



Volumetric and phase behaviour of mixtures of fluoroalkylphosphate-based ionic liquids with high pressure carbon dioxide



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ABSTRACT

The high-pressure solubility of carbon dioxide in ionic liquids based on tris(pentafluoroethyl)trifluorophosphate ([eFAP]) anion, combined with 1-ethyl-3-methylimidazolium ([emim]), 1-butyl-3-methylimidazolium ([bmim]) and 1-hexyl-3-methylimidazolium ([hmim]) cation, was determined experimentally at the temperature of 313.15 K and pressures up to 10 MPa. Measurements of the volume expansion of the liquid phase upon carbon dioxide dissolution are also reported. The obtained results show that the solubility of CO₂ in ionic liquids with the fluoroalkylphosphate anion, as well as the CO₂-induced volume expansion of the liquid, are among the highest so far reported for ionic liquids where CO₂ dissolves through “physical” mechanisms.

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1. Introduction

Ionic liquids have attracted increased attention, in both industry and academia, during the last two decades. They are considered as a new class of alternative solvents and their “green” character is largely related to negligible vapour pressure that prevents air polluting emissions. The field of potential applications for ionic liquids is rapidly growing. As remarked in our recent work on volumetric and phase behaviour of mixtures of tetracyanoborate-based ionic liquids and high pressure carbon dioxide [1], they have been proposed as promising solvents for selective CO₂ capture, in carbon capture and storage processes [2,3], as well as, in combination with supercritical carbon dioxide, for many applications in separations and chemical or biochemical reactions [4–7].

Ionic liquids with fluorinated anions show particularly high CO₂ solubility. However, well-known and widely used imidazolium based ionic liquids with hexafluorophosphate ([PF₆][−]) or tetrafluoroborate ([BF₄][−]) anion are sensitive to moisture and air, especially at elevated temperature [8]. The hydrolytic stability of hexafluorophosphate ionic liquids can be improved by replacing some

fluorine atoms with hydrophobic perfluoroalkyl groups. The new ionic liquids with fluoroalkylphosphate anions [FAP] – [PF₃RF₃] (RF = C₂F₅ [eFAP], C₃F₇ [pFAP], or C₄H₉ [bFAP]), were reported as one of the most CO₂-philic among ionic liquids with physical absorption mechanisms [9–12]. Yet, the high-pressure data on CO₂ solubility in this new family of ionic liquids is scarce [9,13].

One very interesting feature of ionic liquids is their volumetric behaviour in a mixture with CO₂. Contrarily to common organic solvents, where expansion is generally observed on gas dissolution, the volume of ionic liquids barely increases even when large amounts of CO₂ are dissolved [14,15]. For example, the volume expansion of 1-hexylimidazolium bis(trifluoromethylsulfonyl)imide, ([hmim][NTf₂]), with CO₂ at 343 K and 12 MPa is only 25 % despite the fact that the CO₂ solubility at these conditions is approximately 70% mol. It was presumed that this is due to the strong Coulombic forces associated with the ionic nature of ionic liquids and the resultant cohesive structure.

Herein, we report high-pressure data on CO₂ solubility in ionic liquids based on tris(pentafluoroethyl)trifluorophosphate anion paired with a series of 1-alkyl-3-methylimidazolium cations ([C_nmim][eFAP] with n = 2,4,6), at the temperature of 313.15 K and pressures up to 10 MPa. To our best knowledge, the high-pressure solubility data of CO₂ in 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, [bmim][eFAP], has not

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been reported in the literature. We also present the volumetric behaviour of mixtures of those ionic liquids with CO₂.

2. Materials and methods

2.1. Materials

The ionic liquids used in this work, 1-ethyl-3-methylimidazoliumtris(pentafluoroethyl)trifluorophosphate ([emim][eFAP]), 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([bmim][eFAP]), and 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([hmim][eFAP]), were purchased from Merck KgaA, Germany, and used without further purification. The water content, determined by Karl Fischer coulometric titration (Metrohm 831 KF coulometer) was no higher than 250 ppm in all studied cases. Carbon dioxide (99.98% purity) was supplied by Air Liquide and was used as received. Dichloromethane of ≥ 99.9 mass% purity (Sigma–Aldrich) was used in solubility measurements as a solvent, in order to wash the lines and dissolve the salts precipitated after CO₂ expansion from the sample loop, as described below.

2.2. Apparatus and experimental procedure

The measurements of solubility were performed using an isochoric saturation, analytical method in an especially designed apparatus. A detailed description of this facility and methodology has been described in a previous work [16]. The core of the apparatus is a 3.5 cm³, fixed volume, movable-position high-pressure cell, with a sapphire window allowing visualisation of the internal volume. The cell is placed inside an air bath but manipulated from outside. CO₂ is introduced into the cell by a screw injector pump and the whole content is stirred with a magnetic stirrer. After reaching equilibrium, samples are collected in a closed loop. The amount of CO₂ dissolved in ionic liquid is determined by an expansion into a previously calibrated volume at sub-atmospheric pressure. All experiments were performed at least twice and the average result was taken. The reproducibility of the solubility values was 0.02 mole fraction.

The methodology and apparatus used for volume expansion experiments were already described [1]. The core of the experimental setup comprises a high pressure sapphire tube cell (ca. 30 cm³ volume) with a ruler attached to its side. It is placed inside a thermostatic air bath with high-power ventilator ensuring uniform bath temperature.

Ionic liquid is loaded in to the cell up to the level above the magnetic stirrer, and the required temperature is settled. The initial level of the liquid (at atmospheric pressure, P₀, and temperature, T, equalled to 313.15 K) is read out from the ruler and the whole system is flushed with CO₂. An experimental run starts with an addition of a small portion, ca. 0.5 MPa, of CO₂ into the cell. The mixture is stirred for approximately 20 min and then left for equilibration. The stirring and resting periods, if needed, are extended to ensure equilibrium. A new level of the liquid is recorded and an experimental run repeated until no significant change in the liquid level is observed. All experiments were performed twice to ascertain the reproducibility of the measurements. The calculated precision of the volume expansion measurements is $\pm 7\%$ and the estimated uncertainties of the molar liquid volumes are ± 2 cm³/mol.

3. Results and discussion

Table 1 presents high-pressure solubility data of CO₂ in tris(pentafluoroethyl)trifluorophosphate-based ionic liq-

Table 1

Experimental solubility of CO₂ in [emim][eFAP], [bmim][eFAP] and [hmim][eFAP] at 313.15 K. x_{CO2} stands for mole fraction of carbon dioxide.

Ionic liquid	p/MPa	x _{CO2}
[emim][eFAP]	1.98	0.38
	4.02	0.57
	6.07	0.68
	8.07	0.74
	10.24	0.78
[bmim][eFAP]	2.02	0.44
	4.00	0.62
	6.05	0.69
	8.06	0.77
	10.14	0.78
[hmim][eFAP]	2.05	0.50
	3.72	0.62
	6.09	0.73
	8.08	0.79
	9.99	0.80

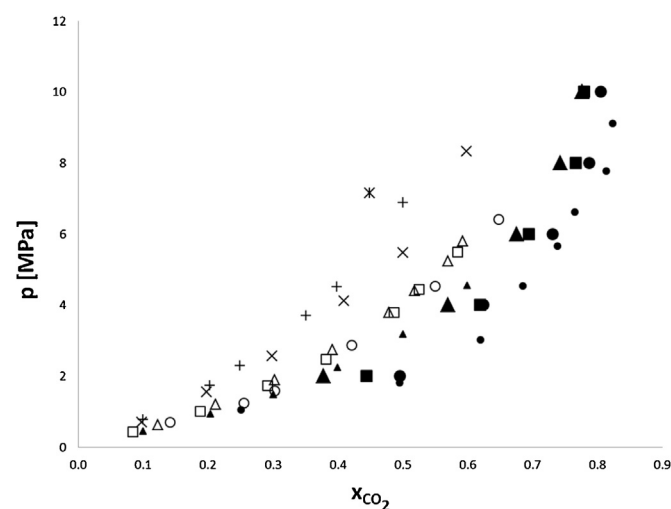


Fig. 1. Solubility of CO₂ in several ionic liquids at 313.15 K: ●, [hmim][eFAP] [this work]; ●, [hmim][eFAP] [9]; ■, [bmim][eFAP] [this work]; ▲, [emim][eFAP] [this work]; ▲, [emim][eFAP] [13]; ○, [hmim][NTf₂] [21]; □, [bmim][NTf₂] [20]; △, [emim][NTf₂] [19]; × [hmim][PF₆] [24]; + [bmim][PF₆] [23]; * [emim][PF₆] [22].

uids: [emim][eFAP], [bmim][eFAP] and [hmim][eFAP], at the temperature of 313.15 K and pressures up to 10 MPa. (Table 2)

Solubility of CO₂ in fluoroalkylphosphate-based ionic liquids at high pressures was measured experimentally by Muldoon et al. [9] and Althuluth et al. [13]. The first group studied CO₂ absorption in [hmim][eFAP] and 1-pentyl-3-methylimidazolium tris(pentafluorobutyl)trifluorophosphate ([p₅mim][bFAP]) at two temperatures, 313.3 K and 333.3 K, and pressures up to 9 MPa. The second group investigated the solubility of CO₂ in [emim][eFAP] in the temperature range of 283.75–364.13 K and pressure up to 12 MPa. A comparison of CO₂ solubility in [emim][eFAP] measured in the current study indicates a very good agreement with the data reported in the literature (Fig. 1). The solubility values obtained for [hmim][eFAP] differ slightly from those found in the literature, but remain mostly within the established uncertainties (Figs. 2, 3)

The compatibility of fluorinated substituents with CO₂ is commonly used to improve the CO₂-philicity of organic compounds [17]. Therefore, it was expected that ionic liquids with anion analogous to [PF₆], where three fluorine atoms are replaced by three fluoroalkyl chains, can absorb more CO₂. Zhang et al. [18], using a computational screening methodology, indeed found that the solubility of CO₂ in ionic liquids with the [eFAP] anion is among the highest, and confirmed it experimentally. For the same 1-hexyl-3-

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