

EXPERIMENTS AND MODELLING OF SYSTEMS WITH IONIC LIQUIDS

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ABSTRACT

This paper presents the high-pressure phase behavior of the binary system 1-octyl-3-methylimidazolium tetrafluoroborate ([omim][BF₄]) + carbon dioxide (CO₂) in the mole fraction range $0.1 < x_{\text{CO}_2} < 0.75$, and in the pressure and temperature range of 0.1-100 MPa and 303-363 K, respectively. High solubilities of CO₂ for $x_{\text{CO}_2} < 0.6$ were established at relatively low pressure, while for $x_{\text{CO}_2} > 0.6$ a dramatic increase of the equilibrium pressure was observed.

The Group Contribution Equation of State (GC-EOS) was applied to predict the phase behavior of binary systems of ionic liquids of the homologous family like 1-alkyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate with CO₂. Pure group parameters for the new ionic liquid functional group [-mim][BF₄] and interaction parameters between these groups and the paraffin (CH₃, CH₂) and CO₂ groups were estimated. The GC-EOS was applied to predict the high-pressure phase equilibria in binary mixtures of the ionic liquids [bmim][BF₄], [hmim][BF₄] and [omim][BF₄] with CO₂. The agreements between experimental and predicted bubble point data for the ionic liquids were excellent for pressures up to 20 MPa and even for pressures up to about 100 MPa the agreements were good.

INTRODUCTION

A new generation of solvents called *Ionic Liquids* (ILs) seems to be promising not only for organic and inorganic chemistry but also for industrial applications. ILs can be imagined as molten salts at room temperature as they are liquids in a wide range of temperatures (approximately 400K). The molten salts at room temperature are composed of one organic cation, most commonly n-alkyl methyl-imidazolium, piridynium, and one inorganic or organic anion like PF₆⁻, BF₄⁻, Cl⁻, NO₃⁻, etc. Depending on the cation and the anion, the physical properties (density, viscosity, hygroscopicity, etc.), may change a lot [1]. All the ILs studied until present show a *negligible* vapor pressure, i.e. we are dealing with a property that makes them attractive to replace volatile organic solvents as they do not affect the environment from the point of view of air pollution.

ILs are known for a long time [2] and are not a novel class of substances. The idea to propose them as a new generation of solvents emerges as a result of the newly discovered wide range of applications for them. ILs are advised to replace solvents in catalytic processes, hydrogenation

and polymerization reactions [3]. The role of the ILs in these reactions differs depending on the characteristic of the anion and cation that compose the IL, for instance, they can fix the polarity of the medium, behave as a solvent and co-catalyst, serve as a solvent and ligand / ligand precursor, and play as a solvent and transition metal catalyst [2].

Together with the exploration of potential applications, the interest in their synthesis and physical properties increased remarkably. The former necessitates for reducing the impurities in the ILs that originates from the synthesis method (for example, small amounts of chloride, water and other impurities) may affect significantly a number of physical properties of ILs [4].

The interest in the physical properties of ILs increased rapidly in the last couple of years as little information on them is available. It is obvious that the knowledge of physical properties should, without any doubt, be requested at the first step of any new application in case a proper IL is involved in the process.

Extraction procedures with supercritical fluids are considered to be highly improved if also ILs are involved. On the basis that ILs dissolve different substances (polar and non-polar), they can be used as the medium for concentrating a non-volatile substance that can be then extracted from the IL with a supercritical fluid (SCF) [5]. The SCF to be used should be the one that offers the following properties: it does not pollute the atmosphere, the non-volatile substance should be sufficiently soluble in the SCF, the IL is not soluble in the SCF, and the SCF is soluble in the IL.

Solubility data of various gases in ILs have been reported in literature [6,7,8]. In the case of [bmim][PF₆], it was shown that CO₂ dissolves better than other gases. Later Shariati et al. [9] studied the same system, and despite the data are different from those of Blanchard et al. [8], the high solubility is still shown for low concentrations of CO₂. CHF₃ also shows a high solubility in ILs. For instance, at 20 MPa and 350 K mole fractions of $x_{\text{CHF}_3} = 0.6$ in the IL can be reached. In addition, a slight solubility of the IL in supercritical CHF₃ was observed.

In this work the solubility of CO₂ in [omim][BF₄] is measured in order to enlarge our knowledge on the solubility behavior of CO₂ in [alkyl-mim] [BF₄] ILs. The data were acquired in a wide range of temperatures and pressures.

Considering the large variety of ILs that may be formed, methods to predict the phase behavior of ILs are needed. Up to now, methods to predict the phase behavior of ILs are mostly based on molecular dynamics simulations [10] and excess Gibbs models such as NRTL [11] and UNIQUAC [11]. In literature, little is mentioned about predicting the phase behavior of systems of ILs using an equation of state approach. Kim et al. [12] used a group contribution non-random lattice-fluid equation of state to predict solubilities of CO₂ in the ILs [hmim][PF₆], [emim][BF₄], [hmim][BF₄], [emim][Tf₂N] and [hmim][Tf₂N] at pressures up to 1 MPa. For the [bmim][PF₆] predictions were made for pressures up to 10 MPa. The agreements between experimental and calculated solubilities were generally good. However, no information was available for higher pressures (>1 MPa). Shariati and Peters [13] used a Peng-Robinson equation of state to model the high-pressure phase behavior of the system fluorofrom and [emim][PF₆]. They showed that the Peng-Robinson equation of state is capable of describing the experimental bubble points of this system and to qualitatively predict the solubility of the ILs in supercritical fluorofrom. In the present study, it is examined if the GC-EOS is capable of predicting the phase behavior of binary systems of ILs of the homologous families 1-alkyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate with CO₂.

EXPERIMENTAL

CO₂ (Messer Griesheim, with an ultra high purity of 99.995%) was mixed with degassed [omim][BF₄]. The IL was synthesized in the group of Organic Chemistry of Delft University of Technology. Different compositions were prepared and measured.

Measurements up to 10 MPa were determined in a Cailletet apparatus with an experimental error of 0.001 MPa and 0.02 MPa for pressures lower than 6 MPa and between 6-10 MPa, respectively. Pressures higher than 10 MPa were measured in an autoclave apparatus [9] with an uncertainty of 0.04 MPa. Both high-pressure facilities were immersed in a water thermostat. The temperature of the Cailletet equilibrium cell was controlled by a Lauda thermostat and measured with a resistance bridge with an uncertainty of 5 mK. The autoclave temperature uncertainty was 70 mK and controlled by a Shimaden DSM temperature control unit.

For each composition the pressure-temperature equilibrium data (isopleths) were carefully determined, i.e., at a fixed temperature the bubble point was determined as the pressure at which the last bubble at equilibrium conditions disappears. For all isopleths, part of the data was acquired by increasing the temperature and part by decreasing the temperature in order to check the chemical stability of the system.

EXPERIMENTAL RESULTS

Experimentally determined bubble points for the system [omim][BF₄] are shown in Figure 1. The measured P-T data (isopleths) indicate the values at which the CO₂ is completely dissolved in the [omim][BF₄]. At higher pressures a homogeneous liquid phase occurs, while at lower pressures two phases coexist: a CO₂-rich and a [omim][BF₄]-rich phase.

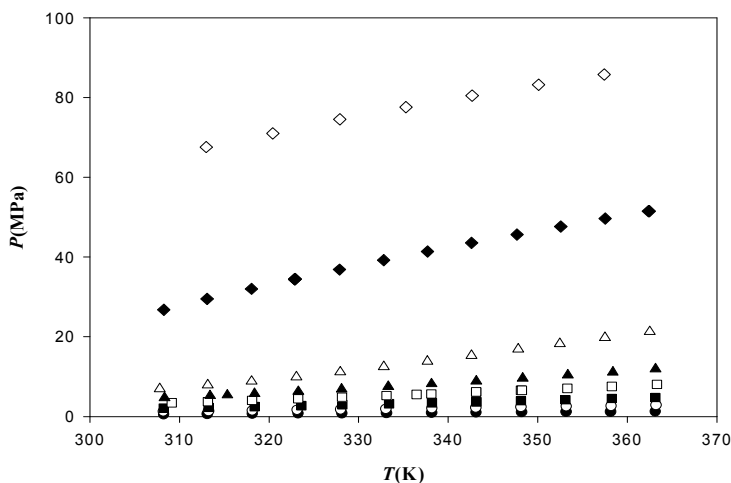


Figure 1: P - T diagram for the system [omim][BF₄]. The symbols represent the isopleths for x_{CO_2} , ●:0.101, ○:0.200, ■:0.299, □:0.412, ▲:0.505, △:0.602, ◆:0.702, ◇:0.752.

The isopleths in Figure 1 show higher separation with increasing concentration. This effect becomes more apparent in Figure 2 where the pressure is plotted against the concentration for 320 K and 360 K. At concentrations of CO₂ up to $x_{\text{CO}_2} \sim 0.6$, the equilibrium pressure increases smoothly and monotonically. However, at mole fractions $x_{\text{CO}_2} \sim 0.6$, pressure increases drastically to very high values indicating a big change in the solubility behavior of CO₂.

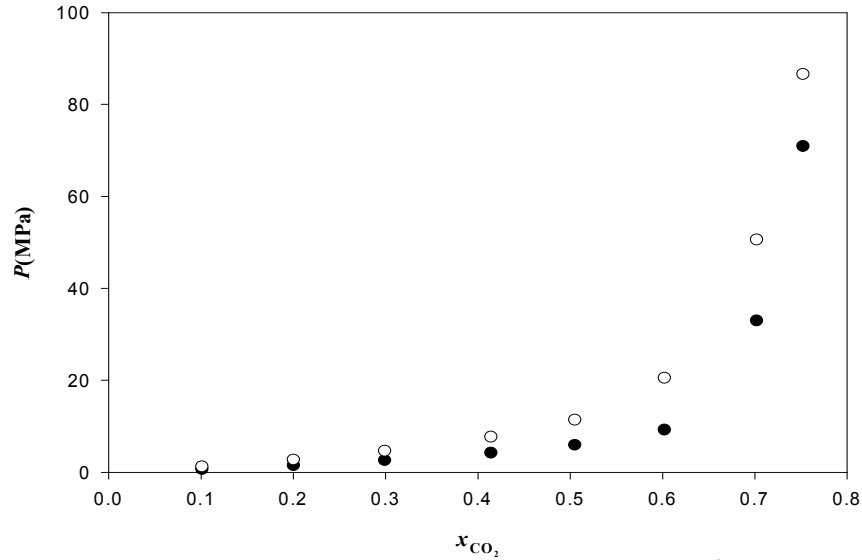


Figure 2: P - x diagram for the system [omim][BF₄] at 360 K (○) and 320 K (●).

Figure 1 also shows the effect of the temperature on the solubility of CO₂, i.e. as can be seen in this figure increasing amounts of CO₂ dissolve in [omim][BF₄] with decreasing temperature.

MODELLING

In this work the GC-EOS equation is used to model binary systems of ILs and CO₂. The GC-EOS was developed in the 1980s by Skjold-Jørgensen [14,15] to calculate vapor-liquid equilibria of non-ideal mixtures up to pressures of 30 MPa. The basis of the GC-EOS is the generalized van der Waals function combined with the local composition principle. In terms of the residual Helmholtz energy.

$$\left(A^R / RT \right)_{T,V,n} = \left(A^R / RT \right)_{att} + \left(A^R / RT \right)_{fv} \quad (1)$$

The free volume term is described by the Mansoori and Leland expression for hard spheres. The attractive part of A^R is a group contribution version of a density dependent NRTL type expression. Details on the modelling and related procedures can be found elsewhere [16].

MODELLING RESULTS

In Figure 4, GC-EOS predictions are compared to experimental values for the ILs [bmim][BF₄] [17], [hmim][BF₄] [18] and [omim][BF₄] at 313 K. For the [bmim][BF₄], deviations between

experimental and calculated values are higher at low CO₂ concentrations and decrease with increasing pressure. The correlations for [hmim][BF₄] and the predictions for [omim][BF₄] are very good over the whole pressure range.

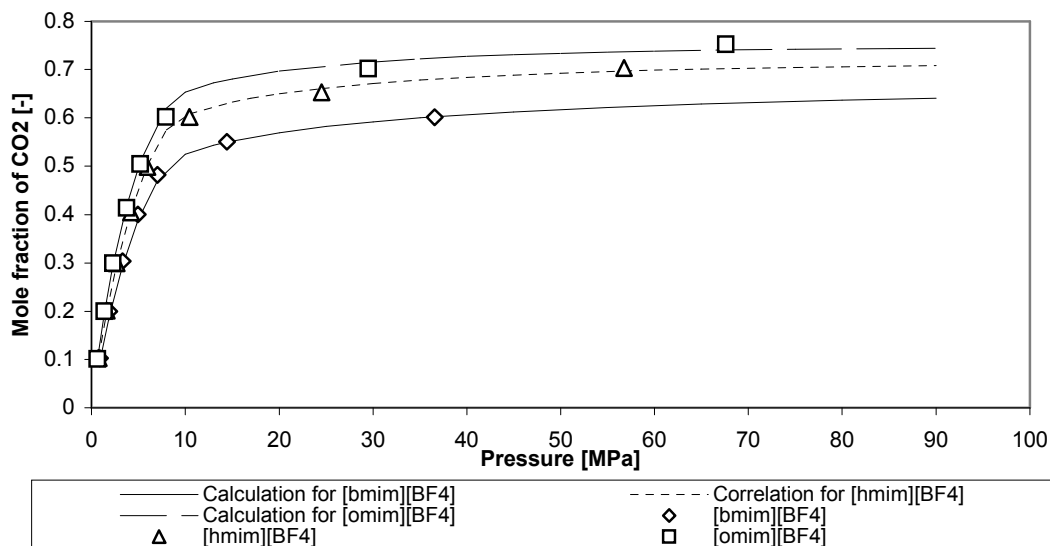


Figure 3: Comparison between GC-EOS predictions and experimental data for binary systems of the ILs [bmim][BF₄], [hmim][BF₄] and [omim][BF₄] with CO₂ at 313 K.

Characteristic of the phase behavior of systems of ILs and CO₂ is that at low concentrations of CO₂, the equilibrium pressure of the system is very low. When the CO₂ concentration is further increased isothermally, the equilibrium pressure increases steeply. The GC-EOS is capable of describing this characteristic phase behavior of ILs.

CONCLUSIONS

The phase behavior of the binary system 1-octyl-3-methylimidazolium tetrafluoroborate + CO₂ was studied. Bubble point measurements showed a change of the solubility of CO₂ in the IL, the pressure needed for completely dissolving the CO₂ increases drastically for high concentrations of the solute. It was shown that the increase of the temperature slightly decreases the solubility of CO₂.

It would be interesting to study the effect of the anion on the solubility of CO₂ when the cation is fixed as [omim]. Further research projects are requested in order to enrich the knowledge on this promising generation of solvents.

The GC-EOS equation was used to model the phase behavior of mixtures of ILs of the homologous family 1-alkyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate with CO₂. For this purpose two new functional groups were defined, consisting of the methylimidazolium cation and the hexafluorophosphate or tetrafluoroborate anion, referred to as the functional groups [-mim][PF₆] and [-mim][BF₄], respectively. The parameter table for the GC-EOS has been extended to include pure group parameters for the [-mim][PF₆] and [-mim][BF₄] groups and interaction parameters for interactions between these groups and the

functional groups CH₃, CH₂ and CO₂. The GC-EOS extended with these parameters is capable of predicting the phase behavior of binary systems of the ILs [emim][PF₆] [19], [bmim][PF₆] [9], [hmim][PF₆] [20], [bmim][BF₄] [17], [hmim][BF₄] [18] and [omim][BF₄] with CO₂. The agreements between predicted and experimental values were very good for pressures up to 20 MPa and even for pressures up to 100 MPa good results were obtained. The results show the capability of the GC-EOS model to describe the phase behavior of binary systems of ILs and CO₂ and its potential for modeling supercritical processes involving ILs.

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