J. Chem. Thermodynamics 40 (2008) 1187–1192

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

High pressure solubility data of carbon dioxide in (tri-*iso*-butyl(methyl)phosphonium tosylate + water) systems

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ARTICLE INFO

Article history:
Received 3 October 2007
Received in revised form 8 April 2008
Accepted 16 April 2008
Available online 24 April 2008

Keywords:
Gas solubility
High pressure
Ternary system
Carbon dioxide
Phosphonium
Water

ABSTRACT

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

In this work, high pressure equilibrium data for the {carbon dioxide (CO_2) + tri-*iso*-butyl(methyl)phosphonium tosylate [$i$$Bu_3$MeP][TOS] + water system were measured at temperatures ranging from (276 to 370) K and pressures up to 100 MPa. Measurements were performed using a high-pressure cell with a sapphire window that allows direct observation of the liquid–vapour transition. Mixtures with different IL concentrations were studied in order to check the influence of the amount of IL on the solubility of CO_2 in the aqueous mixture.

The results show that the presence of IL enhances the solubility of CO_2 in the (IL + water) system revealing a *salting-in* effect of the IL on the solubility of CO_2. The appearance of a three phase region was observed for IL concentrations higher than 4 mol% of IL in water when working at pressures between 4 and 8 MPa and temperatures between (280 and 305) K. In this range, the upper limit of the VLE region observed is shown to increase with the temperature being almost independent of the IL initial concentration in the mixture.

1. Introduction

Ionic liquids (ILs) are a novel class of solvents which are being the focus of much research in recent years due to the interesting conjugation of properties that characterize them [1,2].

ILs are generally composed by a large asymmetric organic cation and either an organic or inorganic anion. A key feature of these compounds is that their physical properties can be tailored by the judicious selection of the cation and/or the anion [3–5]. The asymmetry of the cation is believed to be responsible for the low melting temperatures (<100 °C) of ILs, while the nature of the anion is considered to be responsible for many of the physical properties of these compounds such as their miscibility with conventional solvents, density, viscosity, Lewis acidity, hydrophobicity, hydrogen-bonding capability and hygroscopicity [6]. Moreover their insignificant vapour pressures, reduces environmental pollution and highly reduces working exposure hazards in comparison with the conventional organic solvents currently being used in the industry [7]. These, allied with their thermal and chemical stability and good solvency power for both organic and inorganic materials, polar and non-polar compounds [8,9], turn these compounds in valuable substitutes for traditional solvents.

The higher solubility of gases in ILs when compared to common solvents aroused the interest of the scientific community, as recent literature on the subject reports [5,7,10–16]. 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 primary alkanolamines [17,18] which have been traditionally used in the natural gas processing industry for the sweetening process removal of acid gases according to the following equation:

$$C_nH_{2n}OHNH_2 + CO_2 + H_2O \rightarrow C_nH_{2n}OHNH_3^+ + HCO_3^- \qquad (1)$$

However, there are several drawbacks associated with the use of primary alkanolamines due to their volatility. In this regard and having in mind the actual concerning to largely reduce the CO_2 atmospheric emissions, it is crucial to look for a new kind of

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doi:10.1016/j.jct.2008.04.012

removal agent(s) preferably characterized by negligible vapour pressure and high stability [19]. ILs have been presented as interesting valuable alternatives to traditional removal agents [19,20].

Research regarding the solubility of gases in ILs have been so far most centred on the study of the solubility of gases in imidazolium based ILs. Gases such as light alkanes and alkenes, oxygen, nitrogen, hydrogen, argon, carbon monoxide and CO_2 are among the most studied. Particular attention is being given to CO_2 due to the interesting behaviour observed when this gas is used as supercritical fluid [21–24]. The successful application of supercritical CO_2 for separation and purification of products from ILs, by using the gas as a co-solvent in extractions or as an anti-solvent in precipitations, is the main reason of the attention given to this gas [21,23–26]. The procedure avoids the problems related with traditional separation techniques such as the loss of solvent, cross-contamination, and destruction of thermo-sensible compounds, and allows reactants and products to be extracted from ILs with subsequent recycle and reuse of the IL [26].

Another very interesting aspect is that, the use of 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 [27,28] with relatively low-pressure gaseous CO_2. 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.* [11] and Zhang *et al.* [16,29] for (CO_2 + imidazolium IL + organic) and by Scurto *et al.* [11] and Zhang *et al.* [28] 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.

As mentioned above, there are few works concerning the solubility of gases in phosphonium based ILs. The studied gases include CO_2 [15,30,31] and light alkanes and alkenes [30,31]. Anthony *et al.* [32] studied the solubility of oxygen and CO_2 in [*i*Bu_3MeP][TOS] but only at 323.15 K. Hutchings *et al.* [33] observed that the solubility of one phosphonium based IL in dense CO_2 is surprisingly high in contrast to the solubility behaviour of imidazolium-based ILs. Ion pair formation in the gaseous phase was pointed as the main reason for this behaviour. The ion-paired IL can be viewed as one molecular unit bearing a dipole moment that interacts with the quadrupole moment of CO_2. Recently, Ferguson and Scovazzo [30] have shown that imidazolium and phosphonium based ILs have similar solubilities for several gases. Being about 10 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. 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 required this would also diminish the IL viscosity.

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 CO_2 in aqueous solutions of [*i*Bu_3MeP][TOS] with different IL concentrations, was studied in this work.

Previous studies [28,34] 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 (IL + water) 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. By the addition of water, the viscosity of the system decreases to 'workable' values broadening the application possibilities of the IL. The aim of this study is to see how the reduction in the viscosity of the aqueous solutions of IL will affect its capacity to solubilize gases as CO_2. In addition, a range of (p,x,T) conditions necessary to induce the two liquid phases separation is presented and compared whenever possible to the ones previously reported for the CO_2 + water + imidazolium based IL [27,28,34].

2. Experimental section

The CO_2 used was obtained from Messer with a purity of 99.995% and the [*i*Bu_3MeP][TOS] from Cytec with a purity of 98% checked by n.m.r. The IL was dried under vacuum at 80 °C for 24 h before the measurements. Its final aspect was a very pale yellow colour. The IL's water content was measured with a Metrohm 831 Karl Fischer (KF) coulometer and was about 3585 ppm in mass fraction. This water content was taken into account in the preparation of the mixtures with water.

The apparatus and the measurement procedure followed have been previously described in detail [35–37]. The variable volume high pressure cell sketched in figure 1 consists in a horizontal hollow stainless steel cylinder closed at one end by a movable piston and one sapphire window at the other end allowing for visual observation of the fluid. A video acquisition system, made up of an endoscope plus a video camera, is placed behind the sapphire windows and displays on a computer screen the behaviour of the fluid inside the measuring cell.

The temperature is kept constant by circulating a heat-carrier fluid through 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 0.01 K connected to a calibrated platinum resistance inserted inside the cell close to the sample. The pressure is measured by a piezoresistive silicon

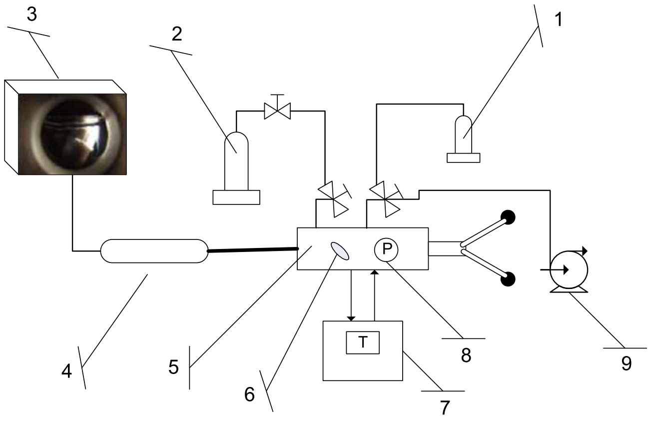

FIGURE 1. Schematic apparatus: 1, aqueous solutions of IL; 2, CO_2; 3, screen; 4, endoscope plus a video camera; 5, high-pressure variable-volume cell; 6, magnetic bar; 7, thermostat bath circulator; 8, piezoresistive pressure transducers; 9, vacuum pump.