

A Fundamental Study of the Transport Properties of Aqueous Superacids as a Model of Proton Conducting Electrolytes

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Superacids are described as systems whose acidity exceeds that of 100% sulfuric acid, that is $H_0 < -12$. Applications include but are not limited to: serving as the electrolyte in electrochemical systems such as lithium batteries and fuel cells, as a polymerization catalyst in the plastic industry, and as a reagent in the pharmaceutical industry.

The incorporation of superacids molecules into host polymers such as Nafion (DuPont) and PEEK has resulted in high proton conductivities in these systems²⁻³. Tremendous effort has been directed at unraveling the ion transport mechanism in these systems⁴⁻⁶. However, the transport properties of aqueous solutions of superacids, which can serve as a very useful model for proton conduction in fuel cell membranes have been largely ignored. Here we will present a fundamental study of the ionic self-diffusion coefficients (D), spin-lattice relaxation times (T_1), ionic conductivity (σ) and viscosity (η) of aqueous superacid solutions. The superacids investigated were Trifluoromethanesulfonic (TFSA), bis(trifluoromethanesulfonyl)imide (TFSI) and p-Toluenesulfonic (PTSA) in the concentration range of 120 down to 5 water molecules per acid. Techniques used include NMR-PGSE for self-diffusion values, AC Impedance spectroscopy for ionic conductivity values, and the falling sphere method for viscosity measurements. All measurements were done at 30°C. Experimental results will be compared with *Ab Initio* calculations, based on density functional theory, of the hydration properties of the gas-phase acids.

Ionic conductivity results are displayed in Figure 1. Of the three superacids TFSA gave the highest σ , it was also the most affected by reduced solvation at high acid concentrations. TFSI gave the lowest σ , which is expected considering its molecular size. All three superacids exhibit a maximum in the range of 15 – 20 water molecules per acid molecule. This suggests that ion transport in these systems is very dependent on the solvation level which is optimum within the range of 15 – 20 water/acid sites, thus affording efficient ion transport.

Proton self-diffusion coefficients exhibited nearly monotonically decreasing behavior as a function of increasing acid concentration expected for acid systems. The anion D 's however displayed a minimum coinciding with the maximum observed in σ for each superacid. T_1 results for the anions also showed a minimum within this range. As an example D and σ results for TFSI are displayed in Figure 2. In addition to this, η measurements displayed in Figure 3 showed no minimum within this range, but rather a monotonic increase with acid concentration, as is expected for these systems. This result implies that the effect is a local rather than a macroscopic one, involving the reordering of the anions in the available bulk water structure to allow efficient proton transport.

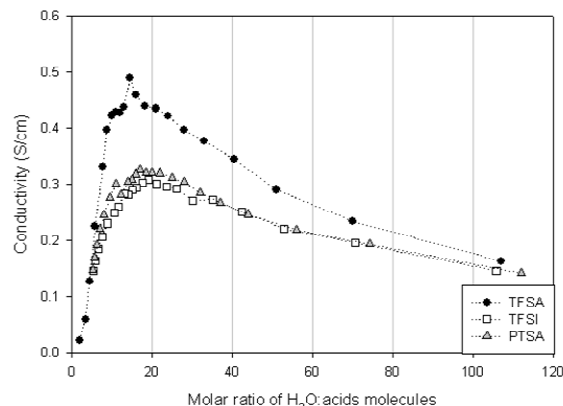


Figure 1. σ results for TFSA, TFSI, and PTSA at 30°C.

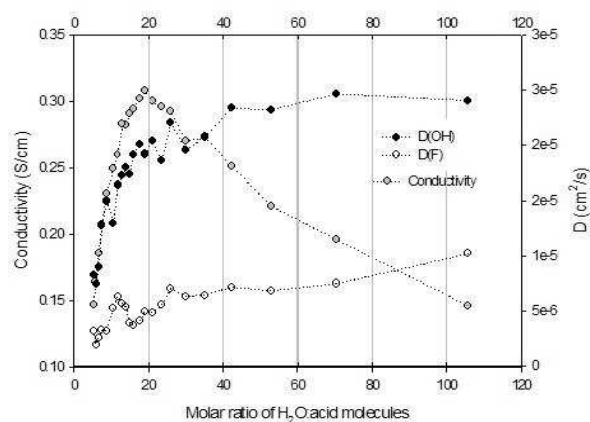


Figure 2. D and σ results for TFSI at 30°C.

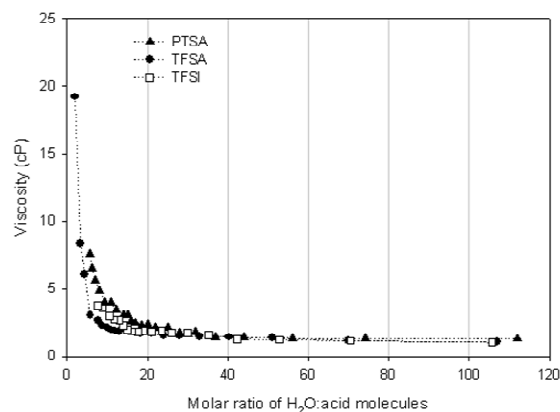


Figure 3. η results for TFSA, TFSI, and PTSA at 30°C.

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