

Hydrogen Structure and Diffusivity in Groups I and II Salts of 12-Tungstophosphoric Acid

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Heteropoly acids (HPA's) are attractive materials for use as components in hydrogen fuel cells because of their potential to provide a proton source in high-temperature applications. HPA's offer a rich variety of structures that can possibly be tuned to maximize the proton diffusivity and hence proton conductivity for some elevated temperature range of interest. A class of compounds that exhibits a somewhat surprising diversity of proton structures are the Groups I and II salts of the Keggin ion based acid, 12-tungstophosphoric acid (HPW). In this paper we describe the structures and dynamics of these salts based on solid-state nuclear magnetic resonance (NMR) techniques.

The NMR techniques used to probe the structure and dynamics of the Groups I and II salts of HPW include temperature dependent ¹H wide-line (non-spinning denoted NS), ¹H and ³¹P magic-angle spinning (MAS), cross polarization magic-angle spinning (CPMAS), rotational-echo double-resonance (REDOR) and pulsed-field gradient spin-echo (PFGSE) NMR experiments. Results from these different NMR experiments provide complimentary information on these HPA's

Figure 1 shows ¹H MAS NMR spectra for HPW as well as the Li, Rb and Sr salts and indicates the strong dependence of the proton structure on the counter cation in the Groups I and II salts of HPW. These ¹H MAS NMR spectra exhibit a variety of resonance lines each with a different value of ¹H chemical shift that corresponds to a different structure as well as acid strength. Generally, a higher chemical shift value means that the proton is more acidic.¹ The relation of acidity to diffusion will be discussed.

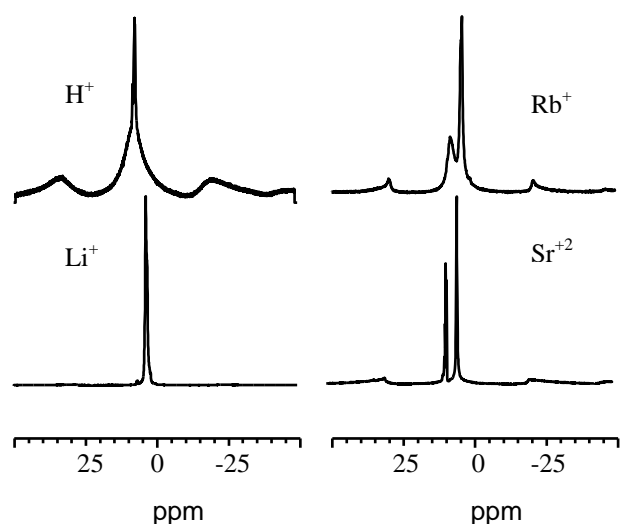


Figure 1. Room temperature 400 MHz ¹H MAS NMR spectra of the limiting hydrated form of HPW and its Li, Rb and Sr salts.

Figure 2 shows ³¹P MAS NMR spectra for HPW and the Li, Rb and Sr salts. The phosphorus structure also exhibits a strong dependence on the counter cation in these

salts. As will be discussed, the ³¹P MAS NMR spectra also indicate that different proton environments exist for individual Keggin anions of a particular salt.²

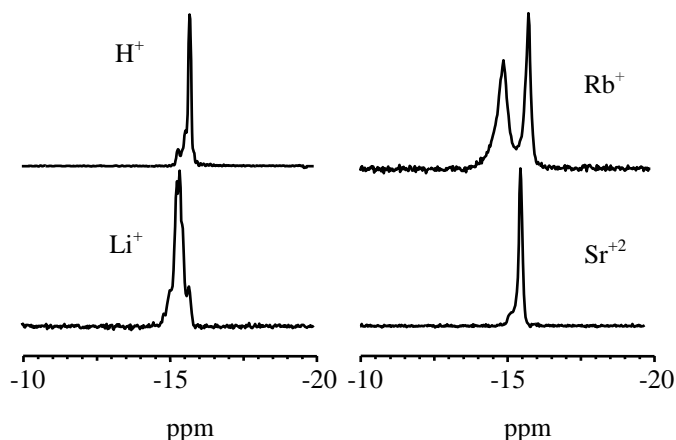


Figure 2. Room temperature 161.9 MHz ³¹P MAS NMR spectra of the limiting hydrated form of HPW and its Li, Rb and Sr salts.

The proton and phosphorus structures of the limiting hydrated form of the Groups I and II salts of HPW derived from MAS, CPMAS and REDOR studies and modeling can be correlated with the proton diffusivity of these salts. The proton diffusion coefficients of these salts are also a strong function of the counter cation, the temperature and the degree of hydration. Figure 3 shows the effect of both water loading and temperature on the diffusion coefficient D of protons in the Na salt of HPW. In this case, the water loading effect becomes more pronounced as the temperature increases. Similar results for the other Groups I and II salts will be presented.

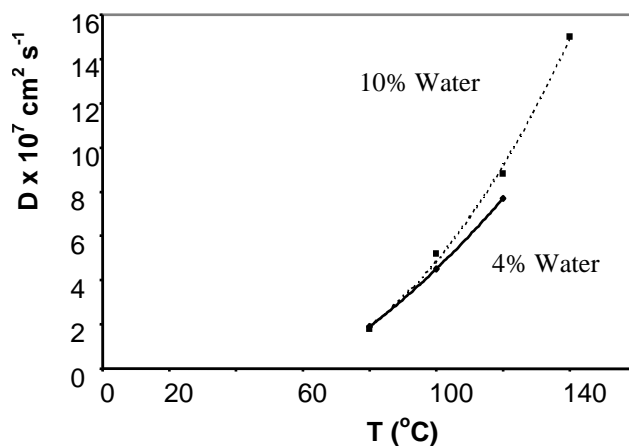


Figure 3. Proton diffusion coefficient of Na salt of HPW as a function of temperature for 4 and 10% water loadings.

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References

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