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Solubilities of Gases in the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide

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Solubility data of carbon dioxide, propane, propene, butane, and 1-butene in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) are presented as a function of pressure at temperatures between 280 K and 340 K. The equilibrium pressure at a given temperature and the amount of gas dissolved into the ionic liquid phase were measured with an experimental technique based on a saturation method at constant volume by use of an apparatus equipped with a cylindrical equilibrium view cell. All measured solubilities were between 0.1 and 0.5 mole fraction gas in ionic liquid. 1-Butene had the highest solubility, followed by butane, propene, and then propane. Carbon dioxide and propane are similarly the least soluble in the [bmim]-[Tf_2N]. Alkene gases were more soluble than alkane gases. From the experimental solubility data, the Henry's constants of each gas in the ionic liquid were estimated as a function of temperature.

Introduction

Ionic liquids are a class of organic salts that are liquid at or near room temperature. They are generally composed of a large asymmetric organic cation and either an organic or inorganic anion. Asymmetry of the cation is believed to be responsible for the low melting points of ionic liquids, while the nature of the anion is considered to be responsible for many of the physical properties of ionic liquids such as their miscibility with conventional solvents and hygroscopicity.[1] A key feature of ionic liquids is that their physical properties can be tailored by judicious selection of cation, anion, and substituents.[2] Unlike molecular liquids, ionic liquids have a number of advantages determined by the unique combination of their properties such as negligible vapor pressure at room temperature, a stable liquid range of over 300 K, and density being greater than that of water.[3] Therefore, these fluids have been proposed as an attractive alternative to volatile organic compounds (VOCs) for "green processing" because they are nonvolatile, nonflammable, and thermally stable.[2,4−6] Replacement of conventional solvents with ionic liquids would prevent the emission of VOCs, a major source of environmental pollution.

Ionic liquids have recently gained great attention in a variety of chemical processes. They are being used as solvents for homogeneous catalysis for a variety of organic reactions,[7−10] media for gas and liquid separations,[11−13] electrolytes for batteries and fuel cells,[14−17] and thermal fluids.[18,19] Ionic liquids are being considered as potential replacements for VOCs in many organic reactions with and without homogeneous transition metal catalysts because they are able to dissolve organometallic compounds; additionally, the use of ionic liquids can enhance activity, selectivity, and stability of transition-metal catalysts. A recently developed commercial technique for the formation of alkoxyphenylphosphine increased productivity by a factor of 80 000 over the previously used process, through the incorporation of ionic liquids.[20] The potential of ionic liquids for new chemical technologies is beginning to be recognized.

Another potential application of ionic liquids is for separation of gas mixtures.[11,12,21] The nonvolatility of ionic liquids would not cause any contamination to a gas stream, and thus this feature gives ionic liquids a big advantage over conventional solvents used for absorbing gases. To select an efficient ionic liquid for use as a gas separation medium, it is necessary to know the solubility of the gas in the ionic liquid phase. Since many reactions in ionic liquids, such as hydrogenation, hydroformylation, and oxidation, involve the reaction of gases in the ionic liquid solutions, collecting the gas solubilities in ionic liquids is important for establishing reaction conditions. However, few data are available in the literature on the solubility of gases in ionic liquids.

Anthony et al.[22] studied the solubilities of nine different gases in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]-[PF_6]) at (10, 25, and 50) °C by means of a gravimetric microbalance. They found carbon dioxide to have the highest solubility in the [bmim][PF_6], followed by ethylene, ethane, and methane. Argon and oxygen had very low solubilities, and carbon monoxide, hydrogen, and nitrogen all had solubilities below the detection limit of the apparatus. They suggested that ionic liquids showed good potential for use as a gas separation medium. Kumelan et al.[23,24] also presented the solubilities of carbon monoxide and oxygen in [bmim][PF_6] for temperatures from (293 to 373) K and pressures up to about 10 MPa. They showed that the [bmim][PF_6] was a poor solvent for carbon monoxide and oxygen. Blanchard et al.[25] presented the high-pressure phase behavior of carbon dioxide with six different imidazolium-based ionic liquids and showed the effect of systematically changing the anionic and cationic components of the ionic liquid on the carbon dioxide−ionic liquid-phase behavior. Large quantities of carbon dioxide dissolved into the ionic liquid phase, but no appreciable amount of ionic liquid solubilized into the carbon dioxide phase. Perez-Salado Kamps et al.[26] also reported the solubility of carbon dioxide in the

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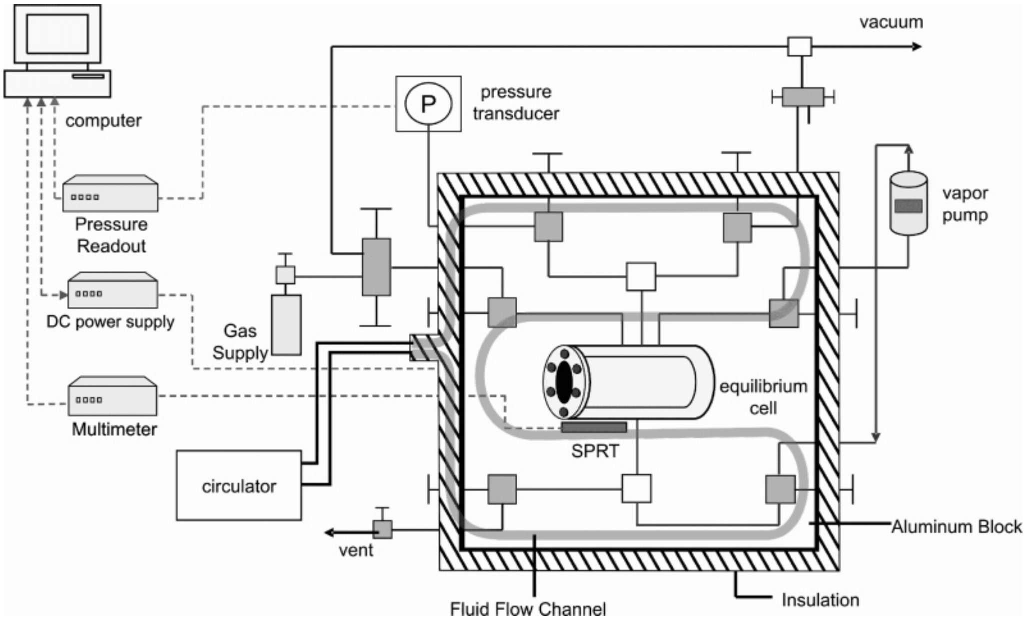

Figure 1. Schematic of the experimental apparatus for measuring solubility of gas in ionic liquid.

[bmim][PF_6] for temperatures from (293 to 393) K and pressures up to about 9.7 MPa. Husson-Borg et al.[27] studied the solubilities of oxygen and carbon dioxide in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) at temperatures between (303 and 343) K and at pressures close to atmospheric. Shariati and Peters,[28,29] Costantini et al.,[30] and Kroon et al.[31] studied the high-pressure phase behavior of binary mixtures consisting of a supercritical fluid (fluoroform or carbon dioxide) and imidazolium-based ionic liquids (1-alkyl-3-methylimidazolium tetrafluoroborate and 1-alkyl-3-methylimidazolium hexafluorophosphate) over a wide range of solute concentration and at pressures up to about 100 MPa. Scovazzo et al.[32] reported gas solubilities and Henry's constants of carbon dioxide in five different ionic liquids under both dry and water-saturated conditions at 303.15 K. The ionic liquids used in their study were [bmim][PF_6], ethylmethylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]), ethylmethylimidazolium trifluoromethanesulfone ([emim][CF_3SO_3]), ethylmethylimidazolium dicyanamide ([emim][dca]), and trihexyltetradecylphosphonium chloride ([thtdp][Cl]). Camper et al.[33] presented the Henry's law constants of hydrocarbon gases such as ethane, ethene, propane, propene, isobutene, butane, 1-butene, and 1,3-butadiene in [bmim][PF_6], [bmim][BF_4], [emim][Tf_2N], [emim]-[CF_3SO_3], and [emim][dca] at 313.15 K. They also discussed the use of regular solution theory to model gas solubility at low pressure with empirically determined constants that depend only on the gas.

In this work, we measured the solubilities of carbon dioxide and light hydrocarbon gases (propane, propene, butane, and 1-butene) in the ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][$(CF_3SO_2)_2N$] or [bmim]-[Tf_2N]), using an equilibrium apparatus equipped with a cylindrical view cell. In our experiments, the determination of solubility was based on a saturation method at constant volume. The mass of gas dissolved into a known amount of the ionic liquid was determined by a change of the system pressure with the introduction of gas into the cell at a constant temperature. The equilibrium pressure and the mole fraction of the gas in the ionic liquid phase were measured as a function of temperature with varying amounts of gas loaded into the system. The Henry's constants of each gas in the ionic liquid were also estimated from the experimental solubility data.

Experimental Section

Materials. The ionic liquid [bmim][Tf_2N] was purchased from Covalent Associates, Inc. (Woburn, MA). [Certain commercial equipment, instruments, or materials are identified in this paper only for completeness of scientific description. Such identification implies neither recommendation nor endorsement by the National Institute of Standards and Technology, nor that the materials or equipment identified are necessarily the best available for the purpose.] A chloride-selective electrode measurement verified the manufacturer's claim that the ionic liquid contained chloride of less than 50 mg/kg. The ionic liquid was dried thoroughly before being introduced into the gas solubility apparatus. The drying was performed at approximately 330 K with the sample being continuously stirred and evacuated by use of a mechanical pump and a liquid nitrogen trap; the ultimate pressure during drying was ≤ 0.1 Pa. Coulometric Karl Fischer titration was performed on a sample of the dried ionic liquid and on a sample of the ionic liquid that was removed from the apparatus following the gas solubility measurements. In both samples, the water content was less than 20 mg/kg. The purity of the ionic liquid was also checked by ^1H and ^{19}F nuclear magnetic resonance (NMR) spectrometry. NMR analysis was performed on a sample of the dried ionic liquid and on a sample of the ionic liquid that had been removed from the apparatus following the gas solubility measurements. In both samples the mass fraction purity of the ionic liquid was no less than 99.4 % by ^1H and ^{19}F NMR.

Carbon dioxide with a purity of 99.99 %, propane with a purity of 99.999 %, propene with a purity of 99.0 %, and 1-butene with a purity of 99.0 % were purchased from Scott Specialty Gases. Butane with a purity of 99.9 % was purchased from Matheson Tri-Gas. These gases were analyzed in our laboratory with a combined gas chromatography−mass spectrometry-infrared spectrophotometry method and found to have no major impurities. They were used as received without further purification.

Apparatus. Figure 1 shows a schematic of the experimental apparatus used for this work. A detailed description of the apparatus was given in our previous publication.[34] The heart of the apparatus is the cylindrical equilibrium cell. The cell, made of 316 stainless steel, has an internal diameter of 2.22 cm and an internal length of 7.62 cm; its internal volume is about 30 cm^3. The cell has a sapphire window at each end to allow visual observation of the fluid being studied. Much of the apparatus is contained in a temperature-controlled aluminum block, which consists of two halves, with an overall dimension of 25.4 cm × 30.5 cm × 10.1 cm. The inside faces of each half of the block were machined to accommodate the equilibrium cell, the valves, and the associated connecting tubing. A standard platinum resistance thermometer (PRT) is located in a thermowell alongside the equilibrium cell.

The temperature of the system within the aluminum block is controlled by fluid circulation in conjunction with computer-controlled electric heating. Flow channels bored through the sides of the block allow for the flow of fluid from a temperature-controlled circulator. The fine temperature control is achieved with six thin-film heaters adhered to the large outside faces of each half of the block. The heaters, used in conjunction with the circulator, are capable of maintaining a set block temperature within ± 0.005 K indefinitely. Temperature was measured with a capsule-type standard PRT read by a multimeter. The calibration of the standard PRT used in this apparatus was checked against the triple points of both gallium (302.9146 K) and water (273.160 K) and adjusted accordingly. The uncertainty in our temperature measurements including the uncertainties in the PRT, voltmeter, and calibration as well as gradients in the aluminum block was estimated to be 0.03 K.

Pressure was measured with a commercially available vibrating quartz crystal pressure transducer with a range of 0 to 6.89 MPa. The transducer reading was recorded at vacuum before each set of measurements and reported pressures were corrected to reflect any offset. The uncertainty of our pressure measurements including the uncertainties in the transducer, calibration and pressure head correction was estimated to be 9.8×10^{-4} MPa.

All instruments were controlled and read by a personal computer over either an RS-232 or an IEEE-488 interface by use of code written in LabVIEW. Every 30 s, measurements of the temperature and pressure of the system were recorded.

Procedure. To conduct solubility measurements, a careful calibration of the internal volume of the apparatus was performed. The calibration was achieved by adding a known amount of high-purity nitrogen gas to the system, then controlling the temperature of the system, and recording the system pressure. Using the REFPROP database[35] to obtain the density of nitrogen at the system temperature and pressure, we were then able to calculate the internal volume. The exact amount of the gas introduced into the cell was determined by weighing the sample cylinder (containing nitrogen) with a sensitive balance/mass comparator before and after loading. The balance has a precision of ± 0.1 mg with an uncertainty of 0.57 mg. The amount of gas lost in the feed line during loading was calculated by multiplying the total dead volume of the feed line by the gas density estimated at the gas loading pressure and temperature. To minimize the amount of gas lost, we used a short feed line of small inside diameter tubing (0.076 cm i.d., 5 cm long). The total dead volume of the gas feed line was calculated from the internal volume of the valves and tubing to be approximately 0.141 cm^3. The calibration procedure was repeated with nitrogen at three different pressures from (1.8 to 4.5) MPa, and the internal volume of the system was calculated to be (35.857 ± 0.024) cm^3. The temperature of the system varied slightly ((294.5, 296.0, and 300.0) K) for the three calibration measurements. However, the volume calibration was not intended to be done as a function of temperature as the thermal expansion of the system over the temperature range of the measurements was calculated to be small and, thus, had negligible affect on the solubility measurement.

Solubility measurements began with loading ionic liquid into the cell using a gastight syringe. The syringe was carefully weighed with the mass comparator mentioned above both before and after loading. High-pressure helium was used to force any ionic liquid remaining in the feed line into the equilibrium cell. The vapor space of the system (containing the ionic liquid) was then evacuated for several hours until a constant pressure reading was achieved when the system was valved off from vacuum. This ensured that the ionic liquid was free of any dissolved gas.

Once the vapor space above the ionic liquid was evacuated, the system was controlled at approximately room temperature, and sample gas was loaded into the cell until a desired system pressure was reached. The amount of the solute gas introduced into the cell was determined by weighing the gas sample cylinder with the mass comparator before and after loading in the same manner as that stated in the calibration procedure.

The equilibrium process began with the addition of the solute gas. After the gas was loaded, the system temperature was lowered to 280.0 K and maintained constant within ± 0.005 K. The system pressure decreased as the gas dissolved into the ionic liquid phase. The system pressure and temperature were recorded every 30 s until equilibrium was attained. The system was considered to have reached equilibrium when the system pressure showed no significant decrease for at least 2 h.

The mass of gas dissolved into the ionic liquid phase must be known to determine the solubility of gas in the ionic liquid. This was calculated by subtracting the mass of gas present in the pure gas phase (above the ionic liquid) at equilibrium from the total mass of gas introduced into the system. The mass of gas present in the pure gas phase was calculated by multiplying the volume of the pure gas phase by the density of the gas at the equilibrium temperature and pressure. Subtracting the volume occupied by the ionic liquid from the total system volume gave the volume occupied by the pure gas phase. Gas densities were obtained from the REFPROP database[35] as functions of temperature and pressure. The volume occupied by the ionic liquid was calculated by dividing the mass of the ionic liquid introduced into the cell by the density of the ionic liquid. The densities of the ionic liquid [bmim][Tf_2N] at different temperatures were obtained from the literature[36] and were linearly correlated as a function of temperature as follows:

$$\rho/\mathrm{g\cdot cm^{-3}} = -9.4824 \times 10^{-4}\, T/\mathrm{K} + 1.7203 \qquad (1)$$

For each gas studied, four loadings were done, and measurements on each loading were done from (280.0 to 340.0) K in 20 K increments. For each loading, the solubilities at different temperatures were measured by raising the system temperature and waiting for a new equilibrium.

Results and Discussion

The solubilities of carbon dioxide, propane, propene, butane, and 1-butene in the ionic liquid [bmim][Tf_2N] were investigated as functions of temperature and pressure. The experimental data for each gas are listed in Tables 1 to 5, respectively. The solubility results are given in terms of the mole fraction of gas (component 1) in the ionic liquid (component 2) phase, x_1. As expected, in all cases the gas solubility increased with the system

Table 1. Experimental Data of Solubility of Carbon Dioxide (1) in [bmim][Tf$_2$N] (2)

T/K	P/MPa	x_1[a]
279.98	0.2918	0.1151 ± 0.0005[b]
	0.7192	0.2472 ± 0.0006
	1.4584	0.4141 ± 0.0007
	2.0595	0.5123 ± 0.0009
299.98	0.4058	0.1063 ± 0.0005
	0.9969	0.2309 ± 0.0006
	2.0636	0.3896 ± 0.0008
	2.9627	0.4837 ± 0.0011
319.98	0.5181	0.0990 ± 0.0005
	1.2929	0.2153 ± 0.0006
	2.6996	0.3659 ± 0.0010
	3.9039	0.4557 ± 0.0014
339.97	0.6350	0.0922 ± 0.0005
	1.5859	0.2020 ± 0.0007
	3.3224	0.3459 ± 0.0011
	4.7999	0.4332 ± 0.0016

[a] Mole fraction of gas in the ionic liquid phase. [b] Uncertainty in solubility measurement, $k = 2$.

Table 2. Experimental Data of Solubilities of Propane (1) in the Ionic Liquid [bmim][Tf$_2$N] (2)

T/K	P/MPa	x_1
279.98	0.0883	0.0175 ± 0.0005
	0.2342	0.0759 ± 0.0005
	0.4285	0.1632 ± 0.0005
	0.4805	0.1818 ± 0.0006
299.98	0.0963	0.0175 ± 0.0005
	0.2972	0.0712 ± 0.0005
	0.5970	0.1500 ± 0.0006
	0.6711	0.1671 ± 0.0006
319.98	0.1049	0.0174 ± 0.0005
	0.3807	0.0650 ± 0.0005
	0.7851	0.1365 ± 0.0006
	0.8850	0.1520 ± 0.0006
339.97	0.1268	0.0160 ± 0.0005
	0.4651	0.0596 ± 0.0005
	0.9599	0.1264 ± 0.0006
	1.0622	0.1427 ± 0.0006

Table 3. Experimental Data of Solubilities of Propene (1) in the Ionic Liquid [bmim][Tf$_2$N] (2)

T/K	P/MPa	x_1
279.98	0.0999	0.0621 ± 0.0005
	0.2285	0.1461 ± 0.0005
	0.2606	0.1651 ± 0.0005
	0.3673	0.2300 ± 0.0005
	0.4265	0.2660 ± 0.0005
	0.4775	0.2946 ± 0.0006
299.98	0.1399	0.0586 ± 0.0005
	0.3414	0.1372 ± 0.0005
	0.3879	0.1553 ± 0.0005
	0.5617	0.2164 ± 0.0006
	0.6599	0.2506 ± 0.0006
	0.7426	0.2780 ± 0.0006
319.98	0.1920	0.0544 ± 0.0005
	0.4731	0.1276 ± 0.0005
	0.5396	0.1446 ± 0.0005
	0.7875	0.2017 ± 0.0006
	0.9322	0.2338 ± 0.0006
	1.0522	0.2596 ± 0.0006
339.97	0.2465	0.0506 ± 0.0005
	0.6105	0.1189 ± 0.0005
	0.6984	0.1346 ± 0.0005
	1.0246	0.1880 ± 0.0006
	1.2182	0.2177 ± 0.0006

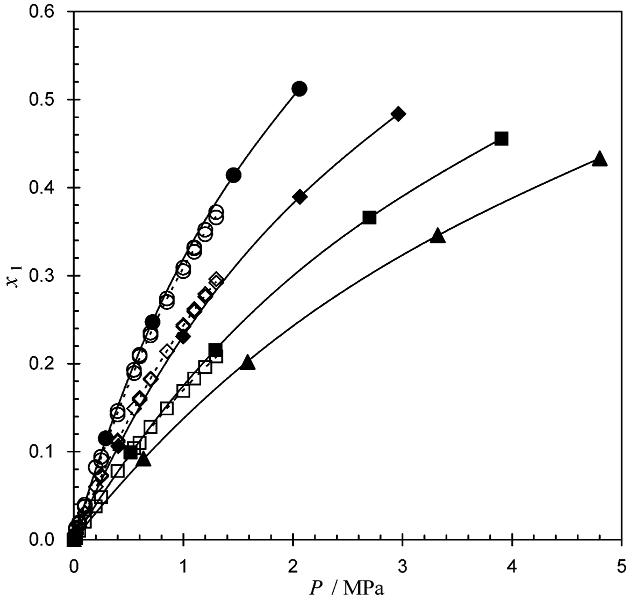

Figure 2. Solubility (x_1) of carbon dioxide in [bmim][Tf$_2$N]: comparison of data from this work (●, 279.98 K; ♦, 299.98 K; ■, 319.98 K; ▲, 339.97 K) with data from Anthony et al.[38] (○, 283.15 K; ◇, 298.15 K; □, 323.15 K).

Table 4. Experimental Data of Solubilities of Butane (1) in the Ionic Liquid [bmim][Tf$_2$N] (2)

T/K	P/MPa	x_1
280.00	0.0334	0.0305 ± 0.0004
	0.0473	0.0440 ± 0.0004
	0.0593	0.0612 ± 0.0004
	0.1037	0.1409 ± 0.0004
300.00	0.0483	0.0291 ± 0.0004
	0.0701	0.0418 ± 0.0004
	0.0879	0.0586 ± 0.0004
	0.1644	0.1358 ± 0.0004
320.00	0.0701	0.0271 ± 0.0004
	0.0998	0.0393 ± 0.0004
	0.1246	0.0555 ± 0.0004
	0.2467	0.1295 ± 0.0004
340.00	0.0949	0.0252 ± 0.0004
	0.1363	0.0364 ± 0.0004
	0.1704	0.0520 ± 0.0004
	0.3041	0.1262 ± 0.0004

Table 5. Experimental Data of Solubilities of 1-Butene (1) in the Ionic Liquid [bmim][Tf$_2$N] (2)

T/K	P/MPa	x_1
280.00	0.0210	0.0328 ± 0.0004
	0.0394	0.0640 ± 0.0004
	0.0760	0.1340 ± 0.0004
	0.0924	0.1663 ± 0.0004
300.00	0.0327	0.0317 ± 0.0004
	0.0640	0.0617 ± 0.0004
	0.1301	0.1294 ± 0.0004
	0.1612	0.1608 ± 0.0004
320.00	0.0504	0.0301 ± 0.0004
	0.0981	0.0587 ± 0.0004
	0.2060	0.1234 ± 0.0004
	0.2565	0.1536 ± 0.0004
340.00	0.0714	0.0284 ± 0.0004
	0.1400	0.0554 ± 0.0004
	0.2867	0.1178 ± 0.0004
	0.3511	0.1475 ± 0.0004

pressure and decreased with the system temperature. The solubility was of the same order of magnitude for all gases. Tables 1 to 5 also show the uncertainty in the solubility measurement for each point. The average uncertainties of the gas solubility in mole fraction were 0.0008 for carbon dioxide, 0.0005 for propane and propene, and 0.0004 for butane and 1-butene. The uncertainty of solubility for each point was obtained from the propagation of the experimental uncertainties in pressure (9.8×10^{-4} MPa) and temperature (0.03 K), the uncertainty in the density calculation, the uncertainty in the system volume measurement (0.021 cm^3), and the uncertainty

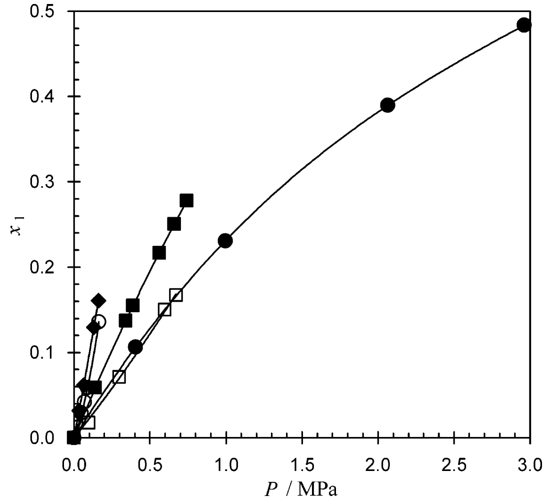

Figure 3. Comparison of gas solubility (x_1) in [bmim][Tf$_2$N] at 300.0 K: ●, carbon dioxide; □, propane; ■, propene; ○, butane; ♦, 1-butene.

in mass determination of the gas and ionic liquid samples (5.7 × 10^{-4} g). The uncertainties were calculated in accordance with the ISO guideline[37] and what is termed in that guide as the "law of propagation of uncertainty". Our reported uncertainties represent a coverage factor, $k = 2$.

Figure 2 shows the solubilities of carbon dioxide in [bmim][Tf$_2$N] at temperatures ranging from (280.0 to 340.0) K and at pressures up to about 4.8 MPa. The isotherms studied in this work exhibited a nonlinear trend as the pressure increased. The solubility data measured in this work were compared with the data reported by Anthony et al.,[38] as shown in Figure 2. Because the two sets of data were measured at slightly different temperatures, a direct, quantitative comparison is not possible; however, the figure shows that our solubility data appear to agree well (at least qualitatively) with those of Anthony et al. At low pressures, the gas solubilities appear linear as a function of the pressure, which seems to confirm the validity of the Henry's law for the given solubility range.

Figure 3 compares the solubilities of five different gases in [bmim][Tf$_2$N] at 300.0 K. As shown in the solubility curves for each gas at a given equilibrium pressure, 1-butene had the highest solubility, followed by butane, propene, and then propane. Among the five gases studied in this work, carbon dioxide and propane are similarly the least soluble in [bmim][Tf$_2$N]. Alkene gases have a higher solubility than alkane gases. The solubilities of butane and 1-butene were higher than those of propane and propene, respectively, when compared at the same pressure and temperature. This implies that hydrocarbon gases with a longer chain are more soluble in [bmim][Tf$_2$N] than those with a shorter chain.

The solubility of a gas in a liquid is frequently described in terms of the Henry's constant, defined as

$$H_{12}(T,P) \equiv \lim_{x_1\to 0}\frac{\hat{f}_1^{\,l}(T,P,x_1)}{x_1} = \lim_{x_1\to 0}\frac{\hat{f}_1^{\,g}(T,P,y_1)}{x_1} = \lim_{x_1\to 0}\frac{y_1\hat{\phi}_1^{\,g}(T,P,y_1)P}{x_1} \qquad (2)$$

Table 6. Henry's Constants of Gases (1) in [bmim][Tf$_2$N] (2)

	$H_{12}^{\mathrm{exp}\ a}$/MPa				
T/K	carbon dioxide	propane	propene	butane	1-butene
280.0	1.88 ± 0.01[b]	3.57 ± 0.03	1.53 ± 0.01	1.19 ± 0.01	0.65 ± 0.01
300.0	2.71 ± 0.01	4.44 ± 0.05	2.30 ± 0.02	1.79 ± 0.02	1.05 ± 0.01
320.0	3.72 ± 0.01	5.88 ± 0.08	3.36 ± 0.02	2.66 ± 0.03	1.67 ± 0.02
340.0	5.05 ± 0.01	8.09 ± 0.11	4.58 ± 0.04	4.07 ± 0.04	2.60 ± 0.03

[a] Henry's constant estimated from the experimental data using eq 3. [b] Uncertainty of the Henry's constant calculation ($k = 2$) derived from the uncertainty of solubility measurement.

where $\hat{f}_1^{\,l}(T, P, x_1)$ and $\hat{f}_1^{\,g}(T, P, y_1)$ are the fugacity of the gas in the ionic liquid and gas phases, respectively; $\hat{\phi}_1^{\,g}(T, P, y_1)$ is the fugacity coefficient of the gas in the gas phase; and x_1 and y_1 are the mole fraction of the gas in the ionic liquid and gas phases, respectively. In our particular case, as the ionic liquid has negligible vapor pressure, the gas phase can be considered to be pure component 2. Furthermore, as the gas phase can be assumed to be ideal at low pressures, eq 2 becomes

$$H_{12}(T,P) \approx \lim_{x_1\to 0}\frac{P}{x_1} \qquad (3)$$

The Henry's constant can be estimated from the experimental solubility data measured in this work. This is done by taking the slope of the tangent line at zero concentration from the plot of the experimental equilibrium pressure in terms of the mole fraction of gas in the ionic liquid phase. The slope of the tangent line at zero concentration was obtained by fitting the *P* versus x_1 curve with a polynomial equation, and then taking the first derivative at $x_1 = 0$:

$$H_{12}^{\mathrm{exp}} = \left(\frac{\mathrm{d}P}{\mathrm{d}x_1}\right)_{x_1=0} \qquad (4)$$

This equation implies that a smaller value for the Henry's constant indicates larger gas solubility.

Table 6 shows the Henry's constants of five gases in [bmim][Tf$_2$N] at four different temperatures. The uncertainty in the Henry's constants was derived from the uncertainty in the solubility measurements. From the solubility data shown in Tables 1 to 5, two additional solubility curves were generated at each isotherm for each gas studied. The first curve was based on the solubility values that were reported plus the uncertainty, and the second curve was based on the reported solubility values minus the stated uncertainty. Each of the curves was fitted with a second-order polynomial equation, and then the Henry's constants were obtained from the slopes of the tangent lines at zero concentration. Finally, the uncertainty of the Henry's constant for each gas and temperature was determined by the difference between the Henry's constant derived from the *P* versus x_1 curve and that from the *P* versus x_1 ± uncertainty in x_1 curves. The average values of the uncertainty of the Henry's constant calculation were observed to be 0.01 for carbon dioxide, 0.07 for propane, 0.02 for propene, 0.03 for butane, and 0.02 for 1-butene. The Henry's constant of a gas in the ionic liquid increased with temperature, which reflected that the gas became less soluble with the temperature increase. As shown in the Henry's constants for the hydrocarbon gases, alkanes had higher values of the Henry's constant than alkenes, indicating that alkanes were less soluble in the [bmim][Tf$_2$N] than alkenes.

Conclusions

The experimental results for the solubility of carbon dioxide, propane, propene, butane, and 1-butene in the ionic liquid [bmim][Tf$_2$N] are presented as a function of pressure at temperatures from (280.0 to 340.0) K. The solubility increased with pressure and decreased with temperature and was of the same order of magnitude for all gases. Alkane gases were less soluble in the [bmim][Tf$_2$N] than alkene gases. The hydrocarbon gases with longer chains had a higher solubility. The Henry's constants for each gas were estimated as a function of temperature from the experimental solubility data.

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