Resolution of Dynamic Processes in Proton-conducting 12-Tungstophosphoric Acid 14-Hydrate by a Combination of Quasielastic Neutron-scattering and N.M.R. Techniques

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Combination of variable temperature incoherent quasielastic neutron-scattering (q.e.n.s.) and ^{1}H n.m.r. relaxation time measurements allows the characterisation of dynamic processes associated with proton transport in 12-tungstophosphoric acid 14-hydrate; q.e.n.s. identifies 180°-flips of H_2O and enables n.m.r. data to be interpreted in terms of this reorientation and H^+ self-diffusion [D_t(295 K) ~10^{-7} cm^2 s^{-1}].

Proton-conducting solid electrolytes are of potential importance in, *e.g.*, H_2/O_2 fuel cells and electrochromic displays. The highest reported protonic conductivities for inorganic materials at temperatures near ambient are those of heteropolyacids,[1,2] which have been included in a patented low-temperature fuel cell.[3] Problems in relating measurements studying the atomic-level processes to the bulk conductivity have been assigned to the presence of previously unrecognized correlation time spectra,[4] arising from the distinct motional processes present.

In this communication we report the resolution of reorientational and diffusive motions in 12-tungstophosphoric acid 14-hydrate [$H_3PW_{12}O_{40}\cdot14H_2O$, (TPA·14$H_2O$)]. In this material an H^+/H_2O mix surrounds the [$PW_{12}O_{40}$]$^{3-}$ anions (a strong acid in the solid state). TPA·14H_2O was prepared by drying damp recrystallised TPA at 25 °C in an atmosphere of 45% relative humidity (over 47% by mass sulphuric acid solution). The powder X-ray diffraction pattern (Cu-K_α radiation, Philips diffractometer) was completely indexed in terms of a triclinic unit cell [a 14.34(1), b 14.47(1), c 13.92(1) Å, α 111.94, β 110.06, γ 61.48°] very similar to that of the molybdenum analogue.[5] Thermogravimetric dehydration confirmed the formula TPA·14($\pm$0.5)H_2O.

Incoherent quasielastic neutron-scattering (q.e.n.s.) experiments were carried out at the Insititut Laue-Langevin using the time-of-flight spectrometer IN5. Measurements were made in the range $250 < T < 295$ K using an incident wavelength λ_0 6.2 Å, an elastic energy resolution ΔE_0 50 μeV (full width at half maximum), a maximum elastic scattering vector Q^{el}_{max} 1.8 Å^{-1} ($Q^{el} = 4\pi \sin \theta/\lambda_0$), and typically 5 h of data acquisition. The ^{1}H n.m.r. relaxation times T_1 and T_2 were recorded at a frequency of 19.25 MHz in the temperature range $140 < T < 295$ K using a purpose-built spectrometer and standard pulse sequences. At low temperatures ($T < 180$ K) T_2 was measured as the time for the solid echo to decay to 1/e of its amplitude, and an additional solid echo 'read pulse' was used in T_1 measurements.

The neutron scattering spectra showed a small (but nevertheless detectable and measurable) temperature-dependent broadening of the resolution functions and an experimental e.i.s.f. (elastic incoherent structure factor) was extracted from the $S(Q,\omega)$ data using standard procedures. Comparison
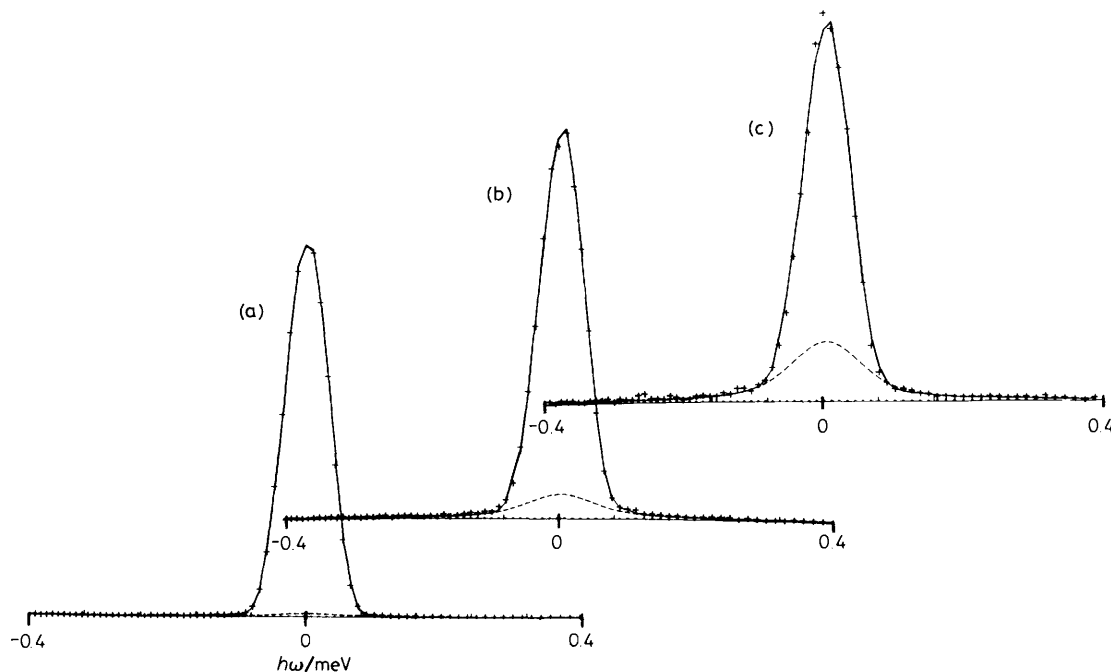

Figure 1. Typical scattering law, $S(Q, \omega)$ at 295 K. The solid curve is a fit of a 2-fold jump reorientation model to the experimental data (+). The dashed line separates the elastic from the quasielastic scattering at Q^{el} (a) 0.352, (b) 1.14, (c) 1.710 Å^{-1}.
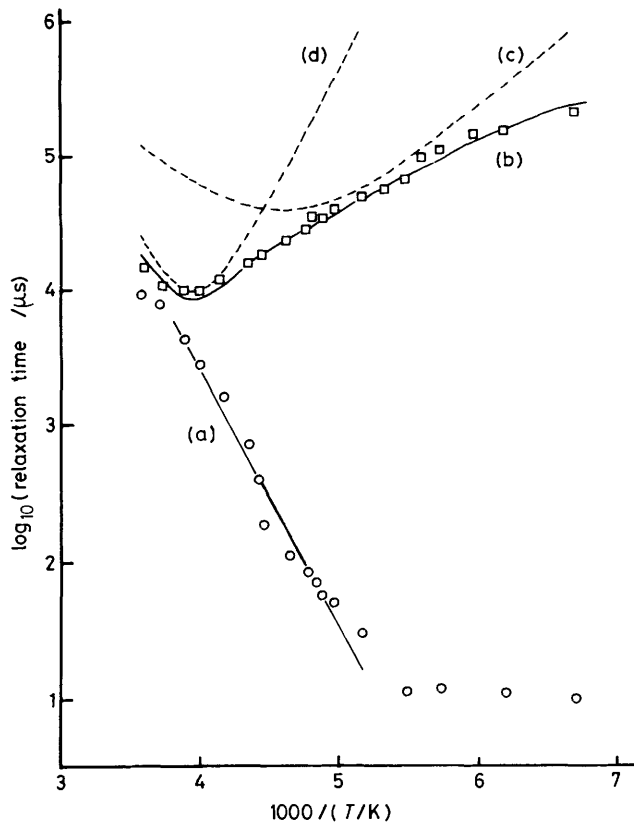
Figure 2. Temperature dependencies of T_1 and T_2 (ν_o 19.25 MHz). The solid lines show the fit to the experimental data, T_2 (a) and $T_{1,obs}$ (b) (see text). The dashed lines show the contributions to $T_{1,obs}$ by the reorientation, $T_{1,ro}$ (c) and self-diffusion, $T_{1,dif}$ (d).

between the experimental and the calculated e.i.s.f. for a variety of simple models for the modes of reorientation for protons in the sample indicated that the observed motion corresponded to a 2-fold reorientation of the H_2O molecule (about the molecular C_2 axis) with either 8 of the formula H_2Os (remaining H in $H_5O_2^+$ units) or 11 of the formula H_2Os (remaining H in H_3O^+) rotating. The full $S(Q, \omega)$ data were therefore fitted with a model corresponding to jump reorientation between 2 sites on a circle, with a radius of gyration of 0.76 Å and with a varying number of static protons, and examination of the qualities of the fits led to the 11 H_2O model being preferred. The corresponding fits to the $S(Q, \omega)$ data at 295 K are illustrated in Figure 1. The fits give values for τ_{res} (the mean site residence time) of 3.2×10^{-11}, 6.6×10^{-11}, 1.4×10^{-10}, and 2.2×10^{-10} s at 295, 280, 265, and 250 K, respectively. Assuming an Arrhenius law, an activation energy E_A 26($\pm$3) kJ mol^{-1} for the 2-fold reorientation is obtained.

In the models above, motions of H$^+$-containing entities are slow (giving a broadening of the q.e.n.s. elastic peak which is small compared to the instrumental resolution) and their contribution to the scattering spectra is purely elastic and constant in the explored Q^{el} range. The precise identity and

dynamics of H$^+$-containing entities are the subject of further studies.

The temperature dependencies of T_1 and T_2 are illustrated in Figure 2. The data are asymmetric, *i.e.* in the plot the low temperature limiting gradient of the T_1 data differs in magnitude from the gradient of the T_2 data. This is typical of crystalline protonic electrolytes[4] and a variety of treatments retaining a model of a single (diffusive) process have been proposed. Attempts to model the data (empirically corrected for the background T_1 contribution from inevitable very low concentrations of paramagnetic reduced W and impurity centres) to a log-normal distribution of correlation times[4] failed to fit simultaneously the T_1 and T_2 data. The q.e.n.s. identification of a C_2-flip of H_2O led to the successful modelling of the data (see Figure 2) assuming BPP formulae to apply to contributory relaxation processes. The T_2 data allow evaluation of a diffusive E_A and τ_c. Subtraction from $T_{1,obs}$ (observed) data of the contributions due to diffusion and paramagnetic centres allows evaluation of a reorientational contribution (and hence E_A and τ_c) because $1/T_{1,obs} = \sum_i (1/T_{1,i})$ for i contributory processes. The quality of the fit is good, for the reorientation $E_A = 15 \pm 1$ kJ mol^{-1} and $\tau_c^{\circ} = 1 \times 10^{-12}$ s, and for H$^+$ self-diffusion $E_A = 36 \pm 3$ kJ mol^{-1}. The difference in reorientational E_A values from n.m.r. and q.e.n.s. can be ascribed to the fact that the n.m.r. measurements are sensitive to other motional modes at this temperature. τ_{res} Values calculated from the n.m.r. data agree with the q.e.n.s. values to within an order of magnitude (good in view of the limited temperature range available to evaluate the diffusive contribution to $T_{1,obs}$).

Fitting the n.m.r. solid echoes obtained in the low temperature region ($140 < T < 185$ K) gave a value M_2 19($\pm$3) G^2. This is again consistent with a C_2 reorientation of H_2O (but not one of higher order), leading to averaging of the intermolecular dipolar interactions but leaving the larger intramolecular interactions unaltered.[6] The position of the minimum in $T_{1,dif}$ corresponds (by BPP theory) to ΔM_2 18 G^2, consistent with a dominant relaxation mechanism at $T > 230$ K arising from diffusion of H$^+$ by chemical exchange (Grotthus mechanism). The self-diffusion coefficient at 295 K estimated (assuming a random-walk model) from the n.m.r. Arrhenius parameters is $D_t \sim 10^{-7}$ cm^2 s^{-1} giving a broadening of the q.e.n.s. elastic peak ($\sim$1 μeV at Q^{el} 1.75 Å^{-1}) too small to be observed with the resolution of the instrument used for this work.

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