Enhancement of oxygen and methane solubility in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide using carbon dioxide

Daniel G. Hert,† Jessica L. Anderson, Sudhir N. V. K. Aki and Joan F. Brennecke*

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The presence of CO_2 increases the solubility of O_2 and CH_4 in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide at 25 °C and pressures to 13 bar.

Due to their volatile nature and associated contributions to air pollution and human health hazards, there has been an emphasis on the development of new solvents to replace volatile organic chemicals (VOCs). Since ionic liquids (ILs) are non-volatile, they have the potential to displace some VOC solvents. In fact, ILs have been shown to be excellent solvents for a wide range of chemical reactions and separations.[1–3] Numerous homogeneously catalyzed reactions including hydrogenations, oxidations, and hydroformylation reactions have been run effectively in these novel solvent media.[1–6] Moreover, since our publication that CO_2 can be used to extract organic compounds from ILs without contamination of the extracted product,[7,8] several research groups have shown that IL/CO_2 biphasic systems can be even more effective as reaction media.[4–6,9] We and others have shown that CO_2 is very soluble in ILs but that H_2, O_2 and CO are not.[10–13] Nonetheless, these reactant gases have been used very successfully in the presence of supercritical CO_2 for hydroformylation, hydrogenation, and oxidation reactions.[4–6,9] For instance, the presence of supercritical CO_2 increases the reaction rates for enantioselective hydrogenation of imines in ILs.[4] Increased H_2 solubility in the presence of CO_2 was observed at high pressures when large amounts of CO_2 were used.[4] Therefore, we are interested more generally in how the presence of CO_2 affects the solubility of lower solubility gases in ILs both at high pressures and at more moderate pressures, as will be presented here. Specifically, in this communication, we present the results for the solubility of O_2/CO_2 and CH_4/CO_2 mixtures in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([hmim][Tf_2N]) at 25 °C in a pressure range of 1 to 13 bar. These results are the first to show that the solubility of O_2 and CH_4 in ILs can be dramatically enhanced with small amounts (and low pressures) of CO_2.

[hmim][Tf_2N] was synthesized in our laboratory according to the published procedures.[10] The IL was dried at 70 °C under high vacuum before use and the water content in the IL was found to be ~160 ppm using Karl-Fischer titration. Coleman instrument grade CO_2, CH_4, CH_4/CO_2, and O_2/CO_2 gas mixtures were purchased from Mittler Supply, Inc. The solubility of pure CO_2, CH_4 and O_2 in [hmim][Tf_2N] at 25 °C was measured in an Intelligent Gravimetric Analyzer (Hiden Analytical Limited, England), the details of which are given elsewhere.[12] The solubility of gas mixtures in [hmim][Tf_2N] at 25 °C was measured in a constant volume view cell and a Varian 3400CX gas chromatograph was used for online measurement of the vapor phase composition. A Heise pressure gauge was used for pressure measurement and the volumes of the cell and the lines were calibrated accurately. In a typical experiment, the cell was loaded with a known amount of sample and was evacuated at 70 °C to remove any dissolved gases. Then the cell was loaded with the feed gas to an initial pressure and the vapor phase was sampled immediately to determine the composition of the feed gas. Then the sample was stirred until equilibrium was attained, as indicated by no further drop in pressure. The final liquid volume and the pressure were measured and the vapor phase was sampled to determine the vapor phase composition. The liquid phase composition was calculated from the difference in the initial and final number of moles of each component in the vapor phase. The moles and fugacity of each component were calculated using the Virial equation of state.[14] Experiments were repeated at several pressures between 1 and 13 bar.

The solubility of pure CO_2, CH_4 and O_2 in [hmim][Tf_2N] at 25 °C is shown in Fig. 1. The solubility of all three gases increases with an increase in pressure and CO_2 was found to be the most soluble gas. These trends were consistent with those reported by our group for the solubility of these gases in other ILs.[12] The low solubility of oxygen in ILs has several implications for performing oxidation reactions. For example, the low solubility of oxygen in

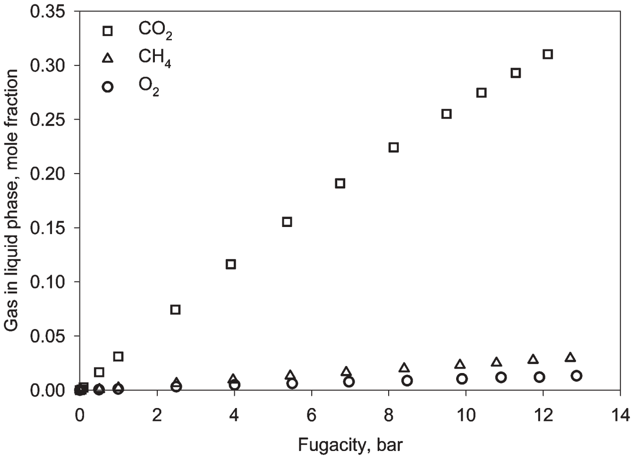

Fig. 1 Solubility of gases in [hmim][Tf_2N] at 25 °C.

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† *Present address*: Department of Chemical and Biological Engineering, 2145 Sheridan Road, Northwestern University, Evanston, USA. E-mail: d-hert@northwestern.edu; Fax: 847-491-3728; Tel: 847-491-2774.
*jfb@nd.edu

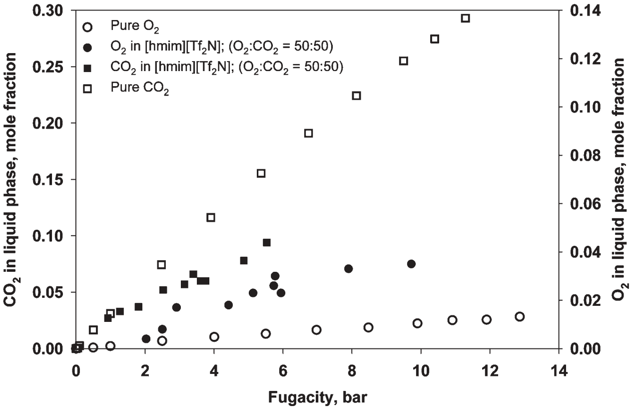

Fig. 2 Solubility of O_2 in [hmim][Tf_2N] at 25 °C in the presence of CO_2. Feed gas composition: O_2/CO_2 = 50/50.

ILs may lower reaction rates, decrease product yields and cause the reaction to be mass-transfer limited. One can overcome this limitation by increasing the oxygen pressure but this may result in safety concerns.

The solubility of oxygen in [hmim][Tf_2N] at 25 °C in the presence of CO_2 is shown in Fig. 2 and Table 1. In the figure, oxygen solubility is given on the right axis with CO_2 solubility indicated on the left axis. The solubility of each component in the gas mixture is compared with the pure gas solubility at the same fugacity. Fugacity, f_i, is defined as $f_i = y_i \phi_i P$, where y_i is the mole fraction, P is the pressure and ϕ_i is the fugacity coefficient, which corrects for vapor phase nonidealities. Here we use the Virial equation of state to calculate f_i for both pure ($y_i = 1$) gases and components in the mixed gas system. The fugacity coefficients are very close to unity for O_2 but range between 0.94 and 1.0 for CO_2. CO_2 solubility is less than the pure gas solubility at all pressures (*i.e.*, fugacities). For example, the solubility at a CO_2 fugacity of 4 bar decreases from 0.12 mole fraction for the pure gas to about 0.07 mole fraction in the mixed gas system. On the other hand, the solubility of oxygen increased substantially compared to the pure gas solubility at all pressures. For instance, with the presence of CO_2 in the liquid phase the oxygen solubility increased from 0.006 mole fraction to 0.03 mole fraction at an O_2 fugacity of 5.7 bar. This is shown in Table 1 in terms of the enhancement factor (EF), which is defined as oxygen solubility in the mixed gas system divided by the oxygen solubility in the pure O_2 system, at the same O_2 fugacity. To aid in these calculations, we give the O_2 solubility (second column from right) if it were a pure gas at the same oxygen fugacity as is present in the mixture (third column from right). The EFs range from 1.7 to 4.9 for the CO_2/O_2/[hmim][Tf_2N] system. Of course, the total pressure when using gas mixtures would be greater than the pressure of pure gas. For example, at an oxygen fugacity of 5.7 bar the total pressure, due to the presence of CO_2, is 9.5 bar for a feed gas with an initial composition of about 50/50 O_2 to CO_2 ratio. However, even if one applied 9.5 bar of pure O_2, the solubility of the O_2 would only be about 0.01 mole fraction. This is less than the O_2 solubility at a total pressure of 9.5 bar, where the initial gas mixture is about half O_2 and half CO_2. These comparisons can be made easily by examination of the data in Table 1. Thus, at a given total pressure the O_2 solubility is enhanced with the O_2/CO_2 mixture, even though the gas phase is "diluted" with CO_2.

Table 1 Vapor–liquid equilibrium for CO_2 (1)–O_2 (2)–[hmim][Tf_2N] (3) at 25 °C

P^{total}	Liquid phase composition			Vapor phase composition					
bar	x_1	x_2	x_3	y_1	y_2	f_{CO_2} bar	f_{O_2} bar	x_{O_2}, pure gas mole fr.	EF
3.0	0.03	0.004	0.96	0.31	0.69	0.90	2.0	0.002	1.7
3.8	0.03	0.008	0.96	0.34	0.66	1.3	2.5	0.003	3.0
4.8	0.04	0.02	0.95	0.39	0.61	1.8	2.9	0.003	5.7
7.0	0.05	0.02	0.93	0.37	0.63	2.5	4.4	0.005	3.8
8.4	0.06	0.02	0.92	0.39	0.61	3.1	5.1	0.005	4.3
9.5	0.06	0.03	0.91	0.40	0.60	3.6	5.7	0.006	4.4
9.5	0.07	0.02	0.91	0.37	0.63	3.4	5.9	0.006	3.7
9.7	0.06	0.03	0.91	0.40	0.60	3.8	5.8	0.006	4.9
13.1	0.08	0.03	0.89	0.39	0.61	4.9	7.9	0.008	4.0
15.7	0.09	0.04	0.87	0.38	0.62	5.5	9.7	0.010	3.5

As shown in Fig. 1, the solubility of methane in [hmim][Tf_2N] is substantially less than the solubility of CO_2. These results suggest that ILs could be used for separating methane from CO_2.[12] Here we present the solubility of methane in [hmim][Tf_2N] in the presence of CO_2 at 25 °C using two different gas mixtures, *viz.*, about 90/10 and 50/50 CH_4 to CO_2 mole ratios. The solubility of the gas mixture is compared with the pure gas solubility of each component in Fig. 3 and in Table 2. Once again the partial pressure of each component in the vapor phase was corrected for nonideality using the Virial equation of state. As with the O_2/CO_2 gas mixture, the solubility of CO_2 decreases compared to the pure gas solubility at all pressures. Methane solubility in the presence of CO_2 increased at all pressures. With the pure gas, the solubility of methane in [hmim][Tf_2N] is 0.03 at a pressure of 13 bar. Interestingly, similar solubilities of methane can be obtained at a methane fugacity of just ~5.7 bar using a 50/50 CH_4/CO_2 gas mixture and at a methane fugacity of ~8.5 bar when a 90/10 CH_4/CO_2 gas mixture was used. The important result is that a small amount of CO_2 increases the CH_4 solubility. For the 90/10 CH_4/CO_2 gas mixture with a methane fugacity of ~8.5 bar the CO_2 concentration in the liquid phase is only 0.01 mole fraction, yet the methane solubility is enhanced to 0.03 mole fraction, which is much greater than the solubility of pure methane at 13 bar, a substantially higher pressure. Note from the data in Table 2 that the enhancement factors for methane are generally lower than those observed for oxygen. Nevertheless, CO_2 does

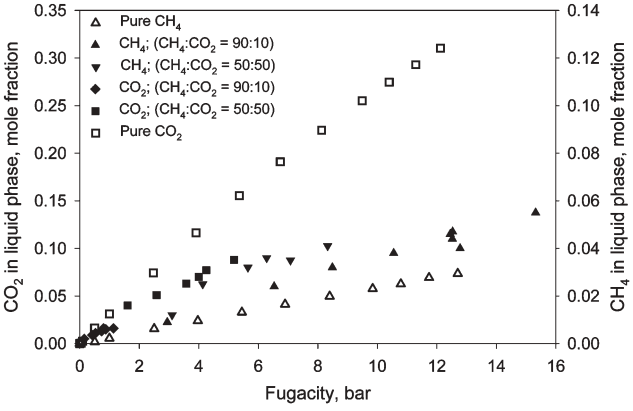

Fig. 3 Solubility of CH_4 in [hmim][Tf_2N] at 25 °C in the presence of CO_2. Feed gas composition: CH_4/CO_2 = 50/50 and CH_4/CO_2 = 90/10.

Table 2 Vapor–liquid equilibrium for CO_2 (1)–CH_4 (2)–[hmim][Tf_2N] (3) at 25 °C

P^{total}	Liquid phase composition			Vapor phase composition		f_{CO_2}	f_{CH_4}		
bar	x_1	x_2	x_3	y_1	y_2	bar	bar	x_{CH_4}, pure gasmole fr.	EF
3.1	0.005	0.009	0.99	0.05	0.95	0.15	2.9	0.007	1.4
7.0	0.009	0.02	0.97	0.06	0.94	0.4	6.5	0.02	1.6
9.2	0.01	0.03	0.96	0.06	0.94	0.5	8.5	0.02	1.6
11.5	0.01	0.04	0.95	0.07	0.93	0.7	10.6	0.02	1.6
13.7	0.02	0.05	0.94	0.07	0.93	0.9	12.5	0.03	1.6
13.7	0.02	0.04	0.94	0.07	0.93	0.9	12.5	0.03	1.5
13.7	0.02	0.05	0.94	0.07	0.93	0.9	12.5	0.03	1.6
13.9	0.02	0.04	0.94	0.06	0.94	0.8	12.8	0.03	1.4
17.0	0.02	0.06	0.93	0.07	0.93	1.1	15.3	0.04	1.6
4.8	0.04	0.01	0.95	0.35	0.66	1.6	3.1	0.007	1.8
6.8	0.05	0.03	0.92	0.39	0.61	2.8	4.1	0.01	2.6
9.5	0.06	0.03	0.91	0.39	0.61	3.8	5.6	0.01	2.5
10.6	0.07	0.04	0.90	0.4	0.60	4.0	6.3	0.01	2.5
11.7	0.08	0.04	0.89	0.38	0.61	4.3	7.1	0.02	2.1
14.0	0.09	0.04	0.87	0.39	0.61	5.2	8.3	0.02	2.1

substantially enhance CH_4 solubility in [hmim][Tf_2N], even at relatively low pressures and concentrations. The implication of this result is that the efficiency of separating CO_2 from methane using ILs may be low and may require additional stages to achieve the desired separation.

These results, decreased solubility of CO_2 relative to the pure gas and increased solubility of O_2 or CH_4 relative to the pure gas, indicate that gas solubility in ionic liquids cannot be described by a regular solution theory (RST) model, as has been suggested by other researchers.[15] For a binary system RST predicts higher solubility when the solubility parameters of the solute and the solvent are more similar. Assuming that the energies of vaporization of most ILs are similar (and large) then ILs with larger molar volumes will have smaller solubility parameters and, thus, more readily dissolve a gas like CO_2, which has a relatively small solubility parameter. This trend does seem to be borne out experimentally for CO_2 solubility in various ILs.[15] However, RST for the ternary mixture would predict that the solubility of both the lower solubility gas (O_2 or CH_4) and the CO_2 should increase. This is not what was observed in this study and, thus, these results cannot be explained by RST. Reduction of the solubility of one or more gases in the mixed gas system compared to the pure gas systems is common with solid adsorbants. There is a competition for adsorption sites by the two gases. A crude extension of this concept to gas solubility in ILs would mean that CO_2, which has been shown to interact strongly with the anion,[16] increases the solubility of the O_2 or the CH_4 through dispersion forces. However, the presence of the O_2 or the CH_4 then takes up some of sites around the anion, thus reducing the solubility of the CO_2 relative to the pure gas. Of course, this is pure speculation and more experiments, modeling and simulations are necessary to fully understand these mixed gas systems.

In this work we have shown that CO_2 can dramatically enhance the solubility of O_2 and CH_4 in [hmim][Tf_2N]. While this makes some gas separations with ILs more challenging, it also provides an easy method to increase the solubility of some low solubility reactant gases. These results suggest that small amounts of CO_2 could be used to enhance the solubility of paraffins and other nonpolar compounds in ILs, as well.

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Daniel G. Hert,† Jessica L. Anderson, Sudhir N. V. K. Aki and Joan F. Brennecke*
182 Fitzpatrick Hall, Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, USA.
E-mail: jfb@nd.edu; Fax: 574-631-5866; Tel: 574-631-5847

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