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Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283 K and 343 K and at pressures close to atmospheric

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Abstract

Experimental values for the solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF_4] – a room temperature ionic liquid – are reported as a function of temperature between 283 K and 343 K and at pressures close to atmospheric. Carbon dioxide is the most soluble gas with mole fraction solubilities of the order of 10^{-2}. Ethane and methane are one order of magnitude more soluble than the other five gases that have mole fraction solubilities of the order of 10^{-4}. Hydrogen is the less soluble of the gaseous solutes studied. From the variation of solubility, expressed as Henry's law constants, with temperature, the partial molar thermodynamic functions of solvation such as the standard Gibbs energy, the enthalpy, and the entropy are calculated. The precision of the experimental data, considered as the average absolute deviation of the Henry's law constants from appropriate smoothing equations is of 1%.

Keywords: Solubility; Gases; Ionic liquids; bmimBF_4

1. Introduction

The main objective of this work is to investigate the interactions between room temperature ionic liquids and a variety of small gaseous molecules. In the current paper we present the study of the solubility of eight different gases in one ionic liquid as a function of temperature and at pressures close to atmospheric. Low pressure gas solubilities can constitute an important source of information about the molecular mechanisms involved in dissolution processes as they are directly related to the thermodynamic properties of solution. The knowledge of the solubility of gases in ionic liquids is also of practical interest as it is useful in the calculation of (vapour + liquid) equilibria in systems of potential technological interest namely in solvents for reaction systems or for the development of new separation processes.

The room temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF_4], was selected for this study. Imidazolium based ionic liquids are amongst the most widely used at present as they seem to be promising solvents for technological applications exhibiting properties that enable their use as reaction media. Although [bmim][BF_4] is commercially available at reasonable prices with a low level of impurities, there is still a lack of solubility data on this particular ionic liquid. Most of the studies described in the literature concerning the solubility of gases in ionic

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liquids are dedicated to systems involving carbon dioxide as solute. This can be explained first by its practical interest especially in separations processes [1]. Furthermore, as it is highly soluble in most room temperature ionic liquids (typical values of the Henry's law constant below 10 MPa) [2], its solubility is relatively easy to measure with a good precision using common experimental techniques.

Our research group has previously studied the solubility of carbon dioxide, oxygen [3] and argon [20] as a function of temperature in [bmim][BF_4]. Carbon dioxide was found to be much more soluble in the ionic liquid than the other two gases for temperatures ranging from $T = 303$ K to $T = 343$ K. The reported solubility decreases with temperature in the former case and increases in the latter. The experimental technique previously used is essentially the same as the one reported here but significant improvements were made both in the experimental apparatus and in the procedure followed so it was chosen to study again the solubility of these gases in addition to other five gaseous solutes measured for the first time in the present work.

Cadena *et al.* [2] have determined the solubility of carbon dioxide in [bmim][BF_4] at three temperatures between $T = 283$ K and $T = 323$ K using a gravimetric microbalance for measurements at pressures up to 1.4 MPa. The Henry's law constants calculated from these measurements increase with temperature (exothermic solvation) and vary from 4.08 MPa to 8.89 MPa. These values agree with our previous measurements at $T = 298$ K, to within the mutual uncertainties, but a significant difference is found at the higher temperature end. These results have been recently recalculated by the same authors and the new Henry's law constant values also increase with temperature varying now from 4.18 MPa to 8.86 MPa. These new values are reported by Anthony *et al.* [5] together with original data on the solubility of gases in several ionic liquids that also include the study of carbon monoxide in [bmim][BF_4] for which the concentration in solution was non detectable. The same research group has studied several systems involving gases and ionic liquids at pressures not far from atmospheric but also at higher pressures using a stoichiometric phase equilibrium apparatus. For example, nine different gases were studied in 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6], at low pressures as a function of temperature [5], and it was observed that carbon dioxide is much more soluble than the other gases, closely followed by ethane and ethylene. Carbon monoxide, hydrogen and nitrogen were observed to be much less soluble and were not detected by the experimental technique used. The same authors found that gas solubilities decrease as a function of temperature except in the case of oxygen and argon for which an endothermic solubilization was observed (the solubility increases with temperature). Other studies by the same authors were devoted to the influence of the nature of the ionic liquid on the solubility of carbon dioxide both experimentally [2,6,7] and by molecular simulation [2]. The two approaches seem to indicate that it is the anion that has the greatest impact on the solubility of the carbon dioxide.

In connection with the study of catalytic hydrogenation in ionic liquid-phase, Berger *et al.* [8] have reported the solubility of hydrogen in [bmim][BF_4] (and in [bmim][PF_6]). Their experimental method was based on the measurement of a pressure drop (at total pressures below 5 MPa), at constant temperature and constant volume. It was found that hydrogen was significantly more soluble in [bmim][BF_4] (Henry's law coefficient of 180 MPa at room temperature) than in [bmim][PF_6]. A much higher value of 580 MPa for the Henry's law constant (corresponding to a lower solubility) was found by Dyson *et al.* [9] using high-pressure ^{1}H NMR spectroscopy. The same authors used ^{13}C high pressure NMR to determine the solubility of carbon monoxide in a series of different ionic liquids including [bmim][BF_4] and [bmim][PF_6] finding values of 337 MPa and 327 MPa for the Henry's law constant at 295 K, respectively [10]. The last value is much higher than the experimental value of 197 MPa at 293 K published by Kumelan *et al.* [11] for the solubility of carbon monoxide in [bmim][PF_6] which should not be significantly different from that in [bmim][BF_4].

Kroon *et al.* [12] have published the high-pressure phase behaviour (pressure above $p = 0.6$ MPa) of the binary system (carbon dioxide + [bmim][BF_4]) between $T = 278$ K and $T = 368$ K using a synthetic method. The Henry's law constants obtained by extrapolation of the experimental results on bubble-point pressures increase with temperature (the solubility decreases) and vary between $K_H = 6.5$ MPa at $T = 323.2$ K and $K_H = 10.4$ MPa at $T = 333.2$ K. These results are in agreement with the ones published by other authors in references [2] and [4] (a value of $K_H = 90.1$ MPa at $T = 323.2$ K was found by extrapolation of the data of [12] and $K_H = 88.9$ MPa, 1.3% lower, and $K_H = 88.6$ MPa, 1.7% lower, are reported in references [2] and [4], respectively).

The solvation of small molecules in ionic liquids has also been studied by molecular simulation [2,13–16] but the particular case of the interactions between gaseous solutes and the ionic liquid [bmim][BF_4] has only been addressed by our research group [15,16]. The molecular simulations reproduce the order of magnitude of the experimental data and give the correct relative solubility for carbon dioxide and oxygen. The temperature dependence of the solubility of oxygen and argon obtained by simulation is, however, opposite to the published experimental trends: the simulated mole fractions always decrease with temperature [16] whereas the experimental solubility of oxygen [3] and argon [20]