ROOM-TEMPERATURE IONIC LIQUIDS FOR SYNTHESIS OF ADVANCED MATERIALS

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ABSTRACT

A short review of our published results using ionic liquids for synthesis of advanced materials has been given. These results demonstrated superior performance of ionic liquids in synthesizing aerogels, nanocomposite materials, and liquid membranes. We expect that these new materials may find applications in areas such as separation, catalysis, and sensors.

INTRODUCTION

Room-temperature ionic liquids have been intensely investigated recently because of their unique solvent properties, which include no vapor pressure, ionicity, and noncomplexing (1, 2, 3, 4, 5, 6, 7). The ionic liquids have been effectively demonstrated as a superior class of solvents for conducting many organic reactions. For example, Chauvin et al. have shown that oligomers of alkenes can be efficiently synthesized using ionic liquid solvents (8, 9). More recently, many new organic reactions in various ionic liquids have been carried out by Seddon's group (10, 11). Green chemistry based ionic liquids have been pioneered by Seddon's group (12). Our interest is in exploring the ionic liquids as solvents to conduct reactions for synthesizing novel materials or tailoring them directly as advanced materials for membrane applications. Here, some aspects of our previous and ongoing research in this area are discussed.

AMBIENT SYNTHESIS OF AEROGELS

Aerogels are a novel class of porous materials with wide-ranging applications. Their unique properties include low density, high surface area, low thermal conductivity, and low dielectric permittivity (13, 14, 15). So far, the synthesis of silica-based aerogels has been accomplished mainly through the controlled condensation of small colloidal particles produced by sol-gel processing in alcoholic aqueous solutions, followed by a supercritical drying process. A highly desirable goal in aerogel synthesis is the elimination of the supercritical drying process, the most expensive and risky aspect of the process. For example, Guo and Guadalupe have succeeded in synthesizing a silica-based aerogel from a metastable lamellar composite through cooperative interaction between silica and surfactant species (16). The surfactant molecules used to generate pores can be
removed from the silica network through conventional solvent extraction. The porous structure is stable during this procedure, and no supercritical extraction is used. We have recently developed a new process to synthesize aerogels using ionic liquids as solvents (17). This ambient process makes use of the unique properties of ionic liquids, allowing the synthesis of stable silica aerogels without use of the supercritical drying step. The key properties of ionic liquids used in our study are (1) negligible vapor pressure and (2) ionicity. The former attribute allows a long aging process to be applied in the synthesis without concern about shrinkage of the network due to the vaporization of solvents. While the latter attribute ensures that no phase separation occurs between silica polymers and solvents. Recently, we have extended this methodology to synthesize silica aerogels containing functional ligands (18). This new type of functional aerogel may find potential application as an advanced sorbent.

A possible mechanism for the aerogel formation in the ionic liquid is shown in Scheme 1. An acid catalyst such as formic acid initiates the formation of the sol particles, which effectively aggregate in the ionic liquid into a sol-gel network (6). Concurrently, the ionic liquid becomes entrapped in the growing covalent silica network, rather than being chemically bound to the inorganic matrix. A long aging time implemented before extraction of the nonvolatile ionic liquid further enhances the stability of the aerogel network. No macroscopic phase separation between the gel and the ionic liquid solvent has been observed. The homogeneity is retained throughout the entire aging process. This indicates that the interaction between the sol particles and the ionic liquids is favored thermodynamically. The ionic liquid forms a homogeneous solution with sol-gel precursors. If other solvents (e.g. DMSO, water) are used in the sol-gel preparation, no appreciable pore volumes (<0.1 cc/g) are found. In fact, similar results have been reported in the literature concerning the doping of silica with organic liquids through sol-gel processes (19).
The mesoscopic structures of our aerogels were also investigated by small-angle X-ray scattering (SAXS) measurements. Figure 1 shows the SAXS patterns for a hybrid aerogel system prepared using the mixture of tetramethylorthosilicate (TMOS) and aminopropyltrimethoxysilane (APTS) as a function of APTS concentration. Scattering intensities at different Q ranges probe different structural features of aerogels (20). In the Porod range, the scattering intensity changes according to $I \propto q^{-D_m}$, where $D_m$ is mass fractal dimension, which is a measure for the degree of branching of the network formed by the primary particles (20). Table 1 summarizes the values of $R_g$ (radius of gyration) and mass fractal dimensions determined from SAXS measurements. All of our aerogel products exhibited a mass fractal structure whose dimension was below 2. This small fractal dimension indicates a highly porous sol-gel network and is consistent with the mass fractal dimension for aerogel materials. The increase of the mass fractal dimension with APTS concentration supports the results obtained through nitrogen adsorption measurements.

Currently, we have extended this synthesis methodology based on ionic liquids further to prepare ordered mesoporous silica materials using 1,3-dialkylimidazolium cations with one of the alkyl-chain substituents lengthened. Here, the ionic liquids function as surfactants, which form micellar structures under sol-gel conditions (21, 22, 23, 24, 25, 26, 27). Figure 2 shows a transmission electron microscope (TEM) image of a hexagonally packed composite material consisting of silica wall and cylindrical ionic liquid phase.
SYNTHESIS OF COMPOSITE MATERIALS

Ionic liquid and organic polymer composites have been recently synthesized (28, 29). Specifically, Carlin and Fuller (28) reported a novel application of a gas-permeable ionic-liquid polymer gel composed of 1-N-butyl-3-methylimidazolium hexafluorophosphate and poly(vinylidene fluoride)-hexafluoropropylene copolymer in catalytic heterogeneous hydrogenation reactions. Applications of these organic composite polymers in a variety of electrochemical devices have been demonstrated by Fuller et al. (28) and Kosmulski et al. (29). Our interest lies in the synthesis of ionic-liquid and inorganic hybrid composite materials. These materials should be more stable under harsh environments because of the ceramic networks. The temperature stability is limited only by that of the ionic liquid. We have recently reported a methodology to immobilize crown ethers in an ionic-liquid nanophase that is entrapped in sol-gel silica for sequestration of metal ions (30). The nanophase is defined as any liquid domain with a size in the range of 1 nm to 50 nm. Here, the liquid nanophase is composed of a room-temperature ionic liquid.
Ionic liquids are attracting increased attention worldwide because they promise significant environmental benefits (7, 12). Unlike the conventional solvents currently in use, ionic liquids are nonvolatile and therefore do not emit noxious vapors, which can contribute to air pollution and health problems for process workers. Accordingly, no losses are induced by vaporization when these ionic liquids are entrapped in solid matrices, even at high temperatures. Unique intrinsic properties of these liquids are that they consist only of ions and can be made hydrophobic! Both Roger's and our groups have recently demonstrated that the novel dual properties of these new ionic liquids make them efficient solvents for the extraction of ionic species from aqueous solutions (5, 31). Whereas conventional solvent extraction of Sr\textsuperscript{2+} and Cs\textsuperscript{+} using crown ethers and related extractants can deliver practical $K$ value of up to two orders of magnitude (10$^2$), tests with ionic liquids as extraction solvents delivered values of $K$ on the order of 10$^4$. These results clearly show the enormous potential that ionic liquids possess for increasing the extractive strength of ionophores such as crown ethers in fission-product separation applications. The same enhancement holds also for ionic liquids entrapped in silica networks (30).

**IONIC LIQUIDS AS SENSING MATERIALS**

Since Sauerbrey (32) published the pioneering article on experimental verification of the mass-frequency shift relation for quartz crystal resonators, the quartz crystal microbalance (QCM) has been widely used to measure mass loadings in the nanogram region (33, 34, 35, 36). Chemical sensing with QCM devices depends on two key elements. The first is a probe device to generate and detect minimal frequency shifts. The second is a chemically sensitive coating that absorbs the chemical species and produces a change in the oscillating frequency that is detectable by the probe device. So far, a variety of materials have been employed as coatings on the surfaces of QCM devices in an effort to modify the sensitivity and selectivity for chemical analytes. These materials have included ceramics, organic polymers, organic dentrimers, self-assembled monolayers, and organic oils and waxes. Several reviews of these types of films have appeared in the literature. We have recently reported the use of room-temperature ionic liquids as sensing materials for a QCM device (37). The use of such ionic liquids to carry out separations of mixtures of organic molecules and inorganic ions has been recently reported (6, 31, 38, 39, 40). Their strong affinities for selected chemical species prompted us to consider the fabrication of vapor-sensing devices based on ionic liquids. As with polymeric films, the vapor pressures of these liquids are essentially undetectable. Accordingly, no loss of the ionic liquids can be induced by vaporization. The salts are usually liquids from about -100°C and are thermally stable to approximately 200°C, depending on the specific structures of the anions and cations. In contrast to solid polymeric films, they are liquidus at ambient temperature, thus implying that fast diffusion can be achieved.
A typical QCM sensor response curve toward repeated exposure to acetone vapor is shown in Figure 3. In general, the QCM sensor modified by the ionic liquids showed sharp responses to organic vapors. The solubility equilibrium of organic vapors in ionic liquids can be reached in few seconds. Different ionic liquids were investigated by our group, with each ionic liquid membrane showing a distinct response for a particular vapor (37). The resonance frequencies of our QCM device modified by the ionic liquids increased sharply when in contact with organic vapors. This response is opposite to that of conventional QCM devices based on detection of mass loadings, where the adsorption of organic vapors to a solid polymeric or metallic film decreases the frequency of the quartz crystal. Accordingly, we cannot rationalize our results based on the equation originally derived by Sauerbrey (32). Frequency shifts of QCM devices result from a comprehensive change in the physicochemical properties of a surrounding medium. In addition to the change of film density on the QCM electrode, the variation of viscosity of a surrounding medium can also give rise to a frequency shift of the resonator. Kanazawa et al. (41) derived the following equations, which express the frequency shift ($\Delta f$) of the quartz crystal in contact with a fluid and the decay length ($\delta$) of the shear wave:

$$\Delta f = -f_0^{3/2}(\eta_L \rho_L / \pi \mu_0 \rho_0)^{1/2}$$

(1)

$$\delta = (\eta_L / \pi f_0 \rho_L)^{1/2}$$

(2)

**Figure 3.** Response of QCM device coated with an ionic liquid toward acetone vapor.
where \( f_0 \) is the oscillation frequency of the free (dry) crystal, \( \eta_L \) and \( \rho_L \) are the absolute viscosity and density of the liquid, respectively, and \( \mu_Q \) and \( \rho_Q \) are the elastic modulus and the density of the quartz.

In general, the solubilities of organic vapors in imidazolium-based ionic liquids are known to be high as compared with those of organic polymers. The dissolution of organic vapors in ionic liquids can induce changes in many physical properties of the ionic liquids (42, 43, 44). The two factors that are relevant to our present discussion are the changes in viscosity and density upon addition of organic cosolvents. Both Hussey's and Seddon's groups have carried out systematic measurements (1, 42) of kinematic viscosity and density as a function of selected cosolvent concentrations for \( \text{AlCl}_3\)-EMIC (EMIC: 1-ethyl-3-methylimidazolium chloride) melts. Their studies have shown that both the viscosity and the density of the \( \text{AlCl}_3\)-EMIC system greatly decrease with the addition of low-viscosity cosolvents. The reduction of viscosity is more pronounced than that of density.

The origin of the strong dependence of viscosity on the cosolvent concentration in ionic liquids is not completely understood. The addition of low-viscosity organic compounds in ionic liquids is believed to decrease ion-pairing or ion aggregation by solvating interacting anions and cations. For example, the addition of 4.4 w% acetonitrile into a basic \( \text{AlCl}_3\)-EMIC ionic liquid results in a decrease in the viscosity from 26.90 cm\(^2\)s\(^{-1}\) to 13.60 cm\(^2\)s\(^{-1}\) and a decrease in the density from 1.2713 g cm\(^{-3}\) to 1.2373 g cm\(^{-3}\). Assuming that a QCM device is coated with this basic \( \text{AlCl}_3\)-EMIC and 4.4 wt% acetonitrile is adsorbed by the ionic liquid on the QCM device, a frequency shift would occur according to equation (1). Insertion of the known values of density and viscosity in equation (1) gives a positive frequency shift of 1640 Hz induced for this hypothetical QCM device using the ionic liquid membrane. If 4.4 wt% acetonitrile were adsorbed on a QCM device coated with a solid film, the corresponding negative frequency shift would be less than 250 Hz based on Sauerbrey's equation.

The general physical properties of the stable ionic liquids used in the present application should be very similar to those of \( \text{AlCl}_3\)-EMIC, with the exception of specific affinities toward different organic vapors. Therefore, our observed large, positive frequency shifts can be rationalized by the decrease in viscosity and density upon adsorption of organic vapors. The frequency response of the QCM device coated with ionic liquids is exceptionally large for a number of the organic vapors. The QCM vapor sensor using ionic liquids can be made to be extremely sensitive to certain chemicals. This sensitivity results primarily from the strong dependence of viscosity on the concentration of organic vapors in the ionic liquids on QCM devices.

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High Temperature Molten Salts