In this interview, Professor Mark B. Shiflett, from the Univeristy of Kanas, talks to AZoM about exploring gas solubility in ionic liquids and why a greater understanding of gas solubility in ionic liquids is important.

What are ionic liquids and how do they interact with gases?

Ionic Liquids (ILs) are defined as salts that melt below 100 degrees Celsius. Room Temperature Ionic Liquids (RTILs) are further defined as salts which are liquid at room temperature.

Gases can interact with Ionic Liquids via a process called absorption. Absorption is a process in which molecules transfer from a gas phase into a liquid phase (in this case the Ionic Liquid).

The difference between absorption and adsorption is that in absorption, the molecules are taken up by a liquid (absorbent), while for adsorption the molecules are fixed onto solid surfaces.

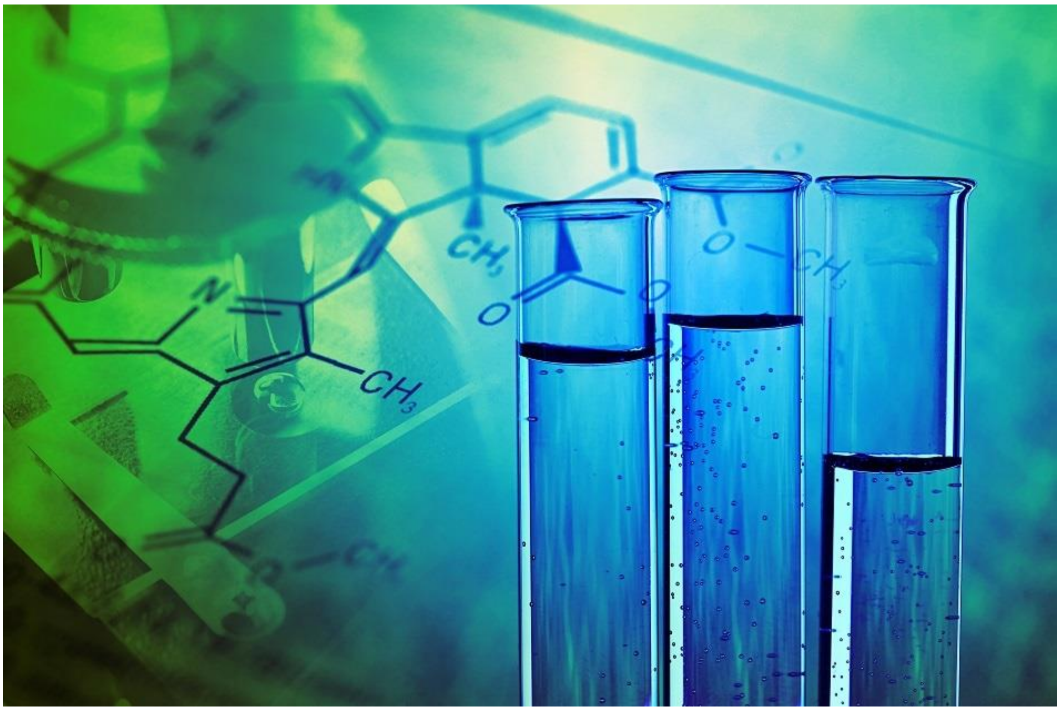
Why is a greater understanding of gas solubility in ionic liquids important?

The solubility of gases has played an important role in the history of ionic liquids, which traditionally have been considered as new solvents for both separations and chemical reactions. In gas separations, the design of the absorption (desorption) column requires solubility data for the gases in the Ionic Liquids.

Absorption can occur by two mechanisms, physical or chemical. Physical absorption involves gas transfer into the liquid by physical forces. Physical absorption also referred to as gas solubility is a function of temperature and pressure.

Chemical absorption includes a chemical reaction occurring between the gas and the liquid. In gas-liquid reactions such as alkylation, hydrogenation, and hydroformylation, both the gas solubility and the mass transfer (diffusivity) of the gas in the ionic liquid phase are needed to design the chemical reactor.

Other applications which require knowledge of gas solubility and diffusion of gases into ionic liquids include absorption cooling, polymerization, membrane separation, lubrication, extraction and gas-expanded liquids to name a few.



What different methods can be used to determine the solubility of gases in ionic liquids?

Several methods have been developed for measuring the solubility of gases in liquids. Those methods include volumetric, gravimetric and analytical techniques such as spectroscopy and chromatography.

Each method requires certain corrections to obtain accurate results so no single method is ideal for all gas liquid systems. A nice feature about measuring the solubility of gases in ionic liquids is the fact that ionic liquids have a very low vapor pressure and thus do not evaporate on practical time scales.

The low vapor pressure of the ionic liquid allows gravimetric methods to be used for measuring gas solubility.

What are the challenges of determining gas dissolution in ionic liquids?

To accurately measure the solubility of a gas in an Ionic Liquid requires:

(1) purification and characterization of the gas and Ionic Liquid;

(2) thorough drying and degassing of the Ionic Liquid;

(3) equilibration of the gas and Ionic Liquid phases under the conditions of known constant temperature and pressure;

(4) measurements that determine the composition of the gas in the Ionic Liquid phase;

(5) proper error analysis to estimate the uncertainty;

(6) use of a thermodynamic model to validate results.

Any paper reporting data on the solubility of a gas in an Ionic Liquid should include an adequate description of these steps and comparison measurements on a standard system to allow the user to judge the reliability of the data.

For this purpose, the International Union of Pure and Applied Chemistry (IUPAC) sponsored a project to make physical property measurements available for comparing the gas solubility of CO2 in a reference Ionic Liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

Another important aspect is ionic liquids can swell when they absorb large quantities of gas and this change in volume must be taken into account in order to accurately calculate the amount of gas absorbed when using volumetric and gravimetric techniques.

What are the advantages of using a gravimetric method over synthetic or chromatographic methods to measure gas dissolution in ionic liquids?

One advantage is gravimetric measurements provide a direct mass measurement as a function of temperature (T) and pressure (P).

Synthetic methods such as volumetric techniques measure volume of gas absorbed which has to be converted to mass using gas density correction as a function of T and P.

How can data collected by the Hiden XEMIS gravimetric sorption analyzer be used to model the relationship between gases and ionic liquids?

The Hiden XEMIS balance provides the mass absorbed as a function of time (t) which can be used for calculating both the gas solubility (x) and diffusivity (D) in ionic liquids using the one-dimensional diffusion equation.

The gas solubility data can be modelled using a solution model such as Non-Random Two-Liquid (NRTL) or Equation of State (EOS) models such as Peng-Robinson or Redlich-Kwong.

The diffusivity data can be modelled using the Stokes-Einstein equation in order to determine the molecular diameter of the absorbing molecules. EOS models can also be used to make predictions of vapor-liquid-equilibria (VLE) at other T and P conditions as well as predict vapor-liquid-liquid equilibria (VLLE) from gas solubility measurements.

Is there much understanding of what occurs on a molecular level when a gas dissolves in an ionic liquid?

Gas solubility measurements provide a macroscopic view (PTx) of how gases dissolve into ionic liquids which can be used to validate molecular simulations that provide a microscopic view (molecular level).

A variety of studies have demonstrated that the physical solubility (physical absorption) of gases in Ionic Liquids can be modelled accurately using atomistic-level simulations.

Force fields for gases and many Ionic Liquids are readily available, and the steady increase in computing power has meant that the time and expense for performing these calculations continues to decrease. Treating reactive systems (chemical absorption) remains a major challenge for the modelling community and advanced methods are required to model such systems.

Could ionic liquids play a role in protecting the environment?

In the past couple of years (2015-2017) we have seen some of the largest scale ionic liquid processes announced which will play a key role in protecting the environment.

For example, the ionic liquids process developed by Queens University Ionic Liquids Laboratory (QUILL) in collaboration with the Malaysian oil and gas company, Petronas for the efficient scrubbing of mercury vapor from natural gas. The process is now operating on an industrial-scale using chlorocuprate (II) ionic liquids impregnated on high surface area porous solid supports.

The supported ionic liquid phase (SILP) approach to heterogenize the ionic liquid allowed the material to be used in standard industrial-scale mercury removal equipment and the rapid commercialization of the process. The SILP containing ionic liquid outperformed the incumbent activated carbon and better manages process upsets such as spikes in mercury concentration.

What commercial applications are there for ionic liquids?

Ionic Liquids are being studied for a variety of applications and several commercial products and processes have been and are being developed. For example, Professor Daniel Armstrong at the University of Texas in Arlington has developed a new class of capillary gas chromatography (GC) columns with stationary phases based on ionic liquids. His group has synthesized dicationic and polycationic ionic liquids which are stable to water and oxygen even at high temperatures. A variety of capillary GC columns are now available based on Ionic Liquid technology.

The technique can also be used for detection of water using a thermal conductivity detector (TCD) at extremely low limits of detection (LOD). Compared with the standard Karl Fischer titration (KFT) method used today with a lower limit of detection (LOD) of 10 µg (1 ppm), the ionic liquid method has a lower LOD of ~2 ng (0.0002 ppm).

Recently, a leading energy company announced in October 2016 the development of a new chloroaluminate ionic liquid alkylation catalyst. The chloroaluminate ionic liquids provide high activity, selectivity and catalyst stability for C_4 alkylation and provided the energy company with an alternative to using corrosive and toxic hydrofluoric acid (HF) as a catalyst.

The energy company stated that they began developing the technology in 1999 and have operated a demonstration unit for the past five years. They plan to start construction in 2017 on a full-scale alkylation plant at their Salt Lake City refinery. After the plant is complete in 2020, they plan to remove all HF specific equipment and its inventory of HF from the site.

Where can our readers go to find out more?

A recent prospective article published by Mark Shiflett and Edward Maginn entitled *The Solubility of Gases in Ionic Liquids* in the *AIChE Journal* (*63(11)* **2017** 4722-4737) provides a detailed discussion of the techniques and methods used for determining the solubility of gases in Ionic Liquids.

This includes various experimental measurement techniques including the Hiden XEMIS microbalance method, EOS modelling and predictive molecular-based simulations.

Many of the key papers from the past 15 years are discussed and put into the context of the latest advances in the field. Limitations of these methods, plus further developments and new research opportunities are discussed. In addition, many excellent books have been written about Ionic Liquids.

A collection of three books which were recently published by editors, Natalia Plechkova and Ken Seddon entitled *Ionic Liquids UnCOILed* (Wiley, 2013), *Ionic Liquids Further UnCOILed* (Wiley 2014) and *Ionic Liquids Completely UnCOILed* (Wiley, 2015) provide critical overviews of the key areas of ionic liquid chemistry.

About Mark Shiflett

Mark B. Shiflett is a Foundation Distinguished Professor in the Department of Chemical and Petroleum Engineering at the University of Kansas.

Mark's research is focused on Green Chemistry and Engineering to develop environmentally friendly and energy efficient chemical processes and products (www.shiflettresearch.com).

Prof. Shiflett retired from DuPont in 2016 as a Technical Fellow in Central Research and Development with 28 years of service. He has published over 70 peer-reviewed articles, is an inventor on 44 U.S. patents and commercialized three refrigerant mixtures used to replace chlorofluorocarbons that have helped heal the Earth's ozone layer.

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