Polarography of the Hydrogen Ion in Concentrated Solutions of Lithium Chloride

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The addition of lithium chloride to an aqueous solution containing the hydrogen ion breaks down the hydrogen-bonded water structure. At 8 molal lithium chloride the hydrogen ion is no longer able to move by the ' proton jump ' mechanism. The half-wave potential of hydrogen on mercury increases markedly between 4·5 and 13 molal. This effect is attributed to a decrease in the degree of hydration of the hydrogen ion, with a consequent increase in its activity. At concentrations greater than 13 molal the hydrogen ion is probably present as H_3O^+ and the half-wave potential remains constant up to 19 molal (*i.e.,* 3 moles of water per mole of lithium chloride). A further increase in half-wave potential occurs between 19 and 20 molal.

RECENT studies by nuclear magnetic resonance and infrared methods have revealed that the structure of water is affected by electrolytes.[1-4] Certain ions have a predominantly polarising effect on the water structure while others tend to break the hydrogen-bonded water structure. Some n.m.r. studies have revealed definite breaks in the plots of proton chemical shift against molality of electrolyte for certain electrolytes, but the breaks are not always easy to detect and have earlier gone un-noticed. We now describe how polarography can be used to study the phenomenon. A small quantity of a strong acid is added to the electrolyte solution and the polarographic wave of the hydrogen ion is recorded. The mobility of the hydrogen ion in a particular solvent

[1] J. N. Shoolery and B. J. Alder, *J. Chem. Phys.*, 1955, **23**, 805.

[2] B. P. Fabricand and S. Goldberg, *J. Chem. Phys.*, 1961, **34**, 1624.

[3] J. C. Hindman, *J. Chem. Phys.*, 1962, **36**, 1000.

[4] K. Buijs and G. R. Choppin, *J. Chem. Phys.*, 1963, **39**, 2035, 2043.

is greatly influenced by the absence or presence of hydrogen bonding and this mobility is directly reflected in the height of the polarographic wave.

The polarographic method also gives information about the overpotential of hydrogen on mercury.

The Ilkovič equation (1) in which i_d = diffusion

$$i_d = 607nD^{\frac{1}{2}}Cm^{\frac{2}{3}}t^{\frac{1}{6}} \qquad (1)$$

current, C = concentration of depolariser, D = diffusion coefficient of the depolariser, m = rate of flow of mercury, n = number of faradays per mole of electrode reaction, and t = drop time, is applicable to any polarographic wave whose limiting current is diffusion-controlled. (The Ilkovič equation is only an approximate
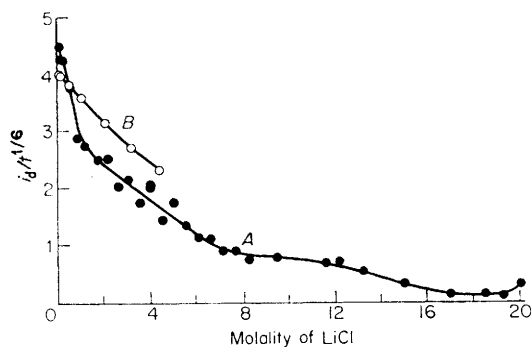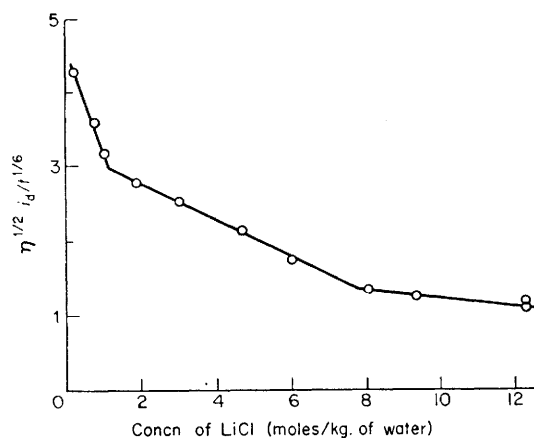

FIGURE 1

FIGURE 2

solution of the diffusion problem, but it is sufficient for our purpose.) It was found that m varied by only 0.5% over the ranges studied, so that the ratio $i_d/t^{\frac{1}{6}}$ should remain constant (see Figure 1; curve A) for a constant concentration of hydrogen ions (10^{-3}M), unless the diffusion coefficient of the hydrogen ion changes owing to change of (a) viscosity of the solution, (b) degree of solvation of the diffusing species, or (c) mechanism of diffusion.

The first factor can be eliminated by determining the ratio $\eta(i_d/t^{\frac{1}{6}})^2$ where η = viscosity of the solution, since, from the Stokes–Einstein relationship, ηD is a constant provided there is no change in the size of the solvated ion (see Figure 2).

3 P

A Yanagimoto A.C.–D.C. Polarograph model P.A. 102 was used. The reference electrode was saturated calomel and all polarograms were recorded at $25.0° \pm 0.1°$.

Viscosities were measured with an Ostwald viscometer. The hydrogen-ion concentration was held constant at 10^{-3}M for all measurements (by the addition of HCl). Lithium chloride was AnalaR grade and all polarograms were corrected for the residual current of lithium chloride solution without added acid.

RESULTS AND DISCUSSION

Diffusion of the Hydrogen Ion.—Figure 2 is virtually identical in form with Figure 1, which indicates that the form of Figure 1 cannot be attributed solely to the increasing viscosity of the solution. Robinson and Stokes [5] have tabulated the diffusion coefficients of the hydrogen ion in aqueous lithium chloride. These were included (Figure 1, curve B) for comparison by calculation of $i_d/t^{\frac{1}{6}}$. Although there is not absolute agreement, the values are parallel to each other above 1 molal. The break in the plot of the polarographic values below 1 molal might indicate that the migration current of the hydrogen ion is important when molal ratio of lithium chloride to hydrogen ion falls below 1000 to 1. However, this value is considerably greater than the ratio of 100 to 1 recommended for other ions and the break is more likely due to the streaming of the solution at low ionic strength.

The other major break in both Figures 1 and 2 occurs at 8 molal; thereafter other changes occur but they are not as pronounced. If the value of $\eta^{\frac{1}{2}}i_d/t^{\frac{1}{6}}$ at 8 molal of *ca.* 1.33 is compared with that obtained by extrapolation of the initial part of the curve (1—8 molal) to infinite dilution a value of 3.2 is obtained. The square of this ratio is 5.8 and can be thought of as expressing the ratio of the diffusion coefficients of the hydrogen ion at infinite dilution and in an 8 molal solution apart from the effects of viscosity. This ratio (*ca.* 6) indicates that the mobility of the hydrogen ion is approaching that of an ordinary univalent ion of comparable size.

The break at 8 molal agrees with the second of the two breaks, 4.5 and 8 molal, observed in the plot of the proton chemical shift against molality.[2] The first break has been attributed to the concentration at which water molecules are first shared between ions, the second has not been explained. An explanation consistent with the n.m.r. and polarographic results is as follows. The hydrogen ion moves through the water structure by diffusion and hydrogen bonding. Increasing concentration of electrolyte causes some of the hydrogen bonds to be ruptured. At 4.5 molal lithium chloride water molecules are first shared between ions, which affects the linear dependence of proton chemical shift on concentration but does not necessarily affect the ability of the hydrogen ion to move by diffusion and hydrogen bonding. This explanation is supported by the work of Buijs and

[5] R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' Butterworths, London, 1957, p. 317.

Choppin on the infrared spectrum of 4·6 molal lithium chloride.[4] They concluded that the hydrogen bonding in pure water is only slightly greater than in 4·6 molal lithium chloride. If C_0, C, and C_2 represent the fraction of water molecules which have 0, 1, and 2 hydrogen bonds per molecule at 21°, the fractions are 0·31, 0·42, and 0·27 for water and 0·30, 0·47, and 0·23 for 4·6 molal lithium chloride respectively. Hence, $i_d/t^{\frac{1}{2}}$ decreases regularly from 1 to 8 molal. At 8 molal the hydrogen-bonded water structure has virtually disappeared and
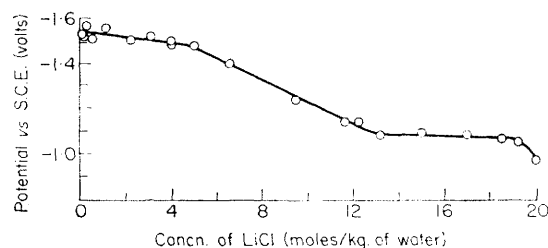

FIGURE 3

the plot of chemical shift against molality shows another break. At this concentration the contribution of ' proton jump ' mechanism to the hydrogen-ion mobility has been eliminated and the plot of $i_d/t^{\frac{1}{2}}$ levels out to a value approaching that of an ordinary univalent ion.

Discharge Potential of Hydrogen on Mercury.—Figure 3 shows a plot of half-wave potential against molality of lithium chloride. The half-wave potential increases from *ca.* −1·55 v *versus* S.C.E. to −0·97 v, an increase of 0·58 v. The main features are that the half-wave potential does not change substantially from 0 to 4·5 molal (0·05 v). From 4·5 to 13 molal the half-wave

potential increases by 0·41 v, and after 13 molal it is remarkably constant (within 0·02 v) until 19 molal where it increases again.

The break at 4·5 molal agrees with that observed in the n.m.r. work on lithium chloride solutions. The second break occurs at 13 molal which is equivalent to $55·5/13 = $ *ca.* 4·3 moles of water per mole of lithium chloride. It seems that the degree of hydration of the hydrogen ion is not markedly affected until a concentration of 4·5 molal, where water molecules are first shared between the lithium and chloride ion. After 4·5 molal the degree of hydration decreases until it reaches a minimum of 13 molal. This decrease in the degree of hydration increases the activity of the hydrogen ion and thus the potential at which it is discharged increases. After 13 molal the proton probably exists as H_3O^+ and no appreciable change occurs in the discharge potential until 19 molal (*i.e.*, in 3 moles of water per mole lithium chloride). This explanation is supported by the work of Critchfield and Johnson [6] who observed that the pH of acid solutions is markedly decreased by addition of strong electrolytes (including lithium chloride). They concluded that the activity of the hydrogen ion increases when it loses water of hydration.

The increase in half-wave potential between 0 and 13 molal of 0·46 v corresponds to a change in activation energy of 10·5 kcal./g.-ion, which is equivalent to the rupture of more than two hydrogen bonds per g.-ion (hydrogen bonding energy in ice is 4·5 kcal. per mole of bonds). This result is in agreement with the suggested mechanism.

⁶ F. E. Critchfield and J. B. Johnson, *Analyt. Chem.*, 1958, **30**, 1247; 1959, **31**, 570.