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Proton Mobility in Water in Glass Pores of 15 μm Diameter

OUR work on hydrogen ion mobility[1-4] led us to compare values of diffusion coefficients measured by polarography and by porous diaphragm cells. When D/D° (D = diffusion coefficient of an ion in a supporting electrolyte solution, D° = diffusion coefficient at infinite dilution, calculated from the Nernst equation) was plotted against concentration of supporting electrolyte, the curves for metallic cations[4] approached a D/D° value of 1 at infinite dilution. Our curves for the hydrogen ion in alkali halides also approached 1 but those obtained by Woolf[5] using porous diaphragm cells approached a lower value.

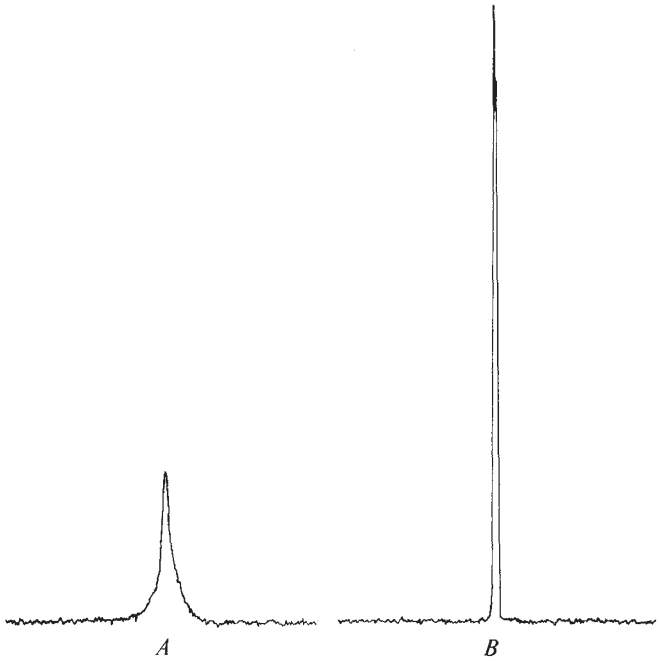

Fig. 1 The n.m.r. spectra of water in sintered glass (*A*) and free water (*B*) recorded under the same conditions.

Mysels and McBain[6] have reported the development of hydrodynamic resistance in fritted glass disks which were in contact with water over an extended period. This had no effect on their conductance measurements on solutions of KCl so they deduced that any changes in the water left the mobility of ions unaffected.

The difference in values of diffusion coefficients of the hydrogen ion obtained by polarography and porous diaphragm cells suggests that hydrogen ion mobility in, or at the surface of, fritted glass is affected by this resistance. Because hydrogen ions move by a different mechanism from other ions in aqueous solution and because rotation of water molecules is the rate-determining step, then it is reasonable to suppose that hydrogen ion mobility would be lessened if water is rigidified in contact with a solid, as suggested by Wentworth[7].

The extent of binding of water molecules can be detected by n.m.r. Slices of sintered glass with a pore size of ~15 μm were inserted in polythene tubing and distilled water was drawn through that for about 30 h. The n.m.r. spectra obtained from the moist sintered glass and from free water in which a piece of glass rod was inserted are shown in Fig. 1. The broadening of the peak in the case of the water sorbed in the sintered glass is readily seen. We suggest that this shows changed environments for some of the molecules, while the time-averaged environments of those free to move is shown as the sharp peak superimposed on a broad band due to immobilized water.

Hechter *et al.*[8] conducted a series of experiments and concluded that the broadening of the water signal in the n.m.r. spectrum of the water in an agar gel-system could best be interpreted as indicating a modification of water structure, and more recent work by Schuffle and Yu[9] on conduction of dilute HCl solutions in glass capillaries from 5 μm to 2,000 μm diameter suggests that this also happens in capillaries of diameter less than 100 μm. We suggest that our spectra also indicate long range modification of the water structure by sintered glass and a consequent effect on proton mobility.

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