

HIGH-PRESSURE PHASE BEHAVIOR OF BINARY SYSTEMS OF CARBON DIOXIDE AND CERTAIN IONIC LIQUIDS

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Abstract

In this work, the high-pressure phase behavior of binary mixtures of carbon dioxide with three ionic liquids from the family of 1-alkyl-3-methylimidazolium hexafluorophosphates have been studied experimentally. A synthetic method was used to measure vapor-liquid boundaries. Pressures up to 97 MPa have been applied. The effect of the different alkyl groups on the CO₂ solubility in the various ionic liquids has been analysed.

Introduction

Ionic liquids are organic salts composed of cations and anions, which are usually in the liquid phase at room temperature. The following physical properties of ionic liquids make them interesting as the next generation of solvents for industrial applications:

- Good solvents for a wide range of substances: organic, inorganic, polar and non-polar.
- Ionic liquids have negligible vapor pressures, which significantly reduces solvent emission to the environment.
- They have suitable densities and viscosities.

Therefore, they may replace today's toxic, flammable, and polluting volatile organic solvents, such as toluene, hexane, and dichloromethane.

Besides the advantages mentioned above, ionic liquids based on the methylimidazolium cation are attractive species in particular, because of their air and water stability and their wide liquidus range. Recently, Brennecke and Maginn [1] gave an extensive perspective for potential industrial applications of ionic liquids in catalytic reactions, gas separations, liquid separations, cleaning operations, electrolyte/fuel cells, lubricants, and heat transfer fluids.

Most of the work in this area has been focused on methods of synthesizing ionic liquids or the application of ionic liquids as solvents in catalytic reactions [2-5]. Although solute recovery from ionic liquids using supercritical fluids is a potential field of applications [6-7], a systematic study on this subject is lacking. Therefore, knowledge of the phase behavior of near-critical fluids + ionic liquids systems are of major interest.

In this work, experimentally obtained phase behavior are presented for the binary systems of carbon dioxide (CO₂) + 1-ethyl-3-methylimidazolium hexafluorophosphate ([emim][PF₆]),

CO₂ + 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), and CO₂ + 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF₆]). The selected ionic liquids are three members of the 1-alkyl-3-methylimidazolium hexafluorophosphate homologous family. The only difference among them is the length of the alkyl chain attached to the cation of each ionic liquid. Temperatures and pressures up to 366 K and 97 MPa, respectively, have been applied. The solubility of CO₂ in this homologous series of ionic liquids has been compared and the effect of the length of the alkyl chain of the ionic liquids on the solubility of CO₂ has been investigated.

Experimental

The high-pressure experiments were carried out in an autoclave for higher concentrations of CO₂. The Cailletet apparatus was used at lower concentrations of CO₂, where equilibrium pressures were not so high. Both facilities operate according to the synthetic method. In both cases, a mixture of fixed and known composition was enclosed in a Pyrex glass equilibrium cell. For example, for the Cailletet facility this was a thick-walled tube. The open end of the glass tube was submerged in mercury, such that the mercury served both as a sealing fluid for the sample and a pressure transmitting fluid. In both facilities, temperature (or pressure) was fixed at desired values, and the pressure (or the temperature) was varied until a phase change is visually observed for a sample with a constant overall composition. Temperatures can range from 250 K to 450 K for both facilities. Pressures can reach up to 15 MPa for the Cailletet apparatus and up to 100 MPa for the autoclave apparatus. A dead weight pressure gauge was used to measure the pressure inside both facilities. A stainless steel ball driven by reciprocating magnets stirred the sample.

The main difference between the two facilities is in the pressure containment. For the Cailletet apparatus the glass tube itself is the pressure vessel, while for the autoclave apparatus, the glass tube is placed inside a windowed stainless steel autoclave containing pressurized water. Again, mercury acts as the sealing fluid between the water and the sample.

The Cailletet tube is placed in a thermostated water bath. The fluctuations of the bath temperature do not exceed 0.04 K. A platinum resistance thermometer is placed just outside the glass tube. The thermometer is connected to a resistance bridge and the achieved accuracy of the temperature measurement is ± 0.01 K. The pressure is kept constant and measured with a dead weight gauge with an accuracy better than ± 0.003 MPa from 0.2 MPa to 15 MPa. Further details of the Cailletet apparatus and the experimental procedure can be found elsewhere [8,9].

In the autoclave apparatus, the equilibrium cell is also placed in a thermostated water bath. A thermometer is placed inside a wall in the autoclave very close to the glass sample cell. The temperature is measured with the same type of equipment as used for the Cailletet apparatus with a fluctuation of less than 0.05 K. The achieved accuracy of the temperature measurements is again ± 0.01 K. The accuracy of the pressure measurements using a dead weight gauge is better than $\pm 0.04\%$ of the reading from 3.0 MPa to 100.0 MPa. A more detailed description of the autoclave apparatus and the experimental procedures are given elsewhere [10].

The CO₂ used for the measurements was supplied by Messer Griesheim and had an ultra high purity of 99.995%. Solid [emim][PF₆], liquid [bmim][PF₆], and liquid [hmim][PF₆] were

purchased from Fluka and had a purity of more than 97.0%. Prior to use, all ionic liquids were dried under vacuum conditions at room temperature for several days.

Results and Discussion

The solubilities of CO₂ in [emim][PF₆], [bmim][PF₆], and [hmim][PF₆] were determined by measuring the bubble point pressures of the binary systems of each of these substances with CO₂ at different temperatures for several isopleths. Figures 1a, 1b, and 1c presents graphically the phase behavior data of the systems CO₂ + [emim][PF₆], CO₂ + [bmim][PF₆], and CO₂ + [hmim][PF₆], respectively. It can be observed for these three binary systems that the equilibrium pressures are reasonably low at lower concentrations of CO₂. However, when the CO₂ concentration further increases, the equilibrium pressures increase dramatically. This can be shown very well on p-x coordinates. Figure 2 illustrates and compares the p-x diagrams of these systems at 333.15 K. This figure shows the similarities of phase behaviors between these three systems. In all these binary systems, CO₂ shows very high solubilities in each ionic liquid at lower pressures, while the equilibrium pressures increase steeply at higher concentrations of CO₂. This is not a common phase behavior, i.e., normally when a large amount of CO₂ dissolves in the liquid phase at low pressures, the system shows a simple

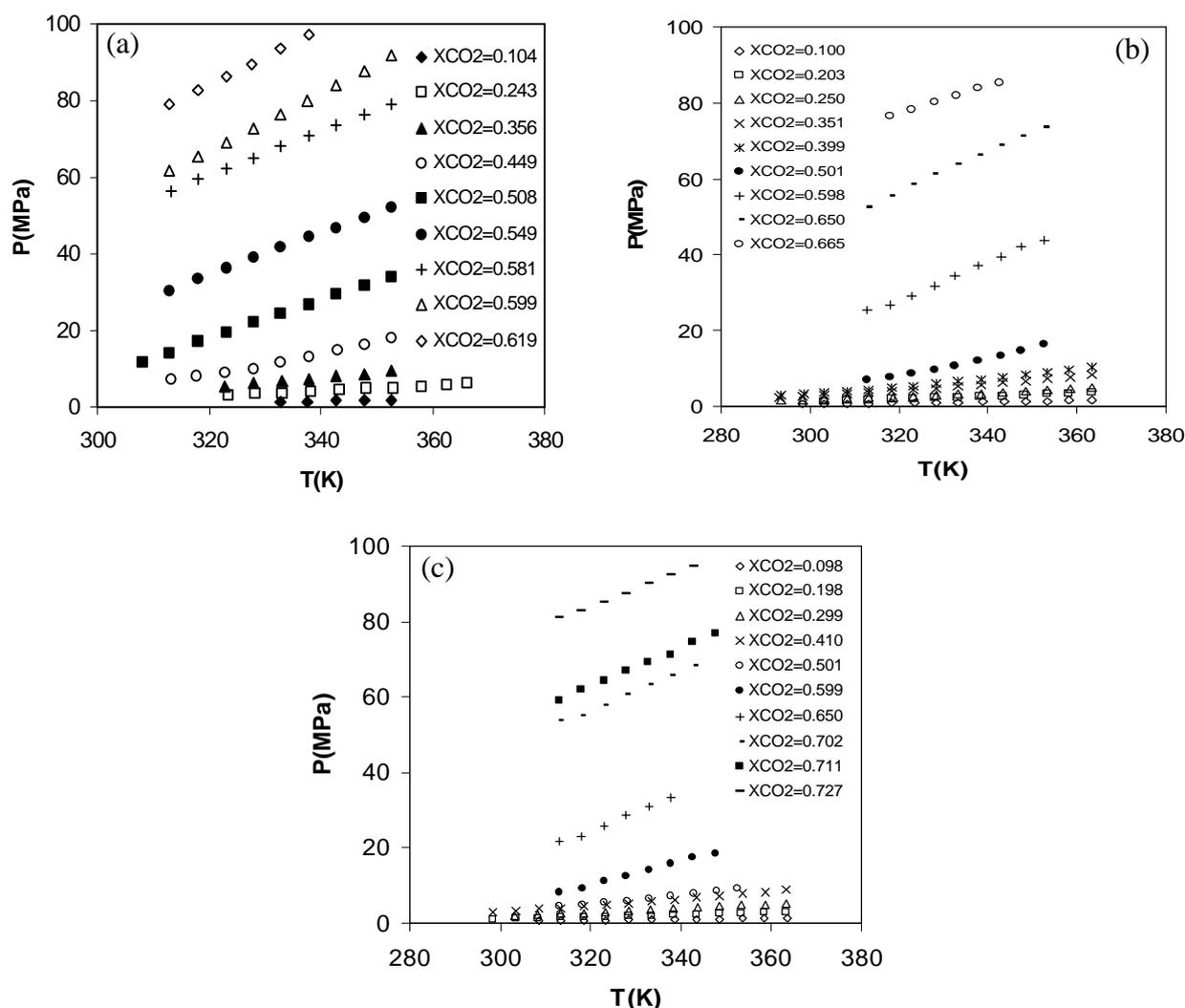


Figure 1. p-T diagrams of the binary systems of CO₂ + 1-alkyl-3-methylimidazolium hexafluorophosphates (a) CO₂ + [emim][PF₆]; (b) CO₂ + [bmim][PF₆]; (c) CO₂ + [hmim][PF₆]

phase envelope with a mixture critical point at moderate pressures. In addition, it is seen that although the solubilities of CO₂ in the three 1-alkyl-3-methylimidazolium hexafluorophosphates are nearly identical for an isotherm at lower pressures, they differ greatly at elevated pressures. Figure 3 shows the effect of the length of the alkyl chain group on the solubility of CO₂ in these ionic liquids at 333.15 K and 10 MPa. It seems that there is an almost linear relationship between the alkyl chain length and the solubility of CO₂ in such ionic liquids at fixed temperature and pressure.

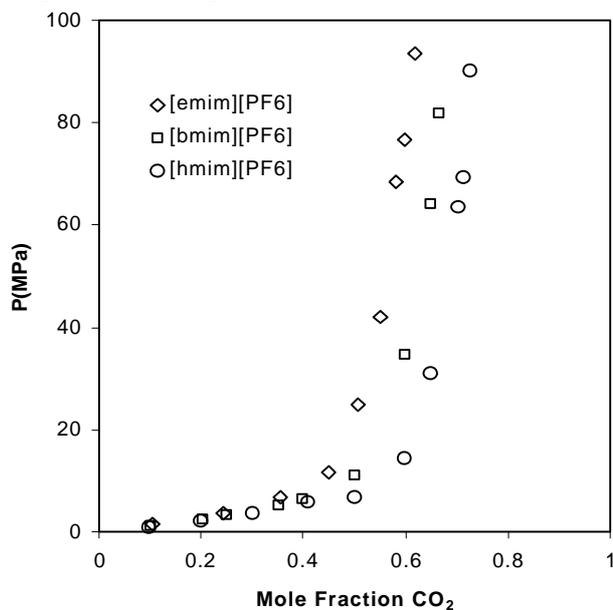


Figure2. p-x diagrams of the binary systems CO₂ + [emim][PF₆], CO₂ + [bmim][PF₆], and CO₂ + [hmim][PF₆] at 333.15 K.

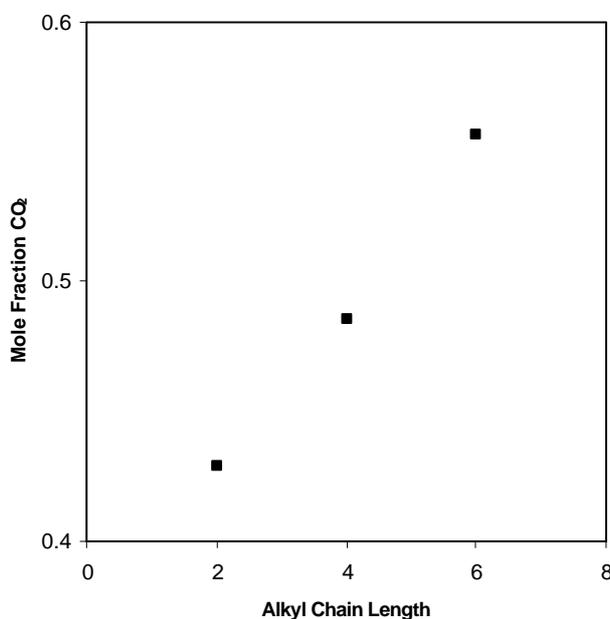


Figure3. The effect of the length of the alkyl chain on the solubility of CO₂ in 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids at 333.15 K and 10 MPa.

Conclusions and Summary

In this work, the phase behavior of binary mixtures of a supercritical fluid (CO₂) and three ionic liquids of the 1-alkyl-3-methylimidazolium hexafluorophosphate family ([emim][PF₆], [bmim][PF₆], and [hmim][PF₆]) have been studied experimentally. We have shown the similarities among the phase behavior of these binary systems. Our study shows that CO₂ has good solubilities in these ionic liquids at lower pressures but instead of having critical points at moderate pressures, their two-phase boundaries extend almost vertically to very high pressures. The effect of the length of the alkyl chain of the three ionic liquids of the same homologous family is also shown on the solubility of CO₂ in each of the ionic liquids. There seems to be a linear relationship between the increase of the alkyl chain length and the increase of the solubility of CO₂ in, at least, the first few members of the 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids.

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