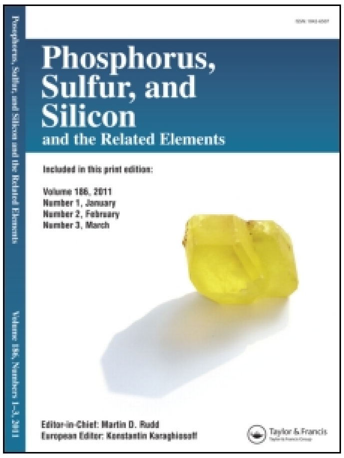

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A NEW CATEGORY OF LIQUID SALT—LIQUID IONIC PHOSPHATES (LIPs)

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Starting with polycationic ammonium and phosphonium salts bearing halide anions previously synthesized in our laboratory, we have prepared a new category of nonaqueous ionic liquids. These new nonaqueous ionic liquids bear either free phosphate anions or partially esterified phosphate anions as the counterions to the ammonium or phosphonium cations. We generally refer to these new species as LIPs (liquid ionic phosphates). We have developed three approaches toward the syntheses of these materials from the halide salts: one using hexafluorophosphoric acid; a classical ion exchange method; and treatment with the free phosphorus-containing acid under vacuum. The new LIPs, although highly viscous, exhibit significantly high specific conductivities. Unlike ionic liquids bearing tetrafluoroborate of tetrachloroaluminate anions, the LIPs are unreactive toward water. Further, the LIPs bearing simple phosphate anions are soluble in water, unlike their corresponding hexafluorophosphate salts. We have also examined the UV/Vis, fluorescence, and mobility characteristics of the new LIPs.

Keywords: Conductivity; molten salt; nonaqueous ionic liquid; phosphate

INTRODUCTION

The preparation of nonaqueous ionic liquids (*NAILs*) has become an area of significant interest in recent years owing to the potential of such materials for a variety of applications, including electrolytic media

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for storage cells, solvents for electrochemical reactions, media for extractions, and catalysis of organic reactions.[1] Most of the previously synthesized *NAILs* have been either water insoluble or water reactive. In the current work we describe the synthesis and investigation of properties for a new category of *NAIL* using phosphate anion as the counterion to ammonium or phosphonium cations.

RESULTS AND DISCUSSION

The several series of polycationic salts previously synthesized by our laboratory[2] held promise as particularly intriguing species, should they be capable of being converted into ionic liquids. In this light, initially these polycationic halides were treated with hexafluorophosphoric acid according to an established procedure for preparation of the hexafluorophosphate (liquid) salts.[3] As previously observed with pyridinium and imidazolium species,[3] water-insoluble materials readily formed which remained solid at room temperature. Investigation of the NMR spectra (^{1}H and ^{13}C) of these materials in DMSO solution corresponded completely with those observed for the parent halide salts. However, the ^{31}P NMR spectra exhibited two sets of signals, a septet at -144 ppm (corresponding to the hexafluorophosphate anion) and a singlet near 0 ppm indicating phosphate anion to be present. As the conversion yields were low, it was presumed that the remainder of the organic salt remained in the aqueous layer. In fact, evaporation of the aqueous layer yielded a sizable amount of a room temperature liquid, soluble in water, which exhibited NMR spectra (^{1}H and ^{13}C) in complete accord with those for the parent halide salts, and ^{31}P indicating only simple phosphate anion to be present. As such, these materials constitute a new class of nonaqueous ionic liquid, the liquid ionic phosphates (LIPs).

An alternative approach toward the preparation of these LIPs was desirable, as the use of hexafluorophosphoric acid 1) was inefficient for the preparation of LIPs, 2) is notably expensive and hazardous to use, and 3) could be determiental to the environment upon accidental release. In this light attempts were made to prepare LIPs by classical ion-exchange using DOWEX 2×8 in the phosphate ion form. While in some instances this approach was successful, often there resulted incomplete conversion with low yield. Finally, treatment of the parent halide salt with a charge equivalent amount of 85% phosphoric acid in aqueous medium, followed by complete removal of water under reduced pressure for an extended period of time, resulted in the isolation of the desired LIPs in high purity (as indicated by ^{1}H, ^{13}C, and ^{31}P NMR) and good yield.

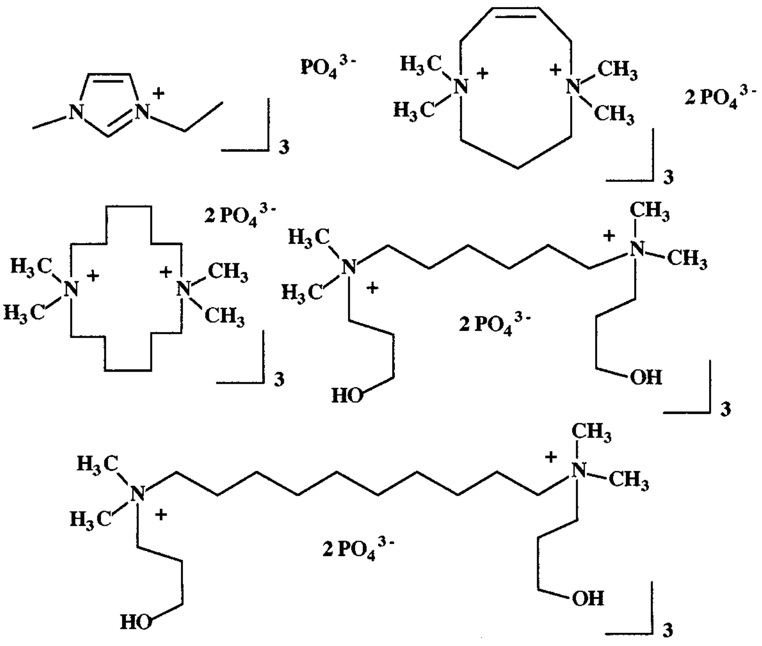

FIGURE 1 Thermally stable LIPs.

For numerous applications it is important that the ionic liquid exhibit thermal stability at elevated temperature. For this determination individual materials were heated at 160°C for four hours, followed by measurement of their NMR spectra to detect degradation products. Those materials exhibiting *no* degradation under these conditions are illustrated in Figure 1.

Other newly synthesized LIPs exhibited degradation under these conditions, particularly those bearing pyridine- or benzene-derived ring systems, diazoniabicyclo[2.2.2]octane ring systems, or terminal hydroxyalkyl chains longer than three carbon atoms. Such systems are, however, stable at lower temperatures and can be of utility for applications not requiring high temperature stability.

As potential applications involve serving as electrolytic media, it was of interest to determine the specific conductivity of these newly synthesized materials. Selected salts are shown in Figure 2 with their specific conductivities as determined.

In addition, several series of spectroscopic measurements were made on the newly synthesized LIPs. In particular, fluorescence in the UV region was observed for those bearing aromatic linkages. Further, diffusion characteristics were measured for the pure liquid salts using

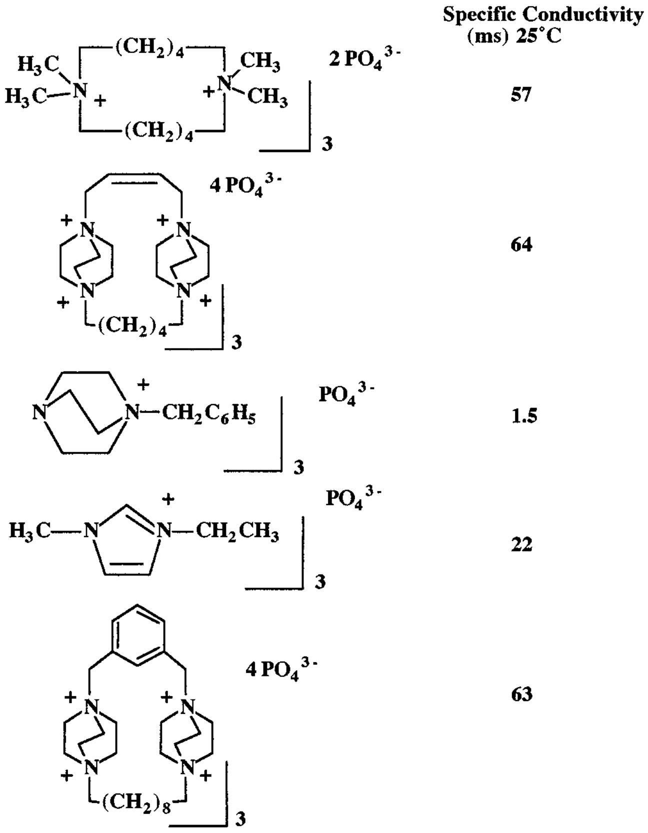

FIGURE 2 Specific conductivities of selected LIPs.

the pulsed gradient spin-echo NMR technique (in collaboration with S. Greenbaum of Hunter College, CUNY). These measurements indicate passive diffusion (in the absence of an applied potential) to be particularly significant for the cationic species, but not for the phosphate anion component of the salts.

Solubility measurements of the full range of newly synthesized LIPs indicate them to be uniformly soluble in water and methanol, but insoluble in other organic media. Attempts have been made (with partial success) toward the preparation of LIPs with partially esterified phosphoric acid (monophenyl phosphate). These materials have exhibited a lower solubility in aqueous medium, but do not exhibit the negligible solubility characteristic of hexafluorophosphate salts. Current efforts are directed toward the development of new phosphorus-containing anions that are significantly hydrophobic, but without the involvement of fluorine.

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