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Solubility of carbon dioxide, nitrous oxide, ethane, and nitrogen in 1-butyl-1-methylpyrrolidinium and trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate (eFAP) ionic liquids

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ABSTRACT

The density and viscosity of the ionic liquids 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate [C_1C_4Pyrro][eFAP] and trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate [P_{66614}][eFAP] were measured as a function of temperature and pressure and as a function of temperature, respectively. These two ionic liquids are more viscous than those based in the same anion associated to imidazolium cations. The effect of the addition of water on the density and viscosity of [P_{66614}][eFAP] was studied at pressures close to atmospheric and as a function of the temperature. This ionic liquid is only partially miscible with water, its solubility being of around $X_{H_2O} = 0.2$ in the range of (303 to 315) K. Experimental values of the solubility of carbon dioxide, nitrous oxide, ethane, and nitrogen were obtained as a function of temperature and at pressures close to atmospheric. Carbon dioxide and nitrous oxide are the more soluble gases with mole fraction solubilities up to $7 \cdot 10^{-2}$. Ethane is four times and 1.3 times less soluble than carbon dioxide in [C_1C_4Pyrro][eFAP] and [P_{66614}][eFAP], respectively. Nitrogen is one order of magnitude less soluble than the others gases in the two ionic liquids studied. In order to understand behavior of the different gases with these ionic liquids, the thermodynamic functions of solvation such as enthalpy and entropy were calculated from the variation of the Henry's law constant with temperature. It is shown that the more favorable interactions of the gases with the ionic liquid explain the larger solubility of carbon dioxide and nitrous oxide in [C_1C_4Pyrro][eFAP]. In the case of [P_{66614}][eFAP], it is the less favorable entropic contribution that explains the lower solubility of ethane in this ionic liquid.

1. Introduction

Ionic liquids are considered as attractive solvents for gas separations [1] as they can be able to selectively and efficiently absorb one gas in a mixture. In particular, they have been indicated as possible alternatives for carbon dioxide removal from flue-gas streams by chemical [2] or physical absorption [3]. Several properties are significant for the evaluation of ionic liquids as liquid absorbers for gaseous solutes – the absorption capacity, the selectivity and the mass transfer – as they will determine the design and cost of possible industrial processes [4].

We are interested in the measurement of the solubility of gases – carbon dioxide, nitrous oxide, ethane, and nitrogen – in ionic liquids based on the anion tris(pentafluoroethyl)trifluorophosphate coupled to the 1-butyl-1-methylpyrrolidinium or the trihexyl(tetradecyl)phosphonium cation. This new class of ionic liquids containing fluorinated anions was first synthesized in 2005 by Ignat'ev *et al.* [5] and have been proposed as replacements for ionic liquids containing other fluorinated anions that might be hydrolytically unstable, especially at elevated temperature.

The solubility of different gases in tris(pentafluoroethyl)trifluorophosphate based ionic liquids has already been reported in the literature but mainly for those containing imidazolium cations. Solubility of carbon dioxide in [C_1C_6Im][eFAP] was measured experimentally by Muldoon *et al.* [6] and Yokozeki *et al.* [7]. Blath *et al.* [8] also studied the solubility of different gases in this same ionic liquid. Recently, Almantariotis *et al.* [9] have measured experimentally the solubility of carbon dioxide, nitrogen, ethane and nitrous oxide in [C_1C_2Im][eFAP], [C_1C_4Im][eFAP], and [C_1C_6Im][eFAP]. Results for the solubility of carbon dioxide in [C_1C_6Im][eFAP], expressed in Henry's law constant, agree to within 2.5% between the different authors except for the values reported by Blath *et al.* [8], that show deviations of up to 12% from the other sets of values.

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Different predictive models have also been used to assess gas solubility in these ionic liquids. The solubility of carbon dioxide in [C_1C_2Im][eFAP], [C_1C_4Im][eFAP], and [C_1C_6Im][eFAP] was predicted by Zhang *et al.* [10] using COSMO-RS and Zhang *et al.* [11] studied the solubility of carbon dioxide in [C_1C_6Im][eFAP] using Monte Carlo simulation.

It was observed that the length of the alkyl chain of the cations does not affect significantly the solubility of carbon dioxide in the tris(pentafluoroethyl)trifluorophosphate based ionic liquids. On the contrary, the nature of the anion has a very significant effect on the solubility of carbon dioxide, the tris(pentafluoroethyl)trifluorophosphate based ionic liquids showing higher solubilities of carbon dioxide when compared to ionic liquids with other anions. For carbon dioxide in [C_1C_4Im][eFAP], an Henry's law constant of 25.0 bar was found at 303.15 K [9], compared with 36.4 [12] bar, 57.1[13] bar and 61.6[14] bar in [C_1C_4Im][NTf_2], [C_1C_4Im][PF_6] and [C_1C_4Im][BF_4], respectively.

The solubility of gases in tris(pentafluoroethyl)trifluorophosphate based ionic liquids with cations different from alkylimidazolium are rare. Blath *et al.* [8] have reported values of solubility of carbon dioxide, nitrogen, carbon monoxide and methane in [P_{66614}][eFAP]. Zhang *et al.* [10] have used COSMO-RS to predict also the solubility of carbon dioxide in [C_1C_4Pyrro][eFAP] at 298 K, and have compared these values with experimental data they obtained at temperatures from (283 to 323) K. The work of Blath *et al.* showed that the solubility of carbon dioxide is higher in [C_1C_6Im][eFAP] than in [P_{66614}][eFAP] when expressed in mass fraction. Zhang *et al.* have measured an higher solubility of carbon dioxide in [C_1C_6Im][eFAP] than in [C_1C_4Pyrro][eFAP] with values of Henry's law constants equal to 23.7 and 28.5, respectively, at 298.6 K.

This work follows previous studies aiming to explain the influence of fluoro-moieties in ionic liquids in the gas absorption by these liquids [15,9]. It has been concluded before that the presence of fluorinated alkyl-side chains in imidazolium cations significantly influences the solubility of carbon dioxide [15]. The effect of the fluorination in the anion was assessed by studying gas solubility in ionic liquids containing the tris(pentafluoroethyl)trifluorophosphate anion coupled with imidazolium based cations [9]. The presence of this anion influences the solubility of gases and such ionic liquids were found to be good absorbents for carbon dioxide, the Henry's law constant for CO_2 in [C_1C_4Im][eFAP] being as low as 25.0 at 303.15 K [9]. To complete these results, we have decided to study the effect of changing the cation in the ionic liquids with the tris(pentafluoroethyl)trifluorophosphate anion.

In the present work, experimental solubilities of carbon dioxide, nitrous oxide, ethane and nitrogen in [C_1C_4Pyrro][eFAP] and [P_{66614}][eFAP] are determined as a function of the temperature from (303.15 to 343.15) K and at pressure close to atmospheric, using an isochoric saturation method. From the solubility data, the Henry's law constants and the thermodynamic properties of solvation were calculated.

2. Experimental

2.1. Materials

The two samples of ionic liquids used were purchased from Merck with mole fraction purities of 0.995. Their decomposition temperatures were determined using a modulated DSC 2920 from TA Instruments and were found to be 503 K for [C_1C_4Pyrro][eFAP] and 473 K for [P_{66614}][eFAP], respectively.

The ionic liquids were kept under vacuum for 15 h at 303 K before each measurement. The water contents of each degassed sample were determined, with a precision of ±5 ppm, using a coulometric Karl Fisher titrator (Mettler Toledo DL31). The water content of the degassed samples was found to be 15 ppm for [C_1C_4-Pyrro][eFAP] and less than 5 ppm for [P_{66614}][eFAP].

The gases used have the following specifications: carbon dioxide from AGA/Linde Gas has a mole fraction purity of 0.99995; nitrous oxide from Linde has a mole fraction purity of 0.995; ethane from AGA/Linde GAZ has a mole fraction purity of 0.995 and nitrogen from SAGA has a mole fraction purity of 0.998. The gases were used as received from the manufacturer.

2.2. Density measurements

Densities were measured using a U-shape vibrating-tube densimeter (Anton Paar, model DMA 512) operating in a static mode, following the procedure described in previous publications [16,17]. Measurements for [C_1C_4Pyrro][eFAP] and [P_{666614}][eFAP] were performed for pressures up to 25 MPa and at temperatures from (293 to 343) K.

The temperature in the densimeter was maintained constant to within ±0.01 K by means of a recirculating bath equipped with a PID temperature controller (Julabo FP40-HP). For measuring the temperature, a 100 Ohm platinum resistance thermometer (precision of ±0.02 K and accuracy of ±0.04 K) was used. Its calibration was performed by verifying a water triple point (triple point cell by Hart Scientific) and by comparison against a 100 Ohm platinum resistance Hart Scientific model 1502A.

The measured period of vibration (τ) of a U tube is related to the density (ρ) according to: $\rho = A\tau^2 + B$ where A and B are parameters that are function of temperature and pressure determined by calibration between temperatures of (293 and 343) K (and pressures of 0.1 and 25 MPa), using as calibration fluids *n*-heptane, bromobenzene, and 2,4-dichlorotoluène following the recommendations by Schilling *et al.* [18]. Density measurements were performed in steps of 10 K. The uncertainty of the density measurements is estimated as 10^{-4} g · cm^{-3}.

2.3. Viscosity measurements

The dynamic viscosities of the two ionic liquids [C_1C_4Pyrro][eFAP] and [P_{666614}][eFAP] previously dried under vacuum were measured using an Anton Paar AMVn rolling ball viscosimeter, as a function of the temperature from (293.15 to 363.15) K (controlled to within 0.01 K and measured with an accuracy better than 0.05 K) and at atmospheric pressure. Before starting the measurements, the 3 mm diameter capillary tube was calibrated as a function of temperature and angle of measurement using a standard viscosity oil from Cannon (N35). The overall uncertainty on the viscosity is estimated as ±1.5%.

2.4. Gas-solubility measurements

The experimental method used for the gas solubility measurements is based on an isochoric saturation technique that has been described in previous publications [13,14]. In this technique, a known quantity of gaseous solute is placed in contact with a precisely determined quantity of degassed solvent at a constant temperature inside an accurately known volume. When thermodynamic equilibrium is attained, the pressure above the liquid solution is constant and is directly related to the solubility of the gas in the liquid.

The quantity of ionic liquid introduced in the equilibration cell is determined gravimetrically. This quantity is equal to the amount of solvent present in the liquid solution, n_1^{liq}, as the ionic liquid does not present a measurable vapor pressure. The amount of solute present in the liquid solution, n_2^{liq} (subscripts 1 and 2 stand for solvent and solute, respectively), is calculated by the difference between two *pVT* measurements: first when the gas is introduced