

# Solubility of Carbon Dioxide in the Ionic Liquid 1-Ethyl-3-methylimidazolium Tris(pentafluoroethyl)trifluorophosphate

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## Introduction

In the last two decades, ILs were recognized as novel solvents for gas separation processes [1]. Reason is that the solubility of various gases (e.g., CO<sub>2</sub>) in ILs is high, while ILs cannot evaporate and contaminate the gas stream, because their vapor pressure at room temperature is negligibly low [2]. Therefore, ILs can be used in gas absorption processes e.g., as solvents for carbon capture [2, 3]. This work investigates the solubility of CO<sub>2</sub> in such an IL i.e., 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([emim][eFAP]) at temperature round 333 K and pressures up to 6.7 MPa. The molecular structure of [emim][eFAP] is schematically shown in Figure 1. To the best of our knowledge the CO<sub>2</sub> solubility in this IL has never been measured before.

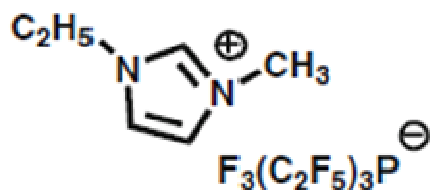


Figure 1: Structure of 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([emim][eFAP])

## Materials

The CO<sub>2</sub> gas was supplied by Hoek Loos with purity of 99.995%. The IL [emim][eFAP] was provided by Merck Chemical Company with a purity of  $\geq 99.0\%$  and was used as such. The water content of the IL was measured using Karl Fischer moisture analysis and was less than 200

ppm. Within the temperature range of the experiments, the IL did not show any decomposition or reaction with the CO<sub>2</sub>.

## **Experimental set-up and procedure**

The solubility of CO<sub>2</sub> in [emim][eFAP] was determined by measuring bubble point pressures at fixed temperature and different compositions using the Cailletet equipment. The temperature was adjusted for a sample at constant composition until a (liquid + vapor)-to-(liquid) phase transition was visually observed.

The main part of the Cailletet equipment is a Pyrex glass tube, which serves as high pressure vessel and equilibrium cell. A known quantity of IL was transferred to the Pyrex tube. Thereafter, the tube was connected to a gas rack, where the IL is degassed first under vacuum. Next, a vessel with calibrated volume was filled with CO<sub>2</sub>. The amount of moles of CO<sub>2</sub> in the calibrated vessel could be calculated using the virial equation of state since pressure, temperature and volume were known. Mercury was used to push the CO<sub>2</sub> into the Pyrex tube, to seal the sample and to act as pressure-transmitter fluid. The pressure was generated by pressing hydraulic oil into the system with a screw-type hand pump, which caused the level of the mercury column in tube to rise and to create the desired pressure in the top. A dead-weight pressure gauge was used to measure the pressure. The temperature of the sample was kept constant by circulating the heat transferring fluid through a thermostat jacket surrounding the Cailletet tube. The temperature was measured with a platinum resistance thermometer inserted in the heat jacket. The sample was kept well-mixed by moving a steel ball with two moving magnets.

The Cailletet equipment allows measurement of phase equilibria within a pressure range of 0.1 to 15 MPa and temperatures ranging from 255 to 470 K, depending on the heat-transferring fluid used. In our experiment the fluid used was water; thus, the temperature range was limited from 275 to 370 K. The uncertainty of the measurements is  $\pm 0.005$  mole fraction in the composition,  $\pm 0.01$  K for the temperature measurements and  $\pm 0.003$  MPa for the pressure measurements.

## **Results and discussion**

The solubility of CO<sub>2</sub> in the IL [emim][eFAP] was determined at various compositions of CO<sub>2</sub> in the IL and pressures up to 6.67 MPa by measuring the bubble point pressures at fixed temperature. The water content was kept below 200 ppm for sample prepared. The results are shown in Figure 2, where the bubble point pressures are plotted against the mole fraction of CO<sub>2</sub> at 333 K. It can be seen that the bubble point pressures increase more than linearly with increasing CO<sub>2</sub> concentration at given temperature, which is the typical behavior for IL + CO<sub>2</sub> systems [4].

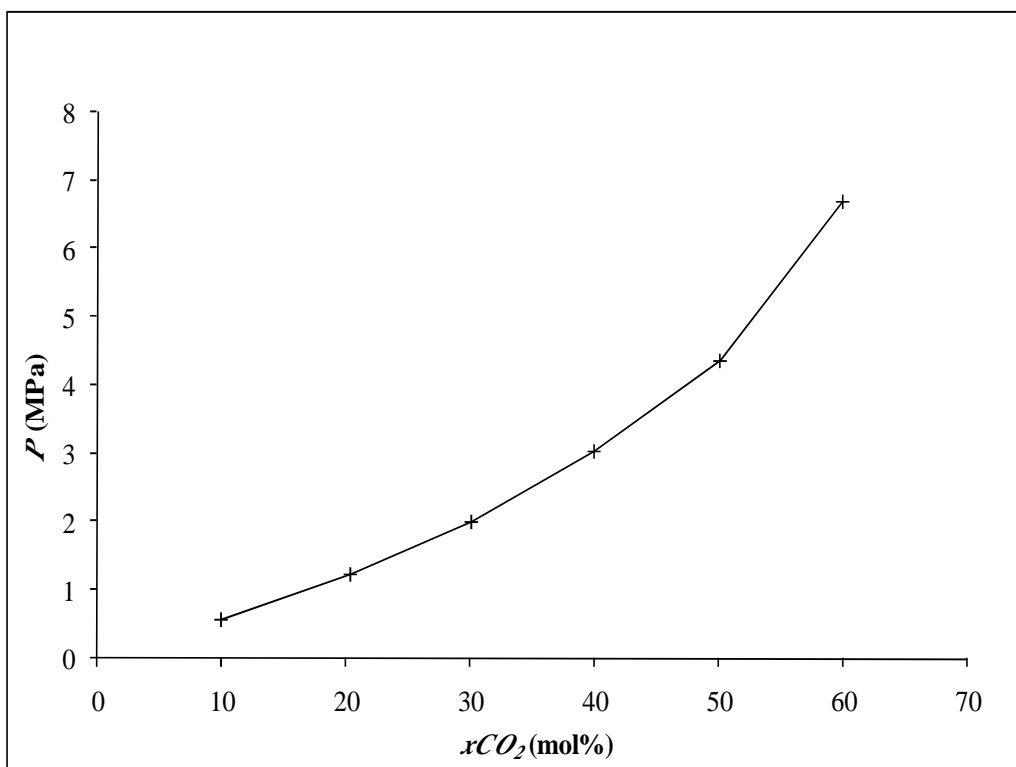


Figure 2: Isotherms of the bubble point pressures at temperature of 333 K of the binary system  $CO_2$  + [emim][eFAP].

The solubilities of  $CO_2$  in [emim][eFAP] at 333 K are compared to the solubilities of  $CO_2$  at the same temperature in other ILs sharing the same cation i.e., 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([emim][Tf<sub>2</sub>N]) [5], 1-ethyl-3-methylimidazolium hexafluoroborate ([emim][PF<sub>6</sub>]) [6], 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF<sub>4</sub>]) [7], and 1-ethyl-3-methylimidazolium ethylsulfate ([emim][EtSO<sub>4</sub>]) [8]. It was found that the solubility of  $CO_2$  in [emim][eFAP] is higher than that in all other ILs with the same cation following the trend: [emim][eFAP] > [emim][Tf<sub>2</sub>N] > [emim][EtSO<sub>4</sub>] = [emim][PF<sub>6</sub>] > [emim][BF<sub>4</sub>]. For example, at 333 K the IL [emim][eFAP] is able to dissolve up to 60 mol% of  $CO_2$  at a pressure of only 6.7 MPa, which is much lower than the required pressure in all other ILs with the same cation. This is most likely due to presence of a large amount of fluorine atoms in the anion, which result in an increase of the  $CO_2$  solubility in the IL [9]. Reason is that the fluorine atoms show specific interaction with  $CO_2$  [10, 11]. Moreover, the IL [emim][eFAP] shows higher stability with respect to moisture and air compared to other fluorinated ILs with smaller anions, such as ILs with the PF<sub>6</sub><sup>-</sup> or the BF<sub>4</sub><sup>-</sup> anion [12]. Therefore, [emim][eFAP] is an attractive solvent for gas separation and carbon capture processes.

## Conclusions

The solubility of CO<sub>2</sub> in the IL [emim][eFAP] has been experimentally determined. It is shown that CO<sub>2</sub> is more soluble in this IL than in any other IL sharing the same cation. Reason is that the anion of this IL is highly fluorinated. Moreover, the anion size is large, resulting in a higher stability with respect to moisture and air, compared to other fluorinated ILs. Therefore, [emim][eFAP] is a promising solvent for industrial gas separation and carbon capture processes.

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