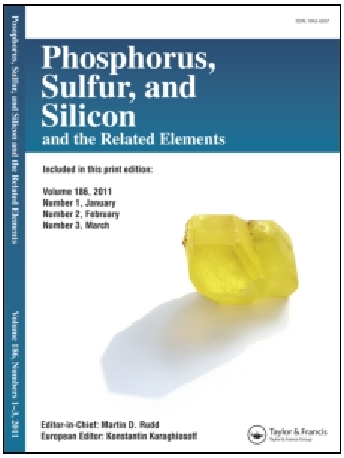

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LIPs--Electrochemical and Spectroscopic Characteristics

Sharon I. Lall[a]; Danny Mancheno[a]; Robert Casiano[a]; Steve Castro[a]; Amir Rikin[a]; Jaimelee I. Cohen[a]; Robert Engel[a]
[a] Queens College, Graduate School, City University of New York, New York

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LIPS—ELECTROCHEMICAL AND SPECTROSCOPIC CHARACTERISTICS

Sharon I. Lall, Danny Mancheno, Robert Casiano, Steve Castro, Amir Rikin, Jaimelee I. Cohen, and Robert Engel
Queens College of the City University of New York and the Graduate School of the City University of New York, New York

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Our recently synthesized polyphosphonium and polyammonium liquid ionic phosphates (LIPs) have been investigated for their electrochemical and spectroscopic characteristics. In particular, the specific conductivities of these new species have been studied in the pure state and in aqueous medium, and measurements of diffusion characteristics have been made using pulsed gradient spin-echo NMR. The abilities of these new species for partitioning of salts with insoluble liquid organic media have been investigated, along with measurements of the electrochemical windows of the pure LIPs. Measurements of the UV/Vis characteristics have been made for the pure LIPs and their aqueous solutions. The behavior in the pure state and solution differ significantly. Further, investigation of the fluorescence in aqueous solution of the LIPs has been performed. While most of the efforts have been directed toward polycationic species, corresponding studies of LIPs based on simple imidazolium cations have also been performed.

Characteristic of particular note include the specific conductivities for the pure LIPs. While significantly viscous, these materials exhibit relatively high specific conductivities. The largest of these are observed for LIPs in which the polycationic portion involves a macrocycle with cationic sites (ammonium) located within the parent macrocycle. Significantly lower values are observed for those LIPs in which the cationic sites are dispersed on chains in the absence of a macrocycle, or on chains attached to a macrocycle (cyclodextrin derivatives). In the instances of highest specific conductivity, values of the order of 30–60 ms

Robert Engel, Department of Chemistry and Biochemistry, Queens College of the City University of New York and the Ph.D. Program in Chemistry, Graduate School of the City University of New York, 65-30 Kissena Boulevard, Flushing, New York, 11367. E-mail: robert_engel@qc.edu

are observed, with values as low as 1 ms observed for linear and cyclodextrin derived LIPs. These values of specific conductivity need be compared with that of a 0.02 M aqueous KCl solution, having a value of 30 ms. While the species are ionic, there is a high degree of order within the liquid matrix, associating cations and anions such that extremely high specific conductivities do not result. Current efforts are directed toward measurement of conductivities of solutions of classic salts dissolved in the LIPs.

Additional efforts have been directed toward understanding of the passive diffusion of species within the LIPs. In collaboration with S. Greenbaum of Hunter College, CUNY, pulsed gradient spin-echo (PGSE) NMR experiments have been performed to determine the self diffusive capabilities of both the cations and the anions of the LIPs. Using ^{31}P PGSE NMR, it was noted that the anions (phosphate) were relatively non-diffusing in the pure LIPs, while the cations (determined using ^{1}H PGSE NMR) were found to be relatively mobile. Again, current efforts are directed toward the determination of changes in these characteristics when classical salts are dissolved in the LIPs.

Further, measurements have been made toward the determination of electrochemical windows for the LIPs. Cyclic voltammetry has been used to establish the range of potential within which neither oxidation nor reduction of the LIPs occurs, allowing the materials to be used as media for the performance of electrochemical reactions. Values for the electrochemical window between 0.5–1.5 V have been measured. This is anticipated to be reasonable for the use of these materials as electrolytes in electric storage cells and as media for the performance of electrochemical reactions, such as the Kolbe reaction of carboxylate salts.