

R74-1

Direct Measurements of Proton Mobilities in Protonated Ice

PROTON mobilities in ice have been calculated previously only on the basis of indirect experimental evidence. Eigen and DeMayer^{1,2} have estimated from discharge experiments that in ice of pure water proton mobility is in the range 0.1-0.5 cm.² sec.⁻¹ V.⁻¹. Conway and Bockris³ calculated from conductivities of ice of pure water that proton mobility is 0.19 cm.² sec.⁻¹ V.⁻¹. Some theoretical estimations⁴ yield proton mobilities in ice of 0.11 cm.² sec.⁻¹ V.⁻¹. These mobilities are all extremely high when compared with

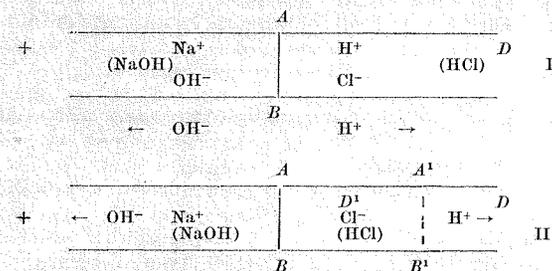


Fig. 1. A sketch for proton boundary movement (hydroxyl ion boundary movement is not considered here). Dye (*D*) used, malachite green; *D*, yellow (frozen) for 0.1 *M* hydrochloric acid; *D*¹, blue after proton depletion; *AB*, initial boundary; *A*¹*B*¹, migrating proton boundary; *AB* - *A*¹*B*¹ region is blue; *I*, boundary positions initially; *II*, boundary positions after electrolysis

the mobilities of protons in liquid water (3×10^{-3} cm.² sec.⁻¹ V.⁻¹).

Protonated ice is a relatively good electrical conductor (Heinmets, F., unpublished results) which suggests that direct measurements of proton movement by the boundary method could be made. Prerequisites for such measurements are the establishment of a sharp moving proton boundary in ice and a proton concentration indicator-molecule to follow the boundary movement. After extensive exploratory work, the conditions for obtaining a suitable boundary have been established and an indicator-dye (malachite green) has been found which exhibits colour change in ice at a suitable proton concentration. I have made such direct measurements of proton mobilities in protonated ice.

Ice was obtained by freezing supercooled 0.1 *M* hydrochloric acid solutions. A U-type conductivity cell (length 30 cm.) was used in which one vertical section was plastic (diameter 1.2 cm. and wall-thickness 0.03 cm.). This facilitated sawing up the tube for sectional analysis. A stable proton boundary, suitable for mobility measurements, is obtained when a boundary is established between hydroxylated and protonated ice (Fig. 1). Half the plastic cell was first filled with 0.1 *M* hydrochloric acid solution (containing indicator dye) and was frozen. Afterwards a layer of 0.1 *M* sodium hydroxide solution, containing also a dye for better boundary indication, was poured on top of the ice and frozen. Some experiments were carried out in the presence of gelatin, since a visually sharper boundary is maintained during the electrolysis. The procedure here was as follows. Half the plastic section was first filled with 0.1 *M* hydrochloric acid solution, containing a proton indicator and 2 per cent gelatin, which gelled and was afterwards frozen. A layer of 0.1 *M* sodium hydroxide solution containing 2 per cent gelatin and metacresol purple was poured on top of this and frozen. This in turn was topped with a non-freezing electrolyte containing a 1 *M* sodium hydroxide solution in 50 per cent glycerol. For the other U-arm a 1 *M* hydrochloric acid solution, also with glycerol, was used. A d.c. potential was applied by means of platinum electrodes. To avoid warming the ice, current values were kept low. The initial boundary of yellow 0.1 *M* hydrochloric acid and purple sodium hydroxide was clear. Shortly after the application of a potential a blue boundary appeared between the purple-yellow interphase, and the blue zone gradually widened. The positions of the boundaries were determined at various time-intervals by switching the current off while the cell was lifted from the bath and the boundary position measured rapidly. During electrolysis at constant voltage, the current value diminished because the blue-zone represents a proton-depleted ice region and its resistance increases with time. In my experiment the current was kept constant by increasing the potential. However, the increase of resistance is not too rapid, since all protons do not migrate out of the region immediately. Apparently all hydrochloric acid molecules are not dissociated in ice and protons migrate only after dissociation. In gel-ice it takes several hours before the resistance in the proton-depleted zone gets very high; during that time the boundary has moved several cm. After completion of boundary measurements, the cell was put into powdered dry ice. Using a duplicate cell, the electric

Table 1. RESISTANCE, pH AND COLOUR OF VARIOUS SECTIONS BEFORE AND AFTER ELECTROLYSIS

Length of section (cm.)	Resistance (ohms)		↑ OH ⁻ NaOH HCl ↓ H ⁺	pH		Colour of ice	
	Before	After		Before	After	Before	After
	—	—		—	—	—	P
1.1	4,000	26,100	1	1.1	3.3	Y	B
1.5	4,000	3,850	2	1.1	1.1	Y	Y
1.5	4,000	3,750	3	1.1	1.1	Y	Y
			↓ A				

Current of 1 m.amp. applied for 180 min. Temperature was kept at -15° . Electric field strength, 0.5 V./cm. A, 0.1 *M* hydrochloric acid, 2 per cent gelatin and malachite green; B, 0.1 *M* sodium hydroxide, 2 per cent gelatin and metacresol purple. P, Purple; Y, yellow; B, blue.

Table 2. VELOCITY OF PROTONS AS A FUNCTION OF TEMPERATURE

Experiment No.	Composition of ice	Temperature (° C.)	Velocity (cm. ²)
			sec.-volt.
1	0.1 <i>M</i> HCl + H ₂ O	-30	2.0×10^{-6}
2	0.1 <i>M</i> HCl + H ₂ O	-25	8.1×10^{-6}
3	0.1 <i>M</i> HCl + H ₂ O + 2 per cent gelatin	-22	2.4×10^{-6}
4	0.1 <i>M</i> HCl + H ₂ O + 2 per cent gelatin	-15	2.2×10^{-4}

In these experiments potential applied at the electrodes varied in the range 200-800 V. The velocity of proton was calculated as follows:

$$V^- = \frac{d}{e \times t}; \text{ in example at } -15^{\circ} V^- = \frac{1.1}{0.5 \times 180 \times 60} = 2.2 \times 10^{-4} \text{ cm.}^2 \text{ sec.}^{-1} \text{ V.}^{-1}$$

where *d*, boundary displacement (cm.); *e*, electric field strength (V./cm.); *t*, time (sec.).

Temperatures reported here are those of bath; ice temperatures are slightly higher due to the passage of current. Electric field intensity for each experiment was determined by d.c. conductivity measurements in a duplicate cell. Same current values were used for conductivity measurements and for electrolysis.

field strength in the hydrochloric acid region was determined for selected current value. Then various sections of plastic cell were sawn off, melted and conductivity and pH determined. A thin section between sodium hydroxide-hydrochloric acid interphase was discarded. In Table 1 the result of a typical experiment is presented. Zone A-1 represents the proton-depleted region. During 180 min. at 1 m.amp. the displacement of the boundary was 1.1 cm. In the blue A-1 zone the pH value was 1.1

before and 3.3 after electrolysis. This was reflected also in resistance increasing from 4,000 ohms to 26,100 ohms. Both measurements reveal a large reduction of proton concentration in *A-1* zone. In two control sections (*A-2*, *A-3*) at the front of the boundary there was no significant change in either the pH or the resistance value, nor was there a change in colour. Additional control experiments with hydrochloric acid solutions and malachite green revealed that the change in colour corresponds to the reduction of the proton concentration. This proton-depleted zone is shown in Fig. 2, which is a black-and-white copy of a colour photograph. All available evidence indicates that the blue zone in ice represents a proton-depleted region, and proton mobility is calculated from the length of the zone. Results are presented in Table 2. Since the conductivity of protonated ice decreases when temperature is lowered, it is expected that proton mobility is also reduced. The results in Table 2 confirm this phenomenon.

It can be questioned how much diffusion contributes to movement of the proton boundary in the ice. A

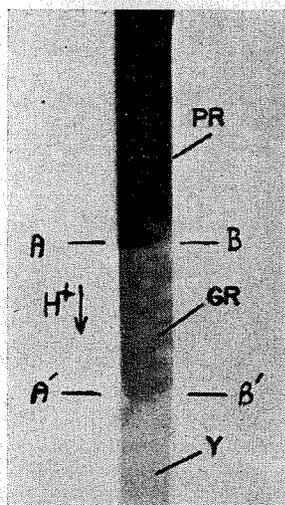


Fig. 2. Proton boundary in ice. *PR*, Purple zone, 0.1 *M* sodium hydroxide plus metacresol purple; *GR*, blue zone, part of 'y' zone whence protons have been removed by electrolysis; depletion of protons changes colour of ice from yellow to blue; *Y*, light yellow zone, 0.1 *M* hydrochloric acid plus malachite green (ice is yellow); *A*—*B*, initial proton boundary position; *A'**B'*, final boundary position

This black-and-white print has been prepared from a colour slide

rough estimate of this has been made on the basis of measurements with a control cell which was stored at -28°C . for six months. Approximate velocity of diffusion boundary was 1×10^{-7} cm./sec. It appears that diffusion displacement of proton boundary is insignificant in experiments lasting only for a few hours.

It is evident that proton mobility in protonated ice is about three orders of a magnitude smaller than previously estimated^{1,3}. This raises the question whether previous indirect estimations and calculations are based on uncertain assumptions or whether, in the ice of pure water, a different mechanism is operating for the proton transfer process. Further work is required to elucidate this point. Unfortunately, moving-boundary methods cannot be used at very low proton concentrations. My experiments were carried out under conditions where current and temperature were regulated manually, and experimental error may be considerable, but the accuracy is definitely better than an order of magnitude. Experiments are in preparation with automatic current and temperature control in order to obtain more accurate proton mobility determinations.

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³ Conway, B. E., and Bockris, J. O'M., *J. Chem. Phys.*, **28**, 354 (1958).

⁴ Conway, B. E., *Canad. J. Chem.*, **37**, 178 (1959).