Measurement of SO$_2$ Solubility in Ionic Liquids

Jessica L. Anderson, JaNeille K. Dixon, Edward J. Maginn,* and Joan F. Brennecke*

Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556

Received: June 7, 2006; In Final Form: June 28, 2006

Measurements of the solubility of sulfur dioxide (SO$_2$) in the ionic liquids 1-*n*-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf$_2$N]) and 1-*n*-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([hmpy][Tf$_2$N]) at temperatures from 25 to 60 °C and pressures up to 4 bar indicate that large amounts (up to 85 mol %) of SO$_2$ dissolve in ionic liquids by simple physical absorption.

Introduction

Combustion of fossil fuels, such as coal and oil, results in the formation of acid gases including carbon dioxide (CO$_2$) and sulfur dioxide (SO$_2$). Methods for avoiding the emission of CO$_2$ to the atmosphere have received increased attention since CO$_2$ is a potent greenhouse gas, attributed to causing approximately 55% of the observed global warming.[1−4] In addition, separation and removal of SO$_2$ before atmospheric release of the flue gas is essential to combat acid rain formation, as specified by the Clean Air Act.[5]

One approach to control acid gas emissions from combustion of fossil fuels is capture and sequestration postcombustion. One of the most attractive approaches for the separation of a target compound from a mixture of gases is selective absorption into a liquid.[6,7] Typical concentrations of SO$_2$ and CO$_2$ in flue gas are 0.2 vol % and 10−14 vol %, respectively. Currently, about 75−90% of CO$_2$ can be captured via processes based on chemical absorption using a monoethanolamine (MEA)-based solvent.[8] Experience with amine-based solvents has identified some major problems. In particular, even though sulfur-bearing compounds are only present in small quantities (500−2500 ppm),[8] they undergo irreversible chemical reactions with amines and cause solvent degradation which reduces the solvent's capacity to capture CO$_2$. This introduces an additional process to first scrub SO$_2$ from the flue gas before contacting in the amine-based scrubbers, typically accomplished with a wet or dry flue gas desulfurization (FGD) system.

Ionic liquids (ILs) have potential to be used as liquid absorbents for flue gas or other combustion off-gas cleanup, since they have shown high CO$_2$ solubility[7,9−22] relative to other common components in flue gases, such as N$_2$.[10] Room-temperature ILs have some natural advantages over the amines used in traditional flue gas scrubbers. These include an extremely low vapor pressure, high thermal and chemical stability so that a wider temperature operating range is accessible, and, potentially, lower corrosivity.[23−27] In addition, if it is found that SO$_2$ is also highly soluble in ILs, it may be possible to simultaneously remove SO$_2$ and CO$_2$ from flue gas in a single absorption step.

TABLE 1: Ionic Liquid Impurities

IL	halide (ppm)	water (ppm)
[hmim][Tf$_2$N]	<10	31
[hmpy][Tf$_2$N]	<10	152

In this letter, we present the results of experimental solubility measurements for SO$_2$ in 1-*n*-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([hmim][Tf$_2$N]) and 1-*n*-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([hmpy]-[Tf$_2$N]). We know of only one other report of SO$_2$ solubility in ILs,[28] where they designed an IL to chemically react with SO$_2$. To our knowledge, this is the first report of SO$_2$ solubility in ILs by pure physical absorption.

Experimental Section

Both ILs were synthesized in our laboratory using standard procedures.[14,29,30] Typical synthesis and purification procedures have been published in our previous work.[30,31]

^{1}H and ^{13}C NMR confirmed no major organic impurities in the ILs. Impurity levels of bromide ions in the ILs were measured using an Oakton Ion 510 Series pH/mV/Ion/°C meter with Cole-Parmer Ion Specific Probes (27502−05 for Br$^-$). Both ILs contained less than 10 ppm Br$^-$. The ILs were dried under vacuum for at least 48 h at 40−70 °C to remove organic solvents and water before use. The samples were further dried in situ prior to the measurements. The approximate water content before use, as determined by Karl Fischer titration or coulometry (Brinkmann Metrohm 756KF Coulometer), is listed in Table 1. SO$_2$ was purchased from Mittler Supply, Inc., with a minimum purity of 99.98% and was used as received. CO$_2$ was also purchased from Mittler Supply, with a minimum purity of 99.99% (Coleman Instrument Grade).

The SO$_2$ gas solubility measurements were carried out in a magnetic suspension balance (Rubotherm, Germany), which has a working range of high vacuum to 500 bar and −200 to 350 °C, with a mass precision of 2 μg. The balance records the weight change of the IL sample upon gas absorption. Since the balance is magnetically coupled to the sorption chamber, the microbalance itself is not exposed to the gas of interest. This allows the use of corrosive gases without harming the delicate
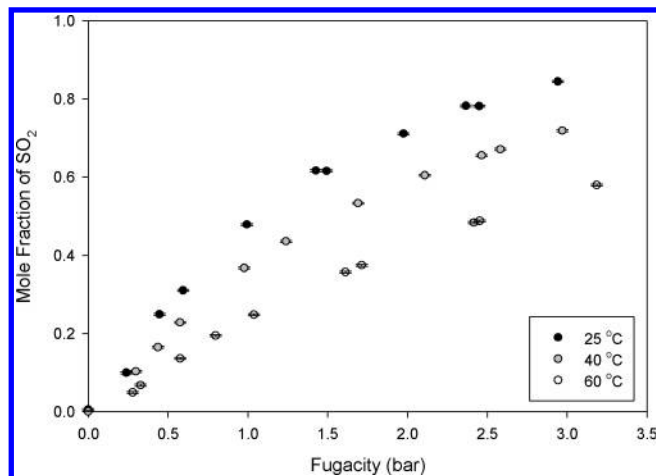
* Corresponding authors. ed@nd.edu; jfb@nd.edu.

Figure 1. Solubility of SO_2 in [hmim][Tf_2N] at various temperatures.

Figure 2. Comparison between SO_2 and CO_2 solubilities in [hmim]-[Tf_2N] and [hmpy][Tf_2N] at 25 °C.

microbalance. A Rubotherm pressure gauge, which has precision of 0.01 bar, was used for pressure measurement, and vacuum was attained and measured using a Pfeiffer Vacuum TSH091 pumping station which can achieve a vacuum of $\sim 10^{-5}$ mbar.

In a typical experiment, a known amount of IL is placed in a quartz bucket and loaded into the absorption chamber. The chamber is then evacuated at 60 °C to remove any dissolved gases, water, or volatile organic compounds until the weight is constant. The chamber is then loaded with SO_2 to an initial pressure, and the weight change of the sample is monitored until equilibrium is attained. The SO_2 pressure is then incrementally increased and the process repeated until a full isotherm is attained. Additionally, once the absorption isotherm is complete, a desorption isotherm is measured by incrementally evacuating SO_2 from the chamber. By measuring both absorption and desorption isotherms, we ensure that equilibrium has been reached and that all absorbed gas has been removed so the IL can be reused. After the run is completed, the sample is removed for NMR analysis to ensure the IL has not been chemically altered by the exposure to SO_2.

Analysis of the results requires a buoyancy correction, which requires knowledge of the sample density and the gas density. SO_2 gas densities were determined from the virial equation of state.[32] While densities of the IL/SO_2 mixtures are needed, we have approximated the liquid densities with the densities of the pure ILs. Previous work with CO_2 has shown relatively small volume expansion even at high CO_2 loadings.[33] Moreover, when the gas solubility is high, as is the case for SO_2, the buoyancy correction is relatively small. For instance, if the buoyancy correction were neglected entirely, it would only change the SO_2 solubility in [hmim][Tf_2N] at 25 °C by 0.5% at 3 bar and 10% at 0.6 bar. However, we do not neglect the buoyancy correction; we approximate it using the density of pure IL and estimate that the error introduced by this approximation to be less than 1%.

Results and Discussion

The temperature dependence of the solubility of SO_2 in [hmim][Tf_2N] is shown in Figure 1, where the solubility increases with increasing pressure and decreases with increasing temperature. This trend is consistent with that seen for other gases, i.e., CO_2, in ILs.[10,17,20] The data are available in tabular form in the Supporting Information. The SO_2 solubility in [hmim][Tf_2N] is extremely high; at 25 °C, the mole fraction of SO_2 approaches 0.9 near the SO_2 saturation pressure of 3.44 bar. By contrast, the mole fraction of CO_2 in this same IL under
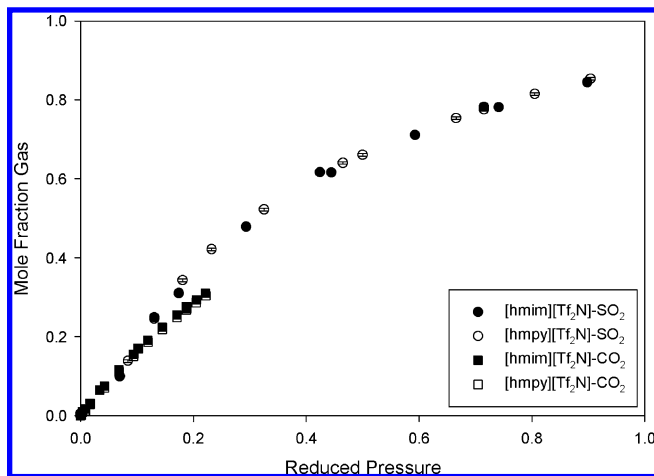
similar conditions is only 0.10.[17,20] The solubility of N_2 is sufficiently low that it is not measurable with our apparatus. The solubility of SO_2 in [hmpy][Tf_2N] is similar to that of [hmim][Tf_2N] at 25 °C. This is expected since in many cases the anion has been found to have the most significant effect on gas solubility.[13]

Although the solubility of SO_2 is much greater than CO_2 in these ILs at a particular temperature and pressure, the solubilities are actually quite similar when they are compared at the same reduced pressure, as shown in Figure 2. Since reduced pressure is defined here as $P_{\text{reduced}} = P_{\text{actual}}/P_{\text{saturation}}$, this corrects for the vastly different saturation pressures of the two gases at 25 °C. If thought of in terms of equifugacity as $y_i \phi_i P = x_i \gamma_i P_{\text{saturation}}$, where $y_i \approx 1$ and ϕ_i is not far from unity, then the slope of the data in Figure 2 is roughly $1/\gamma_i$, implying that the activity coefficients for CO_2 and SO_2 in the ILs are similar. Thus, the SO_2 is more soluble in these ILs than CO_2 at these pressures, primarily because it has a smaller saturation pressure.

Henry's law is the linear relationship between gas concentration and fugacity in the limit of low solute concentrations. Therefore, Henry's law constants can be found by calculating the slope of the isotherm in this limit. For high-solubility gases such as SO_2, Henry's law is only applicable for the lowest pressures used (up to ~ 0.5 bar). The fugacity coefficients were calculated from the virial equation of state[32] and were all between 0.95 and 1.0. In our previous work, the Henry's constants for CO_2 in these ILs were found by fitting a second-order polynomial to the data and calculating the limiting slope as the pressure (or solubility) approaches zero.[10] For this work, the solubility data was fit to a third-order polynomial, as the second-order proved insufficient to capture the SO_2 solubility behavior. Because our previous method used a matrix solution,[10] the extension to a third-order system was a simple one, where the Henry's law constant is still determined from the reciprocal of the linear parameter, β_1. One modification to the error analysis we have used previously is in the uncertainty calculation of the Henry's law constant. In the previous method, the standard deviation of the mole fraction was estimated from the fit residuals. However, this was found to slightly overestimate the error. The modified error analysis simply finds the mole fraction standard deviation of each data point from direct propagation of both the error in the measurement and the calculation of the mole fraction and from the uncertainty in the density measurement of the IL (which is needed for the buoyancy correction). The previously reported results for CO_2 solubility in these

TABLE 2: Henry's Law Constants, Enthalpy, and Entropy of Absorption for Various ILs

ionic liquid	Henry's law constant (bar)			enthalpy (kJ/mol)	entropy (J/mol K)
	25 °C	40 °C	60 °C		
		Sulfur Dioxide			
[hmim][Tf$_2$N]	1.64 ± 0.01	2.29 ± 0.02	4.09 ± 0.06	−20.3 ± 0.4	−64.7 ± 1.2
[hmpy][Tf$_2$N]	1.54 ± 0.01				
		Carbon Dioxide			
[hmpy][Tf$_2$N]	32.8 ± 0.2	46.2 ± 0.3 (50 °C)		−11.5 ± 0.1	−38.1 ± 0.5
[hmim][Tf$_2$N]	31.6 ± 0.2	45.6 ± 0.3 (50 °C)		−11.8 ± 0.3	−38.2 ± 0.9

ILs,[17,20] available in Table 2, were recalculated to reflect the slight modification in the error analysis method.

The Henry's law constants for SO$_2$ dissolution in [hmim]-[Tf$_2$N] and [hmpy][Tf$_2$N] at 25, 40, and 60 °C are shown in Table 2. SO$_2$ is over an order of magnitude more soluble than CO$_2$ in these ILs. Due to the high solubility of SO$_2$ in ILs, even with the low partial pressures of SO$_2$ found in industrial flue gases, it may be possible to remove both SO$_2$ and CO$_2$ in a single processing step, while still enabling reuse of the IL. Both absorption and desorption isotherms were measured to ensure that SO$_2$ was removed from the IL. As mentioned earlier, NMR analysis was used before and after exposure of the IL to SO$_2$ to ensure that no new products were formed and that there was no change in the IL during the gas absorption or desorption. NMR results are available in the Supporting Information.

In addition to Henry's law constants, the partial molar enthalpy and entropy of gas dissolution are calculated by a previously reported method[10] and are available in Table 2 for SO$_2$ dissolution in [hmim][Tf$_2$N]. Values are not determined for [hmpy][Tf$_2$N], as this IL was only investigated at 25 °C due to its similarity to [hmim][Tf$_2$N]. The partial molar enthalpy of gas dissolution gives an indication of the strength of interactions between the gas and IL, while the partial molar entropy illustrates the amount of ordering present in the gas/IL mixture. Results indicate that the interaction between SO$_2$ and [hmim][Tf$_2$N] is about twice as strong as that between CO$_2$ and [hmim][Tf$_2$N], although the magnitudes are still consistent with physical absorption. The partial molar entropy for SO$_2$ absorption is nearly twice that of CO$_2$ in [hmim][Tf$_2$N].

We are aware of one other study of SO$_2$ solubility in ILs.[28] Wu et al. synthesized the IL 1,1,3,3-tetramethylguanidinium lactate ([TMG][lactate]) and reported the solubility of both pure SO$_2$ and SO$_2$ diluted with N$_2$ to simulate flue gas. The reported Henry's law constant at 40 °C of pure SO$_2$ in [TMG][lactate] is 1.2 ± 0.63 bar, after unit conversion. This is slightly lower than our value for [hmim][Tf$_2$N] of 2.3 ± 0.02 bar at 40 °C. [TMG][lactate] was reported to absorb SO$_2$ by both physical and chemical absorption, as evidenced by IR spectroscopy, where the SO$_2$ was shown to complex with the TMG cation. This chemical complexation may account for the slightly higher solubility of SO$_2$ in [TMG][lactate] than we observe at the same temperature in [hmim][Tf$_2$N], where there is only evidence of physical absorption of SO$_2$. Nonetheless, the solubility of SO$_2$ in [hmim][Tf$_2$N] by only physical absorption is extremely high. One could attain solubilities as high as those observed for [TMG][lactate] with [hmim][Tf$_2$N] by simply reducing the temperature of the system slightly, thus avoiding chemical complexation issues, such as larger energy costs associated with solvent regeneration.

Conclusions

In this work, we have shown that the solubility of SO$_2$ in [hmim][Tf$_2$N] and [hmpy][Tf$_2$N] is extremely high. When compared to CO$_2$ solubility in these ILs, there is over an order

of magnitude decrease in the Henry's law constants. Therefore, it may not be necessary to resort to chemical complexation in order to remove SO$_2$ from flue gas, though solubility studies of mixed gases such as N$_2$, CO$_2$, and SO$_2$ should be completed. Since CO$_2$ solubility is also high in these ILs, it may be possible to remove both SO$_2$ and CO$_2$ in a single processing step.

Supporting Information Available: The materials used in this study, including source, grade, and purification method (if any), along with NMR data for the ionic liquids. In addition, the solubility data, Tables S1 and S2, are included. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Yeh, A. C.; Bai, H. L. *Sci. Total Environ.* **1999**, *228*, 121−133.
(2) Wolsky, A. M.; Daniels, E. J.; Jody, B. J. *Environ. Prog.* **1994**, *13*, 214−219.
(3) Parson, E. A.; Keith, D. W. *Science* **1998**, *282*, 1053−1054.
(4) *Intergovernmental Panel on Climate Change; Policymaker's Summary of the Scientific Assessment of Climate Change. Report to IPCC from Working Group*; Meteorological Office: Branknell, UK, 1990.
(5) *The Clean Air Act of 1990*; United States Environmental Protection Agency; Government Printing Office: Washington, DC, 1990.
(6) Astarita, G.; Savage, D. W.; Bisio, A. In *Gas Treating with Chemical Solvents*; John Wiley: New York, 1983; p 493.
(7) Bates, E. D.; Mayton, R. D.; Ntai, I.; J. H. Davis, J. *J. Am. Chem. Soc.* **2002**, *124*, 926−927.
(8) Rao, A. B.; Rubin, E. S. *Environ. Sci. Technol.* **2002**, *36*, 4467−4475.
(9) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. *J. Phys. Chem. B* **2002**, *106*, 7315−7320.
(10) Anthony, J. L.; Anderson, J. L.; Maginn, E. J.; Brennecke, J. F. *J. Phys. Chem. B* **2005**, *109*, 6366−6374.
(11) Baltus, R. E.; Culbertson, B. H.; Dai, S.; Luo, H. M.; DePaoli, D. W. *J. Phys. Chem. B* **2004**, *108*, 721−727.
(12) Baltus, R. E.; Counce, R. M.; Culbertson, B. H.; Luo, H. M.; DePaoli, D. W.; Dai, S.; Duckworth, D. C. *Sep. Sci. Technol.* **2005**, *40*, 525−541.
(13) Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 5300−5308.
(14) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, 5192−5200.
(15) Camper, D.; Scovazzo, P.; Koval, C.; Noble, R. *Ind. Eng. Chem. Res.* **2004**, *43*, 3049−3054.
(16) Gomes, M. F. C.; Padua, A. A. H. *Pure Appl. Chem.* **2005**, *77*, 653−665.
(17) Hert, D. G.; Anderson, J. L.; Aki, S.; Brennecke, J. F. *Chem. Commun.* **2005**, 2603−2605.
(18) Husson-Borg, P.; Majer, V.; Gomes, M. F. C. *J. Chem. Eng. Data* **2003**, *48*, 480−485.
(19) Kamps, A. P. S.; Tuma, D.; Xia, J. Z.; Maurer, G. *J. Chem. Eng. Data* **2003**, *48*, 746−749.
(20) Muldoon, M. J.; Anderson, J. L.; Dixon, J. K.; Aki, S. N. V. K.; Brennecke, J. F. Manuscript in preparation, 2006.
(21) Scovazzo, P.; Camper, D.; Kieft, J.; Poshusta, J.; Koval, C.; Noble, R. *Ind. Eng. Chem. Res.* **2004**, *43*, 6855−6860.
(22) Shiflett, M. B.; Yokozeki, A. *Ind. Eng. Chem. Res.* **2005**, *44*, 4453−4464.
(23) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Edit.* **2000**, *39*, 3773−3789.
(24) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2083.

Letters

(25) Olivier-Bourbigou, H.; Magna, L. *J. Mol. Catal., A: Chem.* **2002**, *182*, 419−437.

(26) Sheldon, R. *Chem. Commun.* **2001**, 2399−2407.

(27) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667−3691.

(28) Wu, W.; Han, B.; Gao, H.; Liu, Z.; Jiang, T.; Huang, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 2415−2417.

(29) Pernak, J.; Rogoza, J.; Mirska, I. *Eur. J. Med. Chem.* **2001**, *36*, 313−320.

(30) Couling, D. J.; Bernot, R. J.; Docherty, K. M.; Dixon, J. K.; Maginn, E. J. *Green Chem.* **2006**, *8*, 82−90.

(31) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. *J. Chem. Eng. Data* **2004**, *49*, 954−964.

(32) Smith, J. M.; Van Ness, H. C.; Abbott, M. M. In *Introduction to Chemical Engineering Thermodynamics*; McGraw-Hill Companies: New York, 1996; p 346.

(33) Blanchard, L. A.; Gu, Z.; Brennecke, J. F. *J. Phys. Chem. B* **2001**, *105*, 2437−2444.