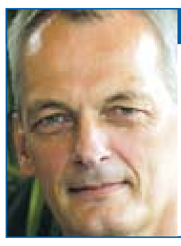
Ionic Liquids

Unique Materials with Multiple Prospects

Unanswered Questions – There is hardly anyone who has never come across the concept of ionic liquids, yet more often than not, certain questions remain unanswered, as they did in the Neil Winterton's article "Ionic Liquids – Help or Hype?" (CHEManager Europe 5/2008). The question is certainly justified, and this article deals with it from the vantage point of an industrial-scale supplier of ionic liquids.

At first sight, it is fairly easy to say what ionic liquids are: salts that are liquid already at low temperatures due to their chemical structure, which comprises mostly rather voluminous, organic cations and a wide range of different anions. And they only consist of these cations and anions; they do not contain any solvents like water. This does not sound very exciting on the face of it, but it results in a combination of unique properties that cannot be achieved with any other material. In a way, these liquid salts combine the properties of solids and liquids in a single material. This paves the way to many innovative solutions like new products or processes.



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To date, ionic liquids are often considered to be "lab curios" that are virtually unaffordable. People tend to overlook that it is not the price that tilts the balance in favor of ionic liquids but the cost at which a kilogram of final product can be manufactured. This cost is usually low because in many cases, a major part of the ionic liquid can be recycled. Moreover, ionic liquids are available nowadays at the ton scale and in high quality from a variety of suppliers. BASF, e.g., offers a portfolio of products that are being manufactured by standard processes on a fairly large scale and cover a wide range of application options.

From the early days, ionic liquids were assumed to merit approval for being "green solvents." This was based on the absence of vapor pressure and has proven to be little help. As with many other chemicals, you can find the entire range from highly toxic to absolutely safe among ionic liquids. So there will never be an across-the-board toxicology or ecotoxicology rating that applies to all ionic liquids alike. Having said that, as in all other cases professional and sustainable management of chemicals is what really makes the difference.

However, the many toxicological studies on ionic liquids that are available today show some clear trends and point the way to toxicologically safe materials. They suggest, e.g., that long-chain alkyl groups should be avoided irrespective of the cation involved in order to achieve lowest possible toxicity levels. 1-ethyl-3-methyl-imidazolium-ethylsulfate is an ionic liquid available today in BASF's portfolio that shows no signs of acute toxicity has been registered in keeping with the law on chemicals and opens up a broad range of applications.

Starting from the original idea that ionic liquids should be used as alternative reaction media for chemical reactions, promising applications today span a wide array of uses. Ionic liquid applications that have actually been put into practice successfully are often distinguished by the fact that they could not have been realized at all if it had not been for the specific properties of these materials, as can be seen from the three examples given below:

Linde – Operating Medium for New Gas Compression Technology

In gas compression, heating the gas to be compressed causes considerable loss of efficiency that translates into increased input of energy. This effect is illustrated clearly by the case of hydrogen, which needs to be compressed to pressures exceeding 400 bar for efficient storage. Linde recently presented a novel compressor technology that has the ionic liquid doing the work of compression as a "liquid piston." This technology, launched by Linde as the "ionic compressor," has obvious benefits: It requires less maintenance as there are significantly less moving parts, and it cuts energy input by about 20%. This is achieved by cooling the operating medium externally, which makes nearly isothermal compression possible.

It is only by means of ionic liquids that this compression technology could be realized, because only ionic liquids offer the combination of physical properties needed here: a liquid that flows relatively freely at temperatures from –20 to +200 °C, virtually no vapor pressure and very low solubility for gases. However, not all ionic liquids meet these requirements equally well. The properties of the ionic liquid must instead be tailored to suit exactly the profile required in this application and other constraints need to be taken into account as well. Linde already operates a number of these compressors for hydrogen and natural gas in a beta test phase in cooperation with selected customers, and general commercial launch of is imminent.

G24i – Electrolyte in Dye-sensitized Solar Cells

The exploitation of solar energy currently represents one of the most promising options for the use of renewable energy. The most widespread technology and also the most advanced in terms of efficiency is the crystalline silicon solar cell. However, the comparatively high cost of this type of cell still poses a major challenge. Dye-sensitized solar cells that can be produced at a much lower cost therefore offer a promising alternative. In addition they are sensitive to far more of the visible spectrum of light, so that they can operate even at relatively low levels of light intensity as for example in diffuse light.

Along with the dye and the electrode materials, the electrolyte used in these dye-sensitized solar cells is crucial. Ionic liquids are the only materials that will produce the desired functionality and long-term stability in these cells. In this case, too, the technology makes use of various properties: the low melting point and negligibly low vapor pressure allow the cells to be used across a broad range of temperatures, from –20 °C to +80 °C; the conductivity of the ionic liquid ensures the charge transfer required, and its electrochemical stability produces the required stability. In addition to that, the ionic liquid stabilizes the dye that is applied over a titanium dioxide layer, and it acts as a solvent in the I-/I3-redox process. This is another case where ionic liquids are the only materials that meet the complex range of requirements.

G24i of Cardiff, Wales, is the first company making commercial use of this dye-sensitized solar cell technology. The technology allows for an extremely favorable roll-to-roll manufacturing process and also gives flexible cells that can be used in many fields. The market launch mainly aims at portable applications such as mobile phone chargers in regions that do not have a universal power supply grid.

BASF – Dissolution and Processing of Cellulose

With 75x109 t regrowing each year, cellulose represents the largest source of carbon available on our planet. Only a very small fraction of that, about 200x106 t, is actually being used nowadays, above all to make paper and pulp. Out of that, the negligible volume of 5x106 t only is used to produce materials in the narrower sense – mainly viscose fibers. Cellulose has not been used more widely to date mainly because there have been no suitable solvents that can be handled easily. Ionic liquids are the first products that can step into this gap.

Based on pioneering work by Professor Robin Rogers of the University of Alabama and in cooperation with additional partners, BASF has developed processes for dissolving and shaping cellulose. Taking things further, the chemical modification of cellulose dissolved in ionic liquids opens up a wide array of potential ways to produce materials based on regenerative raw materials. BASF is cooperating with a number of partners to commercialize these processes and products.

Would-be Limits

Some publications surmise that ionic liquids have come up against certain limits in their applications, or that their potential is being overestimated. This applies in particular to the much publicized use of ionic liquids as reaction media in chemical reactions. Yet that "apparent lack of success" is often due to the approach chosen for the venture. The mere fact that ionic liquids do not have vapor pressure won't be sufficient to make a process more efficient. Applications in this segment that have been implemented successfully are always marked by the fact that the ionic liquid has at least one more very positive influence, in addition to being free of vapor pressure. The following examples of successful applications, which do not claim to be exhaustive, demonstrate that ionic liquids by all means continue to hold great promise as reaction media in chemical reactions, if their specific properties are employed purposefully to optimize these reactions.

In the fluorination process described by Arkema and realized in a pilot plant, the ionic liquid enhances reaction selectivity and prolongs the life of the catalyst. In this process, the ionic liquid supports the catalysis as such, just as it does in the hydrosilylation reactions described by Degussa and Wacker. The beneficial influence of ionic liquids is even more obvious in the processes published e.g. by IFP and Chevron where the ionic liquid itself acts as a catalyst. In the Basil process practiced by BASF, the first ever chemical process to use an ionic liquid, the reaction medium speeds up the reaction dramatically, which makes a totally novel jet reactor concept possible.

Potential Of Ionic Liquids

What has been said with respect to chemical reactions applies in the same way to all other potential applications of ionic liquids: The most promising are those that employ more than one of the properties typical of ionic liquids. Ionic liquids should be seen less as "chemicals" but rather as "system innovations" that make certain products and processes possible for the first time.

Although a broad range of ionic liquids is now available, there is obviously no denying the fact that more work is needed to keep optimizing the properties of these materials. Current research focuses on developing ionic liquids that feature still lower viscosity, higher conductivity while they retain their high electrochemical stability, and improved thermal stability.

Applications that continue to offer major potential for ionic liquids include electrolytes for energy storage media like capacitors or lithium-ion batteries; the deposition of non-noble metals; the transformation of biomass into regenerative energy sources; and the wide area of engineering liquids, which includes applications as interesting as lubricants, hydraulic liquids or sorbents for cold production. Suppliers of ionic liquids, academic researchers and potential customers will definitely have to cooperate closely across their disciplines if we want to tap the full potential available.

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