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Batista**

**Desenvolvimento de uma Escala de Parâmetros de
Solubilidade para Líquidos Iónicos**

**Development of a Solubility Parameters Scale for
Ionic Liquids**



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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 Araújo Pereira Coutinho, Professor Associado com Agregação do Departamento de Química da Universidade de Aveiro

Dedico este trabalho aos meus pais, aos meus irmãos e ao meu avô.

o júri

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palavras-chave

Líquidos Iónicos, Parâmetros de Solubilidade, Parâmetro de Solubilidade de Hildebrand, Teoria das Soluções Regulares, Coeficientes de Actividade a Diluição Infinita, Viscosidade.

resumo

Os biocombustíveis, como bioetanol e butanol, têm se tornado numa área de grande relevância e objecto de investigação, dadas as suas propriedades que possibilitam a substituição dos combustíveis fósseis mais comuns. No entanto, a sua produção tem um problema associado que é a formação de azeotropos sempre que o álcool se encontra na presença de água. Este problema é usualmente ultrapassado pela utilização de Distilação Extractiva, onde os Líquidos Iónicos (ILs) são usados como agentes de separação, com o intuito de quebrarem o azeotropo.

Na última década, os líquidos iónicos, dadas as suas propriedades únicas, têm sido alvo de muita investigação. Entre as mais diversas características, a possibilidade de refinar as suas propriedades para uma tarefa específica, permitiu identificar a necessidade de estudar e perceber qual a relação estrutura-propriedade dos líquidos iónicos, o que levou ao recurso de modelos predictivos. Neste trabalho, o parâmetro de solubilidade de Hildebrand baseado na Teoria das Soluções Regulares, foi utilizado para estimar o parâmetro de solubilidade usando dados experimentais disponíveis para coeficientes de actividade a diluição infinita e também para viscosidade, com o objectivo de obter de uma escala de parâmetros de solubilidade para líquidos iónicos.

Dos resultados obtidos, para os coeficientes de actividade a diluição infinita, foi possível observar que os líquidos iónicos possuem um carácter anfifílico (efeito camaleónico), e utilizando a viscosidade na estimação dos parâmetros de solubilidade verificou-se que, no entanto, os líquidos iónicos comportam-se predominantemente como moléculas polares.

Neste trabalho, também foram medidas solubilidades para o líquido iónico hexafluorofosfato de 1-butil-3-metil-imidazólio em misturas de água e 1-propanol e ainda 1-propanol e tolueno. Este procedimento permitiu a confirmação do comportamento (efeito camaleónico) descrito anteriormente pela utilização de coeficientes de actividade a diluição infinita.

Na estimação dos parâmetros de solubilidade, algumas não conformidades foram observadas. A sua causa poderá estar no facto de que o parâmetro de solubilidade de Hildebrand não detalha a polaridade da molécula ou interações específicas que, os líquidos iónicos sendo moléculas complexas, poderá ser insuficiente para descrever o seu comportamento. Desta forma, extensões ao parâmetro de solubilidade de Hildebrand são sugeridas neste trabalho.

keywords

Ionic Liquids, Solubility Parameters, Hildebrand Solubility Parameters, Regular Solution Theory, Activity Coefficients at Infinite Dilution, Viscosity.

abstract

Bioethanol and biobutanol are biofuels that nowadays are gaining significance due to their physical and chemical properties that enables the replacement of fossil fuels. Nevertheless, their production brings an inherent problem which is the formation of an azeotrope when the alcohol is in the presence of water. Extractive distillation is the process most widely used, where Ionic liquids may act as separation agent, in order to break or shift the azeotrope.

For the past decade, ionic liquids, due to their unique properties, have received an increasing attention by the academic community and industry. Within their characteristics, the possibility of tune their properties allowed identifying the need to understand the relation structure-property which led to the use of predictive models. In this work, Hildebrand solubility parameter based on Regular Solution Theory, was used to estimate solubility parameters using experimental data available for activity coefficients at infinite dilution and viscosity, aiming the establishment of a solubility parameters scale for ionic liquids.

The use of activity coefficients at infinite dilution allowed observing that ionic liquids have amphiphilic (chameleonic) behaviour, and with viscosity it was observed that they act predominantly as polar molecules.

In this work, it was also measured solubilities for 1-butyl-3-methylimidazolium hexafluorophosphate in mixtures of water and 1-propanol and in mixture of 1-propanol and toluene. This procedure allowed to confirm the behaviour (chameleonic effect) described by solubility parameters estimated by activity coefficients at infinite dilution.

In the estimation of solubility parameters, some non-conformities were observed and which can be explained by the fact that the Hildebrand solubility parameter does not detail molecule polarity or specific interactions, and the structure of ionic liquids is clearly more complex than it is taken account. In this matter, other extensions for Hildebrand solubility parameter are suggested.

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NOMENCLATURE

LIST OF SYMBOLS

y	Vapor molar fraction
x	Liquid molar fraction
S	Selectivity
U	Molar cohesive energy
V	Molar volume
G	Gibbs free energy
H	Enthalpy
S	Entropy
T	Temperature
a	Interaction energy
R	Gas ideal constant
f	Volume fraction
z	Compressibility factor
C	Salt category specific Constant
K	Constant or proportionality constant
H	Henry's law constant
b	Constant in equation 23
d	Constant in equation 23
z	Charges of the cation/anion
r	Ionic radius
N, N_A	Avogadro's number
W	Work of cohesion
h	Planck's constant
E	Energy of vaporization

GREEK LETTERS

γ	Activity coefficient
δ	Hildebrand solubility parameter
ρ	Density
Φ	Volume fraction
σ	Surface tension
μ	Viscosity

SUPERSCRIPTS

E	Excess property for a mixture
id	Ideal
∞	Infinite dilution
vap	Vaporization

SUBSCRIPTS

<i>t</i>	Total
<i>d</i>	Dispersion
<i>p</i>	Polar
<i>h</i>	Hydrogen bonding
<i>M</i>	Melt, fusion
<i>c</i>	Cation or cohesion
<i>a</i>	anion
<i>NP</i>	Non-polar
<i>P</i>	polar

ABBREVIATIONS

ED	Extractive distillation
VLE	Vapor-liquid Equilibrium
ILs	Ionic liquids
VOCs	Volatile organic compounds
O.F	Objective function

INTRODUCTION

Fossil fuels in all their forms, such as crude oil, natural gas and coal are and will continue to be the most important source of energy in the foreseeable future.^[1] However, their use implies depletion of scarce non-renewable resources and it is associated to environmental hazardous gases like carbon dioxide, SO_x and NO_x emissions. These emissions are not only responsible for the greenhouse effect and climatic changes, but have also a direct effect upon human health. Furthermore, the continuous increase on their prices and the necessity to reduce our dependence on fossil fuels are bringing into focus to alternative energy sources. The replacement of liquid transport fuels such diesel and gasoline by biofuels, produced from renewable resources such as bioethanol or biobutanol, is now gaining a special interest and demand.^[2-3]

Bioethanol and biobutanol are produced in aqueous medium by the fermentation of sugars such as sucrose and from starch or wood components such as celluloses.^[1, 3] Besides their use as biofuels these alcohols may have many other applications, like solvents in the pharmaceutical, paint and cosmetic industries, they can be used as extraction solvents for natural products and as chemical intermediate, in the manufacture of others high added value chemicals.^[4]

Bioethanol is used mixed with gasoline improving the engine combustion and allowing reduction of hydrocarbon, carbon monoxide and particulate emissions due to their higher oxygen content.^[2-3] It is use in blends where it helps reducing disadvantages like low energy density, significant miscibility with water and toxicity to ecosystems. Alternatively, can be used as a stand alone fuel source with high success in countries like Brazil.^[3]

Biobutanol stands as a better alternative than ethanol as biofuel due to its more favourable chemical and physical properties. Biobutanol has a lower vapour pressure (butanol 5.6 hPa, ethanol 58.5 hPa), a higher flash point (butanol 35°C, ethanol 13°C), lower miscibility with water and it is less corrosive. Owing to these characteristics, biobutanol can replace fossil fuels up to 100% without modifying the engine as well as be blended with gasoline. As disadvantages, biobutanol has a lower octane number, higher viscosity and higher toxicity.^[1]

The production of biofuels by fermentation processes requires a process for the recovery of alcohol (bioethanol or biobutanol) from the aqueous medium. Normally, the distillation process is chosen for that purpose. The distillation is a well known technology that scales

up well and it allows simulation in software programs which enable an easy evaluation of the process.^[5]

The production of bioethanol and biobutanol has, unfortunately, a problem associated. The downstream from the fermentor, is usually a diluted aqueous solution that contains some fraction of alcohol.^[2] The presence of water will form an azeotrope with the alcohol limiting its purification by ordinary distillation.^[2, 5]

The mixture ethanol-water form an azeotrope at 95.6 wt% of ethanol (**Figure 1, A**), which makes ordinary distillation effective only when the mixture has concentrations ranging 5 to 85 wt%, above it, the separation becomes extremely difficult and requires great effort from the process (high flux ratios, additional equipment) and which implies further costs. For the mixture of butanol-water, the azeotrope is located at 55.5 wt% of butanol (**Figure 1, B**). Unlike ethanol, butanol exhibits two liquid phases at the azeotrope point, not only because it is soluble in water up to 7.7 wt% but also because the azeotrope is located above this solubility limit. One of the phases has almost 80 wt% of butanol and the other has 7.7 wt%.^[2, 5]

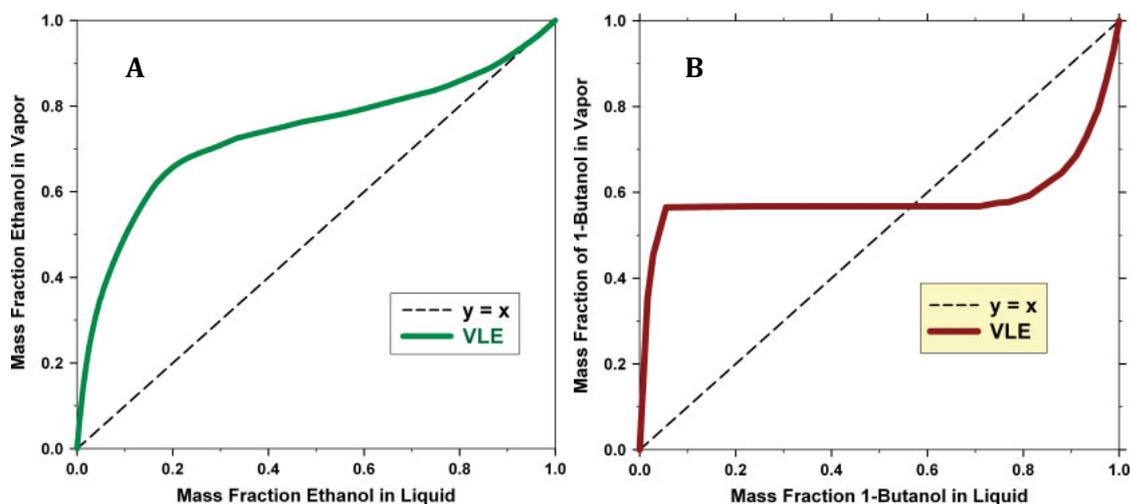


Figure 1- A. VLE of ethanol/water. B. VLE of butanol/water.

To overcome the limitations of ordinary distillation, other processes have been used to break or shift the azeotrope formed. Azeotropic distillation, liquid-liquid extraction, membrane separation (pervaporation), adsorption and gas and steam stripping are some of the techniques that may be used. Nonetheless, these techniques require the use of large amounts of energy, volatile compounds or high pressures. Within the alternatives there is still extractive distillation (ED) which is the process most used to separate the components in an azeotropic system.^[2, 5-7]

Extractive distillation is a vapour-liquid process commonly applied in the chemical industry to separate close boiling point mixtures (like C4, C5, C6 alkanes mixtures) and in mixtures that exhibit azeotrope.^[2, 8] In the ED process, a third component is added to the mixture which is characterized by its miscibility, high-boiling and non-volatile mass-separation agent, usually called as solvent. This solvent is used to alter the relative volatility of the compounds and hence, to improve the separation of components from the mixture.^[2, 8-9] It is, therefore, possible to recover one component of the mixture at the top of the distillation column and the rest at the bottom. If other columns are used in series, it is possible to separate the two other solvents, due to the high boiling point of the separating agent.^[8]

To select the best solvent, the relative volatility (non-ideal) and selectivity parameters are commonly used. The relative volatility gives information on how easy it is to perform the separation of a common mixture with vapour-liquid equilibrium,

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} = \frac{\gamma_i p_i^0}{\gamma_j p_j^0} \quad (1)$$

where y is the molar fraction in the vapor phase, x the molar fraction in the liquid phase, p^0 the pure component vapor pressure and γ the activity coefficient for each component represented by the subscripts i and j .^[8]

As the solvent is introduced in a mixture, the relative volatility should increase. Considering the ratio p_i^0/p_j^0 (ideal relative volatility) constant, the variation of the relative volatility is given by the ratio between the activity coefficient of each component. This ratio, in the presence of the solvent, is called selectivity S_{ij} ,

$$S_{ij} = \frac{\gamma_i}{\gamma_j} \quad (2)$$

A high value of relative volatility and a high value of selectivity are an indicator of a promising solvent for the mixture in question.^[8-9] The activity coefficients depend on the composition, since the role of the solvent tends to increase with an increase in its concentration and for this reason, it is common to consider the situation of infinite dilution so that in the expressions 1 and 2, γ are replaced by γ^∞ .^[8]

The solvent, as a separating agent, can be a liquid, solid salt, a mixture of both or an ionic liquid. Examples for each separating agent, disadvantages and advantages are presented in Table 1.

The extractive distillation with ionic liquids (ILs) has been object of research during the past few years. When an ionic liquid is added to a mixture, it dissolves and acts like an inorganic salt in the way that it dissociates in their ions which interacts with the components of the liquid mixture modifying their chemical potential.^[8, 10] When an IL interacts more strongly with one solvent in the mixture, azeotropes could be broken. Even when this phenomenon does not happen or is not too intense, ILs have considerable solubility in low-polar solvents that allows a greater electrolyte concentration in the mixture, and therefore, a stronger salt effect, i.e., a raise in relative volatility that improves separation.^[10] As is shown in Table 1, the use of an ionic liquid has great advantages in extractive distillation.

Table 1. Characterization of different types of Extractive Distillation.^[2, 8, 11]

Type of ED	Separating agents	Azeotrope	Advantages	Disadvantages
<u>Liquid solvent</u>	Tributylamine	Acetic acid - water	No problems with dissolution, reuse or transport for the liquid solvent;	Very high solvent/feed ratio, leading to high consumption of energy;
	Ethylene glycol	Ethanol - water		
<u>Solid Salt</u>	Potassium acetate; Sodium acetate; Calcium chloride;	Ethanol - water	High production capacity; Low energy consumption; Non-volatility; Environment-friendly;	Potential problems in dissolution, transport and recycle of salt; Potential erosion of equipment;
	Magnesium nitrate	Nitric acid - water		
<u>Liquid solvent + Solid salt</u>	Ethylene glycol - CaCl ₂ Ethylene glycol - KNO ₃	Ethanol - water	Easy operation; High separation ability;	Less availability of suitable salts; Potential corrosion of the equipment by the salt;
<u>Ionic Liquids</u>	[C ₄ MIM][AlCl ₄]	Cyclohexane - toluene	Non-volatility; High selectivities and capacities for regeneration; Ability of properties to be tailored; Low energy consumption; No contamination;	ILs that contains halogen ions are unstable at long-term applications; During his hydrolysis it can form small amounts of corrosive and toxic substance.
	[C ₄ MIM][BF ₄] [C ₂ MIM][BF ₄]	Ethanol - water		

1.1. IONIC LIQUIDS

Ionic liquids (ILs) are a new generation of solvents belonging to the class of molten salts, liquid at room temperature, which are expected to produce an important impact on chemical and biotechnological processes.^[12]

ILs are generally based on a bulky and asymmetric cation such as imidazolium, pyridium, pyrrolidinium, ammonium or phosphonium, and on an anion that ranges from simple halides, inorganic anions like $[\text{BF}_4]^-$ or $[\text{PF}_6]^-$ to organic anions such as trifluoromethylsulfonate $[\text{CF}_3\text{SO}_3]^-$ or bis[(trifluoromethyl)sulfonyl]imide $[\text{NTf}_2]^-$.^[13-14] Illustrative examples of some common cations and anions that are combined to form ILs are shown in **Table 2** and **Table 3**, respectively.

Most ILs exhibit some peculiar properties that, as discussed before, are useful for extractive distillation, such as wide temperature range for liquid (ILs have lower melting point due to their large ions that exhibits reduced lattice energy of the crystalline structure), non-flammable, low toxicity, negligible vapor pressure (this means that they do not contaminate the product of the column in an extractive distillation, so they can be used to produce high-purity products), have a wide range of compounds that are soluble in them, such as organic, inorganic compound and even polymeric materials, that ensures enough solubility for the components to be separated (and therefore increase the relative volatility in the liquid phase), have high thermal and chemical stability (with or without water) under distillation temperature, most of them also have low viscosity at high temperatures (and in presence of water), high density and capacity to be reuse and also have the ability to interact differently in the presence of a polar compound or in the presence of non-polar compound.^[7-8, 10, 12-16]

The different combinations between the cation and the anion allow to fine tune the ionic liquid properties depending on which interactions are required according to specific applications (simply by changing the alkyl chain of the cation, different properties of ionic liquid, such as hydrophobicity, viscosity or density are modified).^[12-13, 17-18] The anion is commonly used to control the water miscibility, but the cation can also influence the hydrophobicity or hydrogen bonding ability.^[19]

Due to their unique properties, ILs are expected to be able to replace volatile organic compounds (VOCs) in a number of applications acting as “green” chemicals, minimizing

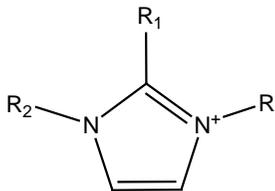
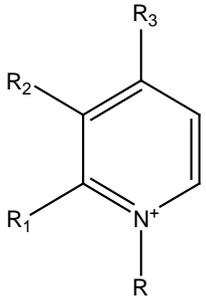
air pollution, climatic changes and human health-related problems. ILs do not only act as excellent solvent for separation processes but also as solvents for catalytic reactions, chemical synthesis or even as electrolytes in batteries, capacitors, solar cells, chemical sensors and can thus be applied in a vast number of chemical products and processes.^[12-13, 20]

Aiming at better understanding the potential of ILs, much work has been carried oriented to obtain the information necessary for a more careful and complete study of their structured-property relationship. Knowing how the structure of ILs influences the physical and chemical properties is very important and has lagged behind. Thus, it is relevant to quantify and qualify fundamental properties such as density, viscosity, surface tension, heat capacity, thermal and electrochemical stability and solubility that allow the assessment of suitability from ILs to specific applications, as well as to design new ILs.^[13, 17] Techniques like UV spectroscopy^[21-22], dynamic methods (visual determination of cloud points)^[13, 23], Hydrogen Nuclear magnetic Resonance spectroscopy (NMR)^[24], gas chromatography (GC)^[25-26], high performance liquid chromatography (HPLC)^[27] and even mass spectroscopy^[28] allow the measure of solubility, however, properties of every conceivable IL cannot be obtained by carrying out appropriate measurements or by using experimental trial an error that would consist in a vast investment. An alternative approach is to develop predictive models, based on limited experimental data.^[13, 17, 20]

It was previously discussed the importance of the purification of bioethanol or biobutanol in the replacement of diesel/gasoline and also how an Ionic Liquid could be advantageous in this process, as a separating agent. The use of predictive methods may allow an easier and more complete scanning of the ionic liquids suitable for a given application. This could allow their design aiming at obtaining a more efficient bioalcohol purification process.

In next section, it will be presented the conception of solubility parameter defined by Hildebrand and Scatchard, and also the various approaches which make use of available data of properties from ionic liquids, for the estimation of solubility parameter.

Table 2. Examples of common cations from ILs.

<u>Imidazolium cation</u>						
Structure	R	R ₁	R ₂	Abbreviation	Name	
	CH ₃	H	CH ₃	[C ₁ MIM] ⁺ or [MMIM] ⁺	1,3 -dimethylimidazolium	
	CH ₂ CH ₃	H	CH ₃	[C ₂ MIM] ⁺ or [EMIM] ⁺	1-ethyl-3-methylimidazolium	
	CH ₃ (CH ₂) ₃	H	CH ₃	[C ₄ MIM] ⁺ or [BMIM] ⁺	1-butyl-1-methylimidazolium	
	CH ₃ (CH ₂) ₅	H	CH ₃	[C ₆ MIM] ⁺ or [HMIM] ⁺	1-hexyl-3-methylimidazolium	
	CH ₃ (CH ₂) ₇	H	CH ₃	[C ₈ MIM] ⁺ or [OMIM] ⁺	1-octyl-3-methylimidazolium	
<u>Pyridinium cation</u>						
Structure	R	R ₁	R ₂	R ₃	Abbreviation	Name
	CH ₃ (CH ₂) ₃	H	CH ₃	H	[C ₄ Mpy] ⁺ or [BMpy] ⁺	1-butyl-3-methylpyridinium
	CH ₃ (CH ₂) ₅	H	CH ₃	H	[C ₆ Mpy] ⁺ or [HMIM] ⁺	1-hexyl-3-methylpyridinium

<u>Pyrrolidinium cation</u>						
Structure	R	R1	R2	Abbreviation	Name	
	CH ₃ (CH ₂) ₃	H	CH ₃	[C ₄ MpyR] ⁺ or [BMpyR] ⁺	1-butyl-3-methylpyrrolidinium	
	CH ₃ (CH ₂) ₅	H	CH ₃	[C ₆ MpyR] ⁺ or [HMpyR] ⁺	1-hexyl-3-methylpyrrolidinium	
<u>Phosphonium cation</u>						
Structure	R	R ₁	R ₂	R ₃	Abbreviation	Name
	CH ₃ (CH ₂) ₁₃	CH ₃ (CH ₂) ₅	CH ₃ (CH ₂) ₅	CH ₃ (CH ₂) ₅	[THTDP] ⁺	trihexyltetradecylphosphonium
<u>Ammonium cation</u>						
Structure	R	R ₁	R ₂	R ₃	Abbreviation	Name
	CH ₃ (CH ₂) ₇	CH ₃ (CH ₂) ₇	CH ₃	CH ₃ (CH ₂) ₇	[Oct ₃ Me] ⁺	trioctylmethylammonium

Sulphonium cation

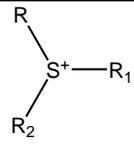
Structure	R	R ₁	R ₂	Abbreviation	Name
	CH ₃ CH ₂	CH ₃ CH ₂	CH ₃ CH ₂	[Et ₃ S] ⁺	triethylsulphonium

Table 3. Examples of common anions from ILs.

<u>Anions</u>			
Abbreviation	Name	Abbreviation	Name
[Cl] ⁻	Chloride	[NTf ₂] ⁻	Bis(trifluoromethylsulfonyl)imide
[Br] ⁻	Bromide	[CF ₃ COO ₂] ⁻	Trifluoroacetate
[CF ₃ SO ₃] ⁻	Trifluoromethanesulfonate	[FAP] ⁻	tris(pentafluoroethyl)trifluorophosphate
[CH ₃ COO] ⁻	Acetate	[CH ₃ CH ₂ OSO ₃] ⁻	Ethylsulfate
[PF ₆] ⁻	Hexafluorophosphate	[SCN] ⁻	Thiocyanate
[BF ₄] ⁻	Tetrafluoroborate	[CH ₃ OSO ₃] ⁻	Methylsulfate
[C(CN) ₃] ⁻	Tricyanomethane	[C(CN) ₂] ⁻	Dicyanamide
[OcOSO ₃] ⁻	Octylsulfate	[NO ₃] ⁻	Nitrate
[TCB] ⁻	Tricyanoborate	[tosylate] ⁻	Tosylate

1.2. SOLUBILITY PARAMETER

Hildebrand and Scott were the authors of the concept of solubility parameter. Usually known as Hildebrand solubility parameter, is defined as the square root of the cohesive energy density:

$$\delta = \left(\frac{\Delta_{vap} U}{V} \right)^{1/2} = \left(\frac{\Delta_{vap} H - RT}{V} \right)^{1/2} \quad (3)$$

V is the molar volume of the pure component and ΔU is the molar cohesive energy (is the energy required to vaporize one mole of the liquid to its saturated vapor).^[29-31] Solubility parameters are sometimes called cohesion energy parameters since they derive from the own cohesive energy per unit volume.^[29-31] The terms of the other equality are enthalpy of vaporization, ΔH , R is the ideal gas constant and T is the temperature.

The solubility parameter term suggests a straight relation with phenomena of solubility or miscibility and those cohesion and vaporization. The solubility parameter is fundamentally a liquid state property and it is used as an important quantity that allows the prediction of solubility relations using only the properties of its individual components.^[29, 31] To achieve a better understanding of the solubility parameter, it is necessary to approach this concept from a thermodynamic point of view.

1.2.1. THERMODYNAMIC CONCEPTS

For a process to occur spontaneously the thermodynamics requires that the Gibbs free energy of mixing must be zero or negative. This free energy of mixing has two contributions, the enthalpic and the entropic,

$$\Delta G = \Delta H + \Delta ST \quad (4)$$

Considering a mixture of components, to measure the deviation of the properties from their ideal behavior, the excess properties are used,

$$G^E = G - G^{ig} \quad (5)$$

This approach is valid and used not only for Gibbs energy but also for enthalpy and entropy energies, in the way that equation 4 can be expressed in terms of excess properties,

$$G^E = H^E + TS^E = U^E + PV^E + TS^E \quad (6)$$

The Hildebrand theory was developed for Regular Solutions, i.e. systems that have negligible excess volume and excess of entropy. With these assumptions,

$$G^E = U^E \quad (7)$$

Using the van der Waals equation of state^[30], the internal energy can be estimated as,

$$U - U^{ig} = -\rho \sum_i \sum_j x_i x_j a_{ij} \quad (8)$$

Noting that $\frac{1}{\rho} = V = \sum_i x_i V_i$, where x is the mole fraction, V is the molar volume and a is

the interaction energy, the internal energy takes the following form,

$$U - U^{ig} = \frac{-\sum_i \sum_j x_i x_j a_{ij}}{\sum_i x_i V_i} \quad (9)$$

For the pure fluid, taking the limit as $x_i \rightarrow 1$, i.e., considering the interactions between the same specie i (the other one is negligible),

$$(U - U^{ig})_i = \frac{-a_{ii}}{V_i} \Rightarrow (U - U^{ig})_i^{is} = -\sum_i \frac{x_i a_{ii}}{V_i} \quad (10)$$

Therefore, for a binary mixture, subtracting the ideal solution the result is,

$$U^E = x_1 \frac{a_{11}}{V_1} + x_2 \frac{a_{22}}{V_2} - \left(\frac{x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22}}{x_1 V_1 + x_2 V_2} \right) \quad (11)$$

Manipulating the equation to a common denominator,

$$G^E = U^E = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} \left(\frac{a_{11}}{V_1^2} + \frac{a_{22}}{V_2^2} - 2 \frac{a_{12}}{V_1 V_2} \right) = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} \left(\frac{\sqrt{a_{11}}}{V_1} - \frac{\sqrt{a_{22}}}{V_2} \right)^2 \quad (12)$$

with $a_{12} = \sqrt{a_{11} a_{22}}$.

Hildebrand and Scatchard reorganized the terms of equation 12, in terms of volume fractions and solubility parameter,

$$G^E = U^E = \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 (x_1 V_1 + x_2 V_2) \quad (13)$$

where

$$\Phi = \frac{x_i V_i}{\sum_i x_i V_i} \quad \text{and} \quad \delta = \frac{\sqrt{a_{ii}}}{V_i}$$

are the volume fraction and solubility parameter respectively.

To estimate the value of δ_i , Scatchard and Hildebrand suggested that experimental data is used according to,

$$\delta_i = \sqrt{\frac{\Delta_{vap}U}{V_i}} = \sqrt{\frac{\Delta_{vap}H - RT}{V_i}} \quad (14)$$

The values of enthalpy of vaporization and molar volume are available in literature for many compounds at a reference temperature that must always be defined (usually the conditions that are defined are saturated liquid at 298 K).^[30]

Another way to predict the solubility parameter, that is often used, is through the plot of mole fraction solubility with solubility parameter of the solvents as the following figure shows,

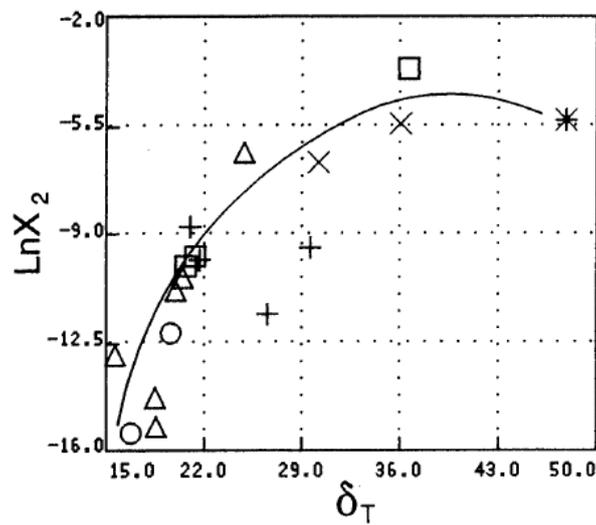


Figure 2- Experimental mole fraction solubility against the solubility parameter of the solvents.^[32]

The maximum visible in Figure 2 corresponds to the point where solvent and solute match, i.e., corresponds to the maximum of solubility of the solute in the solvent and enables the estimation of the overall solubility parameter for the compound in study.

The Regular Solution Theory, as this approach is known, has proved to be useful to predict phase behavior of solutions without detailing molecular polarity or specific interactions. In this matter, other theories appeared as extensions of Hildebrand and Scatchard theory.^{[29, 31,}

^{33]} The most important was proposed by Hansen.^[31]

Hansen^[31] proposed an extension of the Hildebrand solubility parameter, to a solubility parameter divided into three contributions, the dispersion forces (atomic factors), polar forces and (molecular) hydrogen bonding,

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (15)$$

Hansen's total cohesion parameter should equal the Hildebrand parameter, although having different values when different methods are applied to materials with specific interactions. Based on the solubility parameter of ethanol and nitromethane, 26.1 and 25.1 MPa^{1/2} respectively, according to Regular Solution Theory they were supposed to be miscible, but when they are mixed that assumption is not valid. In fact, ethanol and nitromethane have affinities quite different, for e.g., ethanol is miscible with water and nitromethane is not. The Hansen parameter, detailing each interaction that may exist, is capable of explaining such phenomena.^[29, 31] A graphic representation of this three dimensional solubility parameter is shown in **Figure 3**.

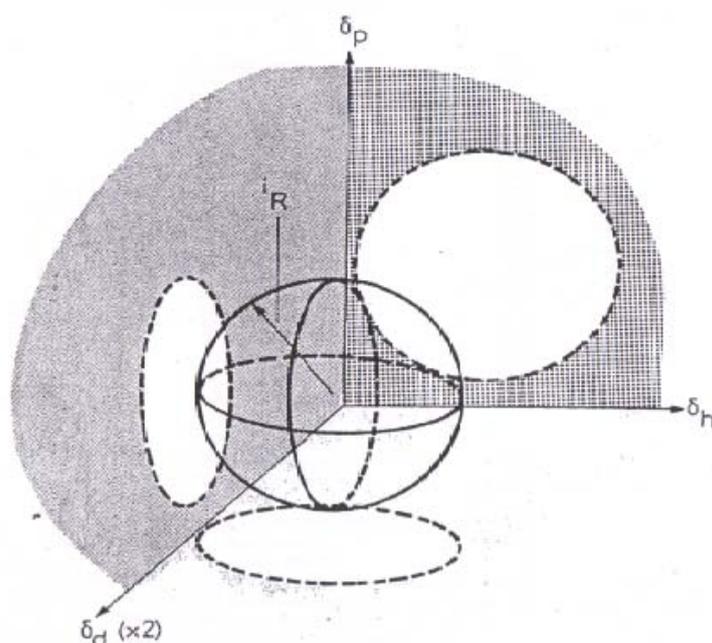


Figure 3 – Solubility parameter representation by three contributions defined by Hansen.^[29]

There is another situation that total Hildebrand solubility parameter cannot account, such as the case of carboxylic acids or glycol ethers (**Figure 4**) where the hydrogen bond dimerization is very significant.

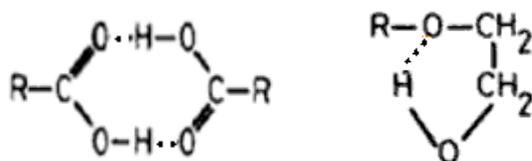


Figure 4 – Examples of strong hydrogen bond dimerization.^[29]

These molecules exhibit different interactions according to the polarity of the solvent molecules. One example is acetic acid which acts as a polar substance in presence of water (polar compound) and in heptane (non-polar compound) tends to behave in a non-polar manner, in an effort to adapt to the solvent medium.^[29]

Hoy^[29] proposed that this ability of a molecule to assume the character of its environment to be called as *chameleonic*, like the reptile that adopts the color of its background. This approach has been applied in drug solutions where the Hildebrand parameter theory undergoes changes, such as the addition of new variable (chameleonic effect).^[29]

Bustamante and co-workers described the chameleonic effect for the first time in a quantitative way using partial solubility parameters in 1994^[34], aiming at that the extension of the Hildebrand solubility approach could describe drug solubility in solvent mixtures which present multiple solubility peaks (unlike as it is shown in Figure 2 which a single maximum corresponds to only one solubility parameter, the overall solubility parameter). A plot of the mole fraction of the drug with the solubility parameter of the solvent mixture allows the identification of the solubility peaks, as shown in **Figure 5**.^[32, 34-39]

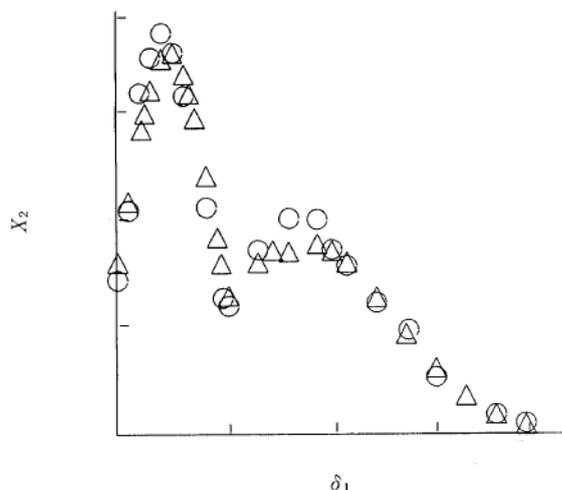


Figure 5- Solubility of Sulfanilamide in Ethanol-Water Mixtures.^[34]

To estimate the solubility parameters from a mixture of solvents, Jouyban-Gharamaleki and Bustamante^[38] used,

$$\delta = \sum f_i \delta_i \quad (16)$$

where δ_i is the solubility parameter of the pure solvents and f_i is their volume fraction in the mixture.

In parallel with this approach Jouyban-Gharamaleki and Barzegar-Jalali proposed a computer optimized model to calculate the solubility of solutes showing two peaks, using ratios of partial solubility parameters.^[38]

As mentioned in the section concerning Ionic liquids, the goal of knowing the factors that influence the performance of ILs as entrainers for extractive distillation has been object of many researches. For that purpose the solubility relations are an important issue and the Hildebrand solubility parameters, though a simple approach, could be a way to predict it.^[19]

The establishment of a solubility parameters scale, based on theory and experimental data, would allow the choice of the best ionic liquid to be used in extractive distillation for a given system.^[29]

1.2.2. ESTIMATION OF SOLUBILITY PARAMETER

One of the most important thermodynamic properties is the activity coefficient. The activity coefficient is related to excess Gibbs energy by,

$$G^E = RT \sum_i x_i \ln(\gamma_i) \quad (17)$$

Differentiating equation 13 with respect one of the components, assuming Regular Solution Theory conditions the relation is,

$$\begin{aligned} RT \ln(\gamma_i) &= V_i \Phi_j^2 (\delta_i - \delta_j)^2 \\ RT \ln(\gamma_j) &= V_j \Phi_i^2 (\delta_i - \delta_j)^2 \end{aligned} \quad (18)$$

At infinite dilution, $\Phi_i=1$ and $\gamma_i = \gamma^\infty$, and equation 18 simplifies to,

$$\begin{aligned} RT \ln(\gamma^\infty) &= V_i (\delta_i - \delta_j)^2 \\ RT \ln(\gamma^\infty) &= V_j (\delta_i - \delta_j)^2 \end{aligned} \quad (19)$$

The activity coefficient at infinite dilution, γ^∞ , by definition describes the non ideality of the maximum of dilution attainable by a compound on a solvent.^[30, 40-41] It gives a direct measure of interactions between unlike molecules in the absence of solute-solute interactions.^[33, 40-42] The activity coefficients are very important for calculations of

selectivity and capacity of entrainers for azeotropic/extractive distillation, liquid extraction, to characterize the behavior of liquid mixtures, estimation of mutual solubilities, fitting the excess Gibbs energy model parameters, predicting the existence of an azeotrope, calculation of Henry constant and partition coefficients, among others.^[33, 43] In fact, the activity coefficients at infinite dilution are the most reliable source of information for the highly diluted region, in which only the interactions between solute-solvent influence the deviation of behavior from the ideal mixture.^[33, 44] Using infinite dilution activity coefficients it is possible to estimate the solubility parameter of a compound.

In spite of all advantages of using activity coefficients, others properties are used in the estimation of solubility parameters. Densities, viscosities, surface tensions, lattice energy and melting points all are properties that can be used to estimate solubility parameters, examples of these cases will be hereforth discussed.^[19, 45]

Scovazzo et al^[46] used melting-point temperatures to estimate solubility parameters in room temperatures ionic liquids (RTIL), by replacing the energy of vaporization ΔU in equation 3) for,

$$-\Delta U = (\Delta H^v - RT)z \quad (20)$$

Where ΔH^v is the heat of vaporization, R is the ideal gas constant, T is the absolute temperature and z is the compressibility factor of the vaporized liquid. But to apply the definition of Hildebrand solubility parameter the author calculate the heat of vaporization for liquids with an empirical relationship typically used for molten salts,

$$\Delta H_M^v = C_T(T_M) \quad (21)$$

ΔH_M^v is the enthalpy of vaporization at salt's melting point, T_M is the salt's melting point and C_T is a specific constant for the salt. Combining equations 20 (with $T=T_M$) and 21, the solubility parameter assume the form,

$$\delta = \left(\frac{K_T T_M}{V} \right)^{1/2} \quad (22)$$

Camper et al^[47] used lattice energies of ILs to estimate solubility parameter through a relationship of low pressure Henry's law with the Regular Solution Theory for different compounds in ILs. The equation derived was,

$$\ln(H_{2,1}(atm)) = b + d(\delta_1 - \delta_2)^2 \quad (23)$$

The lattice energy can be estimated using the Kapustinskii equation as follows,

$$U = 2.40 \times 10^6 \left(\frac{J \overset{\circ}{A}}{mol} \right) \left(\frac{z_1 z_2}{r_c + r_a} \right) \left(1 - \frac{0.345 \overset{\circ}{A}}{r_c + r_a} \right) \quad (24)$$

Introducing the sum of the radius as an estimation for the molar volume,

$$V_1 = 2N(r_c + r_a)^3 \quad (25)$$

Combining these two last equations into the equation of Hildebrand solubility parameter (equation 3), it results,

$$\delta = \left[\left(\frac{2.56 \times 10^6 \left(\frac{J}{mol} \right) z_1 z_2 \left(\frac{cm^3}{mol} \right)^{1/3}}{V_1^{4/3}} \right) \left(1 - \frac{0.367 \left(\frac{cm^3}{mol} \right)^{1/3}}{V_1^{1/3}} \right) \right]^{1/2} \quad (26)$$

Yizhak Marcus^[48] and Sang Hyun Lee^[49] also used lattice energies to predict solubility parameters of distinct compounds in ILs.

Kilaru et al^[50] used surface tension to provide values for solubility parameter by taking into account its definition as the square root of the cohesive energy density (equation 3) and the equation for the work cohesion in terms of surface tension (σ) as shown below,

$$W_C = 2 \times (2 \times 10^{-8}) \sigma V_1^{2/3} N_A^{1/3} \quad (27)$$

Combining equation 27 and equation 3 it is obtained,

$$\delta = \left(\frac{4.78 \times 10^{-8} N_A^{1/3} K_s \sigma}{V_1^{1/3}} \right)^{1/2} \quad (28)$$

Kilaru et al^[45] also used viscosity data to estimate the Hildebrand solubility parameter, where the energy of vaporization, U , included in the equation 3 (that defines Hildebrand solubility parameter) can be estimated by the Eyring's activation energy of viscosity as described below.

The author used the viscosity data, available in literature, through the relationship with molar energy of activation.

$$\Delta G_{vis}^0 = RT \ln \left(\frac{\eta V_1}{h N_A} \right) \quad (29)$$

The energy of vaporization, on its turn, is related to the molar free energy of activation through a proportionality constant, given by,

$$E^{vap} = K_v \Delta G_{vis}^0 \quad (30)$$

Substituting equations 21 and 20 in equation 15, the result is,

$$\delta_1 = \left\{ \frac{K_v RT}{V_1} \ln \left[\frac{(1 \times 10^{-9}) \eta V_1}{h N_A} \right] \right\}^{1/2} \quad (31)$$

where η is the dynamic viscosity of IL (in units of cP), V_l is the molar volume (in cm^3/mol), h is the Plank's constant (in units of J.s), N_A is Avogadro's number and K_v is a proportionality constant. For the value of K_v , two values were obtained, one for the family of the anion $[\text{NTf}_2]^-$ and the other to non- $[\text{NTf}_2]^-$ family.^[45]

Using the information available for activity coefficients at infinite dilution of various solvents in ionic liquids, the solubility parameters will be estimated using equation 19. The approach of Kilaru and Scovazzo^[45] to estimate the solubility parameter with viscosity data, according to equation 31, will be also used in this work. These two approaches were

chosen because they correspond to properties widely available in literature for ionic liquids.

To complete this study, measurements of solubilities of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate in different solvent mixtures was carried out to estimate the solubility parameters from solubility data according to Jouyban-Gharamaleki and Bustamante^[38] approach. These solutions were water with 1-propanol, 1-propanol with toluene. These measurements were made by two different techniques, UV spectroscopy and gravimetric procedure, as described in the next section.

EXPERIMENTAL SECTION

Materials:

In the study of ternary systems the ionic liquid used was 1-butyl-3-methylimidazolium hexafluorophosphate, [C₄MIM][PF₆], acquired from IoLiTec with mass fraction purities > 99 %. The bromide impurity mass fraction is 85ppm. The solutions of solvents used in the ternary systems were water with 1-propanol, 1-propanol with toluene. The water used was double-distilled, passed by a reverse osmosis system, and further treated with a MilliQ plus 185 water purification apparatus. The toluene used were by supplied BDH Prolabo and their purity is > 99 % and for 1-propanol, its purity is > 99.5 % but supplied by Lab-Scan, Analytical Sciences.

Experimental Procedure:

To measure the ILs solubilities, samples at various compositions of the two volatile components prepared by weight and pure IL were, vigorously stirred, and allowed to reach equilibrium by phase separation in 22 mL glass vials (for at least 48 h at 298 K). This period proved to be the minimum time required to guarantee a complete separation of the two phases and it was assumed that no further variations in mole fraction solubilities occurred. The temperature was maintained by keeping the glass vials containing the phases in equilibrium inside an aluminum block previously designed for similar purpose, which is placed in an isolated air bath, and capable of maintaining the temperature within (1±0.01 K). The temperature control was achieved with a PID temperature controller driven by a calibrated Pt100 (class 1/10) temperature sensor inserted in the aluminum block.

Two techniques were used to measure solubilities of these ternary systems, namely UV spectroscopy, using a SHIMADZU UV-1700 Pharma-Spec Spectrometer (**Figure 6**), for the solution of water with 1-propanol, and for the remaining solution a gravimetric procedure was performed applying vacuum for the evaporation of the volatile solvents (**Figure 7**).

- **UV spectroscopy:** For the analysis of the solubility of IL in the propanol-water-rich phase, samples of 0.5 g were taken and diluted by a factor ranging from 0.5:250 to 0.5:25000 (v:v) in ultrapure water. The maximum absorbance for the imidazolium cation was previously established^[28] to be at the wavelength of 211

nm and was here used during all this procedure. At 298 K and at atmospheric pressure, the solubility results at each individual composition are an average of at least five independent measurements, determined from a calibration curve previously established.



Figure 6 – UV spectrometer.

- **Gravimetric procedure:** Samples of 0.1 to 2 g from the solvent mixture rich phase were weighted and the volatile solvents were evaporated under moderated vacuum, in a glass flask designed for the purpose. The IL content was determined by weight. For each composition, at least three individual measurements were performed. All the mass fraction quantifications were performed gravimetrically within a precision of $\pm 10^{-4}$ g, at 298 K.



Figure 7- Equipment used to apply the gravimetric method.

RESULTS AND DISCUSSION

In this work, two approaches to estimate the solubility parameters for ionic liquids were used. Their results will be presented and discussed in this section. Firstly the results for solubility parameters estimation using activity coefficients at infinite dilution data are reported in **Tables 4** and **5**. The results obtained by Kilaru's approach based on viscosities are reported in **Table 6** and **7**. Finally are reported the solubility parameters obtained by the experimental procedure described and are compared with the results previously shown.

1.1 ACTIVITY COEFFICIENTS AT INFINITE DILUTION

Table 4. Solubility parameters organized by the anion of the IL, T=298 K.

Anion	Cation	δ NP/MPa ^{1/2}	δ P/MPa ^{1/2}	Anion	Cation	δ NP/MPa ^{1/2}	δ P/MPa ^{1/2}				
NTf ₂	IM	C ₂ M	22.548	30.197	EtSO ₄	IM	C ₂ M	24.535	26.510		
		C ₄ M	21.725	30.430	Cl	IM	C ₈ M	22.498			
		C ₆ M	20.892	28.611	OcOSO3	IM	C ₄ M	21.082			
		C ₈ M	20.744	30.953	C ₂ H ₅ OC ₂ H ₄ OSO ₃	N	C ₅ H ₆	24.522			
		C ₆ H ₁₃ OCH ₂ M	21.126	28.533	TFA	IM	C ₂ M	24.291			
		(C ₆ H ₁₃ OCH ₂) ₂	19.821	27.355	FAP	IM	C ₂ M	21.541	33.291		
	MIM	C ₂ M	22.797	30.475	TCB	IM	C ₂ M	22.205	29.677		
		py	C ₂	22.455	30.222	Tosylate	phosphonium	tri-iso-butylmethyl	22.335		
	C ₄ M		21.914	29.488	IM		C ₂ M	23.588			
	S	Et ₃	C ₄ M	22.190	30.029	Br	IM	(C ₆ H ₁₁ O ₂)Methyl	25.232	26.515	
								(C ₁₀ H ₁₇ O ₂)Methyl	23.462		
	pBoronicAcid methyl	23.798									
	pBoronicAcid octyl	22.219									
	pyR	C ₄ M	22.409	29.434	MeSO ₄			IM	C ₄ M		25.640
		C ₆ M	21.230						MM	25.497	
	N	Me ₃ B	C ₈ M	22.328	30.626	phosphonium	tributylmethyl	21.549			
OC ₃ Me								16.954	26.984		
P	THTD	17.064	28.778								
BF ₄	IM	C ₂ M	23.974		SCN	IM	C ₂ M	25.274	27.643		
		C ₄ M	23.713	29.208			C ₄ M	24.465	25.502		
		C ₆ M	23.084				HM	23.360	25.095		
		C ₈ M	21.804	27.659			C ₂ M	23.958	28.204		
	py	C ₁₆ M	19.407	28.037	CF ₃ SO ₃	IM	C ₄ M	23.208	30.604		
		C ₄ M	23.714	29.945			C ₆ M	22.485			
		MIM	propyl-M	26.462			29.331	C ₈ M	21.345		
		pyR	C ₄ M	23.679			30.270	pyR	C ₄ M	23.138	26.429
PF ₆	IM	C ₄ M	22.320	32.400	py	C ₄ M	22.484	25.752			
		C ₆ M	21.951	35.229							
		C ₈ M	21.540	33.494							

Table 5. Solubility parameters organized by the cation of the IL, T= 298 K.

Cation	Anion	δ NP/MPa ^{1/2}	δ P/MPa ^{1/2}	Cation	Anion	δ NP/MPa ^{1/2}	δ P/MPa ^{1/2}			
IM	NTf ₂	22.548	30.197	IM	C ₆ H ₁₃ OCH ₂ M	NTf ₂	21.126	28.533		
	BF ₄	23.974			(C ₆ H ₁₃ OCH ₂) ₂	NTf ₂	19.821	27.355		
	CF ₃ SO ₃	23.958	28.204		MM	MeSO ₄	25.497			
	SCN	25.274	27.643		(C ₆ H ₁₁ O ₂)Methyl	Br	25.232	26.515		
	EtSO ₄	24.535	26.510		(C ₁₀ H ₁₇ O ₂)Methyl		23.462			
	TFA	24.291			pBoronicAcid methyl		23.798			
	FAP	21.541	33.291		pBoronicAcid octyl		22.219			
	TCB	22.205	29.677		MIM	C ₂ M	NTf ₂	22.797	30.475	
	Tosylate	23.588		propyl-M		BF ₄	26.462	29.331		
	C ₄ M	NTf ₂	21.725	30.430	py	C ₂	NTf ₂	22.455	30.222	
		BF ₄	23.713	29.208		C ₄ M	NTf ₂	21.914	29.488	
		PF ₆	22.320	32.400			BF ₄	23.714	29.945	
		MeSO ₄		25.640	pyR	C ₄ M	CF ₃ SO ₃	22.484	25.752	
		CF ₃ SO ₃	23.208	26.371			NTf ₂	22.409	29.434	
		SCN	24.465	25.502			CF ₃ SO ₃	23.138	26.429	
		OcOSO ₃	21.082				BF ₄	23.679	30.270	
		NTf ₂	20.892	28.611			C ₆ M	NTf ₂	21.230	
		C ₆ M	BF ₄	23.084		C ₈ M	NTf ₂	20.761		
			PF ₆	21.951	35.229	phosphonium	tri-iso-butylmethyl	Tosylate	22.335	
			CF ₃ SO ₃	22.485			tributylmethyl	MeSO ₄	21.549	
			SCN	23.360	25.095		THTD	NTf ₂	17.064	28.778
	C ₈ M		NTf ₂	20.744	30.953	N	C ₅ H ₆	C ₂ H ₅ OC ₂ H ₄ OSO ₃	24.522	
		BF ₄	21.804	27.659	Me ₃ B		NTf ₂	22.328	30.626	
		Cl	22.498		Oc ₃ Me		NTf ₂	16.954	26.984	
		PF ₆	21.540	33.494	S	Et ₃	NTf ₂	22.190	30.029	
	BF ₄	19.407	28.037							

For the estimation of Hildebrand solubility parameter, through activity coefficients at infinite dilution, equation 19 was used. Manipulating this equation an expression for the solubility parameter, δ_{IL} , is obtained,

$$\delta_i = \delta_j + \left(\ln(\gamma^\infty) \frac{RT}{V_j} \right)^{1/2} \quad (32)$$

For this calculation, the ideal gas constant has the value of $8,314 \text{ cm}^3 \cdot \text{MPa} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, while the molar volume (expressed as $\text{cm}^3 \cdot \text{mol}^{-1}$) and the solubility parameter data, at 298 K for all solvents considered, were obtained from the *CRC Handbook of Solubility Parameter other Cohesion Parameters*^[29] (compiled in the table presented in **Appendix A**). As for the data for the activity coefficients at infinite dilution, a bibliographical research of the available data published was carried.^[18, 33, 40-42, 44, 51-101] It is important to note that these activity coefficients at infinite dilution are of the solvent in the ionic liquid and not otherwise. A large body of data for multiple solvents in a broad range of ionic liquids is available at various temperatures.

A plot of collected data of solubility parameters for solvents versus activity coefficients at infinite dilution (**Appendix B**) demonstrate that ionic liquids possess two different distributions, as it may be seen in **Figures 8 to 10**, at temperature 298 K.

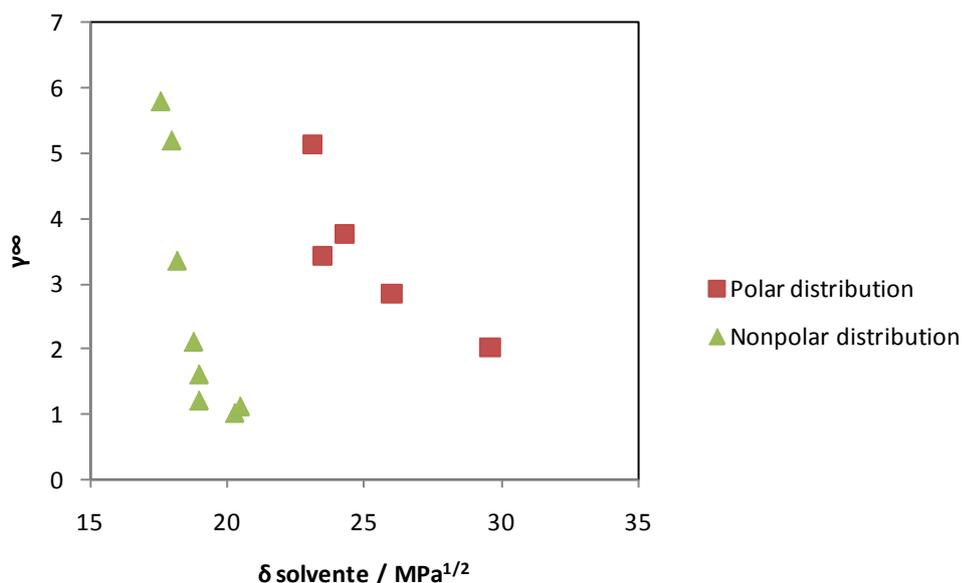


Figure 8 - Activity coefficients at infinite dilution of $[\text{C}_4\text{MIM}][\text{PF}_6]$ in function of solubility parameters of solvents.

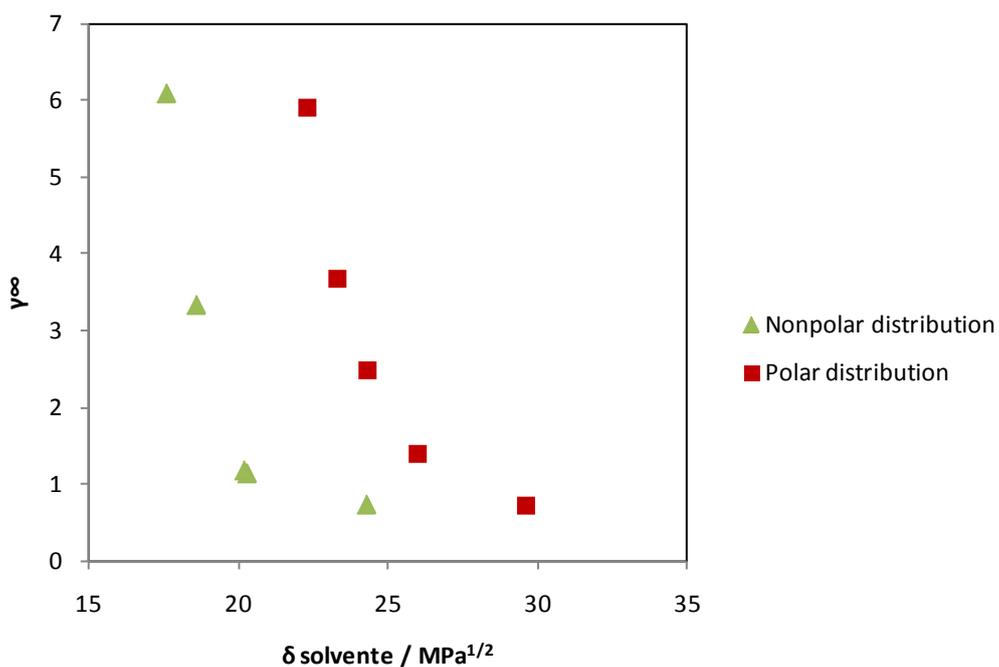


Figure 9- Activity coefficients at infinite dilution of [C₄MIM][BF₄] in function of solubility parameters of solvents

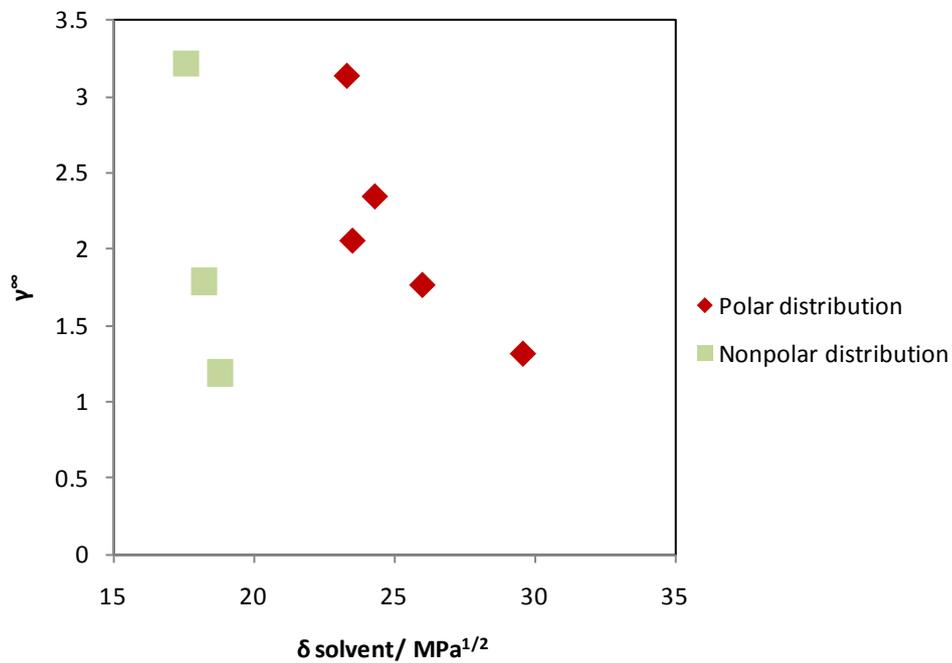


Figure 10 - Activity coefficients at infinite dilution of [C₂MIM][NTf₂] in function of solubility parameters of solvents

This double tendency/behavior may be explained by the concept of chameleonic effect defined by Hoy^[29]. The identification of two values for solubility parameters may result from the fact that ionic liquids exhibit an amphiphilic characteristic (hydrophobic and hydrophilic), behaving differently in the presence of several solvents. These graphics are similar to the ones obtained by Bustamante and Jouyban-Gharamaleki^[38] in Figure 5 with two peaks. The relation between the two properties is given by,

$$\gamma = \frac{1}{x} \quad (33)$$

Instead of having a maximum, the graphic representation of the activity coefficient at infinite dilution presented in Figures 8 to 10 shows the presence of two minima. The results indicate that the ionic liquid is not defined by only one solubility parameter but two, depending on the solvent that is interacting with the ionic liquid.

The green distribution is related to the values obtained using only data from nonpolar solvents such as pentane, hexane, toluene or benzene, which are about up to 24 MPa^{1/2}. For compounds like methanol or ethanol, i.e. alcohols, the value of solubility parameters were up to 30 MPa^{1/2} represented as the red distribution in **Figures 8 to 10**.

These two behaviors observed for polar and nonpolar compounds is related to what is observed in the salvation of compounds in ionic liquids through molecular simulation by Canongia Lopes et al.^[102], where it was stated that “polar and nonpolar species interact in their own way with the different parts of the ions, notably the cation”. Most of the data collected for activity coefficients at infinite dilution were obtained by inverse Gas Chromatography where the IL are used as the stationary phase. This procedure allows observing a separation of polar and nonpolar compounds based on the fact that, after the introduction of the solvent into the column it will be attached locally to the region of the ionic liquid with which it has more affinity. The two sets of values of solubility parameters previously identified are related with the existence of two types of domains in ionic liquids as shown by molecular dynamics simulation. Canongia Lopes et al.^[102-103] was able to show two regions present in each IL as followed in Figure 11 to 13.

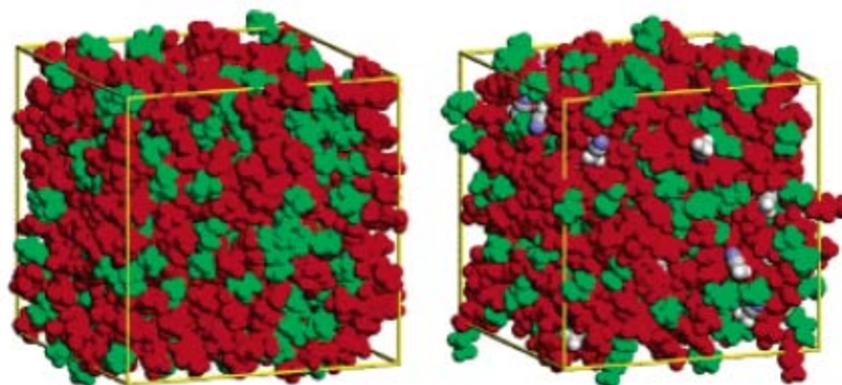


Figure 11 – Snapshots of simulation boxes of [C₄MIM][PF₆] in which atoms belonging to the polar region (imidazolium ring and anion) were colored in red and to regions nonpolar (alkyl side chain) the atoms were colored in green. Left: pure ionic liquid; Right: acetonitrile solution.

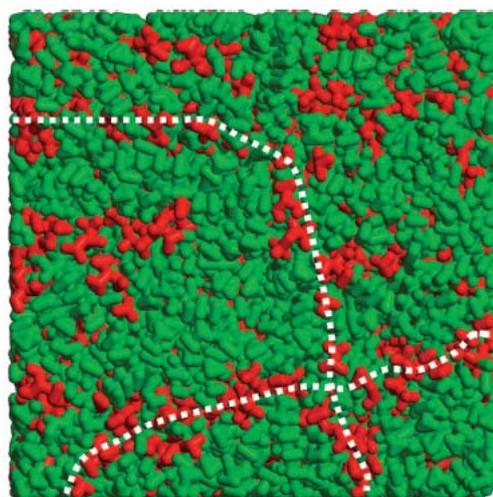


Figure 12 – Snapshot of a simulation for [THTDP][NTf₂], where the region polar is colored in red and the nonpolar region in green. The dotted white lines exemplify the threadline for polar network, which is much less than the nonpolar region.

Recently^[104], the same group investigated the mutual solubility of mixtures of phosphonium-based ionic liquids with alkanes, alkanols, fluorinated alkanes and fluorinated alkanols. A comparison of the phase behaviour of solutions containing phosphonium-based ionic liquids and 1-alkyl-3-methylimidazolium based ionic liquids was also made from which results the following figure.

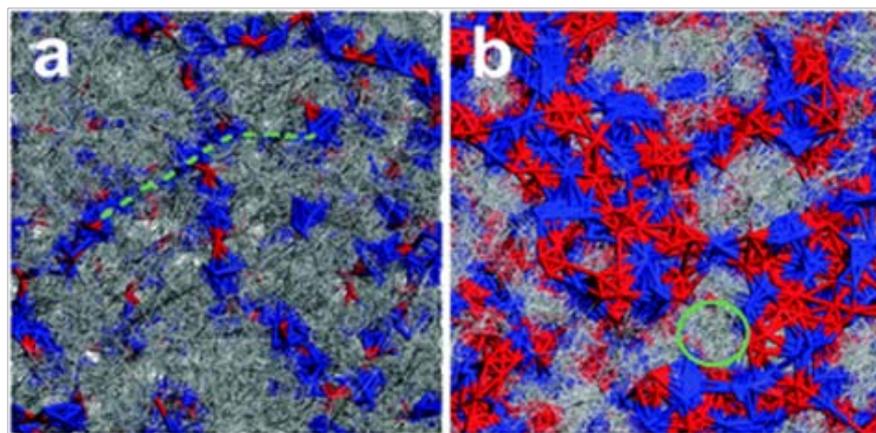


Figure 13 – Snapshots of a pure (a) [THTDP][Cl] and (b) pure [C₁₀MIM][PF₆]. The atoms charged positively (cations) are coloured in blue, the atoms charged negatively (anions) in red, and the region nonpolar (aliphatic chain) are coloured in grey.

In this last figure, the authors could discretize all the present elements, verifying that the [THTDP][Cl] has a predominant nonpolar region compared to the other IL.

Since two different behaviors are observed, two solubility parameters, one for non-polar compounds, δ_{NP} , using data collected for non-polar families and the other for the polar compounds, δ_P , using data collected only for polar families were estimated. The evaluation of the obtained values will be made taking into account the solubility parameters scale for the solvents, where the solubility parameter reference is for water having the value of 47.9 MPa^{1/2}.

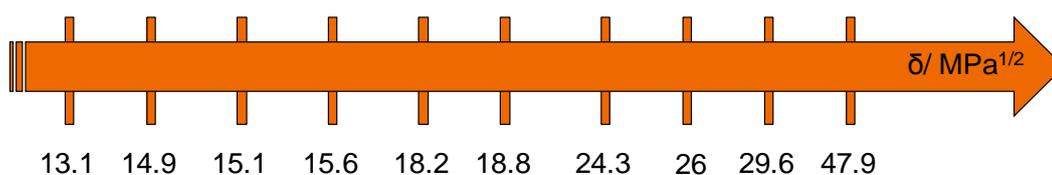


Figure 14- Solubility parameters scale for solvents.

For each solute a value for the solubility parameter was obtained and a value for the solubility parameter of the ionic liquid is estimated, by minimizing the following objective function,

$$O.F = \sum_i (\delta_{IL} - \delta_i)^2 \quad (34)$$

It is important to mention that while the solubility parameter has a slight dependence on the temperature, the data for the pure components were collected only for the temperature of 298 K.

The results obtained were compiled in two tables allowing different analysis. In **Table 4**, is possible to verify the influence of the cation and its alkyl chain length for each anion, while in **Table 5** is possible to study the influence of the anion for a single cation.

Analyzing Table 4 it is possible to observe, for both non-polar and polar solubility parameters, a decrease on the solubility parameters values with the cation alkyl chain length. This tendency is a consequence of the introduction of successive methyl groups (CH_2) in the cation chain which increases the aliphatic character, diminishing the solubility in water, resulting in a smaller value for solubility parameters (**Figure 15**). Though this behavior is in general verified in several ILs, exceptions are observed in the case of the anion $[\text{NTf}_2]^-$, $[\text{PF}_6]^-$ and $[\text{CF}_3\text{SO}_3]^-$ but only for δ_p , as it may be seen in **Figure 16**.

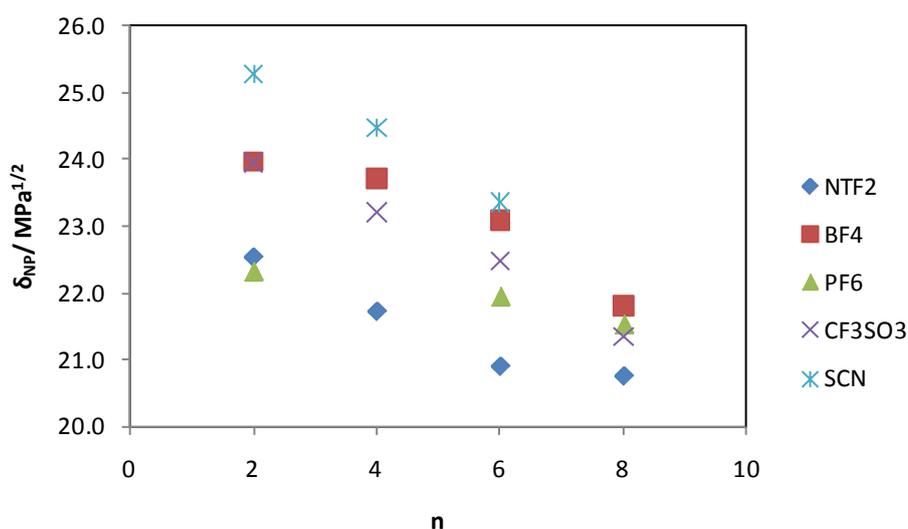


Figure 15 – Effect of the alkyl chain length in δ_{NP} for $[\text{C}_n\text{MIM}][\text{X}]$.

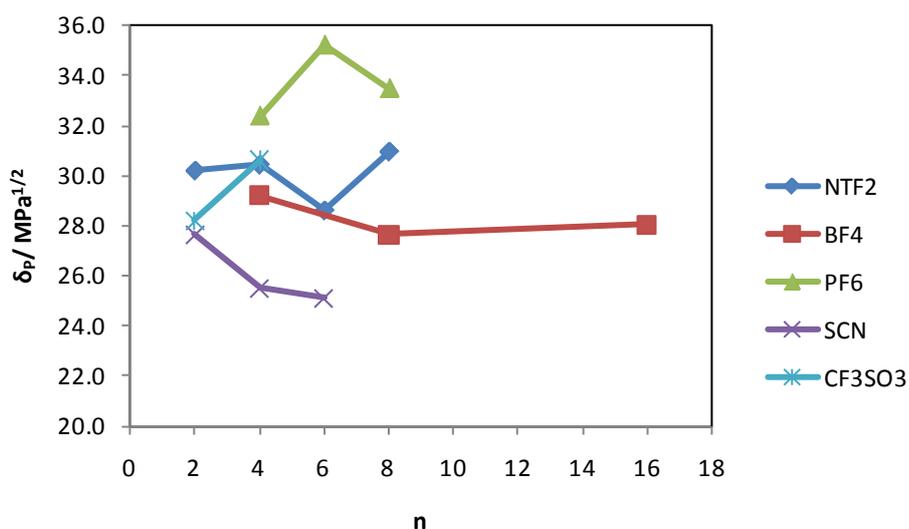


Figure 16 – Effect of the alkyl chain length in δ_p for $[C_n\text{MIM}][X]$.

Table 4 also shows that the increase in the number of substitutions (and longer their chain is) also decrease the values for δ_{NP} and δ_p as it may be seen in the case of anion $[\text{NTf}_2]^-$ for $[\text{C}_2\text{py}]^+$, $[\text{C}_4\text{Mpy}]^+$ and ammonium cations. Nevertheless, this is not verified for the same anion, between the cation $[\text{C}_2\text{MIM}]^+$ and $[\text{C}_2\text{MMIM}]^+$. For the same anion, the introduction of an oxygen atom into the $[\text{C}_6\text{H}_{13}\text{OCH}_2\text{M}]^+$ cation chain increases the value of δ_{NP} but decreases the value of δ_p relatively to $[\text{C}_8\text{MIM}]^+$ since the number of carbons decreases. The reason of this duality may be due to two effects, one is the stereochemical hindrance and the other is the possibility to increase the hydrogen-bonded net which may be the predominant effect in the case of non-polar solubility parameters. The overall trend between cation families, i.e., between imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium and sulphonium cations cannot be evaluated because there is not available data for a common anion. Anyway, there are some tendencies between pairs of families that may be taken. Comparing the values of δ_{NP} , is observed the tendency imidazolium > pyrrolidinium and imidazolium > pyridinium for the common anions $[\text{NTf}_2]^-$, $[\text{BF}_4]^-$ and $[\text{CF}_3\text{SO}_3]^-$. For $[\text{BF}_4]^-$ the tendency for δ_{NP} is imidazolium > pyridinium > pyrrolidinium. This last tendency mentioned is also observed for δ_p for $[\text{NTf}_2]^-$. Unlikely, the inversion of the tendency between imidazolium, pyridinium and pyrrolidinium is observed in the case of the anion $[\text{BF}_4]^-$ for polar solubility parameters. For $[\text{CF}_3\text{SO}_3]^-$ in the case of δ_p , is possible to noticed only the tendency

imidazolium>pyrrolidinium and imidazolium>pyridinium. These interactions are possible to verify in the following figures.

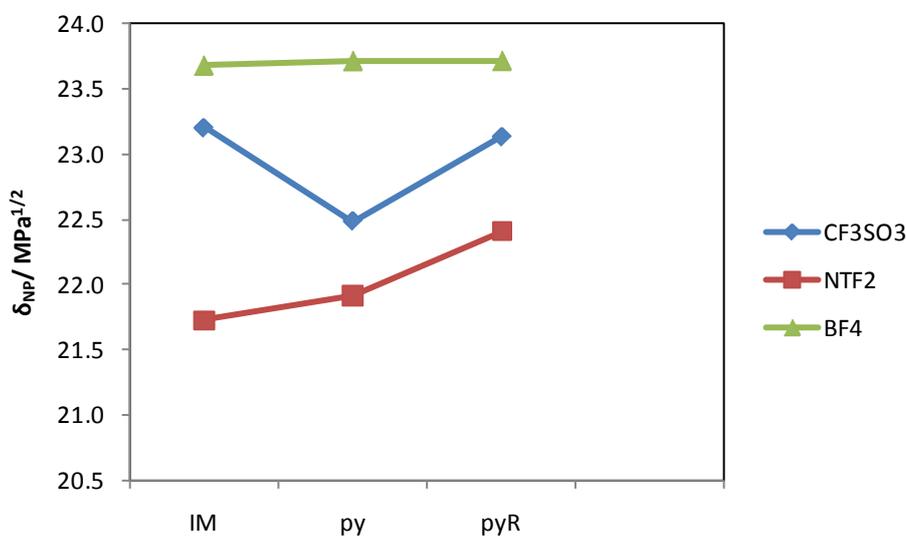


Figure 17 – Cation family effect in δ_{NP} for $[\text{C}_4\text{MX}][\text{X}]$.

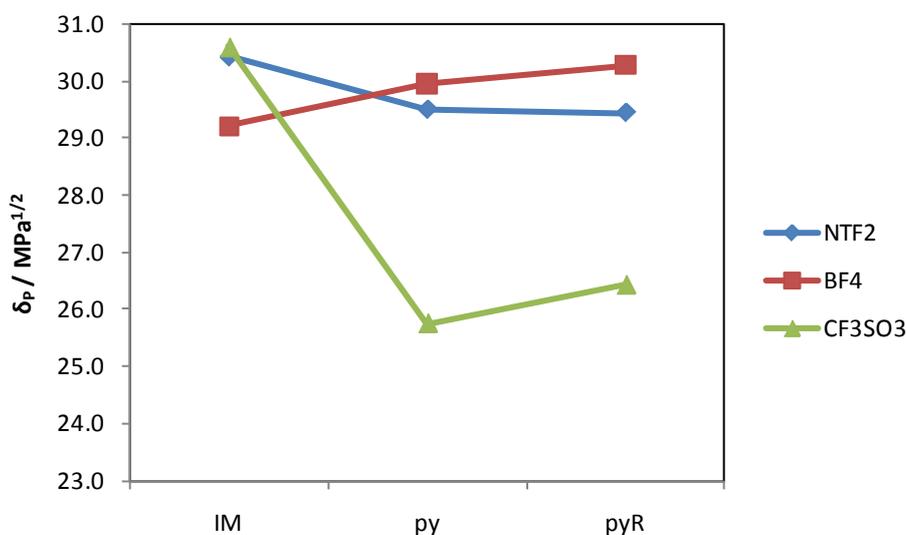


Figure 18 – Cation family effect in δ_P for $[\text{C}_4\text{MX}][\text{X}]$.

Though there is no available data to one specific anion for all cation families, it is also possible to see in this table that values for the cations such as phosphonium, sulphonium and ammonium, the values for solubility parameters are smaller than for imidazolium. The reason for imidazolium cation having usually greater values for solubility parameters, may be due to its aromatic π – bond interactions allowing higher solubility and also due to its acid

hydrogen atom (usually not substituted) that improves its miscibility. These general tendencies were verified through experimental procedures by several research groups.^[105-107]

In Table 5, the solubility parameters may be evaluated by the type of anion. To a better evaluation, the results were graphically represented in **Figure 9 to 13** for δ_{NP} and **Figures 19 to 28** for δ_P as it follows.

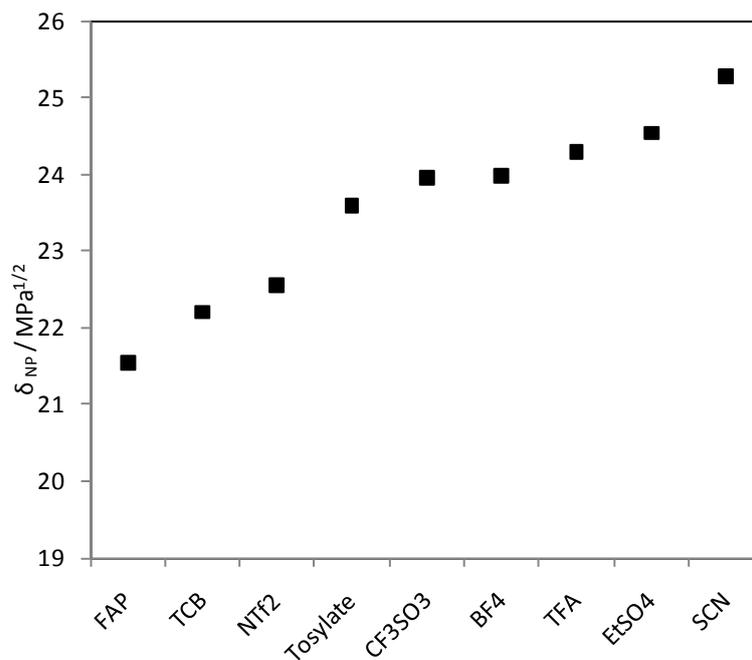


Figure 19 – Values for non-polar solubility parameters for $[\text{C}_2\text{MIM}][\text{X}]$.

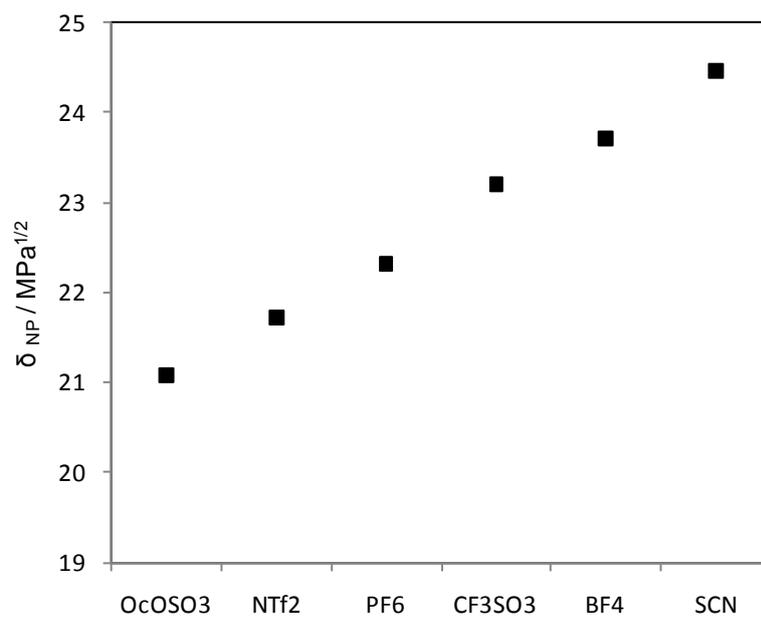


Figure 20 - Values for non-polar solubility parameters for [C₄MIM][X].

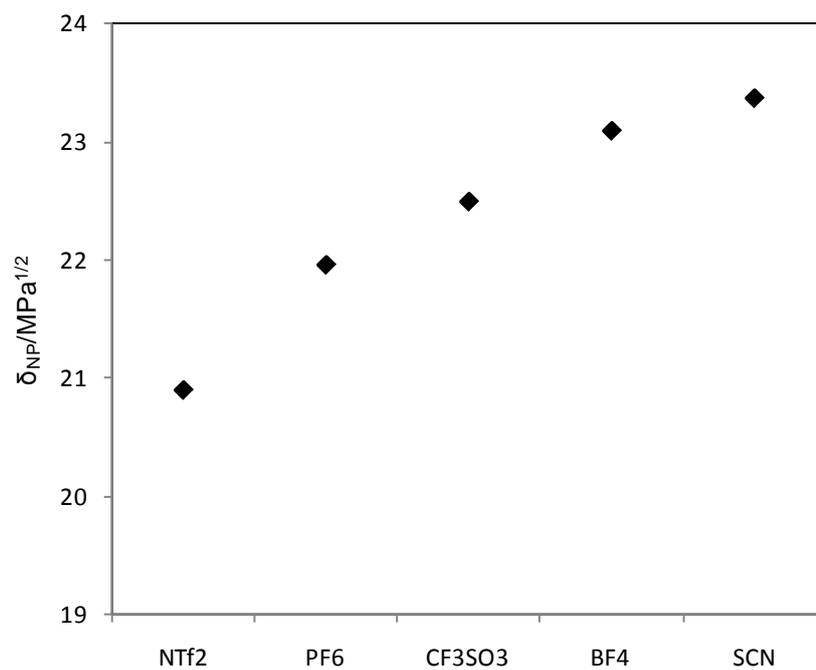


Figure 21 - Values for non-polar solubility parameters for [C₆MIM][X].

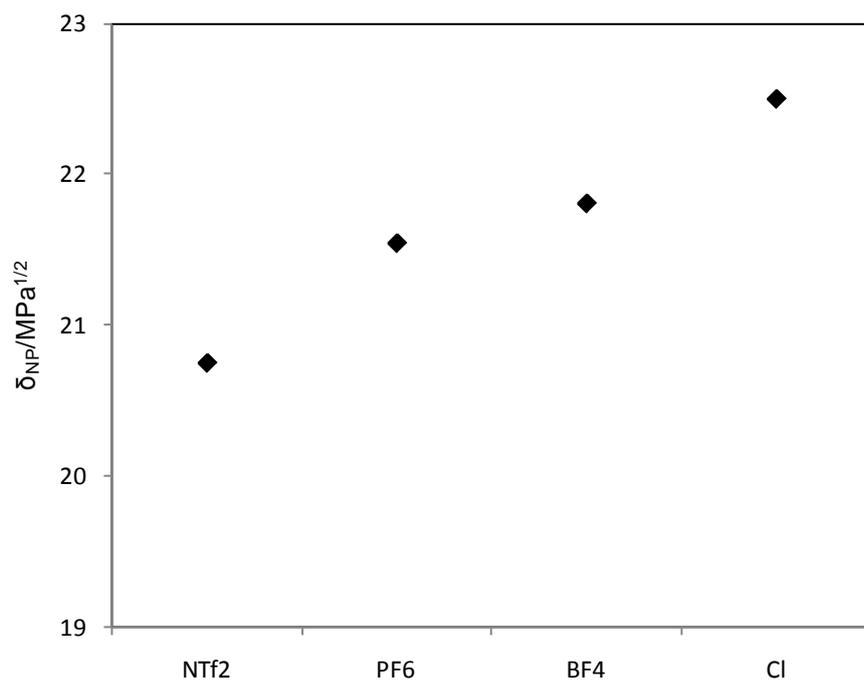


Figure 22 - Values for non-polar solubility parameters for $[C_8MIM][X]$.

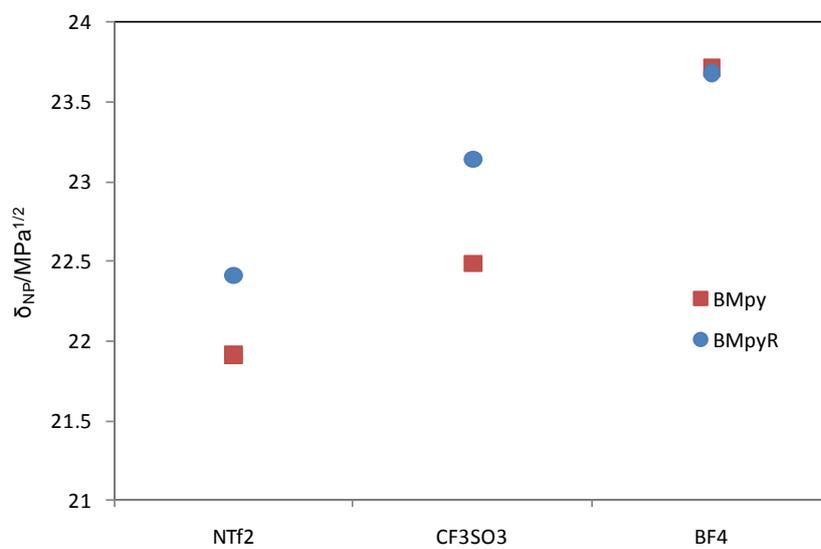


Figure 23 - Values for non-polar solubility parameters for $[C_4Mpy][X]$ (■) and for $[C_4MpyR][X]$ (●).

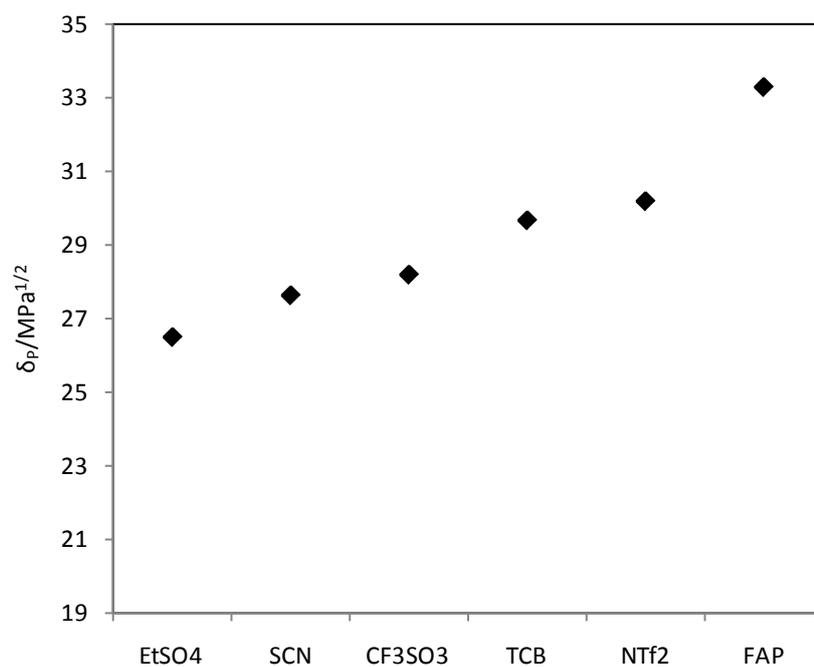


Figure 24 – Values for polar solubility parameters for $[\text{C}_2\text{MIM}][\text{X}]$.

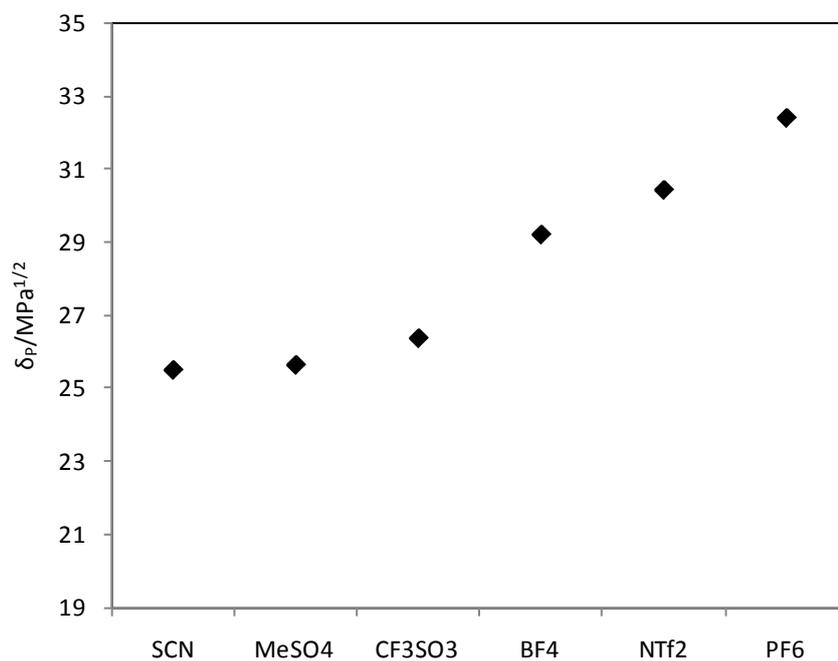


Figure 25 - Values for polar solubility parameters for $[\text{C}_4\text{MIM}][\text{X}]$.

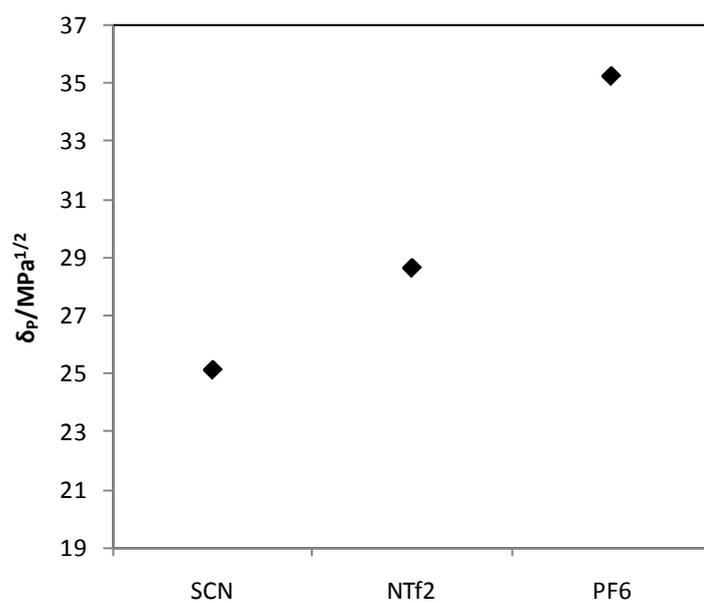


Figure 26 - Values for polar solubility parameters for [C₆MIM][X].

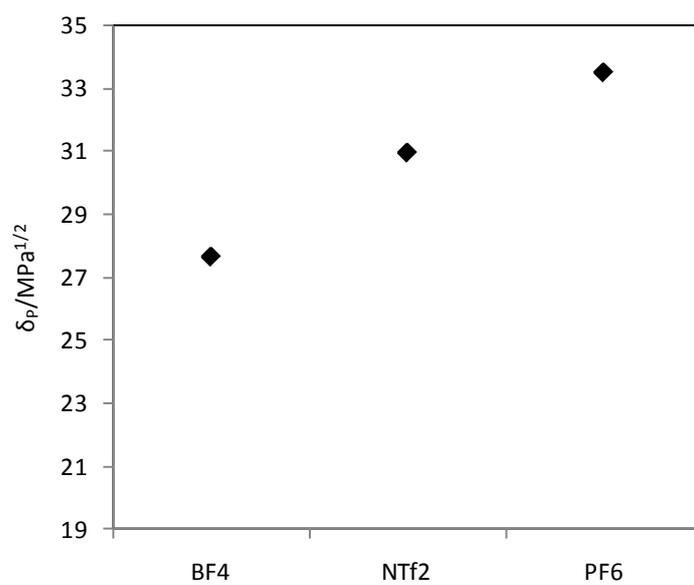


Figure 27 - Values for polar solubility parameters for [C₈MIM][X] .

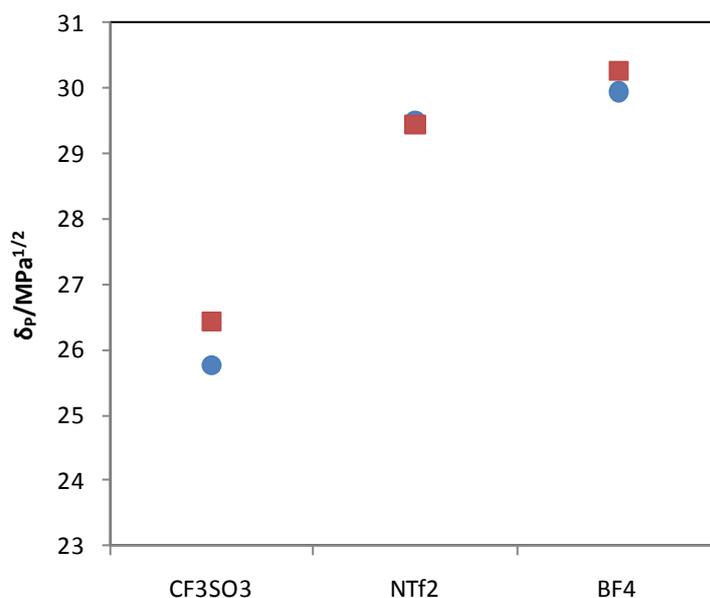


Figure 28 - Values for polar solubility parameters for [C₄Mpy][X] (■) and for [C₄MpyR][X] (●).

Through these graphics it is possible to observe that the highest values for δ_{NP} are, in general for all cations, [SCN]⁻, [BF₄]⁻ and [CF₃SO₃]⁻ and the lowest are for [NTf₂]⁻ and [PF₆]⁻. However, for δ_P the highest values are for [NTf₂]⁻ and [PF₆]⁻ for imidazolium cations, and [BF₄]⁻ for pyridinium and pyrrolidinium cations. The lowest values are given by the [CF₃SO₃]⁻ anion in pyridinium and pyrrolidinium cations and by [SCN]⁻ or [BF₄]⁻ in imidazolium cations.

The solubility of ILs in solvents is influenced by the hydrophobicity of the anions. In some studies^[106-107] it was mentioned that the hydrophobicity followed the order: [BF₄]⁻ < [PF₆]⁻ < [NTf₂]⁻. This order is obeyed by the values obtained for non-polar solubility parameters but the same is not observed for the polar solubility parameters.

These non conformities could be explained by the lack of experimental data, especially for mutual solubilities in alcohols and the fact that measures of activity coefficients at infinite dilution, were made by two different techniques (dilutor technique or gas-liquid chromatography) and were not distinguished on calculation of the overall value for solubility parameter. Dobryakov et al^[54], stated that the technique itself may be the cause for the scattering of the data. Another reason, which probably is the most important, is the limitations of the Hildebrand theory which is based on one-dimensional solubility parameter without detailing molecular polarity or specific interactions.

To confirm the results here obtained and to obtain further information about the solubility parameters of ionic liquids aiming at clarity some issues, the use of other property to estimate solubility parameters was attempted and, according to the discussed above, the viscosity was chosen.

1.2 VISCOSITY

Table 6 - Solubility parameters organized by the cation of the IL using the viscosity for the estimation, T=298 K.

Anion	Cation	$\delta / \text{MPa}^{1/2}$	Anion	Cation	$\delta / \text{MPa}^{1/2}$
PF ₆	C ₂ MIM	29.975	Cl	C ₆ MIM	31.921
	C ₆ MIM	28.805		C ₈ MIM	29.051
	C ₈ MIM	27.158		THTDP	18.593
BF ₄	C ₂ MIM	31.322	CF ₃ SO ₃	C ₂ MIM	28.868
	C ₄ MIM	30.413		C ₄ MIM	31.039
	C ₆ MIM	28.590			
	C ₈ MIM	27.607	NO ₃	C ₈ MIM	29.098
	C ₄ py	31.122			
	C ₄ Mpy	30.019	Ac	C ₄ MIM	32.110
	C ₄ MpyR	24.474			
NTF ₂	C ₁ MIM	28.165	MeSO ₄	C ₄ MIM	29.867
	C ₂ MIM	27.273			
	C ₄ MIM	26.407	EtSO ₄	C ₄ MIM	29.904
	C ₆ MIM	25.472			
	C ₈ MIM	24.671	DCA	C ₄ MIM	27.565
	C ₄ MpyR	26.450		THTDP	18.621
	C ₄ py	26.797			
	butyltrimethylammonium	27.612	C(CN) ₃	C ₄ MIM	26.396

Table 7 - Solubility parameters organized by the anion of the IL using the viscosity for the estimation, at T=298 K.

Cation	Anion	$\delta / \text{MPa}^{1/2}$	Cation	Anion	$\delta / \text{MPa}^{1/2}$
C ₄ MIM	PF ₆	29.975	C ₈ MIM	PF ₆	27.158
	BF ₄	30.413		BF ₄	27.607
	NTF ₂	26.407		NTF ₂	24.671
	CF ₃ SO ₃	31.039		Cl	29.051
	Ac	32.110		NO ₃	29.098
	MeSO ₄	29.867	C ₄ py	NTF ₂	26.797
	EtSO ₄	29.904		BF ₄	31.122
	DCA	27.565	C ₄ MpyR	NTF ₂	26.450
C(CN) ₃	26.396	BF ₄		24.474	
C ₆ MIM	PF ₆	28.805	THTDP	DCA	18.621
	BF ₄	28.590		Cl	18.593
	NTF ₂	25.472	C ₂ MIM	BF ₄	31.322
	Cl	31.921		CF ₃ SO ₃	28.868
				NTF ₂	27.273

For the estimation of Hildebrand solubility parameter now using viscosity data, equation 31 was used.

In this calculation the proportionality constant, K_v , has different values according to the anion that built the ionic liquid, if it has the anion [NTf₂]⁻ the proportionality constant has the value of 7.8 otherwise it has the value of 6.4. The ideal gas constant has the value of 8,314 cm³.MPa.mol⁻¹.K⁻¹, h is Plank's constant with the value of 6.64x10⁻³⁴ J.s, N_A is Avogrado's number 6.02x10²³mol, V is the molar volume in cm³.mol⁻¹ and η is the dynamic viscosity in units of cP. The temperature for this calculation was 298.15K.

The values of η were collected through a bibliographical research of the available data published.^[19, 45, 50, 108-229] This research was complemented with the collection of density and molar mass (**Appendix C**) values which allow the calculation of the molar volume through the following equation,

$$V = \frac{M_r}{\rho} \quad (35)$$

In some cases, the collected data for viscosity does not contain values for the temperature 298.15K. In these cases, a group contribution method for the prediction of the viscosity

proposed by Gardas and Coutinho^[12] at the desired temperature was used. The approach used was,

$$\ln(\eta) = A_{\eta} + \frac{B_{\eta}}{T - T_{0\eta}} \quad (36)$$

where A_{η} , B_{η} and $T_{0\eta}$ are adjustable parameters. This approach was based on the Vogel-Tammann-Fulcher (VTF) equation, also described in the same work.

This method is quite different from the estimation of solubility parameters using the activity coefficients at infinite dilution. The previous method was based on data from binary systems while this method is based only on data for pure ionic liquid in question.

With this approach there are no influences of a second compound on the final value of the solubility parameter and it is possible to obtain an evaluation of the behavior of the pure ionic liquid without interferences. Unlike the previous approach this leads to a single value of the solubility parameter.

Doing the same analysis as with solubility parameter using the activity coefficients at infinite dilution, the result will be evaluated in three aspects beginning with alkyl chain length of the cation, cation family, and finally, anion type. In this evaluation, the solubility parameter of water is again used as reference.

Analyzing table 6 it is possible to observe the tendency of ionic liquids with alkyl chain length of the cation and also with the cation family. In general, the solubility parameter decreases with the addition of a methyl group in the chain of the cation (CH_2) as shown in

Figure 29.

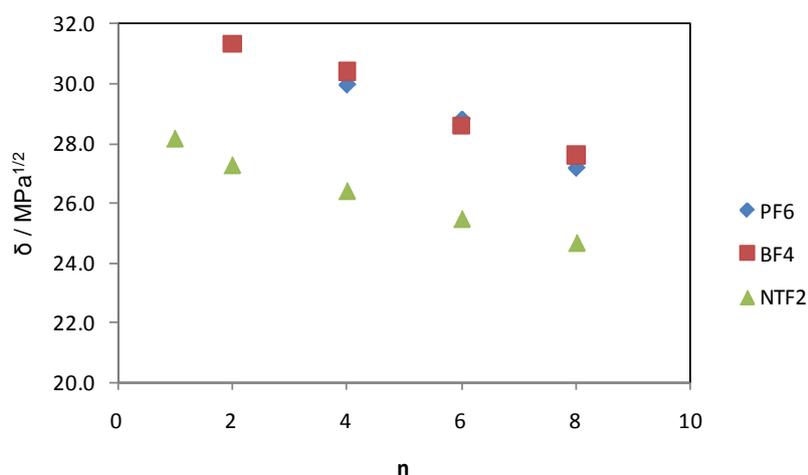


Figure 29 – Effect of the alkyl chain length in $[\text{C}_n\text{MIM}][\text{X}]$.

As for the effect of the cation family, it is only possible to analyze cations with the common anions, $[\text{BF}_4]^-$ and $[\text{NTf}_2]^-$. The tendency imidazolium>pyridinium>pyrrolidinium is verified in the case of $[\text{BF}_4]^-$, but the same is not observed for $[\text{NTf}_2]^-$ where the solubility parameter increase slightly from imidazolium to pyrrolidinium as shown in the following figure.

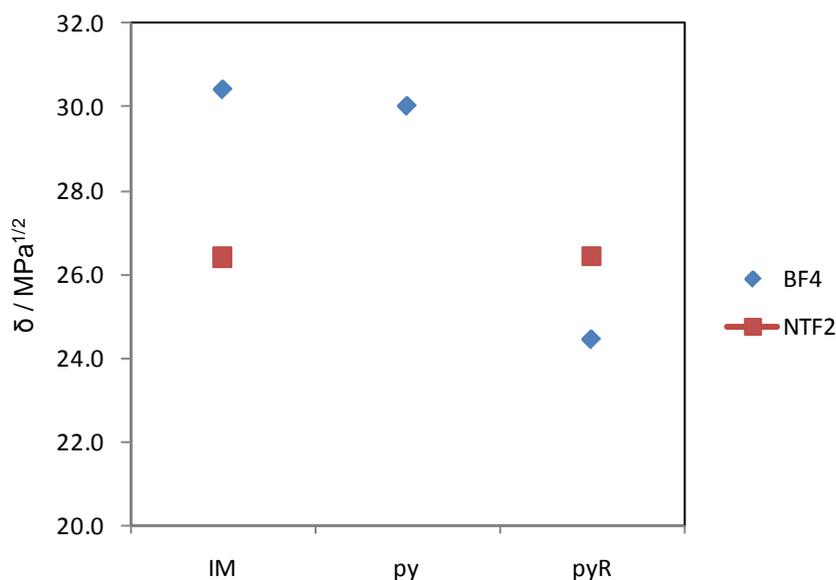


Figure 30 – Effect of the cation family in the solubility parameter for $[\text{C}_4\text{MX}][\text{X}]$.

It is also possible to observe for the anion $[\text{BF}_4]^-$ that when the cation pyridinium has more groups substituting the hydrogen atoms, the solubility parameter is lower as can be observed in Table 6 for $[\text{C}_4\text{py}]^+$ and $[\text{C}_4\text{Mpy}]^+$.

In Table 7, it is possible to evaluate the solubility parameter according to the effect of the anion in the behavior of ionic liquid. In general, for imidazolium, pyridinium and pyrrolidinium cation the tendency is $[\text{NTf}_2]^- < [\text{BF}_4]^-$. For imidazolium cations, with different alkyl chain length the tendency $[\text{NTf}_2]^- < [\text{CF}_3\text{SO}_3]^- < [\text{PF}_6]^- < [\text{BF}_4]^-$ is verified, though there is an exception observed for $[\text{C}_6\text{MIM}]^+$ since $[\text{PF}_6]^- > [\text{BF}_4]^-$ which could not be relevant since the values are similar. This analysis of Table 7 may be seen with a better detail in the following **Figures 31 to 34**.

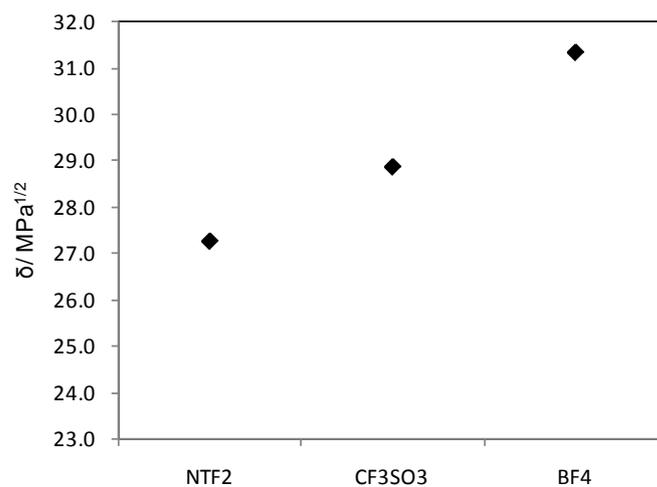


Figure 31 - Effect of the anion for $[\text{C}_2\text{MIM}][\text{X}]$.

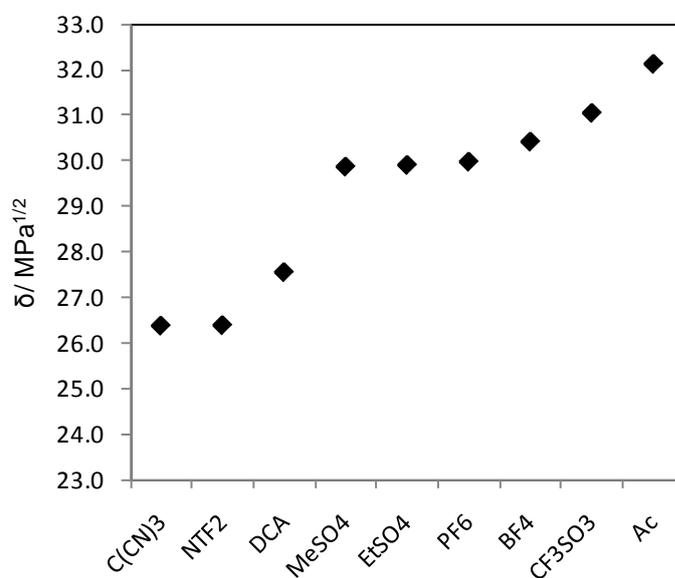


Figure 32 – Effect of the anion for $[\text{C}_4\text{MIM}][\text{X}]$.

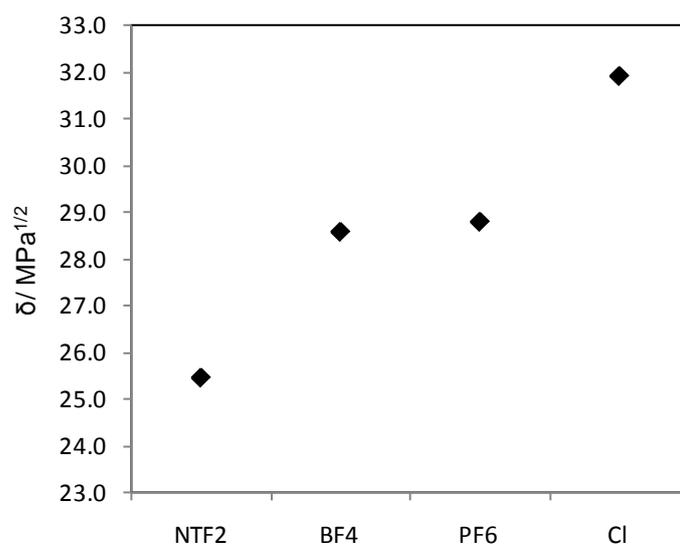


Figure 33 - Effect of the anion for $[\text{C}_6\text{MIM}][\text{X}]$.

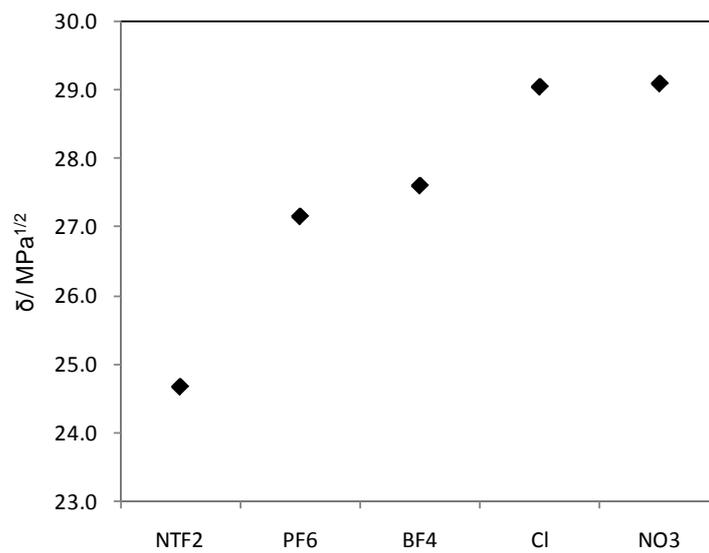


Figure 34 - Effect of the anion for $[\text{C}_8\text{MIM}][\text{X}]$.

1.3 COMPARISON BETWEEN METHODS

Aiming at understanding of how an ionic liquid performs without interference of the medium, it was made a comparison of the values of solubility parameters based on the viscosity which hypothetically are representative of the behavior of the ionic liquid, with the values obtained for activity coefficients at infinite dilution, representing the tendency for the three solubility parameters, i.e., δ_{NP} , δ_P and $\delta(\text{viscosity})$. The comparison was made for three aspects, the effect of the alkyl chain cation, cation family and anion type as may be seen in **Figures 35 to 37**.

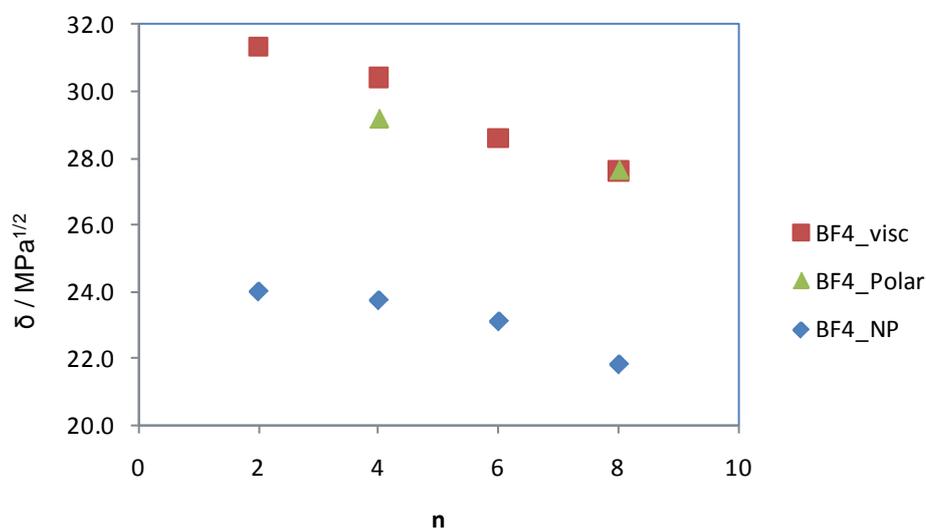


Figure 35 - Representation of the values of solubility parameters obtained from different data evaluating the effect of the alkyl chain of the cation.

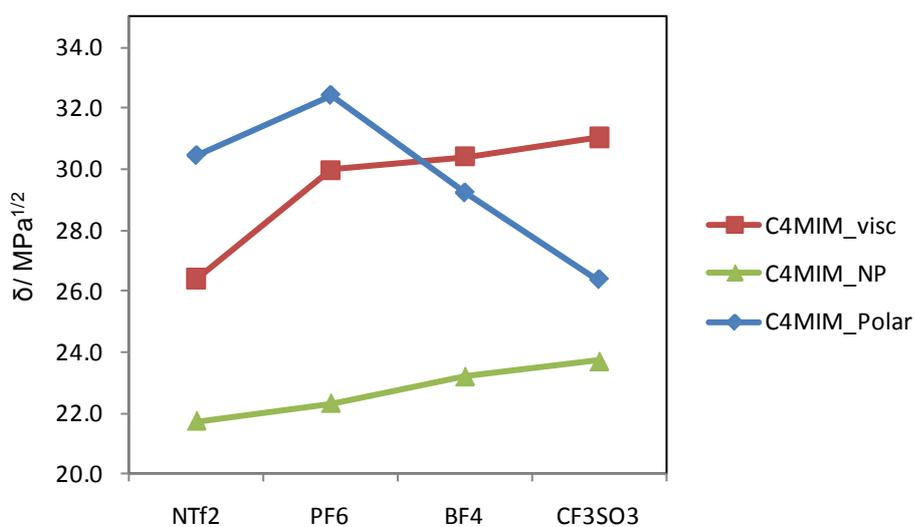


Figure 36 – Representation of the values of solubility parameters obtained from different data evaluating the effect of the anion in [C₄MIM][X].

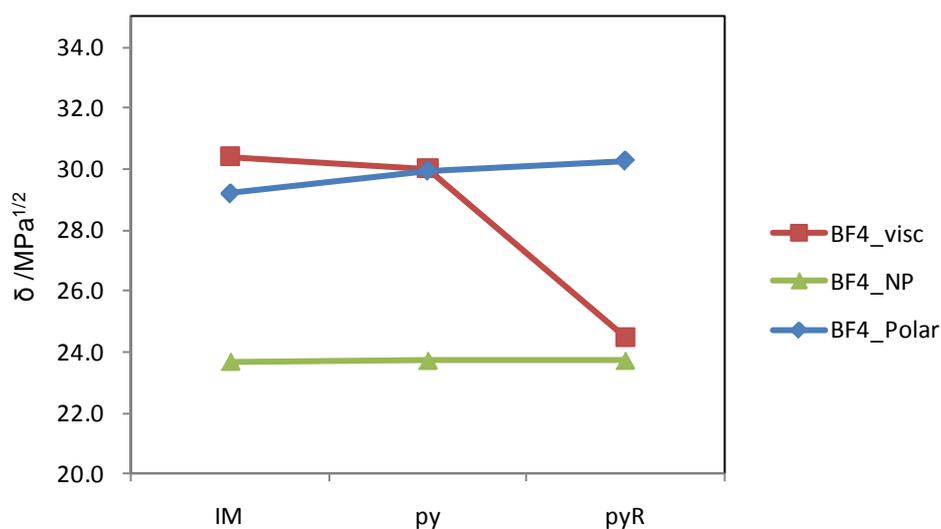


Figure 37 - Representation of the values of solubility parameters obtained from different data evaluating the effect of the cation family in [C₄MX][BF₄].

From these figures it is possible to observe that the solubility parameters based on polar compounds are closer to those obtained for solubility parameter using viscosity data. Nevertheless, the trend observed is more similar with the tendency of solubility parameters obtained with non-polar solvents as shown in Figure 35. Thus, is it possible to say that ionic liquids perform predominantly as polar molecules since the values for solubility parameter are closer to the solubility parameter of water, but how the cation or the anion

influence the solubility parameter of an ionic liquid is not coherent with the solubility parameters estimated with activity coefficient at infinite dilution for polar compounds.

The non conformities observed for solubility parameters obtained with polar compounds may be explained by the fact that, though the Hildebrand solubility parameter can predict solution relations without detailing molecular polarity or specific interactions, ionic liquids having complex structures which lead to complex interactions, the Hildebrand solubility parameter is not enough to capture the complexity of these interactions.

1.4 EXPERIMENTAL PROCEDURE

The experimental measurements of the solubility were carried aiming at investigating if the chameleonic effect observed above was also observed in solubilities. For that purpose the measurement of solubilities for 1-butyl-3-methylimidazolium in mixtures of water and 1-propanol and mixtures of toluene and 1-propanol were carried. The results are represented in the following figures and the data compiled in a table on the **Appendix D**.

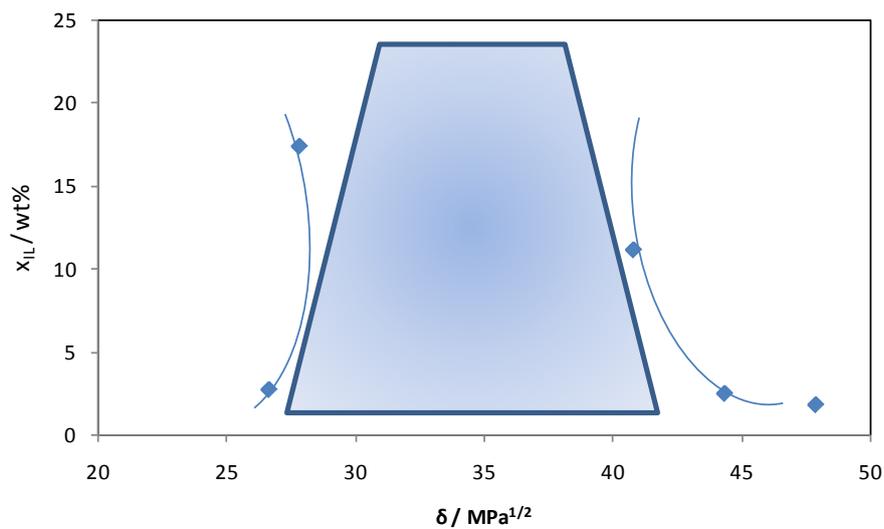


Figure 38 – Mass fraction of Ionic Liquid, $[\text{C}_4\text{MIM}][\text{PF}_6]$ obtained for different compositions of 1-propanol with water.

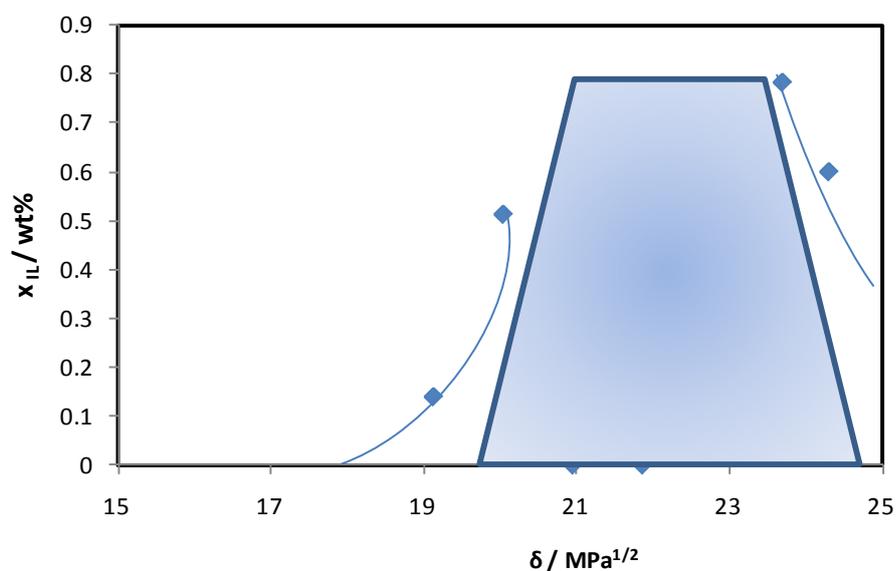


Figure 39 – Mass fraction of Ionic Liquid, [C₄MIM][PF₆] obtained for different compositions of 1-propanol with toluene.

To obtain these graphics, the experimental data were plotted against the values of solubility parameters obtained by equation 16, defined by Jouyban-Gharamaleki and Bustamante approach according to volume fraction for each solvent within the mixture.

In Figure 38, is possible to identify a zone of complete miscibility which, being the mixture of water and 1-propanol, gives the polar solubility parameter, δ_P . In the case of Figure 39, the mixture is 1-propanol and toluene and the maximum solubility is representative of the non-polar solubility parameter, δ_{NP} . The zone of miscibility in the first case goes from 27 to 42 MPa^{1/2}. For the second case it goes from 20 to 25 MPa^{1/2}.

In the case of the solubility in a mixture water and 1-propanol, comparing the values obtained in the estimation of the solubility parameter namely, $\delta_P=32.4$ MPa^{1/2}, $\delta_{NP}= 22.34$ MPa^{1/2} and $\delta=29.98$ MPa^{1/2} (the last obtained from viscosity data), with the solubility parameter of the zones of complete miscibility, the value of δ_P and the solubility parameter estimated from viscosity data are coherent with these values. The same is true for the solubility parameters based on the non polar fluids and the miscibility region on the 1-propanol and toluene. This shows the coherence between the solubility and the activity coefficients at infinite dilution based approaches for the estimation of the solubility parameters and confirms the presence of a chameleonic behavior in ionic liquids that results from their amphiphilic character.

CONCLUSIONS

The determination of a scale of solubility parameters with the purpose of facilitate choosing solvents that better perform given a specific mixture, has great importance and could became a valuable tool for separation processes. Associated to separation processes, ionic liquids exhibit unique properties, as solvents, that enable to overcome problems associated with the production of bioethanol or biobutanol from renewable resources like lignocelluloses. In this work, to predict solubility of ionic liquids, the Hildebrand solubility parameter was used and estimated from activity coefficients at infinite dilution and viscosity.

During the calculation of Hildebrand solubility parameter with activity coefficients at infinite dilution, it was noticed two different behaviors in ILs, leading to the suggestion that they would present a chameleonic behavior as defined by Hoy's theory^[29]. This effect is related to the solvation of the molecules in the ILs. The solvation in different regions of the IL influences greatly the value of solubility parameter and therefore leads to the estimation of two solubility parameters, one using data from non-polar solvents, δ_{NP} , and the other using data from polar solvents, δ_P .

Through the estimation of solubility parameters using the viscosity data was possible to evaluate the ionic liquid without interference of the second compound, since on its estimation only data for pure ionic liquids is needed. This estimation showed that, in comparison with the results obtained with activity coefficients at infinite dilution, ionic liquids act predominantly as polar molecules, leading to values that are closer to the values obtained for δ_P , though the trend with the ILs is similar to the behavior obtained for δ_{NP} .

Some non-conformities were identified in the description of the behavior of ionic liquids using activity coefficients at infinite dilution in the case of the solubility parameter for polar families. These non-conformities may be explained by the fact that the Hildebrand solubility parameter (one-dimensional) does not detail molecule polarity or specific interactions and the structure of ionic liquids is clearly more complex than it is taken into account. In this matter, it would be interesting to use Hansen's theory^[29], where the solubility parameter is now tridimensional taking account each interaction present in the mixture.

The experimental procedure worked as a complementary study which allowed the confirmation of the behavior observed in the solubility parameter estimated by activity coefficients at infinite dilution.

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APPENDIXES

APPENDIX A

This appendix contains the data of the pure components, the solvents, collected in *CRC Handbook of Solubility Parameter other Cohesion Parameter*^[29], namely Molar Volume and the Hildebrand solubility parameter at 298 K.

Solvent	Vmolar(cm ³ .mol ⁻¹)	δ(MPa ^{1/2})
hexane	131,6	14,9
heptane	147,4	15,1
benzene	89,4	18,8
toluene	106,8	18,2
methanol	40	29,6
ethanol	58,7	26
tetrachloromethane	97,1	17,6
ethyl acetate	98,5	18,6
1-butanol	92,8	23,3
2-butanone	90,1	19
acetone=2-propanone	74	20,2
acetonitrile	52,6	24,3
propane	89,4	13,1
1-hexene	125,9	15,1
ethylbenzene	123,1	18
1-pentanol	108,7	22,3
1-propanol	75,2	24,3
octane	163,5	15,6
pentane	116,1	14,3
methylcyclohexane	128,3	15,9
p-xylene	123,9	18
o-xylene=1-2-dimethylbenzene	121,2	18
dichloromethane	63,9	20,3
chloroform	80,7	19
2-butanol	92	22,1
water	18	47,9
diethyl ether	104,8	15,8
1,4-dioxane	85,7	20,5
ethyl acetate	98,5	18,1
2-propanol	76,8	23,5
acetylacetone=2,4 pentanedione	117,7	19,5
propane	85	11,8

APPENDIX B

This appendix contains the data collected for activity coefficients and solubility parameters for solvents, graphically represented in Figures 8 to 10.

Table B1. Data for activity coefficients at infinite dilution of butyl-methylimidazolium hexafluorophosphate and data for solubility parameters of solvents used in Figure 8.

γ^∞	$\delta_{\text{solvent}} / \text{MPa}^{1/2}$
2.13	18.8
3.37	18.2
5.21	18
1.23	19
2.03	29.6
2.84	26
1.63	19
1.04	20.3
5.81	17.6
1.14	20.5
3.77	24.3
3.43	23.5
5.14	23.1

Table B2. Data for activity coefficients at infinite dilution of butyl-methylimidazolium tetrafluoroborate and data for solubility parameters of solvents used in Figure 9.

γ^∞	$\delta_{\text{solvent}} / \text{MPa}^{1/2}$
0.72	29.6
1.39	26
2.48	24.3
1.15	20.3
6.09	17.6
1.19	20.2
0.74	24.3
3.34	18.6
3.68	23.3
5.91	22.3

Table B3. Data for activity coefficients at infinite dilution of ethyl-methylimidazolium bis(trifluoromethylsulfonyl)imide and data for solubility parameters of solvents used in Figure 10.

γ^∞	$\delta_{\text{solvent}} / \text{MPa}^{1/2}$
29.6	1.31
26	1.76
24.3	2.34
23.5	2.05
23.3	3.13
18.8	1.19
18.2	1.79
17.6	3.22

APPENDIX C

In this appendix values of density used to calculate the molar volume, for different ionic liquids, needed for equation 35 are compiled in a table.

Table C1 – Density for different ionic liquids at 298.15 K.

Anion	Cation	$\rho / \text{g.cm}^{-3}$	Anion	Cation	$\rho / \text{g.cm}^{-3}$
PF6	BMIM	1.367	Cl	HMIM	1.040
	HMIM	1.294		OMIM	1.009
	OMIM	1.236		THTDP	0.890
BF4	EMIM	1.28	CF ₃ SO ₃	EMIM	1.385
	BMIM	1.202		BMIM	1.298
	HMIM	1.145	NO ₃	OMIM	1.064
	OMIM	1.104			
	Bpy	1.214	Ac	BMIM	1.053
	BMpy	1.182			
	BMpyR	1.394			
NTF2	C1MIM	1.57	MeSO ₄	BMIM	1.212
	EMIM	1.519	EtSO ₄	BMIM	1.238
	BMIM	1.438			
	HMIM	1.371	DCA	BMIM	1.063
	OMIM	1.321		THTDP	0.899
	bmpyR	1.396			
	Bpy	1.449	C(CN) ₃	BMIM	1.047
	butyltrimethylammonium	1.393			

APPENDIX D

This appendix contemplates the data that gives origin to Figures 38 and 39, respectively Table D1 and Table D2.

Table D1 – Table contemplating the data of solubility of [C₄MIM][PF₆] in a mixture of 1-propanol and water, for different compositions.

1-propanol / vv%	δ / MPa ^{1/2}	x _{IL} / wt%
0	47.9	1.875
15	44.36	2.556
30	40.82	11.202
45	37.28	Miscible
60	33.74	Miscible
85	27.84	17.435
90	26.66	2.787

Table D2 - Table contemplating the data of solubility of [C₄MIM][PF₆] in a mixture of 1-propanol and toluene, for different compositions.

1-propanol / vv%	δ / MPa ^{1/2}	x _{IL} / wt%
100	24.300	0.600
85	19.115	0.140
70	20.03	0.513
55	20.945	miscible
40	21.86	miscible
25	22.775	miscible
10	23.69	0.782