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Room-Temperature Ionic Liquid: A Nanostructured Liquid for High-Vacuum and High-Energy Applications

In recent years, room-temperature ionic liquids (RTILs) have graduated from a green solvent with a wide temperature range to a new medium for synthesis of advanced materials.^{1,2} Two Perspectives in this issue, discuss two relatively unexplored aspects of the expanding horizons of RTILs.^{3,4}

The perspective by Kuwabata et al. describes the ingenious applications of the RTILs in analysis under high-vacuum conditions and in materials synthesis.³ The negligible vapor pressure of RTILs allows studies under vacuum for electron microscopy (TEM and SEM), mass spectrometry (MALDI-MS), and photoelectron spectroscopy (XPS).³ Kuwabata et al. demonstrated that SEM of insulators may be recorded by simply soaking the sample with the highly conducting RTILs. This method avoids irradiation by the electron beam. The TEM of wet nanoparticles in RTILs is free from the complications due to aggregation. The nonvolatile RTILs may be utilized for wet chemistry in ultrahigh vacuum and, in particular, in nanoparticle synthesis by magnetron sputtering, plasma deposition, and high-energy radiation (γ -ray or electron).³ It is shown that nanoparticles may be readily produced in RTILs even in the absence of a covalent stabilizing (capping) agent.³

In his Perspective, Wishart has discussed radiation chemistry in RTILs.⁴ The high-energy ionizing radiations produce spatially inhomogeneous tracks of high-energy particles, photons, and electrons in RTILs. The high viscosity and slow solvation in RTILs dramatically extend the time scales for studying presolvated electrons.⁴ Wishart and co-workers developed the optical fiber single shot technique and detected the difference in the reactivity of presolvated and solvated electrons.⁴ He also discussed the application of electrospray ionization mass spectroscopy to study radiation-induced radicals in RTILs.⁴

A unique feature of RTILs is the presence of persistent local structures of a few nanometer dimensions. SANS studies^{5,6} and computer simulations^{7–10} reveal the presence of nanodomains in RTILs with clear segregation of polar (small anions) and nonpolar (clusters of bulky cations) regions. The presence of nanodomains with high viscosity (and, consequentially, slow diffusion) affords intimate mixing of reactants of differing polarity and produces nanointerfaces. This is akin to phase-transfer catalysis, albeit in nanodimensions, and may give rise to unique reactivity in RTILs. Dynamics in different regions of the spatially heterogeneous RTILs have been studied by femtosecond spectroscopy.^{11,12} Excitation wavelength dependence studies show a drastic difference in the solvent relaxation time from 135 ps in the polar domain to 860 ps in the nonpolar domain.¹² Interestingly, anisotropy decay and isomerization do not exhibit spatial heterogeneity.^{11,12} It seems that when the rotating groups sweep a large volume, it “sees” an average of the polar and the nonpolar domains and hence, does not show spatial inhomogeneity.

The existence of nanodomains may be responsible for the flexible solubility of environmentally important gases (CO_2) in RTILs. This is important in carbon sequestration and development of supported RTIL membranes for CO_2 scrubbing. Recent inelastic state-resolved scattering experiments reveal nonideal behavior of gases dissolved in RTILs and emphasize the role of nonequilibrium dynamics in high-energy collisions.¹³

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