Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Fluid Phase Equilibria 240 (2006) 87–95

FLUID PHASE EQUILIBRIA

www.elsevier.com/locate/fluid

Low-pressure solubilities and thermodynamics of solvation of eight gases in 1-butyl-3-methylimidazolium hexafluorophosphate

Johan Jacquemin, Pascale Husson, Vladimir Majer, Margarida F. Costa Gomes *

Laboratoire de Thermodynamique des Solutions et des Polymères, UMR 6003 CNRS/Université Blaise Pascal, Clermont-Ferrand,
24 Avenue des Landais, 63177 Aubière Cedex, France

Received 19 September 2005; received in revised form 30 November 2005; accepted 1 December 2005

Abstract

Experimental values for the solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon and carbon monoxide in 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6] – a room temperature ionic liquid – are reported as a function of temperature between 283 and 343 K and at pressures close to atmospheric. Carbon dioxide is the most soluble and hydrogen is the least soluble of the gases studied with mole fraction solubilities of the order of 10^{-2} and 10^{-4}, respectively. All the mole fraction solubilities decrease with temperature except for hydrogen for which a maximum is observed at temperatures close to 310 K. 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 better than ±1%.

Keywords: Solubility; Gases; Ionic liquids; bmimPF$_6$

1. Introduction

In the present paper we report the solubility of different gases in one ionic liquid between 283 and 343 K and at pressures close to atmospheric. The knowledge of the gas solubility in this new family of liquid solvents is useful from a practical point of view as these data are valuable in the calculation of vapour/liquid equilibria for reaction systems or separation processes. From a more fundamental perspective, gas solubility measurements provide a reliable way to calculate the thermodynamic properties of solution and to assess the molecular mechanisms involved in the solvation process.

The ionic liquid chosen for this study, 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6] has already been studied by a considerable number of research groups. Some discrepancies have been observed in the literature concerning the phase equilibrium behaviour of this particular ionic liquid and some authors have even recommended that no further investigations should be done in this ionic liquid [1] although it has in the past been considered, among imidazolium based ionic liquids, as a promising solvent for technological applications.

The solubility of gases in [bmim][PF_6] has been determined by several research groups using different techniques and Henry's law constants could be determined both from data obtained at pressures close to atmospheric [2–6,23,24] or by extrapolation of values obtained at higher pressures [1,7–12,25]. When carbon dioxide is the studied gaseous solute, the values in the literature for the Henry's law constants are all in accord approximately to within ±10% [3,4,8,7,10,24–26]. For other gases studied by different research groups, namely oxygen, carbon monoxide and hydrogen, the discrepancies found are much larger, sometimes more than 100%.

In this paper, experimental solubilities of eight gases in one ionic liquid [bmim][PF_6] are reported as a function of temperature between 283 and 343 K near 0.1 MPa using a high precision isochoric saturation method [14,16]. These solubility data allow the calculation of the Henry's law constants as a function of temperature and from there the thermodynamic properties of solvation. The Gibbs energy of solvation considered as the change in Gibbs energy when the solute is transferred at

---

* Corresponding author. Tel.: +33 473407205; fax: +33 473407185.
E-mail address: margarida.c.gomes@univ-bpclermont.fr (M.F.C. Gomes).

0378-3812/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2005.12.003

constant temperature from the pure perfect gas at 0.1 MPa to the infinitely dilute standard state in the solvent is calculated directly from the Henry's law constants and the standard enthalpy and entropy of solvation from their variation with temperature.

2. Experimental

The sample of 1-butyl-3-methylimidazolium hexafluorophosphate used was purchased from Solvionic, France, with a minimum stated mole fraction purity of 0.999. The water content of this ionic liquid, considered as hydrophobic, was carefully determined before and after the solubility measurements as this impurity seems to influence significantly its thermodynamic and thermophysical properties [13]. A Karl-Fischer volumetric titrator from Mettler Toledo (model DL31) was used and a reference value of 150 ± 15 ppm was found after drying the liquid for 15 h at $T = 343$ K under vacuum. Several tests were done to check the time and the conditions for drying and degassing the ionic liquid sample—it is considered that, in the case of [bmim][PF$_6$] the liquid is appropriately degassed and dried after pumping it under a pressure of 1 Pa for 8 h at a fixed temperature between 303 and 343 K.

The gases used have the following specifications: carbon dioxide from AGA/Linde Gaz, mole fraction purity of 0.99995; ethane from AGA/Linde Gaz, mole fraction purity of 0.995; methane from AGA/Linde Gaz, mole fraction purity of 0.99995; oxygen from AGA/Linde Gaz, mole fraction purity of 0.99999; nitrogen from SAGA, mole fraction purity 0.9998; hydrogen from AGA/Linde Gaz, mole fraction purity of 0.999997; argon from AGA/Linde Gaz, mole fraction purity of 0.999997; and carbon monoxide from AGA/Linde Gaz, mole fraction purity of 0.99997. All gases were used as received from the manufacturer.

The experimental method used for these gas solubility measurements is based on an isochoric saturation technique and has been described in previous publications [14–16]. In this technique, a known quantity of gaseous solute is put 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, V_{liq}, is determined gravimetrically. The amount of solute present in the liquid solution, n_2^{liq} (subscript 2 stands for solute and subscript 1 stands for solvent), is calculated by the difference between two pVT measurements: first when the gas is introduced in a calibrated bulb with volume V_{GB} and second after thermodynamic equilibrium is reached:

$$n_2^{\text{liq}} = \frac{p_{\text{ini}} V_{\text{GB}}}{[Z_2(p_{\text{ini}}, T_{\text{ini}}) R T_{\text{ini}}]} - \frac{p_{\text{eq}}(V_{\text{tot}} - V_{\text{liq}})}{[Z_2(p_{\text{eq}}, T_{\text{eq}}) R T_{\text{eq}}]} \tag{1}$$

where p_{ini} and T_{ini} are the pressure and temperature in the first pVT determination and p_{eq} and T_{eq} are the pressure and temperature at the equilibrium. V_{tot} is the total volume of the equilibration cell and Z_2 is the compressibility factor for the pure gas. The solubility can then be expressed in mole fraction:

$$x_2 = \frac{n_2^{\text{liq}}}{(n_1^{\text{liq}} + n_2^{\text{liq}})} \tag{2}$$

or as Henry's law constant:

$$K_{\text{H}} = \lim_{x_2 \to 0} \frac{f_2(p, T, x_2)}{x_2} \cong \frac{\phi_2(p_{\text{eq}}, T_{\text{eq}}) p_{\text{eq}}}{x_2} \tag{3}$$

where f_2 is the fugacity of the solute and ϕ_2 its fugacity coefficient. The fugacity coefficient, which is close to unity in the present case, was included in the calculation of the Henry's law constants for all the gases. It was observed that the values do not change significantly from the ones calculated by taken $\phi_2 = 1$. It was decided however to include the fugacity coefficients in the data reduction as, in the case of carbon dioxide and ethane, the Henry's law constants changed slightly (for example, a maximum change of 0.4% in the Henry's law constant for carbon dioxide was found for the value at 283.15 K).

3. Results and discussion

For each gaseous solute studied, multiple experimental data points were obtained in the temperature interval between 283 and 343 K in steps of approximately 10 K. The experimental solubilities of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon and carbon dioxide in [bmim][PF$_6$] are reported in Table 1. The solubility results are given as Henry's law constants and as mole fractions of solute. These last values are calculated from the experimental data on K_{H} (at slightly different total pressures) assuming a partial pressure of the gaseous solute equal to 0.1 MPa. The relative atomic masses used are the ones recommended by IUPAC [17] and the values of the second virial coefficients for all the gases necessary for the calculation of the compressibility factor and the fugacity coefficient, were taken from the compilation by Dymond and Smith [18]. The density of the sample of [bmim][PF$_6$] used as solvent during the present measurements was determined in our laboratory with a precision better than 0.01% by means of an Anton Paar densitometer (model DMA 512 P) [19]. The density values measured are reported in Table 2 and were fitted to the function (the average absolute deviation of the fit is 0.004%):

$$\rho_{[\text{bmim}][\text{PF}_6]}\,(\text{kg m}^{-3}) = 1388.82 - 8406.83 \times 10^{-4}\,(T(\text{K})) \tag{4}$$

To get representative values of the solubility, the raw experimental data were correlated as a function of temperature by an empirical equation of the type:

$$\ln[K_{\text{H}}(T)\,(10^5\ \text{Pa})] = \sum_{i=0}^{n} A_i (T\,(\text{K}))^{-i} \tag{5}$$

the coefficients A_i obtained are listed in Table 3 together with the average absolute deviations obtained for each solute. These values can be regarded as an estimation of the precision of the experimental data which is in the present case always less than 1%.