

REVERSIBLE IONIC LIQUIDS

Background on Ionic Liquids

Ionic liquids (ILs) are salts composed solely of ions, with melting points near or below ambient temperature. Some ionic liquids can exhibit unusual and advantageous properties like negligible vapor pressure, nonflammability, high thermal stability, wide liquid temperature range, high solvency, high thermal conductivity and immiscibility with many organic solvents. Their physical and solvent properties can be tailor-designed by tuning the pairing and structure of the cations and anions. The most common application of ionic liquids has been their use as chemical reaction solvents. ILs have also been used for electrochemical processes, removal of metal ions, purification of gases, generation of high conductivity materials, extraction solvents stationary phases in chromatography, thermal fluids, lubricants, and propellants.

Solvent properties of ILs are mainly determined by the ability of the salt to act as a hydrogen bond donor and/or acceptor and the degree of localization of the charges on the anions. For example, imidazolium-based ILs are highly ordered hydrogen-bonded solvents and they have strong effects on chemical reactions and processes. Charge distribution on the anions, H-bonding ability, polarity and dispersive interactions are the main factors that influence the physical properties of ILs. Even though some of the ILs such as [EtNH₃][NO₃] were first described in 1914, the phenomenal growth has occurred in industrial and academic interest in the last decade due to their acceptance as a new green chemical with unique properties.

Recently solubilities of gases in ionic liquids have been investigated for purification processes. These experimental studies show that some gases, especially CO₂, are highly soluble in some ILs. The simulations performed explain that the anion of the IL is responsible for high gas solubility, and the relatively high solubility of CO₂ was explained as a result of its large quadrupole moment.

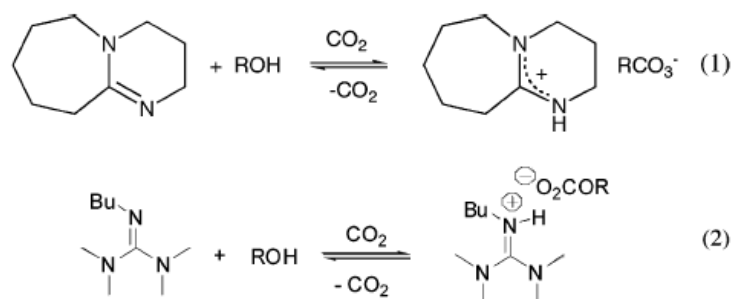
The green character of ILs has been usually related with their negligible vapor pressure; however the toxicity, biodegradation, bio-accumulation, safety, health, and environmental impact data of the conventional ionic liquids have been very limited until now, and are needed immediately. In recent studies it was shown that by pairing and structural tuning of anions and cations, it is possible to design non-toxic ionic liquids. One of the major concerns in applications of ionic liquids, such as imidazolium and ammonium ILs, is their high hydrophilic character, which can lead to decomposition, deactivation of catalysts, and degradation and contamination of solutes in ionic liquids. For example despite their wide spread usage, ILs containing PF₆⁻ and BF₄⁻ have been reported to decompose upon heating in the presence of water and emit HF. Also ILs containing halogen anions generally show poor stability in water, and give off toxic and corrosive species such as HF or HCl. Other challenges of conventional ionic liquids are extreme cost, separation issues, lack of estimated thermophysical and transport properties, and high viscosities. If recycling of an ionic liquid is possible, it generally requires extensive washing with water or organic solvents creating large amounts of wastes and VOCs.

However, the vast majority IL applications to date address only the reaction; they ignore product separation and purification. These are necessary for a full process and it is in the separation and reuse that the greatest problems occur – both in energy consumption and in losses and pollution.

Reversible Ionic Liquids: Facile separation and solvent recovery

We have developed sustainable, reversible ionic liquids in our labs to overcome the separation and purification problems of conventional ionic liquids, while taking the advantage of their beneficial properties. The built-in switch of these systems let us reversibly change the nature and the properties of these liquids from a molecular liquid to an ionic liquid on command, under mild conditions and preferably with mild reagents. This “on and off” chemistry has allowed us explore applications in which we can achieve a synergy of reaction and purification that are both green and economical.

We found that the exposure of a 1:1 mixture of the two neutral liquids 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) and 1-hexanol to gaseous CO₂ at 1 atm, causes an exothermic conversion of the molecular liquid phase to an ionic liquid (Scheme 1). This is akin to going from chloroform to dimethylformamide (DMF) in polarity. The ionic liquid can be converted back to a neutral liquid by bubbling an inert gas, i.e. N₂ or Ar, through the liquid at room temperature. Shown by the thermogravimetric studies, the ionic liquid can also be reversed by heating up to 50-60 °C, which yields higher reversal rates. We have then found many other switchable liquids, each of which can be converted to an ionic liquid upon exposure to an atmosphere of CO₂ gas and then converted back to a neutral organic liquid upon exposure to N₂ or Ar gas, or heat. We have reported another example based on the mixture of an alcohol with 2-butyl-1,1,3,3-tetramethylguanidine (TMBG) (Scheme 2). Our characterization studies of these



Schemes 1 and 2 – New reversible ionic liquids

switchable ionic liquids show that their physical properties such as melting point, viscosity and polarity, and thermodynamic properties such as ΔH and ΔG of reaction can be tuned with the alkyl-chain length of the alcohol and the attached group(s) on the amine base (see below).

The switchable characteristic of the reversible ionic liquids allow facile separation, recovery and reuse of these solvents following a chemical synthesis or extraction, which can be repeated in many consecutive steps. The separation and recycle are viable due to the change in solvent properties change, as the non-ionic liquid is converted to ionic liquid. For example, the mixture of 1-hexanol and DBU under N₂ (neutral form) is miscible with the nonpolar solvent decane, whereas the ionic liquid form (under CO₂) is not. Also a TMBG/methanol equimolar mixture in its neutral form is miscible with the nonpolar solvents pentane, hexane, heptane, and octane, whereas the ionic liquid form is not. In both cases, the nonpolar solvents can be separated simply by decanting, and the ionic liquid can be recycled and reversed. Here therefore we use CO₂ and N₂ at 1 bar as triggers of miscibility and immiscibility,

which can be further tuned by the type of alcohol used and the attached groups on the amine based ionic liquid precursor.

We demonstrated the opportunity of the solvent switchability in chemical reactions by performing the polymerization of styrene in 1:2.5 molar ratio mixture of DBU and 1-propanol (Fig. 1). Styrene was polymerized with $K_2S_2O_8$ initiator in the neutral solvent at 50 °C. After polymerization, the solvent was switched to its ionic form, in which polystyrene has limited solubility. The precipitated polymer was collected by filtration, and the filtered solvent was reconverted to its neutral form and used again for another polymerization. The solvent was used a total of four cycles with an overall yield of polystyrene of 97 %.

A single-component switchable ionic liquid could greatly simplify processing. In preliminary experiments have shown that such ILs can be formed CO_2 and silylated amines without the need of using an alcohol precursor (Scheme 3).

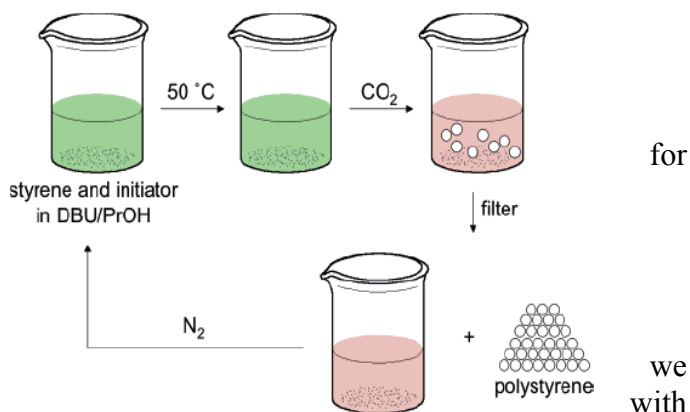
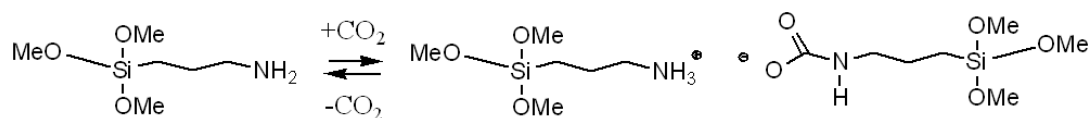


Figure 1: Styrene Polymerization in DBU/1-propanol-switchable IL precursor with recovery of polystyrene and solvent recycle.



Scheme 3

As we observed for the previous amidine or guanidine based ionic liquid systems, the silylated amine ionic liquids physical properties such as melting point, viscosity, and decomposition temperature, and thermodynamic properties such as ΔH and ΔG of reaction vary broadly with the structure of the ionic liquid precursor. A major thrust of this work is tailoring these properties for optimum use as a CO_2 -capture solvent.