Universidade de Aveiro Departamento de Química
2007

Sónia Patrícia
Marques Ventura

EQUILÍBRIOS GÁS LÍQUIDO A ALTAS PRESSÕES

Gas Líquid Equilibria at High Pressures

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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em medição de equilíbrios gás líquido a altas pressões, realizada sob a orientação científica do Dr. João Coutinho Professor associado do Departamento de Química da Universidade de Aveiro e Dra. Ana Dias Estagiária de Pós doutoramento no Instituto de Biotecnologia e Bioengenharia da Universidade do Minho

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Dedico este trabalho a todos os que me deram força para começar este percurso de aprendizagem que é para toda a vida.

Aos meus pais pelo apoio incondicional

À minha irmã pelos maus momentos que passou para me ajudar

Aos meus sobrinhos por todas as traquinices ao longo deste tempo

Aos meus amigos pelas gargalhadas e boa disposição

Aos meus orientadores pela paciência

o júri

presidente

Prof. Dr. José Joaquim Costa Cruz Pinto
Professor Catedrático da Universidade de Aveiro

Prof. Dr. João Manuel da Costa e Araújo Pereira Coutinho
Professor Associado com Agregação da Universidade de Aveiro

Professora. Dra. Isabel Maria Almeida Fonseca
Professora Associada da Faculdade de Ciências e Tecnologia da Universidade de Coimbra

Doutora Ana Maria Antunes Dias
Estagiária de Pós-Doutoramento no Instituto de Biotecnologia e Bioengenharia da Universidade do Minho

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palavras-chave

Célula de altas pressões de volume variável, alta pressão, solublidade, sistema ternário, metano,dióxido de carbono, anilina, líquido iónico, água, salting-in, salting-out.

resumo

Este trabalho tem como objectivo a medição da solubilidade de gases em líquidos a altas pressões. Para a realização experimental foi usada uma célula de altas pressões de volume variável e um método de observação directa para a detecção das transições de fase. As condições usadas neste trabalho experimental foram temperaturas entre 276.00 e 373.15 K e pressões ate 100 MPa.

Numa primeira fase foram efectuadas medições de solubilidade de metano em anilina pura e para uma solução aquosa de composição mássica igual a 5% em anilina. A anilina é fundamentalmente usada em processos como a produção de borracha, de poliuretanos, pigmentos e tintas, fármacos, herbicidas e fungicidas. É usualmente produzida através de processos de redução do nitrobenzeno por reacção com o HCl. De facto, esta síntese é um processo químico complexo onde um grande número de processos compete entre si. Alterações nas condições do processo com a possível formação de produtos intermediários podem afectar a eficiência do processo. Para a sua melhoria foi sugerido que o hidrogénio usado fosse simultaneamente produzido e gasto no reactor principal. Neste caso e para a produção do mesmo, era necessário adicionar metano e água ao reactor. Tendo por base a ideia de que as reacções onde o hidrogénio é reagente e produto ocorrem em simultâneo, torna-se clara a importância do estudo da solubilidade do metano em anilina pura e em soluções aquosas desta.

Numa segunda fase foi estudada a solubilidade do dióxido de carbono em soluções aquosas de tri-iso-butil(metil)fosfónio tosilato, com composições molares são de 4, 8 e 12% em líquido iónico. Este pertencente à família dos fosfónios. Possui uma viscosidade e densidade elevadas, é térmica e quimicamente estável e ainda possui uma elevada polaridade. Apresenta uma miscibilidade completa em água e nos solventes mais usuais, como o diclorometano e tolueno, não sendo no entanto míscivel em hexano. O tri-iso-butil(metil)fosfónium tosilato é usado como solvente nos processos de hidroformilação de olefinas e ainda em processos de captura e conversão de dióxido de carbono.

Neste trabalho experimental, a temperatura e a pressão foram inicialmente aumentadas até o sistema atingir o equilíbrio. A pressão é diminuída lentamente até se verificar o aparecimento/desaparecimento da última bolha de gás. A pressão à qual a última bolha de gás desaparece representa a pressão de equilíbrio para aquela temperatura. Este procedimento foi efectuado para vários sistemas e várias temperaturas

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keywords

Variable volume high pressure cell, high pressure, solubility, ternary system, methane, carbon dioxide, aniline, ionic liquid, water, salting-in, salting-out.

abstract

The aim of this work is the measurement of the solubilities of different gases in different liquids systems at high pressures. A variable volume high pressure cell was used to perform the measurements based on the visual synthetic method for the detection of phase transitions. The conditions used in this work were temperatures ranging from 276.00 to 373.15 K and pressures up to 100 MPa.

The first step of this work was the measurement of methane's solubility in pure aniline and for one aqueous solution of 5% (w/w) in aniline. The main applications of aniline are the manufacture of polyurethane, rubber, dyes and pigments, drugs and agrochemicals (herbicides and fungicides).
This compound is normally produced by reduction of nitrobenzene by reactio
with HCl. In fact, that synthesis is a complex chemical process where a number
competing processes contribute to the final product. Changes in process conditions wit
the possible formation of intermediates can act as catalyst poisons that change th
process's efficiency. For the improvement of the production process it wa
suggested that the hydrogen, used for the reduction of the nitrobenzene, coul
be simultaneously generated and used in the main reactor. In this case for the *i*
situ production of hydrogen it would be necessary the addition of methane an
water in the reactor. Having in mind that these reactions occur simultaneously, i
becomes clear the importance of studying the solubility of methane in anilin
and in its aqueous solutions.

In the second step the solubility of carbon dioxide in aqueous solutions of tri-iso-butyl(methyl)phosphonium tosylate with molar compositions of 4, 8 and 12% molar of ionic liquid, was studied. This compound belongs to the phosphonium - based ionic liquids family. It is characterized by a high viscosity and density. It is thermal and chemically stable and has a high polarity. This compound is totally miscible with water as well as with common organic solvents such as diclorомethane and toluene but is not miscible with hexane.
The main applications of Tri-iso-butyl(methyl)phosphonium tosylate are like solvents in the hydroformylation of olefins and in processes of capture and conversion of carbon dioxide.

In this experimental work, temperature and pressure were slowly increased until the system becomes homogeneous. After that, the pressure is slowly decreased until the appearance/disappearance of the last bubble of gas. The pressure at witch the last bubble disappears represents the equilibrium pressure for that temperature. This procedure was repeated for several systems and several temperatures.

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1. Part

GENERAL INTRODUCTION

The application of high pressures to industrial processes has led to engineering operations that frequently require knowledge of some thermodynamic properties, like solubilities of gases in liquids at pressures higher than those for which such data is ordinarily available. This work focuses on the study of gas solubilities in aqueous solutions of aniline and tri-iso-butyl(methyl)phosphonium tosylate, thus a brief discussion of the characteristics and properties of these compounds is useful to the understanding of the results presented below.

1.1. ANILINE

Aniline, whose IUPAC name is benzenamine, is a primary aromatic amine that is a weak base and forms salts with mineral acids. Aniline was first obtained in 1826 by the destructive distillation of *indigo*. Today it is prepared synthetically and is one of the most important organic bases. Pure aniline is a highly toxic, oily, colourless liquid with a distinctive odour. Its main properties[1] are reported in Table 1.1.1

Table 1.1.1. Properties of aniline.

PROPERTIES OF ANILINE	
Melting point (ºC)	-6
Boiling point (ºC)	184
Relative vapour density at 185ºC	3.22
Vapour pressure at 25ºC (mmHg)	0.7
Specific gravity	1.082
Flash point (ºC)	70
Explosion limits (%)	1.3 - 11
Auto-ignition temperature (ºC)	615

Aniline is a stable compound but incompatible with oxidizing agents, bases, acids, iron an iron salts, zinc and aluminium. This aromatic compound is light sensitive, hygroscopic, moderately soluble in water and miscible with alcohol, benzene, chloroform, carbon tetrachloride, acetone and most organic solvents[2].

In acidic solution, nitrous acid converts aniline into a diazonium salt that is an intermediate in the preparation of a great number of dyes and other organic compounds of commercial interest. This aromatic compound participates in many reactions with other compounds, such as the formation of polymers[3, 4] and the synthesis of dimmers[4, 5] and trimers[4]. When aniline is heated with organic acids, it produces amides, called anilides, such as acetanilide from aniline and acetic acid. Monomethylaniline and dimethylaniline can be prepared from aniline and methyl alcohol. Catalytic reduction of aniline yields cyclohexylamine. Various oxidizing agents convert aniline to quinone, azobenzene[4], nitrosobenzene, *p*-aminophenol, and the phenazine dye aniline black[6].

Aniline have a broad range of applications which include polyurethane manufacture, rubber chemicals, dyes and pigments, pharmaceutical products, agrochemicals (herbicides and fungicides), specialty fibers as well as chemicals used in petroleum refining[7].

This compound is prepared commercially by the catalytic hydrogenation of nitrobenzene or by the reaction of ammonia on chlorobenzene, that was originally carried through the reduction of nitrobenzene by reaction with HCl, in presence of dispersed iron generating aniline and iron oxide sludge[8]. This process produces large quantities of waste and was thus replaced by the catalytic hydrogenation of nitrobenzene[8]. A further step for the improvement of the production process was proposed in the 70's by Polinski and Harvey[9] which suggested that the hydrogen, used for the reduction of the nitrobenzene, could be simultaneously generated in the main reactor avoiding the external production, storage and transport of hydrogen. This process was later optimized and patented[10, 11] being carried at high temperature, between 420 and 450 K and high pressures around 1.5- 2.0 MPa. This new process is summarized by the following reactions:

$$CH_4 + 2H_2O \text{ -------- } CO_2 + 4H_2 \qquad (1.1.1)$$

$$C_6H_5NO_2 + 3H_2 \text{ --------- } C_6H_5NH_2 + 2H_2O \qquad (1.1.2)$$

Having in mind that these reactions occur simultaneously, it becomes clear the importance of studying the solubility of methane in aniline and in its aqueous solutions.

The efficient design, scale-up, optimization and control of chemical process such as aniline's production require the understanding of the process's kinetic and thermodynamic behaviour in as much detail as possible. In fact, the catalytic reduction of nitrobenzene to aniline is a complex chemical process where a number of competing processes contribute to the final product. Changes in process conditions with the possible formation of intermediates that can act as catalyst poisons change the process's efficiency. Moreover, the more stringent safety and environmental concerns and the continuously search for optimized process technologies requires the development and application of new or alternative processes in order to meet efficiency, quality and environmental goals.

Given the industrial importance of this compound it is surprising that the literature data about the solubility of gases in aniline is so scarce. Available in the open literature is the data from Lenoir et al.[12] that studied the Henry's constant of several gases including the constant for methane in aniline at the atmospheric pressure and 298.15K.

1.2. IONIC LIQUIDS

Solvents play an extremely important role in many industrial processes, acting as a media for chemical reactions or for the extraction of products. Typically, these solvents are volatile organic compounds (VOCs). The high volatility of these compounds introduces several health, environmental, and economic concerns. As the VOCs volatilize the risk of human exposure through inhalation increases. VOCs have also been found to increase ozone depletion and smog formation. Lastly, the high volatility increases the loss of these costly solvents. Therefore, it is important to find another class of solvents that still meets the needs of industry while limiting environmental and health risks.

Ionic liquids (ILs), a novel class of compounds, a number of which can be considered "green solvents", have been the focus of much research in recent years[13, 14]. Ionic liquids is the term used to refer to organic salts that are liquids in their pure states at ambient conditions[15, 16]. An idea of the variety of cations and anions that could be combined to make an IL is shown in Figures 1.2.1 and 1.2.2.

The cations correspond to the classes of ionic liquids and these include imidazolium, quaternary ammonium, pyrrolidinium, pyridinium, or tetra alkylphosphonium (Figure 1.2.1).

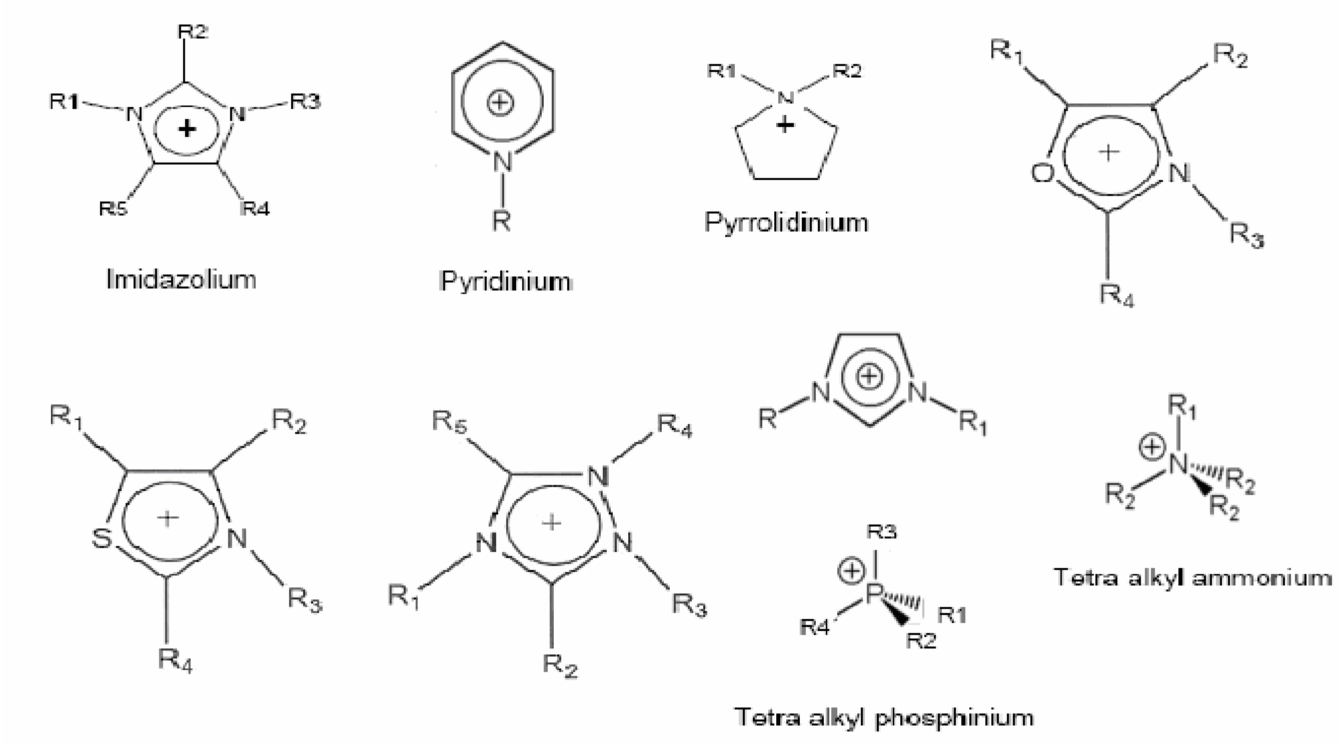

R2
R1
R3
N
+
R5
R4
Imidazolium
⊕
N
R
Pyridinium
R1
R2
N
+
Pyrrolidinium
R1
R2
O
N
R3
R4
R1
R2
S
N
R3
R4
R5
R4
N
N
N
R1
R3
R2
R
N
⊕
N
R1
R3
⊕
P
R4
R1
R2
Tetra alkyl phosphinium
R1
⊕
N
R2
R2
R2
Tetra alkyl ammonium

Figure 1.2.1 Structure of the more common cations in Ionic Liquids. *R* could be methyl, ethyl, butyl, hexyl, octyl or decyl chains[17, 18].

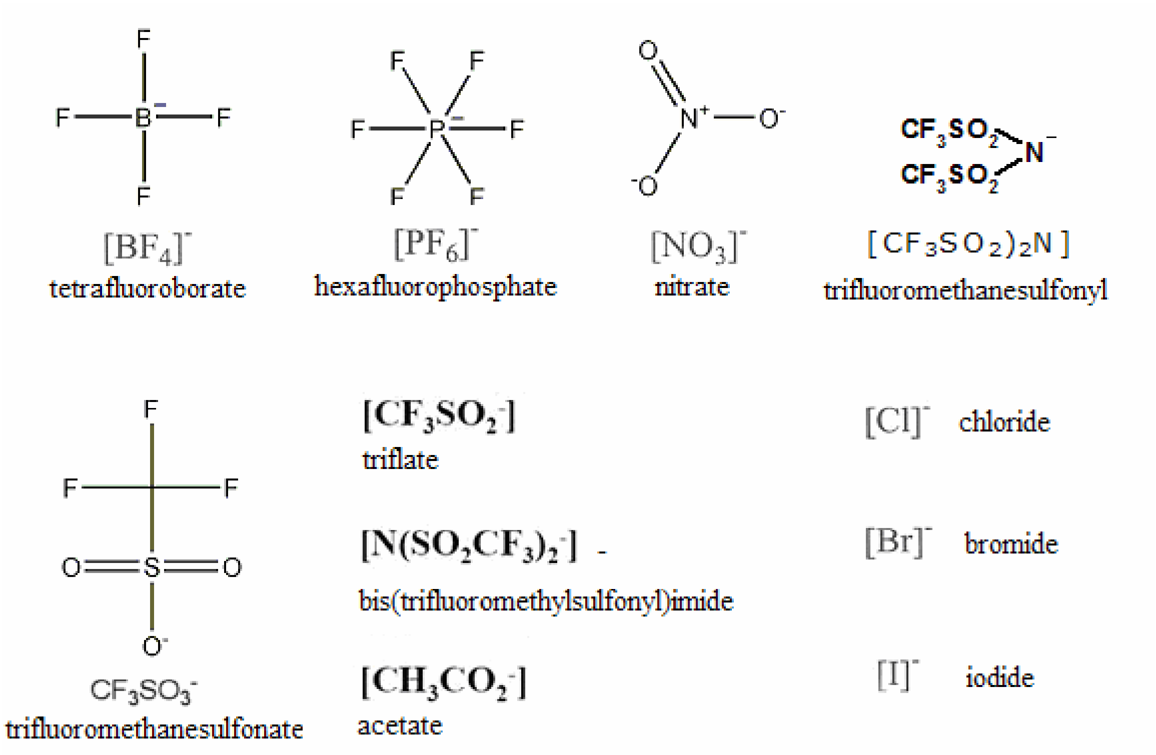

[BF4]-
tetrafluoroborate
[PF6]-
hexafluorophosphate
[NO3]-
nitrate
[CF3SO2)2N]
trifluoromethanesulfonyl
CF3SO3-
trifluoromethanesulfonate
[CF3SO2-]
triflate
[N(SO2CF3)2-] -
bis(trifluoromethylsulfonyl)imide
[CH3CO2-]
acetate
[Cl]- chloride
[Br]- bromide
[I]- iodide

Figure 1.2.2 Structure of the more common anions in Ionic Liquids[17, 19].

In general, Ionic Liquids have many properties that are similar to conventional organic solvents such as good solvency power. Additionally, they have also a wide temperature range (approximately 300ºC) over which they remain liquids and a negligible vapour pressure. These properties depend on the cation, the anion and their substituents[20], therefore making it possible to "tailor" the solvent for a particular application. Researchers have shown that adjusting the structure of either the anion or the cation can have large effects on many properties including melting points and glass transition temperatures[21-26], miscibility with conventional solvents, densities[24, 25, 27], conductivities, viscosities, heat capacities[28, 29], thermal decomposition temperature[22, 23, 25, 30, 31], hydrophobicity, hydrogen-bonding capability[32] and gas and liquid solubilities[33, 34].

Moreover, their insignificant vapor pressures[15, 16] reduces the environmental pollution and highly reduces working exposure hazards, suggesting that ILs should be inherently safer than the traditional organic solvents used in industries[35]. These, allied with their thermal and chemical stability, the halogen and metal free and nonflammable[35] properties turn these compounds in valuable substitutes for traditional solvents.[36]

Based on these properties and in comparison with common solvents, Brennecke and Maginn[37] presented an extensive perspective of the potential industrial applications of ILs in catalytic reactions[38-42], gas separations[43, 44] and liquid–liquid extractions[45, 46]. The knowledge of gas solubility in the reaction media, for example, is required to properly design gas contacting equipment and to determine the intrinsic rate of catalytic reactions. Many of the reactions studied in ILs involve organic liquids or permanent or condensable gases. If a reactant gas has a low solubility in the IL, the mass transfer of the gas into the IL phase will likely be the rate-limiting factor. This limitation would require efforts to be made to increase the interfacial area and/or use high-pressure operations in order to reach the necessary concentration of gas in the IL. In addition to its importance in reactions, understanding the gas solubility process in IL is necessary for assessing the usefulness of ionic liquids in other applications.

The higher solubility of gases in ILs when compared to common solvents aroused the interest of the scientific community to this issue, as recent literature reports.[20, 35, 47-53]

One of the most interesting and valuable application of this property is the possibility of using ILs as CO_2 removal agents from gaseous effluents. This process is usually done through aqueous solutions of secondary amines[54, 55] which have been traditionally used in the natural gas processing industry for the sweetening process removal of acid gases according to the following equation:

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

However, there are several drawbacks associated with the use of alkanolamines as for example the concurrent loss of the volatile amines and the uptake of water into the gas stream, causing intensive energy consumption, cost increases and corrosion problems. In this regard and having in mind the actual concerning to largely reduce the actual CO_2 atmospheric emissions, it is crucial to look for a new kind of sequestering agent(s) preferably characterized by negligible vapour pressure and high stability[56]. ILs have been presented as interesting valuable alternatives to traditional sequestering agents[56,57,58].

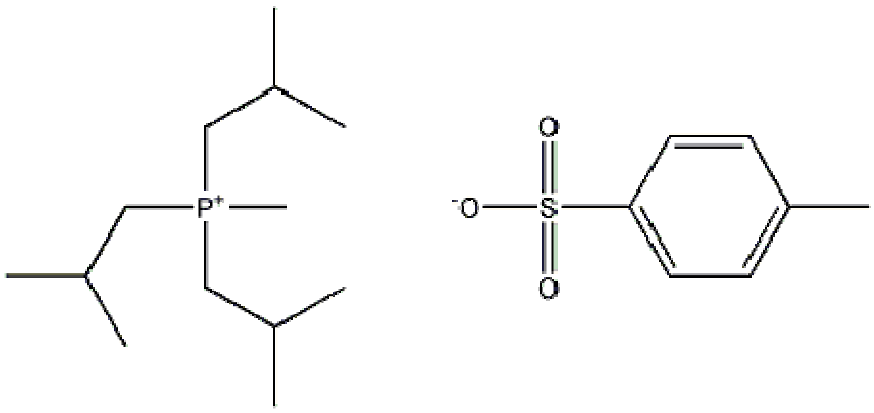
So far the research has been most centred on the study of the solubility of gases in imidazolium based ILs. Gases such as light alkanes[59] and alkenes, oxygen, nitrogen, hydrogen, argon, carbon monoxide and carbon dioxide are among the most studied. Practical examples are given by Dyson et al.[60], in the investigation of the hydrogen's solubility in nine imidazolium, one phosphonium and two pyridinium ILs, Husson et al.[61] and Hert et al.[59] that have investigated the oxygen's solubility in [bmim][BF_4] and [emim][Tf_2N].[62] Finally Buzzeo et al. [63] have studied the fluoroform's solubility in [emim][PF_6].

Particular attention is being given to carbon dioxide due to the interesting behaviour observed when this gas is used as supercritical fluid.[64-67] The successful application of supercritical carbon dioxide for separation and purification of products from ionic liquids by using the gas as a co-solvent in extractions, with subsequent recycle and reuse of the IL[68]. A lot of attention is being given to this issue in the recent literature[64-66, 69]. Another very interesting subject is the use of carbon dioxide like anti-solvent in precipitations. These two applications avoids the problems related with traditional separation techniques such as the loss of solvent, cross-contamination and destruction of thermo-sensible compounds and are the main reason why special attention is being given to this gas[48, 67, 70].

Another very interesting aspect is that, the application of supercritical CO_2 can induce the formation of an additional liquid phase that is rich in IL, even when the original solution is quite dilute in IL. Moreover, besides promoting the separation of IL/organic phases, the technique proved to be able to promote the separation of both hydrophobic and hydrophilic imidazolium based ILs from aqueous solutions[69, 71] with relatively low-pressure gaseous carbon dioxide. For certain P-T-x conditions, ternary CO_2/IL/organic or water systems present a phase split with the appearance of a vapour-liquid-liquid equilibrium (VLLE) characterized by one liquid phase richer in IL, a second liquid phase richer in organic or water and a third gaseous phase rich in CO_2. This behaviour was previously reported in the literature by Aki et al.[48] and Zhang et al.[53] for CO_2 + imidazolium IL + organic and by Scurto et al.[67] and Zhang et al.[71] for CO_2 + imidazolium IL + water ternary systems. The interesting aspect to point out is that the VLLE is observed at relatively mild thermodynamic conditions. At those conditions, a slight increase in pressure enriches each of the phases in a preferential component, promoting the separation of the ternary mixture at economic and safe conditions.

Recently, Ferguson and Scovazzo[72] have shown that imidazolium and phosphonium based ILs have similar solubilities for several gases. Being about ten times cheaper, phosphonium based ILs can represent a low-cost alternative to imidazolium ILs however, their higher viscosities difficult the diffusion of gases through the liquid structure. A possible way to overcome this problem consists in the use of an aqueous solution of the IL instead of the pure compound. Besides reducing the total amount of IL needed this would diminish the IL viscosity.

Considering the potential alternative that phosphonium ILs represent, in this work, the solubility of carbon dioxide in an aqueous solutions of tri-iso-butyl(methyl)phosphonium tosylate, [*i*Bu3MeP][TOS], (CHYPHOS IL 106) (Figure 1.2.3) was studied. The aim of this study is to see how the reduction in the viscosity of the aqueous solutions of Ionic Liquid will affect its capacity to solubilize gases as carbon dioxide.



Tri-iso-butyl(methyl)phosphonium

Tosylate

Figure 1.2.3. Tri-iso-butyl(methyl)phosphonium tosylate, [*i*Bu3MeP][TOS].

Phosphonium - based ionic liquids have some different particularities when compared with imidazolium-based ionic liquids. The phosphonium cation contains four substitutes and the various combinations along with the multitude of various available anions represent an enormous number of possible salts. Of course, not all of such phosphonium salts are liquids at room temperature but by a judicious selection of the alkyl chain and anion, there are numerous phosphonium salts which are liquid at room temperature and many more which fall within the broad general definition of ionic liquids as salts which have low melting points. In this regard, phosphonium salts are much more thermally stable than the corresponding ammonium salts. This is very important for processes which operate at temperatures greater than 100 °C. In addition to being slightly less thermally stable, the imidazolium cation contains protons which are not entirely inert.

Many researchers consider that phosphonium-based ionic liquids are low-cost alternatives to the imidazolium-based ionic liquids for reaction media or separation agents.[72] A comparison between imidazolium and phosphonium based ionic liquids shows that these two families have similar thermodynamic (gas solubility on a volume basis) and transport properties (magnitudes of the diffusivities) [72]. On the other hand alkylphosphonium salts are, in general, less dense than water and this can be beneficial in product work-up steps while decanting aqueous streams which contain inorganic salt by-products.

Tri-iso butyl(methyl)phosphonium tosylate in particular, is prepared from triisobutylphosphine and methyltosylate and consequently is totally halogen free. Due to the presence of the aromatic anion the density is increased and consequently this IL is one of the few phosphonium based ILs with a density greater than water. A plot of density as a function of temperature for this IL is presented in Figure 1.2.4.

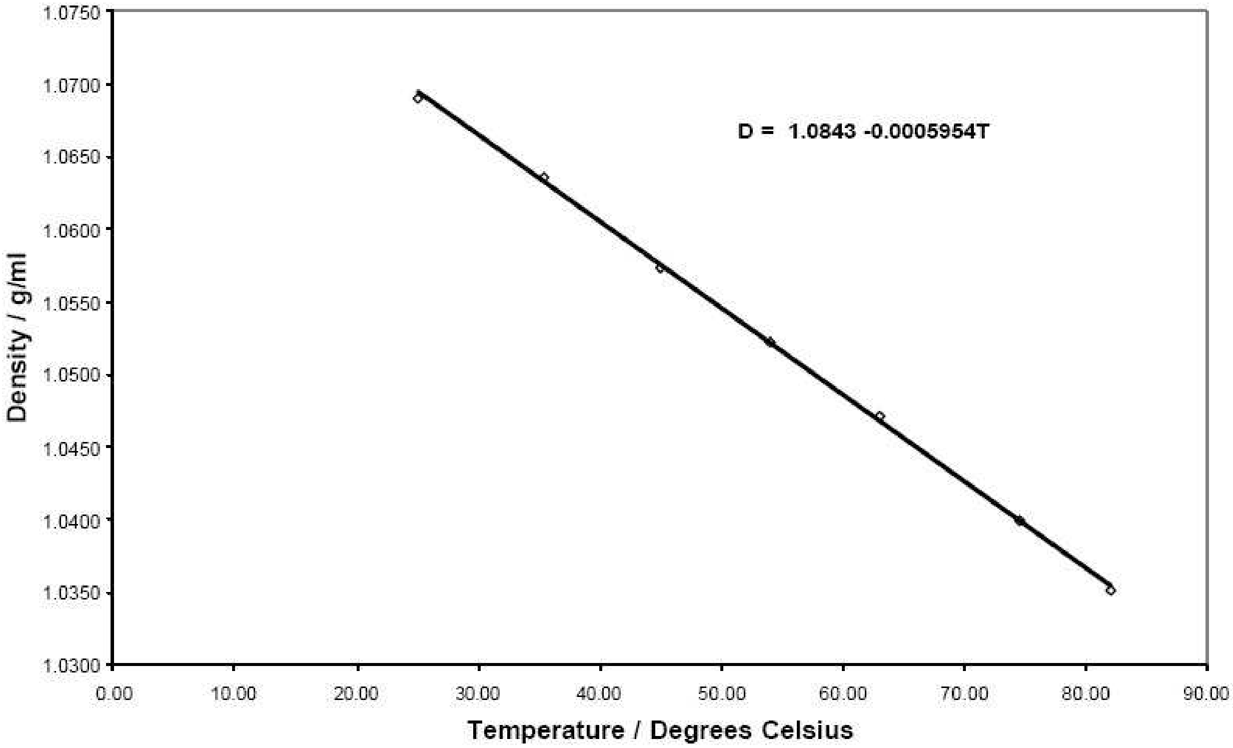


Figure 1.2.4. Effect of the temperature in the density of [*i*Bu3MeP][TOS].[73]

Phosphonium is ten times cheaper than imidazolium-based IL. However, its viscosity is higher when compared to imidazolium and this is an important characteristic that has influence in the application of phosphonium ILs in the industry. This difference in the viscosity is attributed to different microviscosities of ionic liquids. High viscosity means that the diffusion of the gas through the liquid structure is more difficult.[72] The viscosity can be influenced by temperature (Figure 1.2.5) and the presence of water (Figure 1.2.6).

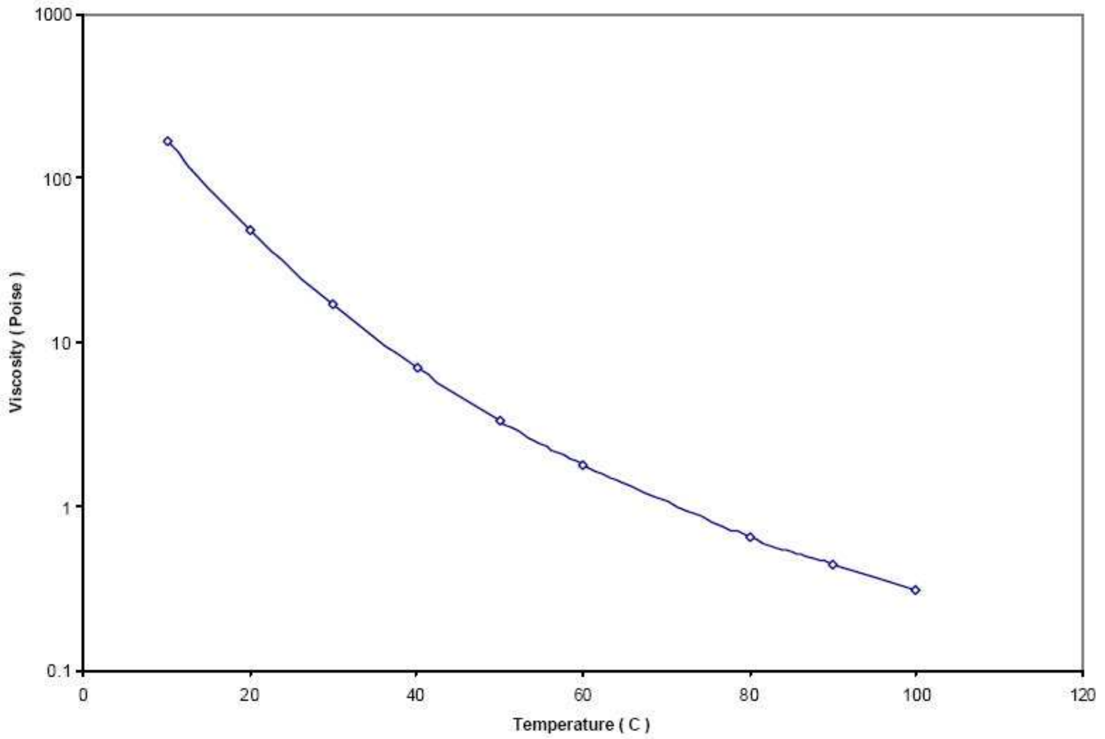


Figure 1.2.5. Effect of the temperature in the viscosity of [*i*Bu3MeP][TOS].[73]

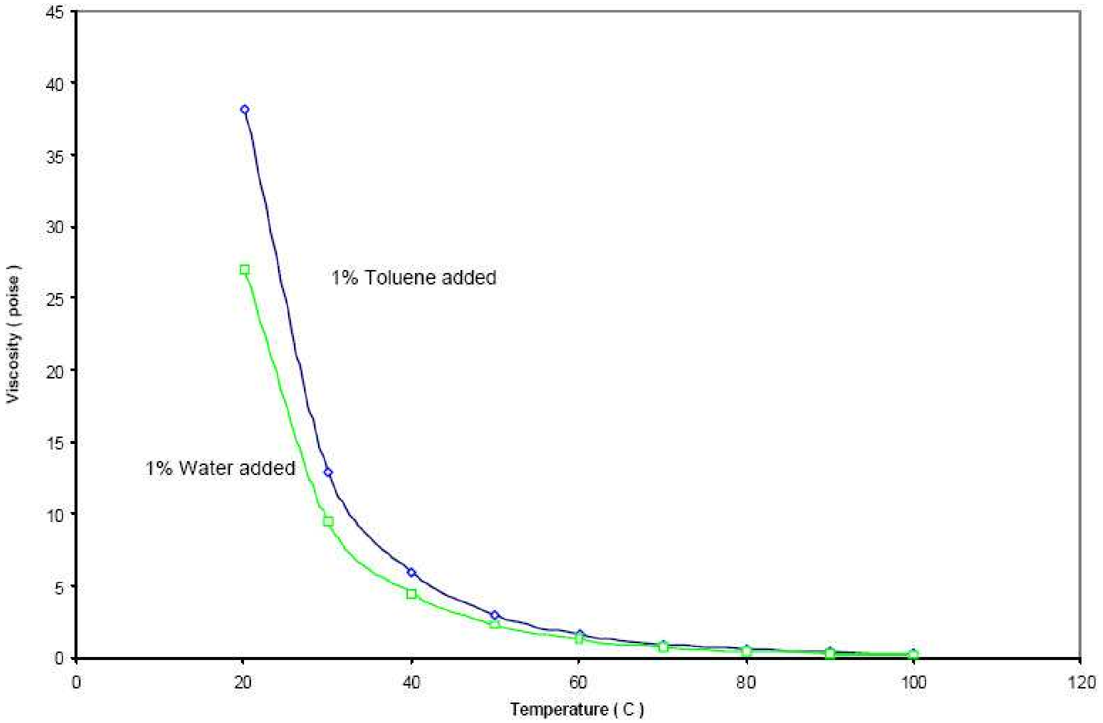


Figure 1.2.6. Effect of water and toluene in the viscosity of [*i*Bu3MeP][TOS].[73]

The viscosity decreases exponentially with temperature (Figures 1.2.4 and 1.2.5), so at typical reaction temperatures of 80 to 100 °C the [*i*Bu3MeP][TOS] will become quite water- like in terms of viscosity.[73]

As usual with ionic liquids, the addition of the slightest amount of solute will have a singular effect on lowering the viscosity as shown in Figure 1.2.6. Considering the possible problems in future applications of [*i*Bu3MeP][TOS] in industry due to its high viscosity, aqueous solutions of IL are considered in the experimental measurements performed in this work.

Phosphonium tosylates have been reported as novel solvents for the hydroformylation of olefins.[74] Bio-transformations are often limited to the concentration of either the substrate or products due to toxicity effects on either the enzymes or organisms. However, the bio-degradation can be carried out in a two phase system such as [*i*Bu3MeP][TOS]/(aqueous phenol), in which the phenol will partition into the IL phase at a concentration which is non-toxic to the organisms.[36]

Literature data regarding the IL system studied in this work is scarce. There are some works concerning the solubility of gases in binary mixtures of phosphonium based ILs. The studied gases include carbon dioxide[52, 72, 75] and light alkanes and alkenes[72, 75].Anthony et al.[76] studied the solubility of oxygen and carbon dioxide in [*i*Bu3MeP][TOS], but only at 323.15 K. These works indicate that imidazolium and phosphonium based ILs both present similar solubilities for the studied gases. This information allows the consideration of phosphonium-based ionic liquids as low-cost alternatives to the imidazolium-based ionic liquids for industrial applications. Another very interesting feature of phosphonium based ILs is that their solubility in dense CO_2 is surprisingly high in contrast to the solubility behaviour of imidazolium-based ionic liquids. Ion pair formation was pointed as the main reason for this behaviour[77]. The ion-paired ionic liquid can be viewed as one molecular unit bearing a dipole moment that interacts with the quadrupole moment of CO_2. Although the study of ternary systems involving CO_2 + IL + organics is being increasingly reported in the recent literature[53, 78] little information is available concerning the phase behaviour of multicomponent systems consisting in CO_2 + IL + water, despite the mechanistic and practical implications that these data may represent for both reaction and separation systems using ILs with water. To our knowledge only Scurto et al.[69] and Zhang et al.[71] have studies about ternary systems composed by CO_2 + water + imidazolium based ILs.

Previous studies[71, 79] have reported the influence of the presence of water on the solubility of gases in ILs showing that the solubility decreases with the increase of the water content in the solution, which can be explained by the lower solubility of the gases in water when compared to their solubilities in the IL. In this work, the focus goes to the study of the solubility of CO_2 in an IL/water mixture in which water is the main component in molar terms. It is important to notice that the mixtures studied composed by 3, 8 and 12 mol% of IL in water actually contain 47.35, 65.24 and 74.64% in terms of IL mass fractions.

I.3. MOTIVATION

Despite the current interest in these compounds, there are questions relating their behaviour that are still unanswered, most of the times due to lack of experimental data. For many of the applications discussed above, the importance of gas solubility data is clear. This work intends to be a contribution in the effort devoted to the characterization of aqueous solutions of aniline and tri-iso-butyl(methyl)phosphonium tosylate. The main objective is to present new experimental data that, besides the practical direct interest, can help to answer some gaps in literature data and contribute to enhance our knowledge about these systems.

The thesis is organized in two parts. The first part deals with the experimental data measured of methane's solubility at high pressures in pure and aqueous solutions of aniline. The second part addresses the experimental data measured about solubility of carbon dioxide in aqueous solutions of [*i*Bu3MeP][TOS] at high pressures.

2. Part

EXPERIMENTAL METHODS

2.1- INTRODUCTION

The increasing number of applications of aniline and [*i*Bu3MeP][TOS] in the industry requires a precise knowledge of the thermophysical properties of these compounds and their phase equilibria. We are particularly concerned with the solubility of gases at high pressure on these compounds. Experimental methods for the measurement of high-pressure phase equilibria can be divided into two main classes, depending on how the composition is determined: the analytical/direct sampling methods and the synthetic/indirect methods. In this work we used a synthetic method. It consists in the preparation of a mixture of known composition followed by observation of the phase behaviour in an equilibrium cell upon change of temperature or pressure. After known amounts of the components have been placed into an equilibrium cell, values of temperature and pressure are adjusted so that the mixture is homogeneous. Then, the temperature or pressure is changed until the formation of a new phase is observed.[80]

Each experiment gives one point of the P–T–x phase diagram. This kind of methods are used when analytical methods fail, for example, when phase separation is difficult due to similar densities of the coexisting phases, near or even at critical points. Since no sampling is necessary, the experimental equipment can be rather inexpensive and the experimental procedure is usually easy and quick.

In the present work the solubility of gases such as methane and carbon dioxide were measured at high pressures and temperatures and a high-pressure cell with a sapphire window that allows the visual detection of the point at which the phase boundary is crossed. The systems were studied at pressures up to 100 MPa and temperatures ranging from 278.15 to 373.15 K.

The main objective is to collect data for these systems that are being used for different applications. Whenever possible, experimental data measured is compared with literature data available.

2.2. MATERIALS

Chemicals used for the measurements were methane (4.0) from Linde Gas, aniline (99.5 %) from Aldrich.

The Carbon dioxide used (99.995 %) was obtained from Messer and the Tri-iso-butyl(methyl)phosphonium tosylate (CYPHOS IL 106) from Cytec. The ionic liquid was dried under vacuum at 80 ºC for 24 h before the measurements. Its final aspect was a very pale yellow colour. This ionic liquid is halogen free, and its purity was checked by NMR.

2. 3- APPARATUS AND PROCEDURE

In this work, high pressure solubility measurements were carried out using a visual synthetic method. Figure 2.3.1 shows the schematic diagram of the variable volume high pressure cell which is described below.

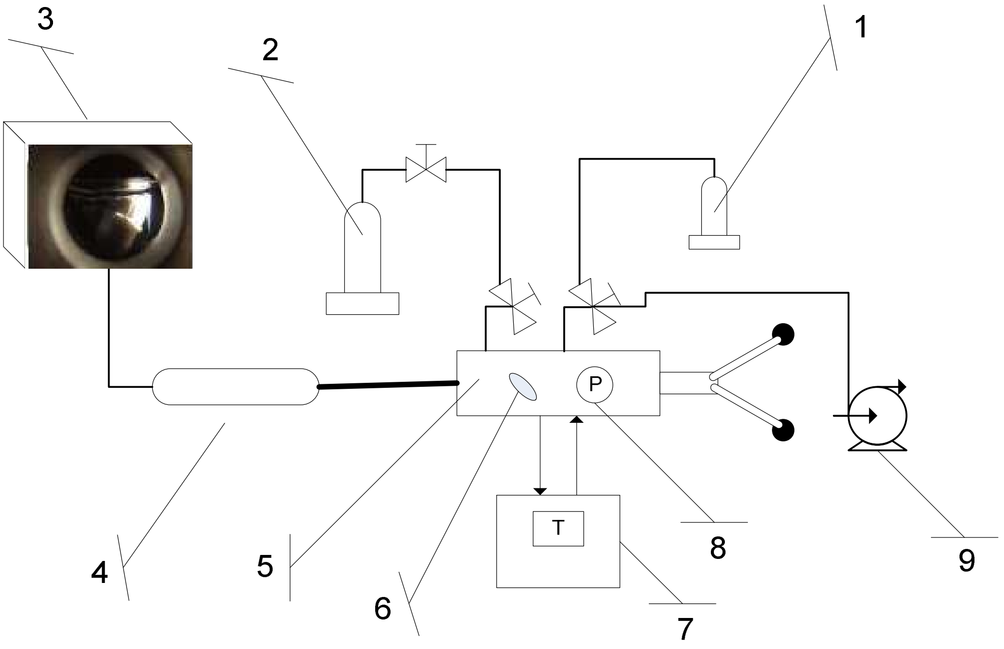


Figure 2.3.1. Schematic apparatus: 1-Liquid; 2-Gas; 3-Screen; 4-Endoscope plus a video camera; 5- High-pressure variable-volume cell; 6-Magnetic bar; 7-Thermostat bath circulator; 8-Piezoresistive pressure transducers; 9-Vacuum pump.

The cell consists in a horizontal hollow stainless steel cylinder closed at one end by a movable piston. One sapphire window closes the other end allowing visual observation of the entire fluid in study. A video acquisition system made up of an endoscope plus a video camera is placed behind the sapphire windows in order to display on the screen of a computer what happens inside the measuring cell. A small magnetic bar is placed inside the cell for the homogenization of the mixture by means of an external magnetic stirrer. Due to the presence of this magnetic stirring bar as well as of the second window, the minimum internal volume is limited to 8 cm^3 whereas the maximum volume was fixed to 30 cm^3 to limit the size of the cell and thus reduces thermal inertia and temperature gradients within the cell.

The temperature is kept constant by circulating a heat-carrier fluid thought three flow lines directly managed in the cell. This heat-carrier fluid is thermo-regulated with temperature stability of 0.01 K by means of a thermostat bath circulator (Huber Ministat CC1). The temperature is measured with a high precision thermometer, Model PN 5207 with an accuracy of 0.01K connected to a calibrated platinum resistance inserted inside the cell close to the sample.

The pressure is measured by a piezoresistive silicon pressure transducer (Kulite) fixed directly inside the cell to reduce dead volumes. The accuracy of the transducer in the experimental range studied is 0.2 MPa.

The experimental procedure can be described as follows. First, a fixed amount of liquid is introduced in the cell, by vacuum extraction. The aqueous solutions were prepared outside the equipment and then introduced in the equilibrium cell by the same method. The exact mass introduced is determined by weighting the liquid holder during its introduction with a precision balance (Ohaus) with an accuracy of 0.1 mg. Gas (Methane or carbon dioxide) is then introduced under pressure. For this purpose, the gas is initially loaded at saturation pressure in an aluminium reservoir tank (Gerzat) fixed in the plate of high weight/high precision balance (Sartorius) having a maximum weighting capacity of 2000 g with an accuracy of 1 mg and connected to the measuring cell by means of a flexible high pressure capillary. The exact mass of gas injected into the measuring cell is determined by weighing the reservoir tank while filling. After preparation of a mixture of known composition, this is allowed to reach the desired temperature at low pressure; the pressure is then slowly increased at constant temperature until the system becomes homogeneous. The pressure at which the last bubble/drop disappears represents the equilibrium pressure for the fixed temperature. For each temperature the measurement is repeated 3 times. During the experiment, the mixture is continuously stirred at high frequency to keep the system in equilibrium during the compression.

In the present experimental work was possible to measure the three phase zone for some of the compositions of gas. This measurement follow the next steps: the piston is fixed in a certain position allowing high pressures and the temperature is kept constant in the high values. At this moment the presence of two different liquid phases is registered. After that, the pressure is decreased until the appearance of the third phase vapour of carbon dioxide. This procedure is repeated for all the possible conditions (composition of IL and gas). In that experimental part, the mixture was stirred at low frequency.

3. Part

EXPERIMENTAL RESULTS AND DISCUSSION

3.A Part

SOLUBILITY OF METHANE IN PURE AND HYDRATE ANILINE AT HIGH PRESSURES

3 A.1 – Bibliographic Revision

Literature data regarding the systems studied in this work are scarce or even inexistent. In the open literature, there is data for the mutual solubility of aniline/water system[81] and for the solubility of methane in aniline at atmospheric pressure at a single temperature.[12] Data for the solubility of methane on water is far more frequent.[82, 83] In order to improve the thermodynamic knowledge of these systems, the solubility of methane in pure aniline and in an aniline-water mixture with 5% (w/w) water content was studied. From this work the influence of water on the methane's solubility in aniline was evaluated.

3 A.2 – Experimental Results and Discussion

Experimental results obtained for the solubility of methane in aniline and in the 5% (w/w) water/aniline mixture are reported in Table 3.A.2.1.

Table 3.A.2.1. Experimental P (MPa)-x_{CH4}-T (K) data measured for methane-aniline and methane-aniline-water mixtures at temperatures from 303 to 370 K.

CH_4 + Aniline

x_{CH4}	**302.99K**	**312.68K**	**322.51K**	**332.19K**	**341.79K**	**351.59K**	**361.16K**	**370.06K**
0.034	8.27	7.97	7.64	7.50	7.35	7.17	6.89	6.73
0.064	19.18	18.21	15.62	16.00	14.25	13.39	13.00	12. 69
0.092	30.04	25.72	21.22	21.95	18.63	17.41	17.02	16.54
0.122	61.65	53.16	44.27	40.66	34.82	31.20	28.57	25.20
0.130	66.30	59.82	48.03	46.00	37.23	33.66	30.49	28.80
0.167		74.42	59.75	57.54	45.58	41.07	37.58	36.36

CH_4 + Aniline + Water

x_{CH4}	**303.08K**	**312.68K**	**322.37K**	**332.05K**	**341.73K**	**351.43K**	**361.35K**	**369.97K**
0.030	13.11	12.54	11.91	11.08	10.61	10.09	9.50	9.14
0.061	27.73	25.31	22.98	22.17	20.87	20.08	19.02	18.88
0.090	55.99	48.01	42.62	38.58	34.95	30.44	29.37	29.18
0.116			61.89	53.62	46.17	43.83	40.35	36.55
0.126			73.91	61.54	55.09	49.79	43.99	41.67

The temperature dependence of the experimental solubility of methane in both systems is similar and data for the solubility of methane in pure and aqueous solutions of aniline is shown in Figure 3.A.2.1. It can be seen that at low pressures, corresponding to methane's mole fractions up to 6%, the solubility is a weak function of the temperature. However, the equilibrium pressure required to solubilize higher amounts of gas is much more markedly dependent on the working temperature. Moreover, it was observed that the solubility of methane in aniline increases with temperature. It is interesting to notice that this behaviour is opposite to what usually happens with the solubility of gases in liquids. However the same tendency was observed by other authors when studying the solubility of methane in amines.[84] It would be interesting to further explore this uncommon behaviour.

The figure also makes clear the influence of water on the solubility of methane in aniline. The solubility of methane in aniline decreases in presence of water, considering a fixed methane molar fraction. This behaviour can be explained by the solvation of water by the aniline through hydrogen bonds that reorganize the bulk allowing fewer interactions between aniline and methane.

Attempting a better understanding of the solubility process of the methane–aniline system the data measured in this work were compared with experimental data taken from the literature[12, 85] for the solubility of methane in four different aromatic compounds, namely benzene, toluene, m-xylene and phenol. In this last case, as no data were found for direct comparison, the solubility of methane in phenol was derived from its Henry's constant at atmospheric pressure[12]. The aim of the comparison is to see the influence of different substitute groups and their consequently different liquid structures on the solubility of methane.

The data shown in Figure 3.A.2.2 indicates that the solvents here presented fall into two different groups. One made up by benzene, toluene and m-xylene showing similar solubilities for methane while in the other group appears aniline and phenol. Although the methane solubility obtained as an extrapolation from the atmospheric pressure Henry Constants is not valid within the entire pressure range presented, the dashed lined in Figure 3.A.2.2 can be seen as an upper limit for the solubility of methane in phenol. The much lower solubility of methane in the polar compounds compared to the non polar hydrocarbons suggests that both the misfit of interactions between the solute and solvent molecules and the more organized liquid structure that exists in those compounds due to polar interactions or hydrogen bonding, increasing the energy required for cavity formation, will contribute to the much lower solubility observed for methane on these solvents.

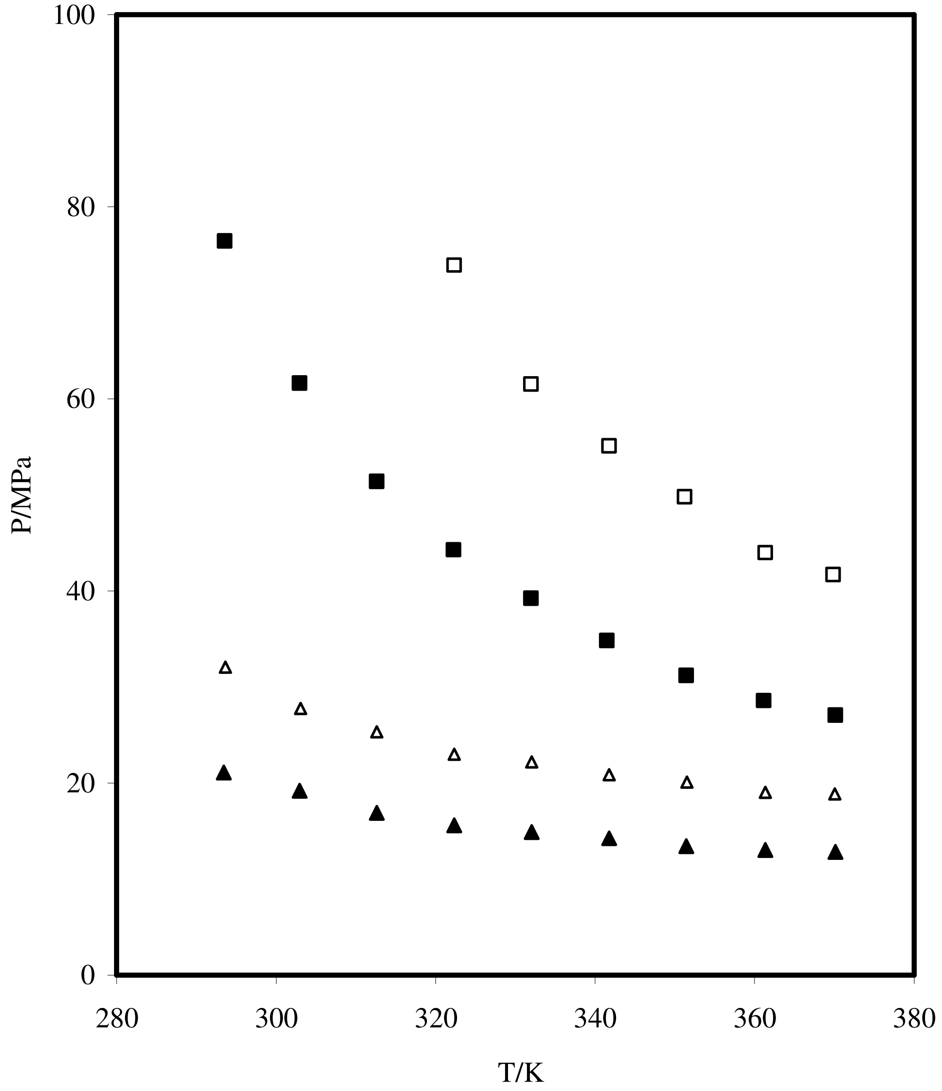


Figure 3.A.2.1. Pressure-Temperature diagram for the solubility of methane in pure aniline and aqueous aniline at different mole fractions of the gas: 12.58 mol% (□), 12.37 mol% (■), 6.06 mol% (Δ) and 6.35 mol% (▲). Open symbols represent the solubility of methane for the ternary system.

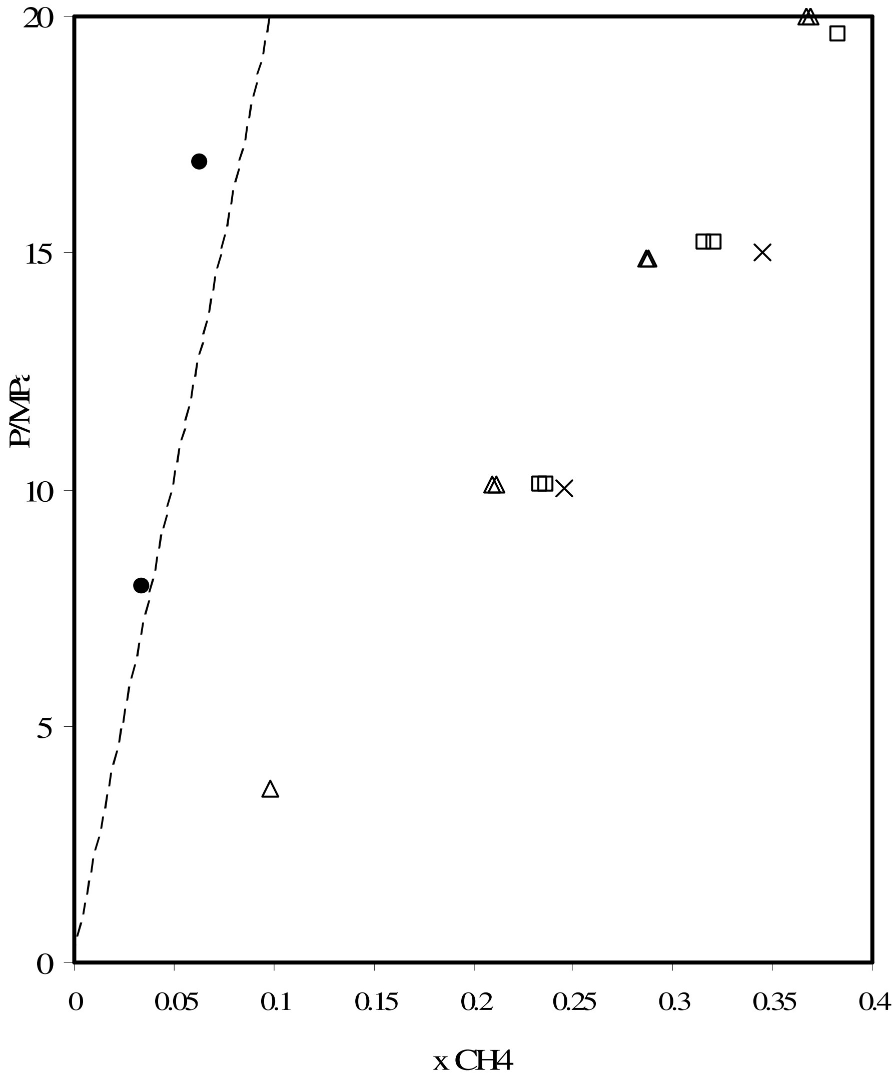


Figure 3.A.2.2. Experimental solubility data for methane in four aromatic compounds around 315 K: data measured in this work for aniline (●) and data taken from the literature[85] for benzene (Δ), toluene (□), m-xylene (×) and for phenol[12] (dashed line). The solubility in phenol was estimated from its Henry constant at atmospheric pressure.

3.B Part

SOLUBILITY OF CARBON DIOXIDE IN AQUEOUS SOLUTIONS OF TRI-ISO-BUTYL(METHYL)PHOSPHONIUM TOSYLATE AT HIGH PRESSURES

3 B. 1 – Bibliographic Revision

Despite the mechanistic and practical implications that ternary CO_2/IL/water solubility data may represent for both reaction and separation systems, the fact is that literature data regarding these systems is still scarce. Considering the potential alternative that phosphonium ILs represent, the solubility of carbon dioxide in aqueous solutions of tri-iso-butyl(methyl)phosphonium tosylate, [iBu3MeP][TOS], (CHYPHOS IL 106), with different IL concentrations, was studied in this work. On the other hand, this work intends to extend these studies to aqueous solutions of ionic liquids as a means to reduce their viscosity to use in absorption columns for CO_2 capture. To check the influence of the addition of water to the phosphonium IL, the measurements of the viscosity for various solutions with different composition of water were done.

3 B. 2 – Experimental Results and Discussion

The viscosity of aqueous solutions of Tri-iso-butyl(methyl)phosphonium tosylate are reported in Table 3.B.2.1. A very strong variation of the viscosity with water concentration is observed in particular for solutions very rich in ionic liquid with variations of one order of magnitude in the viscosity when less than 10 mol% of water content is observed. The mixtures studied present viscosities that are less than twice the viscosity of water being easily manipulated with conventional pumps. By the addition of water, the viscosity of the system decreases to 'workable' values broadening the application possibilities of the IL.

Table 3.B.2.1. Viscosity data for the mixtures used in the experimental measurements.

Mass composition IL % (w/w)	Viscosity ($x10^3$) (Pa.s)
0.000[86]	0.89
0.125	1.65
0.250	2.61
0.375	4.00
0.500	6.89
0.625	11.60
0.750	23.00
0.872	68.50
1.000	1320

The solubility of carbon dioxide in aqueous solutions of 4, 8 and 12 mol% of Tri-iso-butyl(methyl)phosphonium tosylate was measured at pressures up to 100 MPa and temperatures from 275 to 370 K. The solubility is reported in Table 3.B.2.2 while Table 3.B.2.3 presents the studied thermodynamic conditions for which the second liquid phase appears.

Table 3.B.2.2. Experimental data P (MPa)- x_{CO2}-T (K) measured for the CO_2-IL-water system for different IL molar compositions and at different temperatures ranging from 276 to 370 K.

4 mol% IL

x_{CO2}	3.0%	5.0%	8.0%
T(K)	P(MPa)	P(MPa)	P(MPa)
288.4	4.50	69.81	
289.0	4.52	66.05	
291.6	4.74	61.42	
295.1	5.42	53.50	
314.8	6.47	27.54	
324.4	6.70	21.50	
329.9	7.52	19.25	
349.4	8.47	17.31	93.76
369.3	10.37	17.50	57.03

8 mol% IL

x_{CO2}	3.2%	5.0%	8.1%	10.3%	12.3%
T(K)	P(MPa)	P(MPa)	P(MPa)	P(MPa)	P(MPa)
288.2	2.82	5.68	39.18		
295.4	3.59	5.90	27.83		
314.1	4.07	7.83	14.21	56.40	
332.6	5.21	10.03	14.23	33.52	76.08
351.8	6.15	10.23	15.21	26.09	46.55
369.5	6.36	11.19	15.18	24.14	36.19

12 mol% IL

x_{CO2}	3.0%	5.0%	8.0%	10.1%	12.0%	14.0%
T(K)	P(MPa)	P(MPa)	P(MPa)	P(MPa)	P(MPa)	P(MPa)
276.8	0.78	3.97	8.22	35.10	99.75	
280.6	1.17	4.08	8.43	26.33	84.66	
282.6	1.34	4.15	8.54	22.67	77.50	
285.15	1.53	4.22	8.68	21.31	75.43	
287.70	1.71	4.30	8.82	18.01	59.07	
291.45	1.96	4.42	9.04	13.34	51.80	
293.60	2.09	4.85	9.13	12.13	45.14	
312.55	3.09	4.78	10.17	10.95	23.65	57.57
322.62	3.47	5.53	11.09	9.53	20.17	43.72
331.87	3.76	5.69	11.99	13.89	18.71	34.42
351.45	4.30	7.23	13.27	14.40	17.90	28.09
369.32	5.38	7.97	14.76	15.49	18.49	26.25

Table 3.B.2.3. Dependence of the Lower critical end point (LCEP) on the initial ionic liquid concentration and temperature for the ternary Tri-iso-butyl(methyl)phosphonium tosylate/water/CO_2 system.

4 mol% IL and 5 mol% CO_2

T/ K	278.85	284.05	288.05	293.25	298.15	306.15	307.35
P/ MPa	3.92	4.46	4.92	5.30	6.09	6.35	6.80

4 mol% IL and 8 mol% CO_2

T/ K	278.75	279.25	284.15	288.25	293.65	297.15	305.65
P/ MPa	3.88	3.94	4.50	4.98	5.65	6.23	7.52

8 mol% IL and 8 mol% CO_2

T/ K	280.65	281.65	286.35	290.25	295.25
P/ MPa	4.11	4.30	4.67	5.03	5.20

8 mol% IL and 10 mol% CO_2

T/ K	278.65	283.45	288.95	294.95
P/ MPa	4.02	4.49	5.22	5.92

8 mol% IL and 12 mol% CO_2

T/ K	279.15	284.45	293.35	298.25	303.55
P/ MPa	3.95	4.56	5.68	6.49	7.20

12 mol% IL and 12 mol% CO_2

T/ K	282.35	283.65	286.15	287.85	290.75	293.65	298.35
P/ MPa	4.47	4.52	5.15	5.19	5.46	5.99	6.65

12 mol% IL and 14 mol% CO_2

T/ K	279.45	285.05	288.95	293.45	297.45	302.35
P/ MPa	4.14	5.07	5.30	5.89	6.38	7.23

The solubility of CO_2 in the 8 mol% IL-water solution is depicted in Figure 3.B.2.1, as an example. The vapour liquid equilibrium (VLE) lines present a regular behavior with the gas solubility decreasing when temperature increases. When attempting to solubilize CO_2 concentrations higher than 8 mol%, a liquid-liquid region appears at low temperatures when pressure is increased.

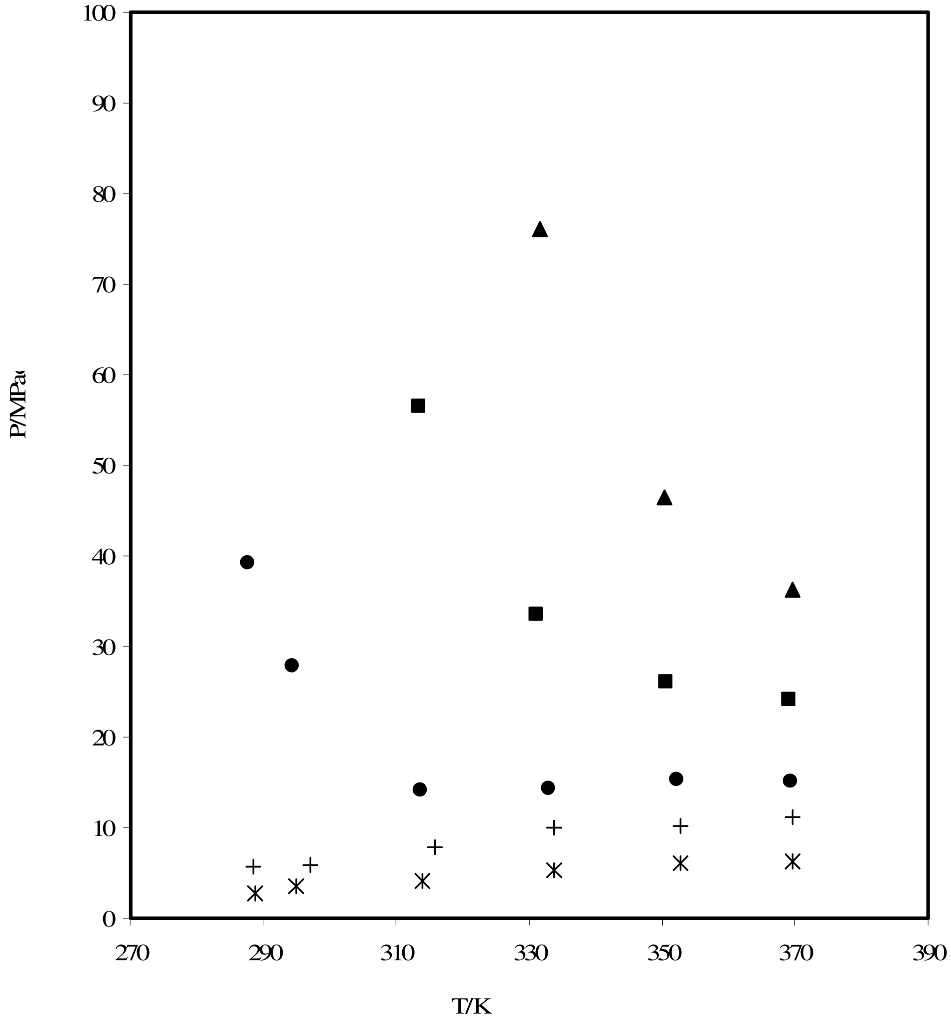


Figure 3.B.2.1. Pressure-Temperature diagram for the solubility of CO_2 in aqueous solution with 8 mol% of IL for various gas contents: 3.16 mol% (+), 5.00 mol% (×), 8.06 mol% (●), 10.28 mol% (■) and 12.31 mol% (▲).

The pressure-composition projection of the same system is presented in Figure 3.B.2.2. for different temperatures. It is clear from the figure that it is possible to solubilize up to 10% of CO_2 in the IL/water mixture with pressures lower than 20 MPa. However, the equilibrium pressure increases very sharply for increasing concentrations of CO_2 with the appearance of a two-phase region extending up to very high-pressures. A similar behaviour was observed by Shariati and Peters[35, 87, 88] when studying binary systems of carbon dioxide plus imidazolium based ILs. As mentioned by the authors, this is a very unusual behaviour when comparing with the traditional closed phase envelope usually observed for the solubility of carbon dioxide at high pressures.

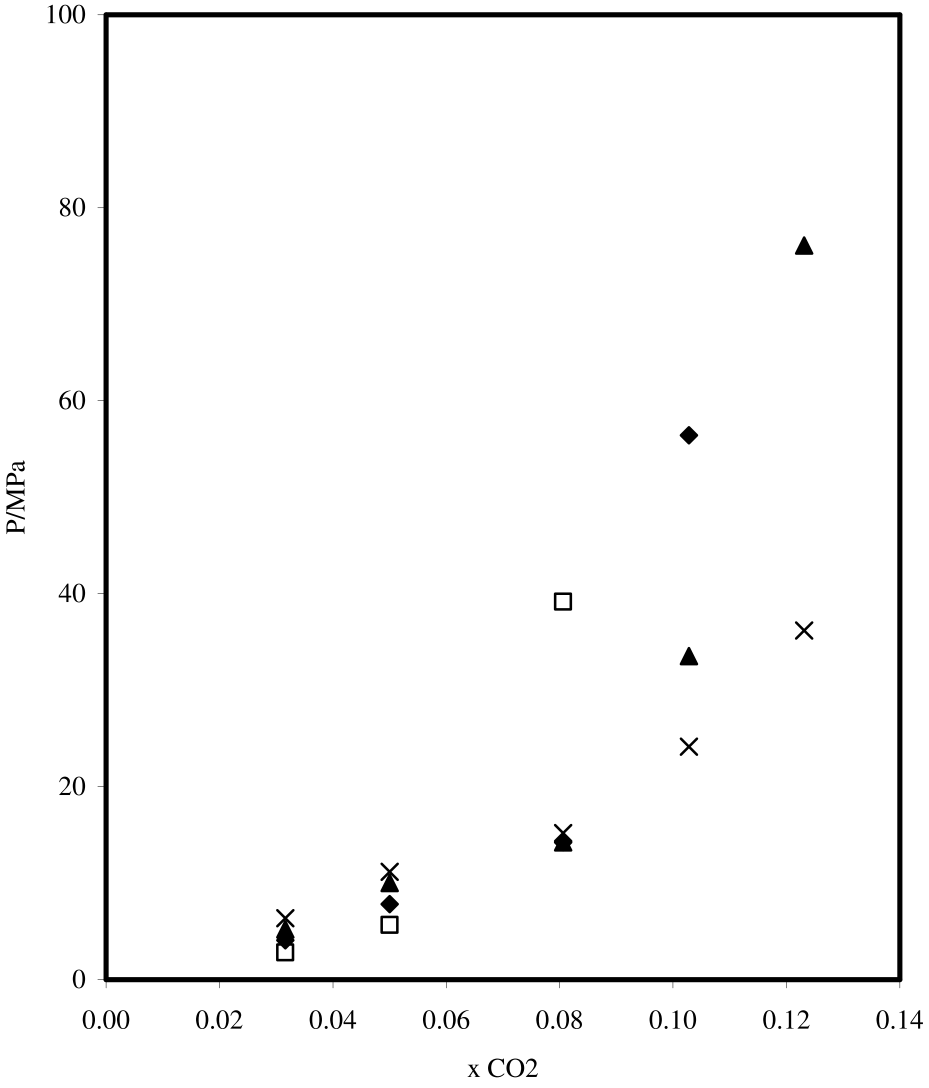


Figure 3.B.2.2. Experimental solubility data for CO_2 in an aqueous solution of 8 mol% of IL at various temperatures: 288.22 K (□), 314.15 K (♦), 332.63 K (▲), 369.49 K (×).

The influence of the amount of IL on the solubility of CO_2 in the mixture is shown in Figure 3.B.2.3 where the Henry's constants for different systems are represented as a function of the temperature. The Henry's constants (K_H) were calculated as a function of temperature for the ternary systems studied in this work using interpolated experimental data from Table 3.B.2.2. Solubility data for carbon dioxide in pure water[89] and in pure [iBu3MeP][TOS][76] are also shown for comparison. The figure clearly shows that the solubility of CO_2 decreases with the increase of the temperature for all the mixtures represented. The solubility of the gas in the IL/water mixture is between the gas solubility in pure water and in the pure IL. The solubility of the gas increases with the IL content in the liquid phase meaning that [iBu3MeP][TOS] promotes a salting-in effect on the solubility of carbon dioxide in water.

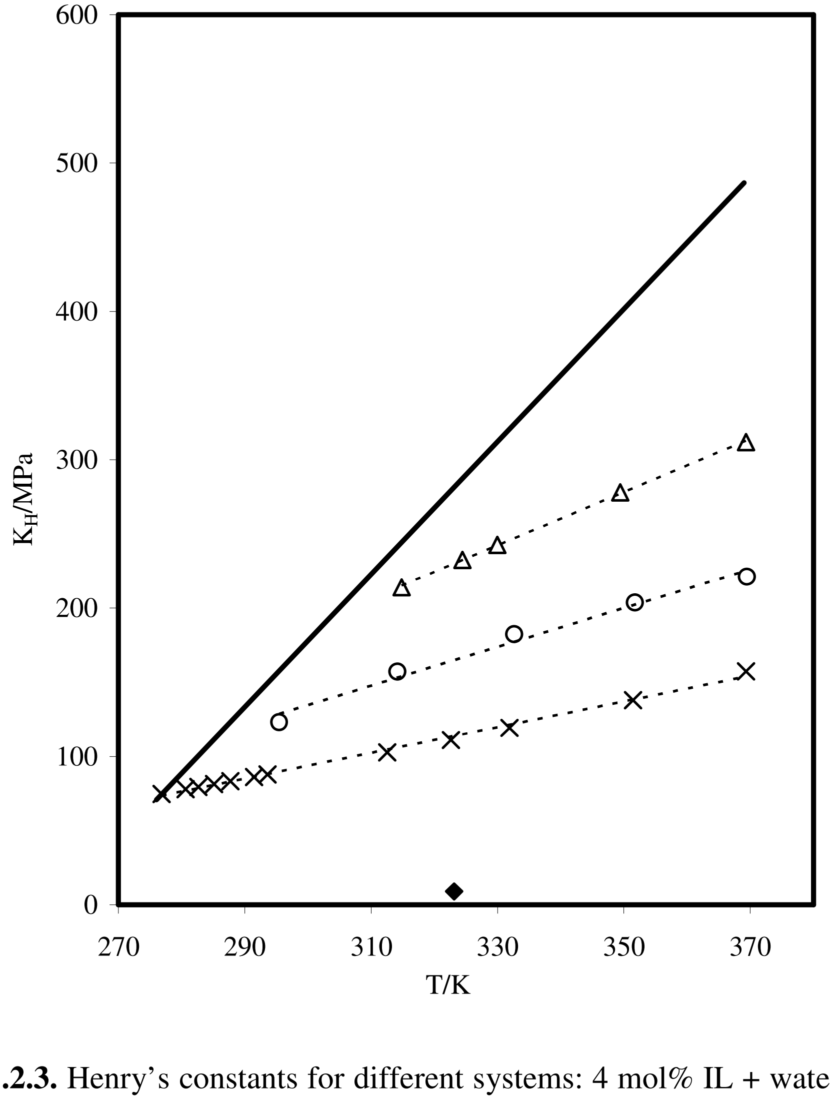


Figure 3.B.2.3. Henry's constants for different systems: 4 mol% IL + water + CO_2 (Δ), 8 mol% IL + water + CO_2 (○), 12 mol% IL + water + CO_2 (×), [*i*Bu3MeP][TOS] + CO_2 (♦)[76] and water + CO_2 (■)[89].

The knowledge of Henry's constant for CO_2 in the aqueous mixtures studied allows for the calculation of the solution thermodynamic properties namely the Gibbs energy ($\Delta_{sol}G°$), enthalpy ($\Delta_{sol}H°$) and entropy ($\Delta_{sol}S°$). These thermodynamic functions are associated with the hypothetical changes that happen in the solute neighbourhood when the solute molecules are transferred to a hypothetical dilute ideal solution where the mole fraction of solute is equal to one and can be calculated according to:

$$\Delta_{sol}G° = RT(\ln K_H) \tag{3.B.2.1}$$

$$\Delta_{sol}H° = R\left(\frac{\partial \ln(K_H / P°)}{\partial(1/T)}\right)_p \tag{3.B.2.2}$$

$$\Delta_{sol}S° = (\Delta_{sol}H° - \Delta_{sol}G°)/T \tag{3.B.2.3}$$

where P° is the standard pressure of 0.1 MPa. Table 3.B.2.1 reports the thermodynamic data calculated at 298.15 K for the aqueous mixtures with 4, 8 and 12 mol% of IL. The thermodynamic functions calculated for the solubility of CO_2 in pure water are also presented for comparison. The positive Gibbs energy values indicate that the process is not spontaneous under the studied conditions. It seems that the solubilization process is entropy driven with a low interaction between the gas and the solvent.

Table 3.B.2.4 Gibbs Free Energy $\Delta_{sol}G°$, Enthalpy $\Delta_{sol}H°$ and Entropy $\Delta_{sol}S°$ of solution for CO_2 in [*i*Bu3MeP][TOS]-water systems at standard temperature and pressure (T= 298.15 K, P = 0.1 MPa).

Aqueous mixture	**$\Delta_{sol}G°$ kJ.mol^{-1}**	**$\Delta_{sol}H°$ kJ.mol^{-1}**	**$\Delta_{sol}S°$ J.K^{-1}.mol^{-1}**
0 mol% IL	18.76 ± 1.10	-12.18 ± 0.82	-103.76 ± 2.44
4 mol% IL	18.67 ± 0.17	-6.65 ± 0.12	-84.94 ± 0.37
8 mol% IL	17.96 ± 0.43	-5,95 ± 0.32	-80.21 ± 0.95
12 mol% IL	16.84 ± 0.19	-7,23 ± 0.14	-80.74 ± 0.43

As mentioned previously, ternary CO_2 + IL + organic or water systems are characterized by the appearance of a liquid-liquid phase split over certain P-T-x conditions with the appearance of a second liquid phase along with the gaseous CO_2 rich phase. This behaviour was also observed in this work and, Figure 3.B.2.4 represents on a P-T diagram, the upper limit of the VLLE region observed. The VLE line for pure CO_2[86] as well as the results previously reported in the literature for analogous systems[48, 53, 90] are also represented in the figure. There are a number of curious features related to this line marking the upper limit of the VLLE region. In all cases it increases with the temperature and for the IL composition range studied in this work, it is essentially independent of the initial IL concentration in the aqueous solution. This line is also within the experimental uncertainty, coincident with the VLE line for pure CO_2[86] and the appearance of the three phase region only occurs while the working conditions are below the critical point of pure carbon dioxide.

These observations are not novel as Aki et al.[48] observed the same behaviour for mixtures with IL concentration higher than 5% but they give a clear indication that the second liquid phase results from the condensation of the carbon dioxide as it crosses, with increasing pressure, the dew point line that, for mixtures with less volatile compounds, will occur at pressures somewhat below those of pure carbon dioxide. The boiling point line for the carbon dioxide rich phase will occur for higher pressures, close to those of pure carbon dioxide, due to very high concentrations of carbon dioxide in this phase. The mixture will thus behave almost as pure carbon dioxide showing a bubble point very close to the saturation line of carbon dioxide. The high CO_2 content of the second liquid phase is also observed in other works[53].

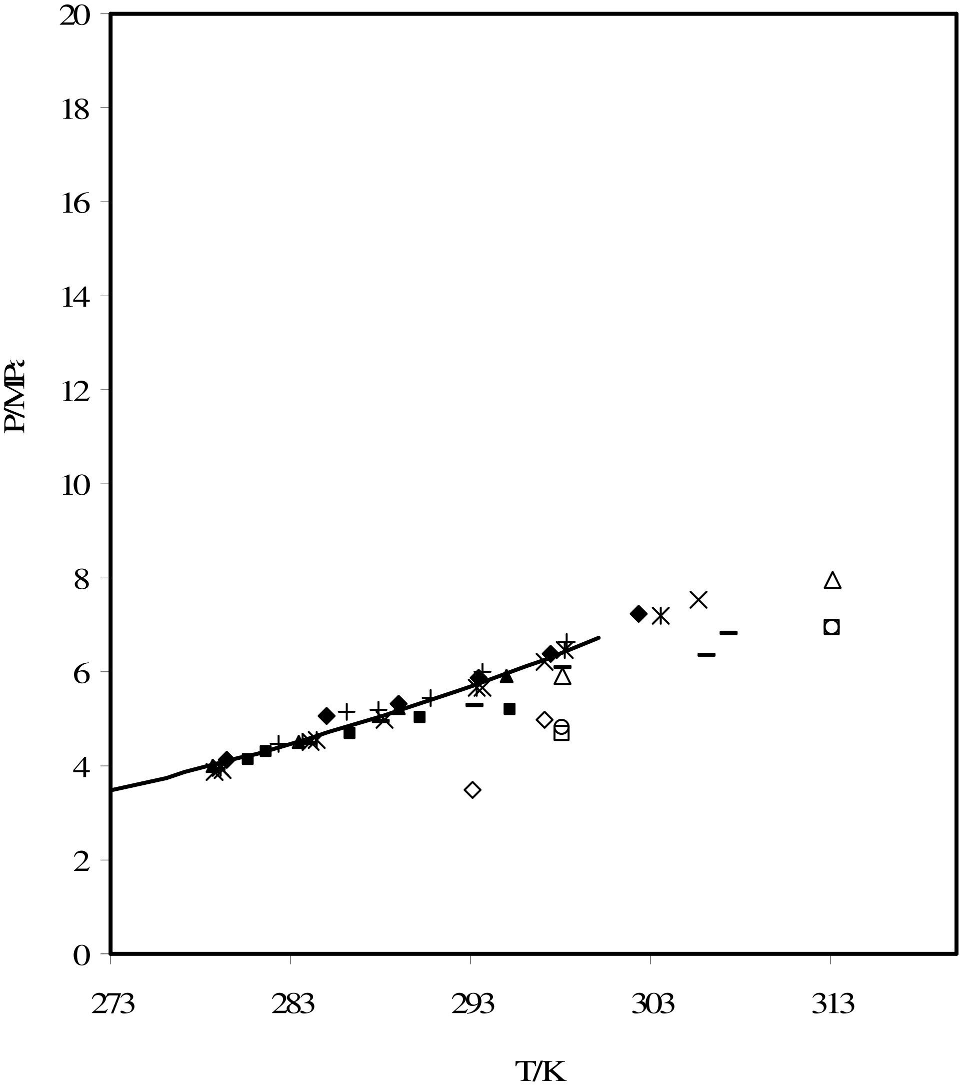


Figure 3.B.2.4. Diagram for the upper limit of the three phase zone for all the studied systems: 5 mol% of CO_2 and 4 mol% of IL (—), 8 mol% of CO_2 and 4 mol% of IL (×), 8 mol% of CO_2 and 8 mol% of IL(■), 10 mol% of CO_2 and 8 mol% of IL (▲), 10 mol% of CO_2 and 8 mol% of IL (*), 12 mol% of CO_2 and 12 mol% of IL (+), 14 mol% of CO_2 and 12 mol% of IL (♦) and data reported in the literature: 0.1 mol% (Δ), 4.9 mol% (○) and 9.0 mol% (□) of [bmim][PF_6][48] plus CO_2 until phase separation is observed; 7.7 mol% of [bmim][PF_4] and 2.3 mol% of CO_2 in the IL rich phase[71] (◊) and pure CO_2[86] (line).

4. Part

CONCLUSIONS

4.1. Conclusions

Alternative approaches to the reduction of nitrobenzene for the aniline production using methane are being investigated. Solubility data of gases in aniline or aqueous aniline solutions are very scarce. In this work, high pressure equilibrium data were measured for methane-aniline and methane-aniline-water systems at temperatures ranging from 293.15 to 373.15 K and pressures up to 100 MPa using a visual static method for detection of the phase transitions. It has been shown that the solubility of methane in aniline increases with temperature and decreases with the system water content. A comparison with literature data for other aromatic compounds indicates that the solubility of methane in aniline is lower than on other aromatic compounds most probably because of the more organized bulk structure of liquid aniline favoured by the hydrogen bonds.

Ionic liquids are attracting great attention nowadays due to their interesting properties which able them to be used in a broad range of applications including reaction media, separation and capture of environmentally hazardous gases as carbon dioxide. In many cases, for practical and/or economical reasons, the use of the aqueous solutions of the ILs would be preferable to their use as pure compound.

In this thesis, high pressure equilibrium data for the CO_2 - [*i*Bu3MeP][TOS] - water systems were measured at temperatures ranging from 276 to 370 K and pressures up to 100 MPa. Such as in the aniline's case, those measurements were done using a high-pressure cell with a sapphire window that allows direct observation of the liquid vapour transition. Different mixtures with different IL compositions were studied in order to check the influence of the amount of IL on the solubility of CO_2 in the aqueous mixture. VLLE data was also observed and the thermodynamic conditions at which the vapour phase appearance is observed were also reported.

The gathered data shows that the temperature dependence of the CO_2 solubility presents a regular behaviour with the gas solubility decreasing with an increase in the temperature. The results also show that the solubility of carbon dioxide in the aqueous [*i*Bu3MeP][TOS] system increase with the increase of IL molar composition revealing a salting-in effect promoted by the IL. It is shown that although the solubility of CO_2 in the aqueous mixture is, as expected, lower than in pure IL, it is still possible to solubilize significant amounts of gas in the aqueous mixtures, hopefully promoting gas diffusion and reducing operational constrains on the use of these fluids.

The formation of two liquid phases, one rich in carbon dioxide and the other rich in water, which was observed at mild thermodynamic conditions can represent an interesting alternative for separation processes involving systems similar to the ones reported in this work. Moreover, it was observed that the upper limit of the VLLE region was almost independent of the initial composition of IL in the solution and that it coincides with the VLE data for pure CO_2, a clear indication that the condensed phases are mainly constituted by condensed CO_2.

5. Part

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