

# Ionic Liquids for CO<sub>2</sub> capture

F. Stiemke<sup>\*</sup>, G. Adamová,<sup>\*\*</sup> B. Iliev,<sup>\*\*</sup> T. J. S. Schubert, G. Romanos,<sup>\*\*\*</sup> M. Kroon<sup>\*\*\*\*</sup>

<sup>\*</sup>Iolitec Inc., 720 2nd Street AIME Bldg. Tuscaloosa, AL 35401, USA, info@iolitec-usa.com

<sup>\*\*</sup>Iolitec GmbH, Salzstrasse 184, D-74076 Heilbronn, Germany, info@iolitec.de

<sup>\*\*\*</sup>NCSR Demokritos, Institute of Physical Chemistry, 15310 Athens, Greece

<sup>\*\*\*\*</sup>Eindhoven University of Technology, Dept. Chemical Engineering and Chemistry, 5600 MB Eindhoven, Netherlands

## ABSTRACT

The main motivation for research on energy efficient processes and environment friendly solvents for CO<sub>2</sub> capture are economical and environmental aspects. Ionic liquids might be suitable candidates for a replacement of conventional solvents such as monoethylamine (MEA) in these processes, because of their low volatility and other beneficial properties. The diversity in cation/anion combinations is enormous, therefore the main challenge is to design and test the most suitable ones.

**Keywords:** ionic liquids, CO<sub>2</sub> capture

## 1 INTRODUCTION

Ionic liquids (ILs) are a class of compounds composed entirely of ions which maintain their liquid state below 100°C and have enjoyed an increased popularity in the past decade due to a unique combination of physical and chemical properties. Since it is possible by changing the cation/anion combination to fine-tune some of these properties for a specific purpose or application, they have earned the name of “designer solvents”. Their low volatility, non-flammability, tunable conductivity and viscosity, combined with high electrochemical and thermal stability make them promising candidates for a number of applications including CO<sub>2</sub> capture. Since it is known that IL have the tendency to retain CO<sub>2</sub> both physically (physical sorption) as well as chemically (chemisorption)<sup>[1]</sup>, they can be used for the direct capture of CO<sub>2</sub> replacing the current process based on highly corrosive and volatile aqueous amine solutions. This is leading to increased CO<sub>2</sub> loading, and absorption/stripping rates, while reducing water consumption, release of solvents to the atmosphere and corrosion impact on plant components.

## 2 IONIC LIQUIDS

The number of possible ionic liquids for every application is very large and choosing the most suitable material is often difficult. The most common cations and anions of ionic liquids are shown in Figure 1, where R represents alkyl chains of various lengths.

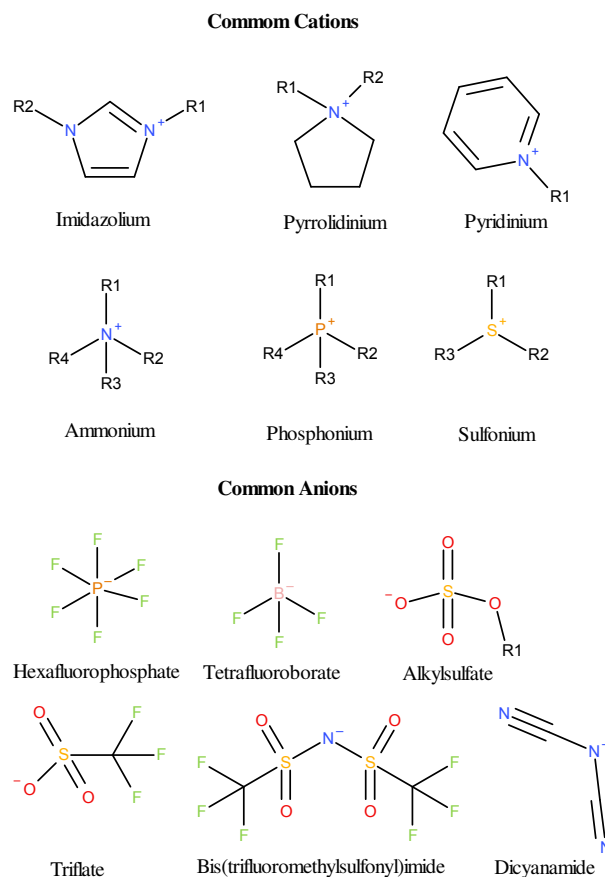


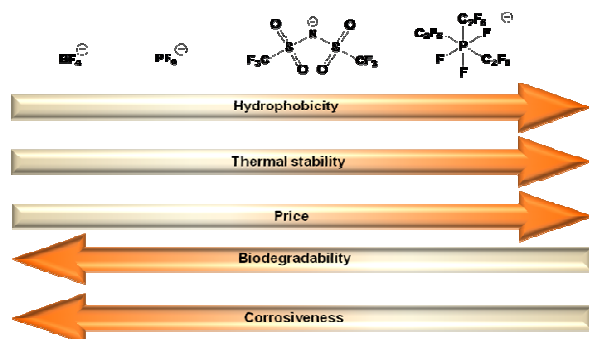
Figure 1: Commonly used cations and anions of ionic liquids

As mentioned above, ionic liquids have a tendency to capture CO<sub>2</sub> both physically and chemically, therefore they can be divided to physisorption ionic liquids, functionalized ionic liquids (chemisorption) and reversible ionic liquids, which can be reverted back to nonionic initial state.

### 2.1 Ionic liquids for physical sorption

Initial research on CO<sub>2</sub> capture with ILs focused mostly on the phase behaviour of CO<sub>2</sub> with different physical (nonfunctionalized) ionic liquids. In that case it is believed that the anion plays the primary role and cation secondary<sup>[2]</sup>. However, this also depends on various other

factors. One of them could be a level of fluorination which can significantly improve the CO<sub>2</sub> solubility when compared to ionic liquids without fluorine, as the CO<sub>2</sub> solubility increases as the number of fluor atoms in the anion increases<sup>[3,4]</sup>. Despite the fact that the cation plays a secondary role in enhancing the solubility, its fluorination can significantly improve the solubility although to lesser extent than the anion-fluorination<sup>[5]</sup>. There are other aspects which have to be considered when designing suitable ionic liquids, such as thermal stability, biodegradability, corrosiveness and last but not the least, the price.



## 2.2 Functionalized ionic liquids

Ionic liquids exhibiting only physisorption of CO<sub>2</sub> are not suitable for large scale, as the absorption is lower at postcombustion conditions. By incorporating amine moiety into the cation, the CO<sub>2</sub> absorption capacity increases due to reaction of amine group with CO<sub>2</sub> forming carbamate salt<sup>[6]</sup>. In this case the high viscosity might be the main issue, however the authors didn't observe dramatic viscosity increase after CO<sub>2</sub> reacted with amine functionalized cation of ionic liquid. It has to be noted that the viscosity of amine functionalized ionic liquids is still high and in order to overcome this problem to certain extent Camper et al.<sup>[7]</sup> proposed the use of nonfunctionalized ionic liquid-amine solutions. Such solution with 50% of MEA is capable of rapid and reversible capture of CO<sub>2</sub>, with stoichiometry close to 1 mol of CO<sub>2</sub> per 2 mols of MEA. The lower viscosity also influenced absorption rate, which was much higher when compared to functionalized ionic liquid, however the presence of MEA can negatively influence the corrosiveness of this material.

## 2.3 Reversible ionic liquids

Jessop et al.<sup>[8]</sup> reported that the room temperature ionic liquids could be also formed by reaction of an alcohol and an amine base, by exposing it to CO<sub>2</sub>. This ionic liquid can be then reverted back to its nonionic initial state when

exposed to nitrogen or other inert gas. These kind of solvents are also referred in literature as a switchable solvents, as the polarity of the solvent can be tuned upon the reaction with CO<sub>2</sub><sup>[9]</sup>. Bases such DBU, TMG or Hunig's base form a liquid alkylcarbonate when they are exposed to CO<sub>2</sub> in alcohol mixtures. It was reported that they bind chemically and reversibly with high CO<sub>2</sub> capacity (up to 19 % by weight) and also exhibited high selectivity in the presence of nitrogen<sup>[10]</sup>. The drawback in this case can be the fact that an undesired bicarbonates are formed in the presence of water, which can be problematic as the flue gas contains substantial water.

## 3 CONCLUSIONS

Ionic liquids design allows to tune their physical properties in the direction which can be attractive for CO<sub>2</sub> capture processes. On the other hand developing a cost efficient IL-based CO<sub>2</sub> capture system is a whole another task. In terms of price, up to now, ionic liquids are still not able to compete with conventional solvents. Therefore, the true innovation lies within development of the process which will be more environmental friendly, less energy demanding and will have a lower sensitivity to the flue gas composition. This can be achieved through a development of process based on hybrid absorption bed/membrane systems that will incorporate TSIL modified porous materials and membranes (Supported ionic liquid phase systems (SILPS) and Supported Ionic Liquid Membranes-SILMs). Iolitec cooperates within FP 7 EU project IOLICAP with researchers from various fields with the goal to establish such IL based PCC technology that will address the legislative mandates and reduce the cost of the carbon capture.

## REFERENCES

- [1] Wang C., Luo H., Jiang D., Li H., Dai S., *Angew. Chem. Int. Ed.*, 49, 5978–5981, 2010.
- [2] Aki S. N. V. K., Mellein B. R., Saurer E. M., Brennecke J. F., *J. Phys. Chem. B*, 108, 20355–20365, 2004.
- [3] Maiti A., *Chem. Sus. Chem.*, 2, 628–631, 2009.
- [4] Sistla Y. S., Khanna A., *J. Chem. Eng. Data*, 56, 4045–4060, 2011.
- [5] Almantariotis D., Gefflaut T., Padua A. A. H., Coxam J. Y., Costa Gomes M. F., *J. Phys. Chem B*, 114, 3608–3617, 2010.
- [6] Bates E. D., Mayton R. D., Ntai I., Davis J. H., *J. Am. Chem. Soc.*, 124, 926–927, 2002.
- [7] Camper D., Bara J., Gin D. L., Noble R., *Ind. Eng. Chem. Res.*, 47, 8496–8498, 2007.
- [8] Jessop P. G., Heldebrandt D. J., Li X., Eckert C. A., Liotta C. L., *Nature*, 436, 1102, 2005.

- [9] Liu Y., Jessop P. G., Cunningham M., Eckert C. A., Liotta C. L., *Science*, 313, 558-560, 2006.
- [10] Heldebrandt D. J., Yonker C. R., Jessop P. G., Phan L., *Energy Environ. Sci.*, 1, 487-493, 2008.