	
6	Methanesulfonate	
7	Hydrogenphosphate	
8	Toluene-4-Sulfate	
9	Nitrate	

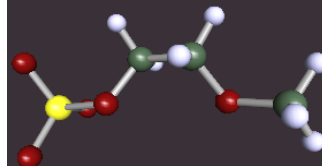
10 Tosylate



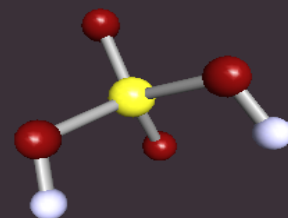
11 Methylsulfate



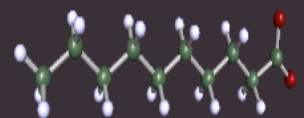
12 Methoxyethylsulfate



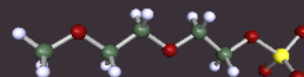
13 Hydrogensulfate



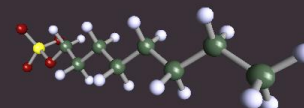
14 Etoxyethylsulfate



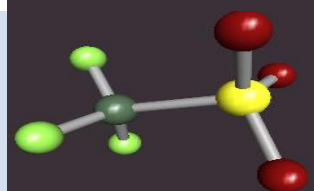
15 MDEGSO₄



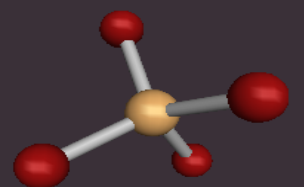
16 Octylsulfate



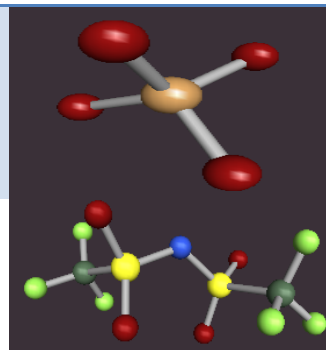
17 Trifluoromethane-sulfonate



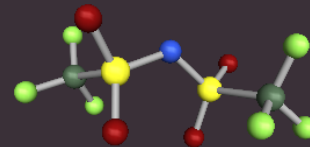
18 ClO₄



19 Perchlorate



20 TF_2N

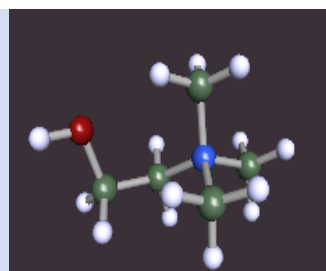


21 Chloride

Cl^-

Cation

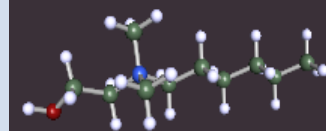
22 Choline



23 Ethyl-2-hydroxyethyltrimethylammonium



24 Hexyl-3-hydroxyethyltrimethylammonium



25 O-ethyl-N,N,N,N-tetramethylisouronium



26 O-methyl-N,N,N,N-tetramethylisouronium



