Ionic Liquids as Novel Absorbents for Acid Gas Removal

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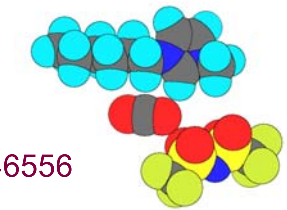

What are Ionic Liquids?

Ionic liquids (ILs) are organic salts which are liquid below 100 °C. ILs are being investigated for a variety of applications including reaction media, separation solvents, non-volatile electrolytes, heat transfer fluids, and gas capture.

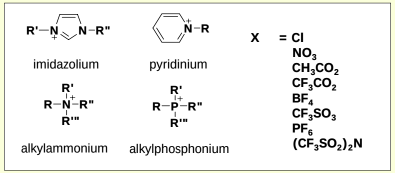

Fig. 1. Some common ILs

ILs are liquid over a wide range of temperature, having high thermal and chemical stability; hence, ILs can be used as solvents. They have demonstrated success as reaction solvents for a variety of reactions such as olefin dimerization, metathesis, isomerizations, Diels Alder, Friedel-Crafts alkylations and acylations, hydrogenations, and C-C coupling.

ILs have ***negligible vapor pressures*** which means that fugitive gas emissions are not a problem. This reduces worker exposure, decreases flammability danger, and disallows contamination of the IL into any gas phase.

Perhaps the most important property of an IL is its ability to be tailored by choice of cation and anion for a particular function. This tunability can exploit differences in solubility of various gases in ILs, allowing for specific and selective gas absorption.

Objectives and Motivations

Our research interest focuses specifically on how ILs can be designed for specific and selective gas separations. One potential application for this research is the separation of industrial flue gases for removal of environmentally hazardous gases. The ILs' negligible vapor pressure and tunable properties make them ideal to replace volatile and/or corrosive solvents currently being used for these processes. To this end, gases of interest to our study include carbon dioxide, sulfur dioxide, oxygen, and nitrogen.

Selection of different combinations of anions and cations influences the physical properties and functionality of an IL. Thus, one focus of this work is to understand the structure property relationship needed for enhanced gas solubility.

Materials and Methods

Gas solubility in several ILs was determined using a Magnetic Suspension Balance (Rubotherm, Germany). The balance records the mass 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 microbalance. CO_2 solubility has also been measured using a different microbalance (Hiden Isochema., UK).

Fig. 2. Photograph of Rubotherm setup

In a typical experiment, a known amount of IL is placed into a quartz bucket and loaded into the absorption chamber. The chamber is then loaded with gas to an initial pressure and the mass change of the sample is monitored until equilibrium is attained. Both absorption and desorption isotherms are measured to ensure all absorbed gas can be removed.

Fig. 3. Photograph of quartz bucket loaded with IL

Results

Pure gas solubilities have been measured in imidazolium- and pyridinium-based ILs. The anion of the IL has been found to have a greater effect on gas solubility than the cation (Cadena, et al.). Thus, the cation can be used to "fine-tune" IL properties.

Physical absorption of the gas in the IL increases with increasing fluorination, with anion fluorination having the largest effect. *Note that by simply changing the anion from [PF_6] to [bFAP], one can **double** the CO_2 solubility!*

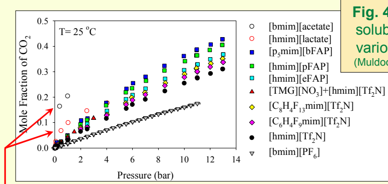

Fig. 4. CO_2 solubility in various ILs (Muldoon, et al.)

In contrast to fluorination, our research has also developed compounds which are generally less expensive and lead to increased gas solubility through chemical complexation of the gas to the IL, as shown with the [bmim][acetate] and [hmim][lactate] ILs. Chemical absorption increases gas solubility at low CO_2 pressures; at higher pressures the solubility levels out, becoming comparable to that of physical absorbents.

Another method for improving CO_2 solubility in ILs via chemical complexation is to append functional groups to the IL, such as amines, which are specifically intended to bond with CO_2. One such compound has been made (Bates, et al.) which contains an amine appended to a imidazolium cation and has been shown to complex CO_2.

Importantly, CO_2 has high solubility when compared to other gases frequently occurring in flue gases such as O_2 and N_2 (see Fig. 5). The tunability of ILs is of great importance for improving the CO_2 absorbance and selectivity of gases in ILs.

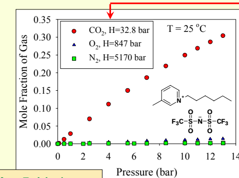

Fig. 5. Various gas solubilities in [hmpy][Tf_2N] (Muldoon, et al.)

$$H(T) = \lim_{x_i \to 0}\left(\frac{f_i^l}{x_i}\right) \approx \frac{P}{x_i}$$

Another important gas solubility to investigate is that of SO_2. In current CO_2 removal technologies such as amine scrubbers, the presence of SO_2 degrades the amine solvent and thus must first be removed from the flue gas before CO_2 scrubbing commences.

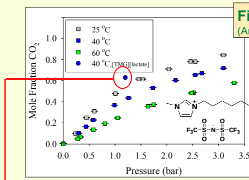

Fig. 6. SO_2 solubility in [hmim][Tf_2N] (Anderson, et al., 2006)

Wu et al., SO_2 solubility in [TMG][lactate] at 40 °C. SO_2 solubility makes use of both physical and chemical absorption which increases the SO_2 solubility in this IL.

The first studies of SO_2 solubility in an IL were measured in [hmim][Tf_2N] where the temperature dependence was determined (Fig. 6). SO_2 solubility increases with decreasing temperature or increasing pressure, similar to many other gas solubilities such as CO_2.

SO_2 was found to have the highest solubility when compared to other gases frequently occurring in flue gases. As shown in Fig. 7, SO_2 solubilities are similar in the two ILs. This is expected since the anion is mainly responsible for the bulk solubility properties.

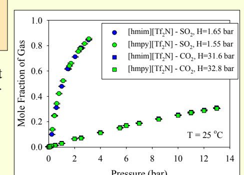

Fig. 7. SO_2 solubility vs. CO_2 solubility in [hmim][Tf_2N] and [hmpy][Tf_2N] (Anderson, et al., 2006)

As shown, SO_2 is *dramatically* more soluble in these ILs than CO_2. Note that the Henry's Law constant is less than 2 bar for SO_2, compared to ~ 30 bar for CO_2! This high solubility shows great potential, even at the low partial pressures of SO_2 typically found in industrial flue gas, as all the SO_2 could be removed simultaneously with CO_2. This requires verification with mixed gas solubility studies.

Conclusions

- Ionic liquids are tunable solvents with wide variety of potential applications
- Gas solubilities in ILs vary significantly and can be exploited for gas separations
- Fluorination of the IL increases CO_2 solubility, with the anion fluorination having the largest effect
- Compound with best CO_2 solubility from physical absorption ([$p_5$mim][bFAP]) has H=20.2 bar at 25 ºC
- Potential H~15 bar for fluorinated anion AND cation
- Higher carrying capacity of CO_2 obtained through chemical complexation, $H_{[bmim][acetate]}$=4.8 bar at 25 °C!
- High physical absorption of SO_2
- Applicability for simultaneous removal of CO_2 and SO_2

Literature Cited / Recent Publications

J.L. Anderson, J.K. Dixon, E.J. Maginn, J.F. Brennecke, "Using Ionic Liquids as Absorbent for the Desulfurization of Flue Gas", *Manuscript in preparation*, **2006**.

J.L. Anthony, J.L. Anderson, E.J. Maginn, J.F. Brennecke, "Anion Effects on Gas Solubility in Ionic Liquids", *J. Phys. Chem. B*, **2005**, *109(13)*, 6366-6374.

M.J. Muldoon, J.L. Anderson, J.K. Dixon, S.N.V.K. Aki, J.F. Brennecke, "Improving Carbon Dioxide Solubility in Ionic Liquids", *Manuscript in preparation*, **2006**.

J.L. Anderson, J.L. Anthony, E.J. Maginn, J.F. Brennecke, *Gas Solubilities in Ionic Liquids*, in *Ionic Liquids in Synthesis*, P. Wasserscheid,T. Welton, Editors. 2005.

D.G. Hert, J.L. Anderson, S. Aki, J.F. Brennecke, "Enhancement of Oxygen and Methane Solubility in 1-Hexyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl) Imide Using Carbon Dioxide", *Chem. Comm.*, **2005***(20)*, 2603-2605.

C. Cadena, J.L. Anthony, J.K. Shah, T.I. Morrow, J.F. Brennecke, E.J. Maginn, "Why is CO_2 so Soluble in Imidazolium-Based Ionic Liquids?" *J. Am. Chem. Soc.*, **2004**, *126(16)*, 5300-5308.

E.D. Bates, Mayton, R.D., Ntai, I., and Davis, Jr., J.H., "CO_2 Capture by a Task-Specific Ionic Liquid", *J. Am. Chem. Soc.*, **2002**, *124(6)*, 926-927.

W. Wu, Han, B., Gao, H., Liu, Z., Jiang, T., and Huang, J., "Desulfurization of Flue Gas: SO_2 Absorption by an Ionic Liquid", *Angew. Chem. Int. Ed.*, **2004**, *43(18)*, 2415-2417.

Acknowledgments

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