

High pressure solubility of CO₂ in a new low-viscosity ionic liquid based on the tetracyanoborate anion

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High Pressure Solubility of CO₂ in a New Low-Viscosity Ionic Liquid Based on the Tetracyanoborate Anion

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Introduction

Ionic liquids, thanks to their unique properties such as the negligible vapor pressure at room temperature [1, 2] and high thermal stability have been proposed as alternative solvents for several applications. Among the potential applications of ionic liquids in chemical processes is their use in separation technology, including gas separation and supercritical extraction.

One of the most interesting characteristic of ionic liquid systems is that carbon dioxide (CO₂) is highly soluble in the ionic liquid rich phase, but no detectable quantity of ionic liquid is dissolved in the CO₂ [3]. Therefore, it was found to be possible to extract organic solutes from ionic liquids using supercritical CO₂ without any detectable traces of ionic liquid in the supercritical phase.

The application of ionic liquids as solvents for gas separation is interesting because their low volatility prevents the cross-contamination of the gas phase with the liquid, reducing the post-processing of the stream. Determining the optimum conditions where the gas separation is maximize is crucial for the industrial application of ionic liquids. For that reason, abundant information about ionic liquid + gas systems can be found in literature [4].

Improving the solubility of CO₂ in ionic liquids can be achieved by tuning the chemical structure of the cation, and especially of the anion forming the ionic liquid. We present the phase behavior of CO₂ in a new low-viscous ionic liquid, the 1-hexyl-3-methylimidazolium tetracyanoborate ([hmim][TCB]).

Material and methods

The [hmim][TCB] ionic liquid was provided by Merck KgaA, Germany, and no further purification was done upon its use. The only precaution was to keep the ionic liquid in dry storage under vacuum conditions. Ionic liquids are known to be highly hygroscopic [5] and small variation of the water content can modify its properties[6]. Karl-Fischer moisture analysis was done for every sample, and it was found that the water content was less than 400 ppm for all cases. No traces of fluorine were found in a NMR analysis. Within the temperature range of the experiments the ionic liquid did not show any decomposition or reaction with CO₂.

The CO₂ used for the measurements was supplied by Hoek Loos, The Netherlands, and had an ultrahigh purity of 99.995

The solubility of CO₂ in [hmim][TCB] was determined using the Cailletet apparatus. A well known amount of the ionic liquid, whose water content was checked to be below 400 ppm before the filling, was placed in a thick-walled Pyrex glass. The tube is connected to a gas rack where the sample is degassed prior to the addition of a calibrated volume of CO₂ at a registered temperature and pressure. The tube is sealed with mercury, which acts both as sealing agent and as pressure transmitter. More information can be found somewhere else [7].

The experimental procedure is based on the adjustment of temperature and pressure until the occurrence of a phase transition is observed. In the temperature and pressure range studied (from 273 to 373 K and pressures up to 14MPa) only the liquid-vapor (LV) to liquid (L) phase transition was observed.

Results and discussion

The solubility of CO₂ in [hmim][TCB] was determined by measuring the bubble point pressures of the system in the Cailletet apparatus. Preliminary results are shown in Figure 1, where the bubble point pressures of the binary system CO₂ + [hmim][TCB] are presented in form of isopleths at three different mol compositions.

It can be noticed that the CO₂ solubility in [hmim][TCB] is very high. Moreover, it was found that the solubility of the gas in the ionic liquid decreases when the temperature is increased, resulting in higher bubble point pressures. Finally, it was found that the solubility can be enhanced by isothermally increasing the pressure. This is common behavior for ionic liquid + CO₂ systems.

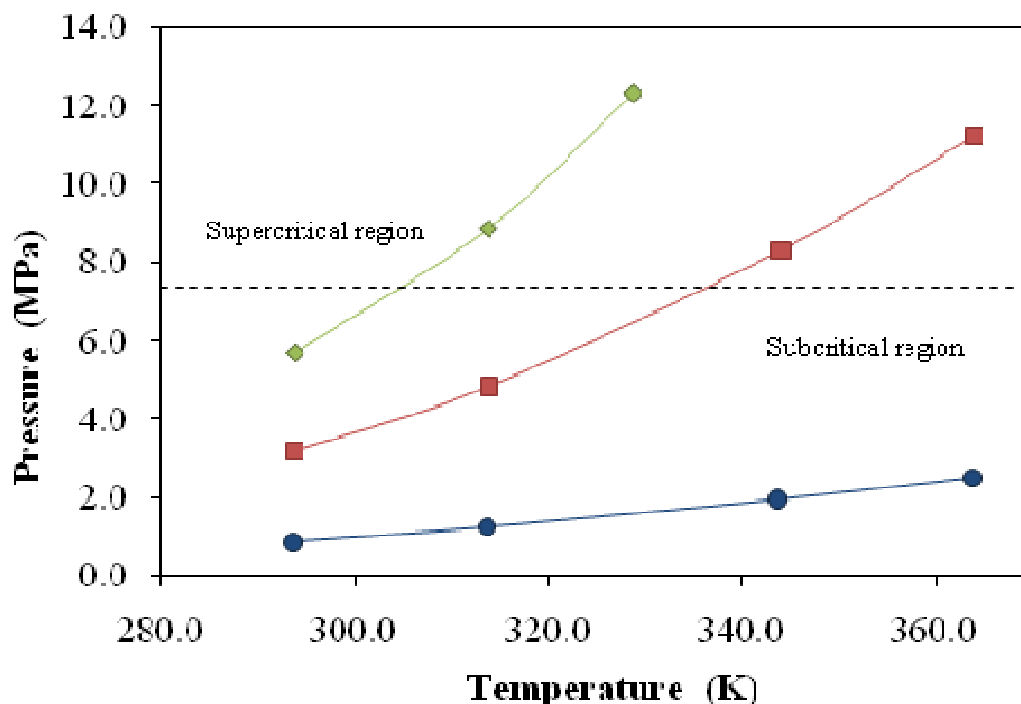


Figure 1: Isoleths of the bubble point pressures for the binary system CO₂ + [hmim][TCB] at different molar composition of CO₂: ●, 25.18%; ■, 60.07%; ◆, 70.16%.

The solubility of CO₂ in [hmim][TCB] is much higher compared to that in other ionic liquids. For example, at the supercritical conditions of 313 K and 8 MPa [11], the solubility of CO₂ in the frequently studied ionic liquid [hmim][BF₄] is roughly 60% mol, while for [hmim][TCB] is almost 70%. Therefore, [hmim][TCB] is especially interesting for gas separation applications.

Conclusions

The tendency of ionic liquid developers moves towards the direction of finding the optimum anion-cation combination to improve the solubility of CO₂ in order to reduce the pressure required for the potential industrial applications for ionic liquid technology. But this also promotes the supercritical application of the CO₂ + IL systems, since the solubility of CO₂ in supercritical conditions is enhanced.

The [hmim][TCB] is a good example of this solubility improvement and its low viscosity makes it an excellent candidate for applications in processes related with CO₂ capture.

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