

## **A REVIEW: SOLUBILITY BEHAVIOUR OF NATURAL REFRIGERANTS WITH IONIC LIQUIDS**

**T. Altamash<sup>1\*</sup>, D. Salavera<sup>1</sup>, A. Kumar<sup>2</sup>, K.R. Patil<sup>2</sup>, C. Nieto de Castro<sup>3</sup> and A. Coronas<sup>1</sup>**

<sup>1</sup>CREVER, Dept. Mechanical Engineering Universitat Rovira i Virgili, Tarragona, Spain

<sup>2</sup> National Chemical Laboratory, Pune, India

<sup>3</sup> Faculdade de Ciências da Universidade de Lisboa, Lisboa, Portugal

\*Corresponding author: [tausif.altamash@urv.cat](mailto:tausif.altamash@urv.cat)

**Keywords:** Ionic liquids, Refrigerants, Solubility, Review

**Introduction:** Now, it is well accepted in the field of chemical science and engineering that ionic liquids have become an important class of novel solvents. Ionic liquid exists as liquid from wide range of temperature to room temperature due to asymmetry. The technology of absorption heat pumps and refrigeration has received growing attention in the past years from air-conditioning and refrigeration applications especially in connection with energy efficiency. Recently, absorption cooling cycles using ionic liquids + water / ammonia / carbon dioxide have been proposed as replacement for classical working fluids such as LiBr + H<sub>2</sub>O and H<sub>2</sub>O +NH<sub>3</sub> system due to a unique set of material properties, like non-volatility, high thermal stability, and large liquid ranges that are available neither from molecular compounds nor from typical crystalline salts, that is the true advantage of ionic liquid. In absorption technology one pair of working fluids are needed, first fluid with strong volatility is used as refrigerant e.g. Carbon dioxide / Ammonia / Water etc, whereas a second fluid with much smaller volatility but strong affinity to the former is used as absorbent like ionic liquid. So, there is need of systematic study of interaction of phase behaviour in terms of mutual solubility or other parameters.

This review deals with the solubility properties of ionic liquids with natural refrigerants (Carbon dioxide / Ammonia / Water) at high pressure and temperature as well as focused on interactions.

**Discussion:** We have discussed solubility or phase behaviour between ionic liquid and natural refrigerants under following points.

**Ionic Liquid + CO<sub>2</sub> / NH<sub>3</sub> Systems:** The phase behaviours of IL-CO<sub>2</sub> systems are studied very extensively in the literature to understand the interaction in term of solubility behaviour of CO<sub>2</sub> with ionic liquids. During literature survey it has been found that fluorinated anion (Tf<sub>2</sub>N, BF<sub>6</sub> and BF<sub>4</sub>) containing ionic liquids have been extensively used for CO<sub>2</sub> gas at high pressure. NH<sub>3</sub> interacted more strongly with imidazolium cation than anion due to hydrogen bond interaction. However, the detail studies of phase behaviour of IL-NH<sub>3</sub> are scarce, but NH<sub>3</sub> solubility in ionic liquids discussion included according to availability of their literature [1-4].

**Effect on Phase behaviour of Pressure and Temperature:** It has been found that solubility of CO<sub>2</sub> or NH<sub>3</sub> increases on increasing the pressure and decreases on increasing the temperature. Solubility of CO<sub>2</sub> in Ionic liquids increases with increasing pressure but the exact amount of CO<sub>2</sub> dissolved in the liquid phase varies significantly. In the study of Blanchard et al. [5], it is found that at 70 bar the solubility of CO<sub>2</sub> in [C<sub>2</sub>mim][EtSO<sub>4</sub>] was 0.36 (mole fraction) whereas, it was 0.63 in [C<sub>8</sub>mim][PF<sub>6</sub>]. Although there are some numerical differences in the mole fraction of CO<sub>2</sub> dissolved, the general trend of the phase behaviour is nearly identical for all Ionic liquids. The solubility of CO<sub>2</sub> in the ionic liquid-rich phase changes slightly with the temperature as in the case of [C<sub>4</sub>mim][PF<sub>6</sub>]-CO<sub>2</sub> system. Since the qualitative phase behaviour of almost all ionic liquids seems similar, it can easily be concluded that scCO<sub>2</sub> can be used to recover solutes not only from [C<sub>4</sub>mim][PF<sub>6</sub>] but also from all kind of Ionic liquids.

**Ionic Liquids + H<sub>2</sub>O Systems:** With respect to solubility behaviour of water, there are two types of ionic liquids; hydrophobic and hydrophilic ionic liquids. Even hydrophobic ionic liquids are known to be highly hygroscopic, and the H<sub>2</sub>O solubility in these ionic liquids amounts to nearly 10–30 mol % (0.7 – 4.0 mass %). H<sub>2</sub>O + hydrophobic ionic liquids are partially miscible systems with a typical immiscibility gap of about 20–100 mol % (2.4–100 mass %) at room temperature. On the other hand, hydrophilic ionic liquids are completely mutually soluble at room temperature. The solubility behaviour is largely controlled by the chemical structure of the anion, and various empirical rules for the H<sub>2</sub>O solubility in ionic liquids have been found experimentally [6].

**Summary:** As noted above, solubility of gases depends upon pressure and temperature of system. On increasing the pressure the solubility of gases increases and on increasing the temperature decreases, all gases solubility increases on elongation of alkyl chain of an ionic liquid due to free volume increment. It is clear from experimental, computational and theoretical studies that the ionic structure with the ability of the ionic liquid to dissolve the gas molecules. CO<sub>2</sub> dissolve more easily in fluorinated anion having ionic liquids, so CO<sub>2</sub> called as CO<sub>2</sub>-philic. The molecular characteristics proposed by Beckman [7] for a “CO<sub>2</sub>-philic” material hold for specifically designing the Ionic liquids to enhance the solubility of the gases having strong interactions with the Ionic liquids. The first two features, i.e., flexible and high free volume materials with weak self-interactions, apply to the design of new Ionic liquids for enhancing the solubility of the gases having weak interactions with the Ionic liquids, where as Hu and co-author [8] reported in his concluding remark that decreasing the anion size will generally exert greater influence on the gas pair selectivity than shortening the cation chain length. In case of NH<sub>3</sub> interaction, NH<sub>3</sub> interacted more strongly with imidazolium cation than anion due to hydrogen bond interaction and also depend on free volume of ionic liquid like CO<sub>2</sub>. Hydrophobic ionic liquids are partially miscible in aqueous systems with a typical immiscibility gap, whereas hydrophilic ionic liquids are completely mutually soluble at room temperature. The solubility decreases in H<sub>2</sub>O on increasing the alkyl chain length and depends on anion rather than cation core of an ionic liquid.

**References:**

1. W. Shi and E. J. Maginn, Molecular simulation of ammonia absorption in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf<sub>2</sub>N]), *American Institute of Chemical Engineers Journal* 55 (2009) 2414-2421.
2. G. Li, Q. Zhou, X. Zhang, L. Wang and S. Zhang, Solubilities of ammonia in basic imidazolium ionic liquids, J. Li, *Fluid Phase Equilibria* 297 (2010) 34-39.
3. A. Yokozeki and Mark B. Shiflett, Ammonia solubilities in room-temperature ionic liquids, *Industrial & Engineering Chemistry Research* 46 (2007) 1605-1610.
4. A. Yokozeki and Mark B. Shiflett, Vapor–liquid equilibria of ammonia + ionic liquid mixtures, *Applied Energy* 84 (2007) 1258–1273.
5. L.A. Blanchard, Z. Gu and J.F. Brennecke, High-Pressure phase behavior of ionic liquid/CO<sub>2</sub> systems, *Journal of Physical Chemistry B* 105 (2001) 2437–2444.
6. A. Yokozeki and M.B. Shiflett, water solubility in ionic liquids and application to absorption cycles, *Industrial & Engineering Chemistry Research* 49 (2010) 9496-9503.
7. E. J. Beckman, A challenge for green chemistry: designing molecules that readily dissolve in carbon dioxide, *Chemical Communications* (2004) 1885-1888.
8. Y-F. Hu, Z-C. Liu, C-M. Xu and X-M. Zhang, The molecular characteristics dominating the solubility of gases in ionic liquids, *Chemical Society Reviews* 40 (2011) 3802-3823.