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Ionic liquids: A most promising research field in solution chemistry and thermodynamics*

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Abstract: Modern room-temperature ionic liquids (RTILs) consisting of large and asymmetric organic cations and small inorganic anions exhibit a special class of recently developed liquids unifying the property of the liquid state and strong Coulomb interactions acting as the prevailing intermolecular interactions in the liquid state. Several selected examples of the most promising chemical and technical applications of ILs are presented, which underline the importance of thermophysical properties of ILs and their role of being particular solvents in catalytic and separation processes as well as in special fields of electrochemistry.

Keywords: ionic liquids; applications of ionic liquids; solution chemistry of ionic liquids.

INTRODUCTION

Interest in room-temperature ionic liquids (RTILs) has dramatically grown in the scientific community during the last years. While until 1999 the number of papers published worldwide was 50 to 100 per year, in 2003 this number increased to more than 900 and is still increasing every year. The fields of chemical and technical applications range from the development of new chemical syntheses where RTILs are used as solvents and catalysts to chemical engineering and electrochemical applications such as special kinds of batteries, new techniques of electrodeposition, dye-sensitized solar cells (DSSCs), hazardous gas storage systems, chemical separation processes, supported liquid membranes, and the use of RTILs as lubricants and as thermal fluids in heat transporting systems. Several recent review articles and proceedings of congresses on RTILs give a survey of this most promising variety of applications [1–7], which are based on the following unique features of RTILs.

• RTILs are ionic compounds consisting of relatively large and asymmetric organic cations such as imidazolium derivatives, pyridinum derivatives, quaternary alkylammonium ions, and relatively small anions such as Cl⁻, BF₄⁻, PF₆⁻, and others which are liquid at room temperature due to relatively small enthalpies of fusion ΔH_{melt} and large entropies of fusion ΔS_{melt} resulting in low melting temperatures T_{melt} according to the general relationship

$$T_{\text{melt}} = \frac{\Delta H_{\text{melt}}}{\Delta S_{\text{melt}}}$$

A selection of modern RTILs is shown in Fig. 1. Most of them are stable liquids up to 400 °C or even higher temperatures.

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- RTILs have a nondetectable vapor pressure in the whole range of temperature available for applications. Their ionic character is mainly responsible for an unusual solubility behavior of substances, which are hardly soluble in normal solvents.
- RTILs show good electrical conductivities and moderate viscosities, which make the technical usage of RTILs attractive for many purposes [3,8].
- Many RTILs available today show an interesting mixing behavior with other liquids, including selective solubilities of gases [8].
- Toxicity and ecotoxicity of RTILs turned out to be low at least as long as the alkyl groups in the organic cation contain fewer than 5 carbon atoms [9].



Fig. 1 A selection of modern RTILs.

Compared to the wide extent of chemical and engineering applications of RTILs, the corresponding knowledge of their physicochemical properties (i.e., thermodynamic, spectroscopic, and transport properties) is far less developed although the recent activities in these basic research fields indicate that an increasing number of research groups become attracted by RTILs. Efforts have been made recently to understand better the molecular structure and intermolecular interactions in RTILs and mixtures of other fluids with RTILs on the basis of quantum mechanical ab initio calculations and molecular dynamics (MD) using force field techniques [10–14].

This article's purpose is to present some selected examples of innovative applications of RTILs and to point out the fact that there is a particular interest in basic research studies from the point of physical chemistry, solution chemistry, and thermodynamics.

SELECTED EXAMPLES OF APPLICATION

The first example concerns a serious problem arising in the petrochemical industry. Gasoline and other petrochemical products contain undesired amounts of aromatics and/or sulfonated organic compounds. An effective procedure to selectively remove such chemicals from the fuel prior to the combustion process is most desirable. RTILs are known to show a preferred solubility for aromatics and sulfonated organics compared to saturated hydrocarbons. This can be demonstrated by comparing Henry's coefficients of aromatic compounds and saturated hydrocarbons. Activity coefficients at infinite dilution γ_i^{∞} are proportional to Henry's coefficient and provide a direct measure for the solubility. The higher γ_i^{∞} or Henry's constant is, the less soluble is the corresponding compound in the RTIL. Figure 2 shows some results of γ_i^{∞} values in RTILs, demonstrating clearly the preferred solubility of aromatics in RTILs [15].

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Fig. 2 Activity coefficients at infinite dilution at 313 K for solutes in \blacktriangle [4-nBPyr] [BF₄], \bigcirc [C₂MIM] [NTf₂], and \times [C₂MMIM] [NTf₂]. Left: (6) *n*-hexane, (7) *n*-heptane, (8) *n*-octane, (9) *n*-nonane, (10) *n*-decane. Right: (6) benzene, (7) toluene, (8) ethylbenzene, (9) iso-propyl-benzene, (10) *tert*-butyl-benzene.

As a consequence, aromatics and also sulfonated compounds can effectively be stripped from a gasoline stream using an RTIL as extracting medium. Most important is the fact that no RTIL can enter the gasoline stream owing to the nondetectable vapor pressure of the RTIL. A further remarkable property of most of the RTILs is the good solubility of CO_2 in RTILs [8]. Combining these properties of RTILs, a separation unit can be designed to extract the aromatic compound dissolved in the RTIL in a first stage, exposing in a second stage supercritical CO_2 to the RTIL saturated preferably with the aromatic compound, which can now be extracted from the RTIL by CO_2 . The aromatics can be condensed from the CO_2 stream, and the purified RTIL as well as the CO_2 can be used again without loosing any RTIL owing to the fact that no RTIL is soluble neither in gasoline phase nor in the supercritical CO_2 phase. Such a possible process is sketched in Fig. 3. Regardless of the economic efficiency, it demonstrates an interesting alternative way to remove aromatics and sulfonated organics from gasoline. This example demonstrates also the importance of basic research work concerning solubility measurement of fluids and compressed gases in RTILs.



Fig. 3 Schematic of extraction of aromatics and sulforized compounds from gasoline.

Another interesting example of exploiting the fact that RTILs can absorb remarkable amounts of gases without being dissolved in the pressurized gaseous phase is the hazardous gas storage technique, which has recently been developed [16]. Hazardous gases like BF₃ and PH₃ have widely been used in the electronic chip industry for ion implantment technique. Figure 4 shows schematically the sorption

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isotherm of PH_3 and BF_3 in the RTILs $[C_4MIM] [Cu_2Cl_3]$ and $[C_4MIM] [BF_4]$, and it can be seen from the figure that quite large amounts of these gases can be absorbed and stored at ambient pressure, allowing the release of an easily controllable gas stream of these hazardous gases. Using this technique, intensive safety installations of gas reservoirs normally operated at high pressure can be avoided, providing a safer and less expensive handling. Figure 4 also shows that the special complexation of the gases with the anions of the RTILs is the reason for the good solubility of PH_3 and BF_3 at low pressure.



Fig. 4 Sorption isotherms of PH₃ (left) and BF₃ (right) and anion complexation.

A most successful and unique example of a chemical production process where RTILs play an essential role is the so-called BASIL process (biphasic acid scavenging process utilizing ILs) developed by the BASF company [17].

The production of $R_1R_2P-O-C_2H_5$, an important intermediate product is conventionally synthesized by reaction of R_1R_2P-Cl with ethanol, whereas a tertiary amine, traditionally triethylamine, is used as acid scavenger (see Fig. 5). Since it is difficult to remove the solid quarternary alkylammonium compound ([$(C_2H_5)_3NH$]⁺Cl⁻) from the reaction mixture and to separate the desired product, *N*-methylimidazole has been used instead of trialkylamines. Above 75 °C, the [HMIM]Cl is a liquid and can easily be separated from the phase containing the product $R_1R_2P-O-C_2H_5$ and, in addition, the [HMIM]Cl is acting as a good nucleophilic catalyst from which the *N*-methylimidazole can be recovered by simple deprotonation of [HMIM]Cl with sodium hydroxide.



Fig. 5 Synthesis of phosphorus compounds using the BASIL process by BASF.

A possible and most exciting application of RTILs is their usage as a nonvolatile electrolyte system in DSSCs [18–20]. Figure 6 shows the cross-section of a sheet consisting of surface electrodes connected by an electrolyte. The sheet acts as flexible electrochemical cell with the cell reaction

$$\frac{3}{2}I^- \rightarrow \frac{1}{2}I_3^- + e^{-\frac{1}{2}I_3^-}$$

at the electrode consisting of TiO2-nanoparticles covered by the dye and the reverse reaction

$$\frac{1}{2}I_3^- + e^- \to \frac{3}{2}I^-$$

at the counterelectrode.



Fig. 6 Dye-sensitized solar cells (DSSCs)-working principle.

The cell provides a voltage and consequently an electrical current across the cell and an external load with the resistor R if the dye electrode is illuminated and electrons of the dye are excited by a photon absorbed from the light source. The electrons are transferred from the dye to the TiO₂-particles closing the electric circuit. The weak point of such mechanically flexible solar cells is the liquid electrolyte located between the electrodes. The problem of using solvents for carrier electrolytes such as acetonitrile or 2-methoxypropionitrile is their volatility and incompatibility with sealing materials of the cell.

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Since RTILs have been available, unifying the properties of acting as liquid electrolyte and having an extremely low volatility the prospects of developing DSSCs with a long life time and good efficiency using RTILs are very promising.

A further interesting example where the properties of RTILs as nonvolatile electrolytes are used is their application as hygrometers. Water-soluble RTILs change their electrical conductivity by dissolving or evaporating gaseous water depending on partial pressure of water in the surrounding atmosphere to which they are exposed. Long-time stabilized instruments for measuring humidity have been developed on this basis [21].

We present a last example that shows in a particular manner the unexpected properties of new RTILs opening interesting prospects of applications. Japanese scientists have developed magnetic RTILs [22] by a simple synthesis shown in Fig. 7 where the chloride anion of 1-alkyl-3-methylimidazolium chlorides is substituted by complexated FeCl_4 anion, which carries a permanent magnetic moment. Since the iron atoms in the liquid phase are separated far enough from each other, the liquid shows a strong paramagnetic behavior. Such liquids could be used as mechanical devices (e.g., magnetically operated switches) or as transport media that can be moved by magnetic fields in a controlled way inside closed network systems. Medical as well as engineering applications can be thought of in the future.



Fig. 7 [C₄MIM] [FeCl₄] and [nC₄MIM] [FeCl₄]—magnetic ILs.

CONCLUSIONS AND PROSPECTS

We have presented some selected examples of possible or already utilized applications of modern ILs.

The wide and promising areas where RTILs can be used exhibit also a challenge for more basic research work required in particular in the following branches of physical chemistry and solution chemistry.

- There is a need for systematic measurements of transport properties in RTILs and mixtures containing RTILs covering a wider range of temperature and composition. This concerns in the first place electrical conductivity and mutual diffusion coefficients in mixtures containing RTILs. These data are important for designing devices where these properties dominate the technical process.
- It would be highly desirable to have solubility measurements of mixed gases at elevated pressure in RTILs to study synergistic effects and their influence on separation processes.
- Surface properties such as surface tension measurements and interfacial tension measurements in RTIL + solvent mixtures exhibiting liquid–liquid demixing are of interest since mass transport across interfaces dominates the separation and extraction processes where RTILs are involved.
- The largest defficiency concerns data and information of the molecular structure and the intermolecular interaction in RTILs. Experimental methods like NMR and Fourier transform infrared (FTIR) spectroscopy as well as scattering data using small-angle X-ray scattering (SAXS) or neu-

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tron scattering would provide such information to reveal the connection between molecular structure and macroscopic properties. These efforts must be accompanied by computational methods such as MD simulation in combination with quantum mechanical ab initio calculations. Recently, more activities are visible in the literature regarding theoretically based studies, e.g., in refs. [10–14].

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