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Polycations. Part X. LIPs, a new category of room temperature ionic liquid based on polyammonium salts

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A series of polyammonium halide salts have been converted to the phosphate ion form. The resultant salts constitute a new category of non-aqueous ionic liquid (NAIL); these new ionic liquids (Liquid Ionic Phosphates) have been characterized by standard methods and have been investigated for their electrical conducting characteristics.

Previously we have reported the preparation of several series of polycationic organic salts.[1] Subsequently, we considered the possibility of converting these new (solid) polyammonium salts into a unique category of ionic liquids through conversion of the gegenion. Numerous reports have been made of the conversion of monoammonium (solid) salts to non-aqueous ionic liquids by such anion conversion. The most extensively investigated series of NAILs include those in which the organic cation is either an *N*-alkylpyridinium or an *N*-alkyl-*N′*-alkylimidazolium species.[2–5] These species have involved *only* organic *mono*cations, with the single exception of a dicationic species involving two imidazolium sites at opposite ends of a long alkyl chain.[6] Of particular interest to us was the use of hexafluorophosphoric acid[7] to generate the corresponding hexafluorophosphate liquid salts from the polycationic species previously synthesized in this laboratory.

Using the established procedure for preparing such salts, with our polycationic organic salts it was observed that only a relatively low yield of such hexafluorophosphate salts could be isolated. Attempts to improve the yield through vacuum evaporation of the aqueous medium resulted in the isolation of a totally new and intriguing category of ionic liquids, liquid ionic phosphates (LIPs). It is with these new materials that the present report is concerned.

Using two separate anion exchange methods we have prepared a series of rt LIPs. The first of these involves vacuum evaporation of the aqueous supernatant solution from the preparation of the hexafluorophosphate species. Moderate yields of clear viscous liquids that exhibit NMR spectra (^{1}H, ^{13}C and ^{31}P) in accord with the assigned structures are isolated (*vide infra*). The second approach involves the more traditional anion exchange using an insoluble resin. Passage of the parent halide salts through a bed of DOWEX™ 21K in the phosphate ion form followed by vacuum evaporation of the eluent also yields the clear, highly viscous liquids providing the same analyses as noted above. A series of LIPs prepared by these methods and so analyzed is illustrated in Fig. 1. LIPs **1–8** are derived from the polycationic halide salts prepared in this laboratory. Species **9** has been prepared from the corresponding chloride prepared by a reported procedure,[4] and was included as a general reference to previously available NAILs derived from imidazolium salts.

The ^{1}H and ^{13}C spectra (measured in D_2O) are in total accord with those previously reported[1] in the preparation of the parent halide salts. The ^{31}P NMR spectra (also in D_2O) exhibit sharp singlet signals between $\delta = 0.91$ and 1.20 (relative to 85% phosphoric acid). A representative example of these salts and

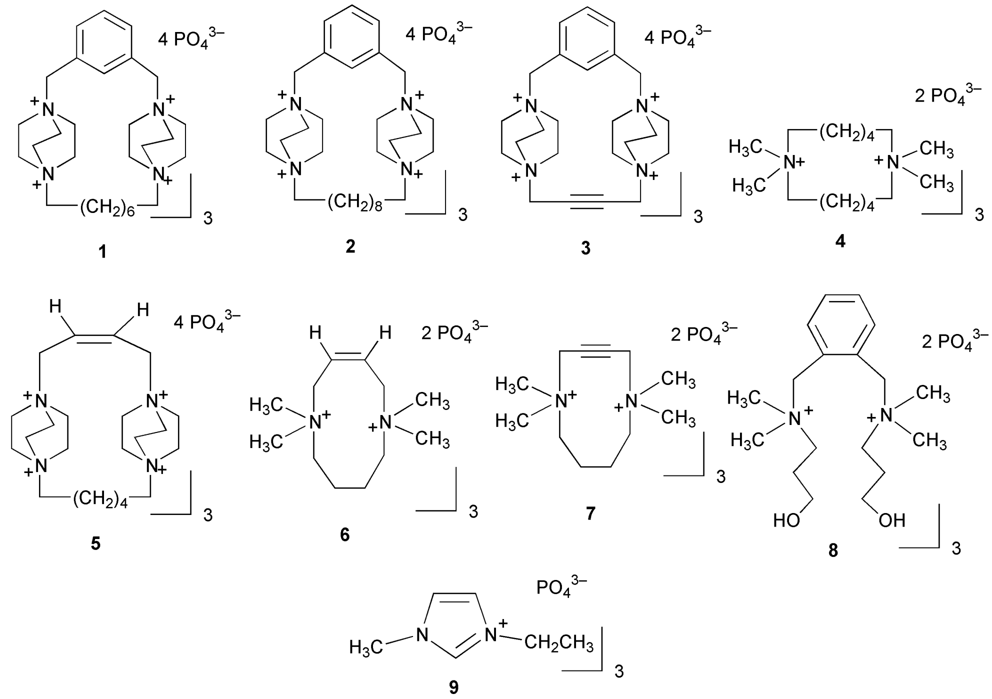

Fig. 1

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Table 1 Densities and specific conductivities of LIPs

LIP	Density/ g mL^{-1}	Specific Conductivity, σ/Ω^{-1} cm^{-1}			$\sigma/\sigma_{\mathrm{KCl\ Ref.}}$^{a}
		25 °C	40 °C	60 °C	
1	1.78	0.057	0.063	0.061	19
2	1.86	0.063	0.052	0.082	21
3	1.96	0.026	0.027	0.042	9
4	1.82	0.063	0.06	0.071	21
5	1.58	0.064	0.081	0.087	21
6	1.82	0.038	0.052	0.05	13
7	1.58	0.053	0.056	0.071	18
8	1.9	0.042	0.053	0.067	14
9	1.98	0.022	0.03	0.037	7

[a] 0.02 M KCl(aq) reference, specific conductivity = 0.03 Ω^{-1} cm^{-1} at 25 °C.

their spectra is provided by **7**: δ_{H}: 1.86, br s, 4H; 3.16, s, 12H; 3.49, br s, 4H; 4.35, s, 4H. δ_{C}: 20.87, 51.98, 56.28, 65.41, 81.35. δ_{P}: 1.20.

The hexafluorophosphate salts also isolated in these reactions exhibit corresponding ^{1}H and ^{13}C NMR spectra, but the ^{31}P signals appear as symmetrical septets centered at $\delta \sim -144$. Further, the isolated hexafluorophosphate salts appear to be universally contaminated with phosphate. Through quantitative measurement of the ^{1}H NMR spectra for these LIPs their anhydrous nature can be established, although they are fully soluble in water and adsorb water from room air. Specifically, from ^{1}H NMR measurements it is determined that the water content of the new LIPs is below the limit of reliable measurement, that is less than 0.5%. Unlike the hexafluorophosphate salts which are insoluble in water to the point that NMR measurements can not be made, the new LIPs are fully soluble in water. Both types of salts are soluble in DMSO allowing measurement of the ^{1}H and ^{13}C NMR spectra of the crude reaction products.

In addition to the measurement of their densities, specific conductivity measurements were performed on the LIPs **1**–**9**. A YSI Model 31 conductivity bridge was used for these measurements, with a constant temperature bath to maintain temperature of the sample during measurement at several temperatures (25, 40 and 60 °C). A 0.02 M solution of KCl in water was used as reference material (specific conductivity of 0.03 Ω^{-1} cm^{-1} at 25 °C). The results for these determinations are shown in Table 1.

In comparison with previously prepared rt NAILs, the presently described LIPs exhibit particular advantages. These include: (a) ease of preparation, requiring only ordinary ion-exchange in aqueous medium rather than the use of the quite reactive (and under certain circumstances hazardous) hexafluorophosphoric acid, tetrafluoroboric acid or aluminum chloride, which require controlled atmospheric conditions; (b) the resultant salts are unreactive with water; (c) although viscous, the LIPs are liquids at rt, while the hexafluorophosphate salts of monocations melt above rt and the hexafluorophosphate salts of polycations we have synthesized remain solid up to 75 °C; (d) particularly high specific conductivities; and (e) the potential for use as media for electrochemical processes requiring a large electrochemical window.

We are in the process of exploiting this new category of NAILs for utility in a variety of processes, including electrochemical conversions, media for “green” chemical reactions, catalysts for chemical conversions, syntheses of related species exhibiting water-insolubility, and the performance of separations without the use of volatile solvents. Further, determinations of the diffusion coefficients, mobilities of ions within the viscous media, and potential applications for electrochemical storage cells are being made.

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