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PROTON TRANSFER CONDUCTANCE IN AQUEOUS SOLUTION

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Proton Transfer Conductance in Aqueous Solution

Part 1.—Conductance of Concentrated Aqueous Alkali Metal Hydroxide Solutions at Elevated Temperatures and Pressures

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Measurements of the electrical conductivity of aqueous solutions of KOH, NaOH and LiOH are presented within the ranges 25-200°C, 1-3000 atm and 0.1-6.68 molal. These indicate that with increasing concentration there is a transition in the primary mechanism of conductance in these solutions from the proton transfer mechanism to the hydrodynamic mechanism. In LiOH solutions, however, saturation occurs before this transition is established. It is suggested that at high concentrations most of the water molecules are dominated by their proximity to an ion and so cannot participate in the proton transfer mechanism of conductance by the hydroxyl ion. This mechanism is disrupted most by KOH and least by LiOH at a given concentration in excess of 1 molal, and this is related to the greater ionic association of the latter solute.

With increasing concentration of KOH the Walden product becomes more nearly independent of temperature and pressure. Data for the viscosity of water have been surveyed and a table covering the ranges 10-200° and 1-3000 kg cm^{-1} is presented. The pressure dependence of the conductance of these solutions is virtually independent of concentration to the unexpectedly high value of about 1 molal, but it alters markedly in the range 1-2 molal. The observations are discussed qualitatively.

Electrostatic theories of electrolyte solutions, which consider only the Coulombic forces between ions dissolved in a continuous dielectric solvent, are only adequate for the prediction of the concentration dependence of the thermodynamic and transport properties in the limit of extremely high dilution, and other, more localized intermolecular forces, e.g., those between ions and solvent molecules and between the solvent molecules themselves, must also be taken into account in a complete theory applicable to high concentrations. Hence most of the current literature on electrolyte processes essentially describes efforts towards the understanding of ionic solvation, and usually the studies seek correlations between electrolyte properties and the structure of the solute and solvent. The present contribution, e.g., is concerned with how the transfer of protons between water molecules is affected by the close proximity of dissolved ions.

The importance of ion-solvent interactions is exemplified in the relation between the limiting ionic conductance and the crystallographic radius. Thus, contrary to expectation, the mobility of the alkali metal cations in water increases with increasing crystallographic radius until it reaches a maximum value for such ions as Cs^+ and I^-, when the crystallographic radius is of similar magnitude to the radius of a water molecule. For the tetralkylammonium ions, on the other hand, the mobility decreases normally with increasing ionic radius. The limiting mobilities of the hydrogen and hydroxyl ions in water are much greater than this maximum hydrodynamic mobility, and this observation has received considerable discussion. Little attention,

however, has been given to the mechanism of conductance by these ions in concentrated aqueous solutions, and the effects of temperature and pressure on such processes do not appear to have been considered previously.

The primary empirical approach to the conductance of aqueous solutions has been the examination of the concentration dependence in very dilute solutions at 25° and atmospheric pressure; indeed, much of the most precise conductance work was stimulated to confirm the Debye-Hückel-Onsager theory. Recently, however, there has been considerable interest in the effects of temperature and pressure on the properties of aqueous solutions.[1] There are two primary reasons for this increased interest: first, the studies have application to such technologies as boiler corrosion, hydrothermal synthesis and oceanography, and secondly, the short-range structure which persists in water when ice melts is broken down by increasing both temperature and pressure. This is reflected e.g., in the wide variation of the dielectric constant [2, 3] (from about 100 to less than 10), and has marked effects on ionization equilibria and transport processes in water. Change of temperature and pressure therefore provides a valuable means of studying these phenomena.

A considerable volume of conductance data for aqueous solutions covering wide ranges of temperature and pressure has consequently been recorded. The concentration ranges studied, however, have usually been in the very dilute region so that the measurements could be extrapolated to infinite dilution to eliminate ionic interaction effects, and few measurements on solutions more concentrated than 0.1 molal at high temperatures and pressures have been reported. Several Russian workers, however, have published data for high temperatures at the saturation vapour pressure of the solution, (which corresponds to pressures up to about 200 bar for temperatures up to 300°C). Rodnyanskiĭ and Galinker [4] and Gorbachev and Kondrat'ev [5] have studied the alkali metal chlorides to a concentration of 3 M at temperatures to 300°C. Mil'chev and Gorbachev [6] investigated the sulphates of K, Li, Zn and Cd from 0.1 to 0.5 M up to 200°C, and Kondrat'ev and Nikich [7] investigated the alkaline earth chlorides from 0.5 to 1 M up to 300°C. Maksimova and Yushkevich [8] report conductances of NaOH solutions to 12 M, and sodium metaborate solutions to 4 M, over the range 20-300°C. No measurements, however, of the effect of pressure on the conductance of concentrated aqueous solutions at temperatures above 100° appear to have been published.

Unfortunately, few systems have been studied over the complete range from very dilute solution to fused salt,[9] though several workers have studied the effects of small concentrations of water on the properties of molten salts.[10] It still seems debatable, however, whether the problems presented by concentrated solutions will ultimately prove more tractable by studies at the extreme molten salt end of the concentration scale. The present paper illustrates that studies of the conductance as functions of temperature, pressure and concentration over wide ranges of these variables can contribute significantly to our understanding of the mechanism of ionic migration in solution. Thus, although no precise quantitative theory exists to be tested using the results presented, qualitative discussion leads to some new conclusions and predictions. Finally, there is an acute need in chemical industry for more data on the transport properties of concentrated electrolytes at high temperatures and pressures,[11] to which this paper is in part directed.

EXPERIMENTAL

The general requirements for the design of a conductance cell for use at high temperatures and pressures have been discussed previously.[12] To measure the conductance of concentrated aqueous alkaline solutions, however, it is additionally necessary to use a cell which

has a very high cell constant and is extremely chemically resistant. The need for a large cell constant arises because the solutions are so highly conducting that the cell resistance would otherwise be too small to measure with adequate precision. Moreover, if the resistance of the cell is very low the capacitative component of its impedance becomes dominant with consequent loss in definition of the balance point of the a.c. conductance bridge. The bridge (type 4896, H. Tinsley and Co. Ltd.) showed optimum accuracy in the range 3-30 kΩ, so the dimensions of the cell were designed accordingly.

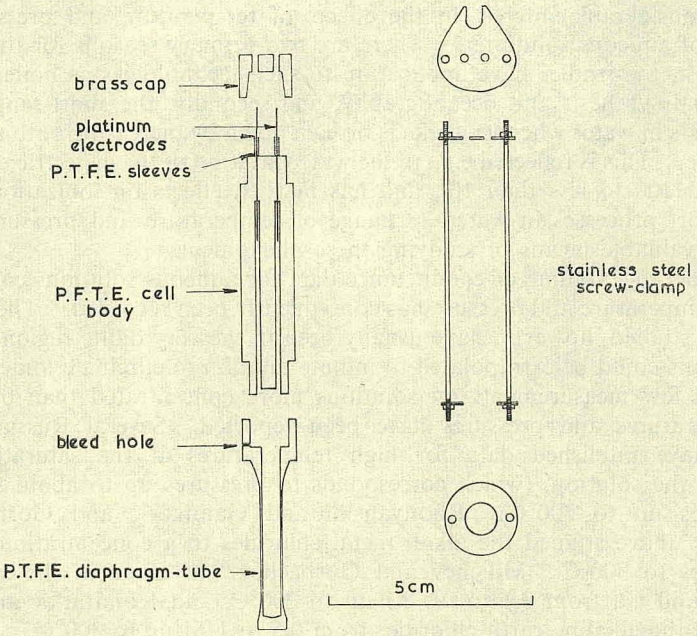

FIG. 1.—Exploded view of PTFE conductance cell for use with concentrated aqueous solutions at elevated temperatures and pressures.

The PTFE cell shown in fig. 1 has proved satisfactory over the ranges 1-3000 atm and 25-200°; it is a modification of the cell used previously for dilute aqueous solutions.[12] The solutions came into contact only with PTFE and platinum, which are chemically resistant to the aqueous alkalis used. Changes in volume of the solutions resulting from alterations of temperature and pressure were allowed by distortion of the PTFE diaphragm tube. The platinum wire electrodes were heavily platinized to reduce polarization errors, and were sealed into the cell by forcing them through a slightly undersized bore when the PTFE component was heated to about 200°. The cell constant alters very slightly with temperature and pressure as a result of the expansion and compression of the PTFE. This was an unavoidable compromise, however, because ceramic materials which might otherwise be used to hold the electrodes at a fixed distance apart are dissolved by the alkaline solutions. High pressure PTFE conductance cells have been used for very dilute solutions by other workers,[13] and Hamann [14] has discussed the correction for the change in cell constant with pressure. This is an uncertain procedure, however, because the PVT behaviour of PTFE varies between samples [15] so no cell constant correction was applied to the present results, but this would not affect our general conclusions.

The cells were completely filled with solution using a PTFE syringe fitted with a flexible PTFE delivery tube. Rapid checks with an Avometer were used to test for gas bubbles which occasionally lodged in the cells causing an open circuit. All filling operations were performed in a glove box using CO_2-free conditions. The tension to retain the seals on the cell was provided by the screw clamp, which also served for mounting the cell in position

in the pressure vessel. Several cells were used together in a 350 ml capacity pressure-vessel which was pressurized with phenyl-methyl silicone oil. Pressures to 3000 atm were generated by a hand pump and intensifier and measured by Bourdon gauges. The pressure-vessel was maintained at constant temperatures ($\pm 0.01°$) in the range 25-200°C by a silicone oil thermostat bath. Further details of this equipment have been described previously.[3]

MATERIALS

Solutions were prepared under CO_2-free conditions and stored in polythene vessels. KOH and NaOH solutions were obtained by dilution of carbonate-free B.D.H. volumetric standard solutions. CO_2 was removed from the conductance water by boiling followed by cooling using a soda lime guard-tube. LiOH solutions were prepared by weight from BDH lithium hydroxide monohydrate without further purification.

PROCEDURE

A pressure cycling procedure at constant temperature was adopted. Initially the thermostat was adjusted to 25°C and the cell resistances were measured at approximately 500 atm intervals from 1 to 3000 atm. Resistances were normally measured at a constant frequency of 1 kHz because the ratios $\kappa_p/\kappa_{p=1}$ were negligibly dependent on frequency over the range 1-30 kHz. Plots of cell resistance against time indicated when thermal equilibrium conditions were regained following an adiabatic expansion or compression. The thermostat was then set to a higher temperature and the pressure cycle repeated. For temperatures above 100°, however, the pressure was not taken below the vapour pressure of the solution as this could damage the cells. Finally, each series of measurements was completed by re-adjusting the thermostat to 25° and repeating the measurements at atmospheric pressure. This ensured that the solutions had not significantly changed in composition during the cycles. Cell resistances at integral pressures were interpolated from large-scale isothermal plots of resistance against pressure. The results were expressed in terms of the relative specific conductances $(\kappa_p/\kappa_{p=1\text{ atm}})_T$ and $(\kappa_T/\kappa_{T=25°C})_P$ for a solution of a given molality. The use of these relative specific conductances rather than relative equivalent conductances obviates the need to correct for the change in volume of the solution with temperature and pressure. For very dilute solutions this is easily effected by assuming that the *PVT* behaviour of the solution differs negligibly from that of the pure solvent, but for concentrated alkaline solutions such an assumption would be invalid and, moreover, the relevant *PVT* data for these solutions are not available.

RESULTS AND DISCUSSION

Table 1 gives the effect of pressure to 3000 atm on the specific conductance of KOH solutions at 25° and concentrations to 6.68 molal. The equivalent conductance as a function of pressure may be calculated from these data by combining them with the concentration dependence of the equivalent conductance at atmospheric pressure, and compressibility data to 3000 atm. Table 1 shows that the pressure dependence of conductance in KOH solutions is affected little by concentration up to about 1 molal, but at higher concentrations $(\delta\kappa/\delta P)_{25°C}$ is markedly dependent on the concentration. Thus, in dilute solutions the conductance increases with pressure, whilst in very concentrated solutions it decreases with pressure and at about 3.5 molal $(\delta\kappa/\delta P)_{25°C}$ is zero. This is illustrated in fig. 2, from which data for the more dilute solutions have been omitted for the sake of clarity. Such a striking transformation in behaviour suggests a change in the mechanism of conductance in KOH solutions as the concentration is increased. In terms of the transition state theory of transport processes,[16] the *formal* volume of activation for conductance is negative in dilute KOH solutions and positive in very concentrated solutions. (The word *formal* here denotes the composite volume of activation for all the steps contributing to the

TABLE 1.—EFFECT OF PRESSURE ON THE SPECIFIC CONDUCTIVITY OF POTASSIUM HYDROXIDE SOLUTIONS AT 25°C; RATIO OF THE SPECIFIC CONDUCTIVITY AT P atm TO THAT AT ATMOSPHERIC PRESSURE

P/atm	0.1 m	0.5 m	1.0 m	1.78 m	2.85 m	3.56 m	4.68 m	5.35 m	6.68 m
1	1	1	1	1	1	1	1	1	1
500	1.0287	1.0297	1.0277	1.0155	1.0087	1.0007	0.9932	0.9882	0.9782
1000	1.0501	1.0499	1.0481	1.0390	1.0145	1.0014	0.9879	0.9778	0.9597
1500	1.0663	1.0654	1.0627	1.0404	1.0183	1.0020	0.9833	0.9687	0.9442
2000	1.0775	1.0769	1.0749	1.0505	1.0204	1.0027	0.9796	0.9606	0.9303
2500	1.0857	1.0851	1.0838	1.0584	1.0215	1.0034	0.9765	0.9537	0
3000	1.0908	1.0906	1.0897	1.0637	1.0218	1.0034	0.9739	0.9483	0

models of the conductance mechanism, and these have been discussed by Eigen and De Maeyer [18] and by Conway.[19] The accepted view is that the conductance of the hydrogen and hydroxyl ions in water arises from an hydrodynamic mechanism plus a more rapid proton transfer mechanism. The hydrodynamic process involves ionic movement by a diffusive mechanism in the electric field, analogous to the migration of, say, K^+ or F^- ions. The proton transfer process accounts for about 79 % of the conductance of the hydrogen ion and about 62 % of the conductance of the hydroxyl ion in water at 25°C and atmospheric pressure. It occurs as a consequence of the ability of H^+ and OH^- to be readily incorporated into the short-range, tetrahedral, H-bonded structure of water.[20] The electronic charge can easily move within this H-bonded structure, as verified by the very high proton mobility in ice observed by Eigen and De Maeyer, and the rapid exchange of a proton between two favourably orientated water molecules occurs within the distance of an H-bond and results in the proton moving a distance of about 0.35 Å whilst the centre of charge moves through an O—O distance of about 2.76 Å. (The precise values of these dimensions are still subject to discussion.) Once a water molecule has passed a proton to an adjacent water molecule, however, it cannot accept another proton travelling in the same direction without being reorientated through approximately 120°.

By estimating the energetics of the proton tunnelling and structural reorientation processes, Conway, Bockris and Linton [21] concluded that the latter is the rate-determining step in the conductance mechanism, whilst Eigen considers the rotation of a water molecule on the periphery of the $H_9O_4^+$ (and corresponding $H_7O_4^-$) complex to be rate-determining, i.e., the structural diffusion of the whole complex by formation and breakdown of H-bonds at its boundary. To the extent that both the normal, hydrodynamic mechanism of ionic conductance and the proton transfer mechanism probably both involve the disruption of H-bonds in the vicinity of the ion, we believe these two processes are essentially similar. (This view may partially explain why the Debye-Hückel-Onsager theory apparently applies equally well to aqueous solutions fo both HCl and KCl.) The structural diffusion of the H^+ and OH^- hydration complexes involves a similar mechanism to that proposed by Frank and Wen [22] for the formation and disappearance of H-bonded clusters in water. Thus, the overall conductance process involves the net structural migration in the direction of the applied electric field.

Hamann and Strauss [13] explained the increase in mobilities of the hydrogen and hydroxyl ions with pressure by suggesting that pressure assists the proton exchanges by providing some of the repulsion energy needed to bring the oxygen atoms close enough for a proton switch to occur. The current interpretation is that high pressure reduces the extent of H-bonded association in water thereby facilitating the rotation of water molecules which is regarded as the rate-determining step in the proton transfer mechanism. The volume of activation for this process would be expected to be negative because the rotation of a water molecule involves the breakage and reformation of H-bonds, and hence a contraction of the system on entering the transition state. This view is fundamentally little different from that of Hamann and Strauss.

It is now necessary to discuss the change-over in the effect of pressure on the conductance of aqueous KOH solutions as the concentration is increased. We suggest that as the concentration is increased above about 1 molal, the proton transfer mechanism is increasingly hindered because there are fewer " bulk " water molecules, (i.e., those not governed in their energetics and orientations by proximity to an ion), to participate in the successive proton switches. The contribution of the proton transfer mechanism to the total conductance of the solution therefore decreases.

In discussing this concept that only a proportion of the total number of water molecules are free to participate in the proton transfer chains, we consider how the ratio of the number of molecules of water to molecules of solute varies with concentration. We do not imply a rigorous division of all the water molecules into those free to participate in successive proton transfers and those bound to cations, or other solute molecules, as there is no clear boundary between these two extreme categories. The total number of molecules of water available for solvation of one molecule of solute, assuming that the solute is undissociated, falls drastically as the concentration is increased. At 3.5 M, e.g., there are 16 water molecules per solute molecule, and at 10.5 M, only 5. If, however, the solute is dissociated there will be even fewer water molecules available for each solute species, and it is not surprising, therefore, that there is evidence for extensive ion pairing in solutions of 6-7 M NaOH and KOH.[23] Thus, at these high concentrations almost all of the water molecules in the solution will be dominated by their proximity to a solute species and hence it is unlikely that the proton transfer mechanism of conductance could be established to any appreciable extent.

TABLE 2.—VISCOSITY OF WATER AT ELEVATED TEMPERATURES AND PRESSURES [35]

pressure/ kg cm^{-2}	10°C	25°C	30°C	50°C	75°C	100°C	150°C	200°C
1	12.99	8.949	8.004	5.49	3.81	2.839	1.86	1.36
200	12.94	9.0	8.06	5.55	3.87	2.90	1.88	1.40
400	12.84	9.1	8.15	5.6	3.94	2.97	1.91	1.43
600	12.82	9.15	8.25	5.65	4.0	3.02	1.94	1.46
800	12.83	9.25	8.35	5.7	4.05	3.07	1.98	1.5
1000	12.83	9.3	8.42	5.8	4.12	3.14	2.03	1.53
2000	13.28	9.9	9.0	6.25	4.44	3.50	2.2	1.68
3000	14.36	10.7	9.76	6.75	4.83	3.85	2.4	1.83

$\eta(H_2O)$ millipoise.

At high enough concentrations of KOH, the solution conductance decreases with pressure as it does for dilute aqueous solutions having the maximum hydrodynamic mobility. Moreover, fig. 2 shows that the conductance decreases with pressure roughly in parallel with the increase in viscosity of the solvent, and the Walden product is almost independent of pressure up to about 1000 atm at 25°C for 6.68 molal KOH. This supports our suggestion that conductance occurs almost entirely by the hydrodynamic mechanism at very high concentrations. Table 2 gives the viscosity of water to 200°C and 3000 kg cm^{-2} obtained by graphical analysis of the available data.[24] There are considerable discrepancies between the few sets of published data, so high precision is not claimed for these values.

TABLE 3.—EFFECT OF PRESSURE ON THE CONDUCTIVITY OF AQUEOUS NaOH SOLUTIONS AT 25° AND CONCENTRATIONS TO 4 molal; RATIO OF THE SPECIFIC CONDUCTIVITY AT P atm TO THAT AT ATMOSPHERIC PRESSURE

P/atm	1 m	2 m	4 m
1	1	1	1
500	1.0107	1.0132	0.9968
1000	1.0377	1.0262	0.9939
1500	1.0505	1.0375	0.9924
2000	1.0541	1.0466	0.9895
2500	1.0637	1.0532	0.9879
3000	1.0685	1.0578	0.9869

Table 3 shows, as might be expected, a similar behaviour for NaOH as for KOH solutions, but for LiOH solutions the different situation occurs as shown in table 4. With increasing LiOH concentration above about 1 molal, there is a noticeable reduction in the pressure dependence of conductance but saturation occurs before the concentration can be increased sufficiently for $(\delta\kappa/\delta P)_{25°C}$ to become zero. This suggests that the conductance in LiOH solutions at 25° and atmospheric pressure occurs primarily by the proton transfer mechanism at *all* concentrations up to saturation. Thus, in this respect, LiOH contrasts in behaviour with KOH and NaOH.

TABLE 4.—EFFECT OF PRESSURE ON THE CONDUCTIVITY OF AQUEOUS LiOH SOLUTIONS AT 25° AND CONCENTRATIONS TO 5 molal; RATIO OF THE SPECIFIC CONDUCTIVITY AT P atm TO THAT AT ATMOSPHERIC PRESSURE

P/atm	0.976 m	3 m	5 m
1	1	1	1
500	1.0416	1.0348	1.0354
1000	1.0738	1.0605	1.0531
1500	1.0980	1.0815	1.0663
2000	1.1164	1.0972	1.0756
2500	1.1319	1.1096	1.0840
3000	1.1435	1.1185	1.0893

This difference is also noticeable in the concentration dependence of the specific conductance of these solutions, which is shown in fig. 3. These data were taken from the Landolt-Börnstein tables.[25] Indeed, there appears to be a relationship between the observations that the specific conductance exhibits a maximum in its concentration dependence and that the pressure dependence of the conductance passes through zero with increasing concentration (subject to the restriction of solubility). This relationship is satisfying because it would appear that these two phenomena can be explained by essentially the same concepts. With increasing concentration the specific conductivity initially increases because more charge carriers are available per unit volume. As the concentration is further increased the ions come closer together for a longer time, and the orientation and motion of more of the water molecules become dominated by their proximity to an ion. Thus, the proton transfer mechanism of hydroxyl ion conductance is gradually obliterated and the Coulombic energy of attraction between anions and cations is increased sufficiently for ion-pairs to form with significant lifetimes : the specific conductance of the solution therefore no longer increases as more solute is added. With further increase in concentration the specific conductance would be expected to fall because the viscosity of the solution increases [26] and the hydrodynamic mechanism of ionic migration will be hindered.

This difference between LiOH on the one hand and NaOH and KOH on the other is a significant observation which requires explanation. It appears that the destructive effect of increasing concentration on the proton transfer conductance in the alkali hydroxides studied is greatest for K^+ and least for Li^+. This effect is clearly illustrated in fig. 4. It seemed logical to appeal for some indication of an explanation to the data [26] for the variation of viscosity with concentration, because the rate-determining steps in the mechanism of proton transfer conductance and viscous flow in these solutions might well be closely related, viz., probably the rotation of water molecules in the vicinity of OH^- and alkali metal ions, which is limited by the breakage of H-bonds in the evanescent water structure. One might therefore expect that as the viscosity of the alkali hydroxide solutions increases markedly with concentration in the range 1-5 molal at normal temperature and pressures, so the proton transfer conductance and also the hydrodynamic conductance should be

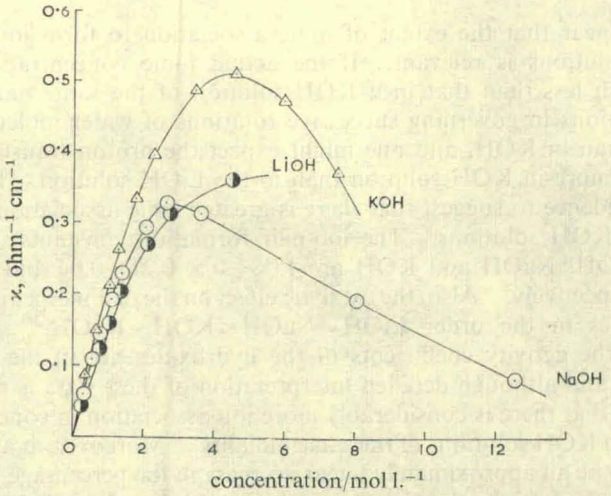

FIG. 3.—Concentration dependence of the specific conductance of aqueous KOH, NaOH and LiOH solutions at 25° and atmospheric pressure; data from ref. (25). ⊙, NaOH; ◑, LiOH; △, KOH.

reduced as the concentration is increased. However, (*a*) the viscosity of KOH solutions increases less with concentration than does that of LiOH and NaOH solutions, and (*b*) the viscosity of LiOH and NaOH solutions increases with concentration to almost the same extent for concentrations up to 4 M. The viscosity data, therefore, do not explain the relative trends shown by Li^+, Na^+ and K^+ in fig. 4.

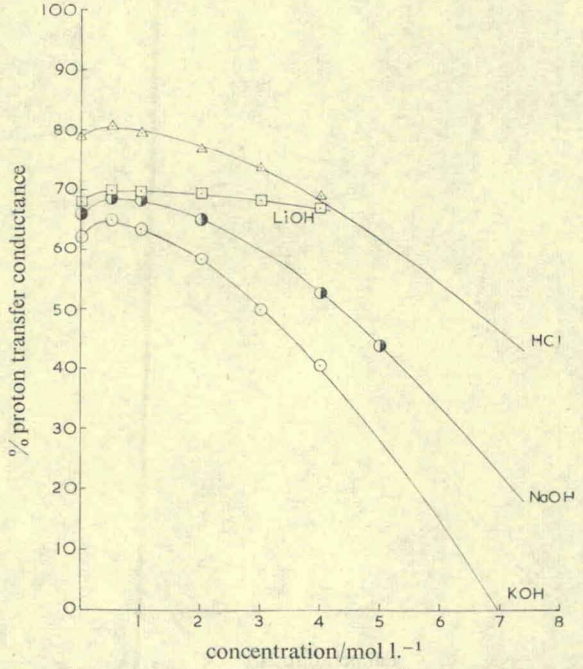

FIG. 4.—Concentration dependence of the percentage contribution of the proton transfer mechanism to the conductance of hydrogen and hydroxyl ions in aqueous acids and alkalis at 25° and atmospheric pressure. △, HCl; ⊡, LiOH; ◑, NaOH; ⊙, KOH.

It would appear that the extent of ionic association to form ion-pairs in these concentrated solutions is relevant. If the actual ionic concentration in a LiOH solution is much less than that in a KOH solution of the same molality, then the effect of the cations in governing successive rotations of water molecules should be less in LiOH than in KOH, and one might expect the proton transfer conductance to be hindered more in KOH solution than in the LiOH solution. In fact, there is considerable evidence to suggest that there is greater ionic association in LiOH than in NaOH and KOH solutions. The ion-pair formation constants [27] at zero ionic strength for LiOH, NaOH and KOH are 1.06 ± 0.5, 0.21 ± 0.06 and approximately zero l. mol^{-1} respectively. Also, the catalytic effect on the dedimerization of diacetone alcohol increases in the order LiOH < NaOH < KOH ~ RbOH.[28] At any given concentration, the activity coefficients of the hydroxides are in the order LiOH < NaOH < KOH, and although detailed interpretation of these data is not yet possible they do suggest that there is considerably more ion association in concentrated LiOH solutions than in KOH solutions of the same molality. Moreover, at a given molality, there appears to be an approximately linear decrease in the percentage proton transfer conductance as the activity coefficient increases in going from LiOH to NaOH to KOH. It therefore seems that differences in the mechanism of conductance in very concentrated solutions of LiOH, NaOH and KOH is related to differences in the degrees of association in these solutions. The more extensive ion association in concentrated LiOH than in KOH of the same molality implies that fewer water molecules are required for solvation of ions, so more are available for the proton transfer conductance of the hydroxyl ions.

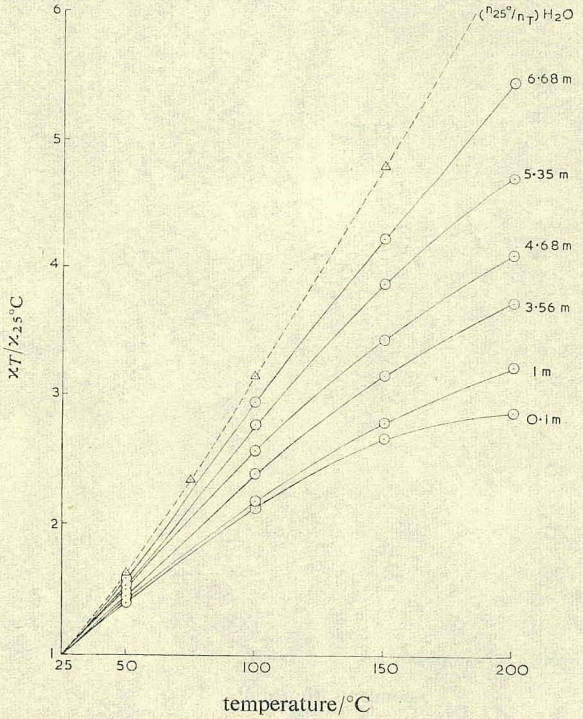

FIG. 5.—Temperature dependence of the conductance of aqueous KOH solutions at concentrations to 6.68 molal. Broken line shows temperature dependence of the fluidity of water relative to the value at 25°C; data from table 2.

The temperature dependence of the conductance of aqueous alkali metal hydroxide solutions also corroborates our view that the mechanism of conductance in very concentrated solutions is of the hydrodynamic type rather than the proton transfer type. Fig. 5 shows that with increasing concentration of KOH, e.g., the temperature dependence up to 200°C of the conductance approaches that of the fluidity of the solvent. The data used for fig. 5 are recorded in tables 2 and 5. Dilute KOH solutions show a maximum in $\kappa = f(T)$ at about 200°C, which moves to higher temperatures with increasing concentration.

TABLE 5.—EFFECT OF TEMPERATURE ON THE CONDUCTIVITY OF AQUEOUS KOH SOLUTIONS AT CONSTANT PRESSURES IN THE RANGE 1-3000 atm AND AT CONCENTRATIONS FROM 0.1 TO 6.68 molal.

Values $(\kappa_T/\kappa_{25°C})_P$, the ratio of the specific conductivity at temperature T to that at 25°C. These ratios are independent of pressure in the range 1-3000 atm (within the limit of accuracy implied by the number of quoted significant figures).

T/°C	0.1 m	1.0 m	3.56 m	4.675 m	5.346 m	6.68 m
25	1.0	1	1	1	1	1
50	1.41	1.44	1.46	1.50	1.53	1.59
100	2.12	2.18	2.39	2.56	2.76	2.94
150	2.66	2.78	3.16	3.44	3.87	4.23
200	2.87	3.22	3.72	4.11	4.72	5.46

When employing the Walden rule, however, ionic conductance and solvent viscosity are implicitly but not explicitly related properties.[29] The hydrodynamic mechanism of ionic mobility and the mechanism of viscosity in the pure solvent, though similar, cannot be identical because the former is complicated by the effect of the ionic charge on the solvent intermolecular forces near the moving ion. With this limitation, however, this use of the Walden rule to distinguish between the hydrodynamic and proton transfer mechanisms of ionic migration would seem to be justified.

The change in sign of $(\delta\kappa/\partial P)_T$ as the concentration is increased was observed for NaOH and KOH solutions at all the temperatures studied in the range 25-200°C. The pressure dependence of the conductance of concentrated LiOH solutions also remained essentially unchanged over this temperature range. This is illustrated in fig. 6, and some typical data are recorded in table 6. These indicate that our proposals concerning the effect of concentration on the conductance mechanism are also applicable at these elevated temperatures. Presumably the conductance of dilute alkaline solutions still occurs primarily by the proton transfer mechanism at these higher temperatures. Fig. 7 shows the effect of temperature on the estimated percentage contribution of the proton transfer mechanism to the total conductance of the hydrogen and hydroxyl ions in 0.01 molal HCl and KOH respectively. (These percentages are little different from those at infinite dilution.) The line for the conductance of the hydrogen ion has been included for comparison.

The percentage proton transfer conductance for the OH^- was estimated as

$$\left(\frac{\Lambda_{KOH}-\Lambda_{KCl}}{\Lambda_{KOH}-0{\cdot}5\Lambda_{KCl}}\right)\times 100 = \left(\frac{\lambda_{OH^-}-\lambda_{Cl^-}}{\lambda_{OH^-}}\right)\times 100,$$

and that for the H^+ as

$$\left(\frac{\Lambda_{HCl}-\Lambda_{KCl}}{\Lambda_{HCl}-0{\cdot}5\Lambda_{KCl}}\right)\times 100 = \left(\frac{\lambda_{H^+}-\lambda_{K^+}}{\lambda_{H^+}}\right)\times 100.$$

TABLE 6.—EFFECT OF PRESSURE ON THE CONDUCTANCE OF AQUEOUS HYDROXIDE SOLUTIONS AT ELEVATED TEMPERATURES; VALUES OF $(\kappa_P/\kappa_1)_T$ AT MOLALITIES IN THE RANGE 0.1-6.68 m.

KOH solutions at 50.2°C

P/atm	0.1 m	1 m	2.851 m	4.68 m	5.346 m	6.68 m
1	1	1	1	1	1	1
500	1.0230	1.012	0.9991	0.9974	0.9873	0.981
1000	1.0383	1.025	1.0018	0.9902	0.9781	0.967
1500	1.0488	1.038	1.0086	0.9865	0.9711	0.954
2000	1.0568	1.050	1.0129	0.9837	0.9654	0.944
2500	1.0635	1.059	1.0155	0.9812	0.9606	0.936
3000	1.0686	1.061	1.0168	0.9792	0.9574	0.928

KOH solutions at 101.7°C

P/atm	1 m	1.78 m	2.851 m	4.678 m	5.346 m	6.68 m
1	1	1	1	1	1	1
500	1.0099	1.0068	0.9983	1.0045	0.9869	0.9855
1000	1.0191	1.0130	0.9974	1.0080	0.9767	0.9754
1500	1.0283	1.0187	0.9988	1.0095	0.9506	0.9685
2000	1.0373	1.0234	1.0026	1.0085	0.9624	0.9626
2500	1.0450	1.0279	1.0079	1.0080	0.9584	0.9583
3000	1.0520	1.0316	1.0159	1.0085	0.9552	0.9549

	KOH solutions at 150.1°C			KOH solutions at 200.7°C	
P/atm	1 m	2.851 m	4.678 m	5.346 m	2.851 m	6.68 m
1	1	1	1	1	1	1
500	1.014	0.9906	1.0033	0.9807	0.9996	0.981
1000	1.028	0.9872	1.0060	0.9697	1.0004	0.967
1500	1.041	0.9891	1.0080	0.9615	1.0040	0.954
2000	1.053	0.9943	1.0094	0.9565	1.0125	0.944
2500	1.064	1.0038	1.0107	0.9545	1.0276	0.936
3000	1.074	1.0178	1.0114	0.9530	1.0538	0.928

	LiOH solutions at 101.8°C			LiOH solutions at 150°C		
P/atm	0.976 m	3 m	5 m	0.976 m	3 m	5 m
1	1	1	1	1	1	1
500	1.0236	1.0207	1.0163	1.0267	1.0311	1.0276
1000	1.0458	1.0419	1.0323	1.0536	1.0616	1.0547
1500	1.0671	1.0652	1.0487	1.0798	1.0947	1.0801
2000	1.0864	1.0883	1.0647	1.1052	1.1235	1.1028
2500	1.1046	1.1114	1.0804	1.1292	1.1498	1.1240
3000	1.1233	1.1345	1.0955	1.1521	1.1736	1.1434

These calculations involved the following assumptions: (*a*) the hydrodynamic conductance of the hydrogen ion is approximately equal to that of the K^+, (*b*) the hydrodynamic conductance of the hydroxyl ion is approximately equal to that of the Cl^-, and (*c*) the transport numbers of K^+ and Cl^- in dilute aqueous KCl are 0.5 are independent of temperature. Whilst these assumptions are questionable,[30] they are probably acceptable as a first approximation. Assumptions (*a*) and (*b*) are necessary in order to divide the total conductance of H^+ and OH^- into the contributions from the two mechanisms. If is possible that F^- might be slightly preferable to Cl^- in assumption (*b*), but data for the fluorides are much less complete than for the chlorides. Assumption (*c*) is necessary only because transport number data for aqueous solutions at high temperatures are insufficient.[28] The available

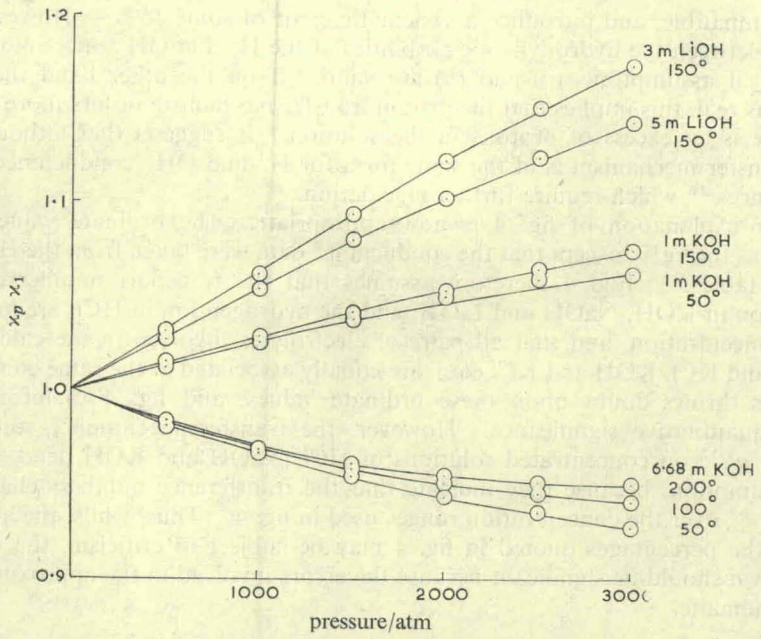

FIG. 6.—Pressure dependence of the conductivity of concentrated aqueous KOH and LiOH solutions at elevated temperatures.

data to 45° do indicate, however, that this assumption might only lead to an error of about 1 or 2 %. Therefore, the percentages quoted in fig. 7 are only estimates. They were calculated using the data of Noyes [21] and of Lown *et al.*[3]

The two lines in fig. 6 are almost parallel to one another, but their wide separation poses a problem. A possible explanation is that assumptions (*a*) and (*b*) are not

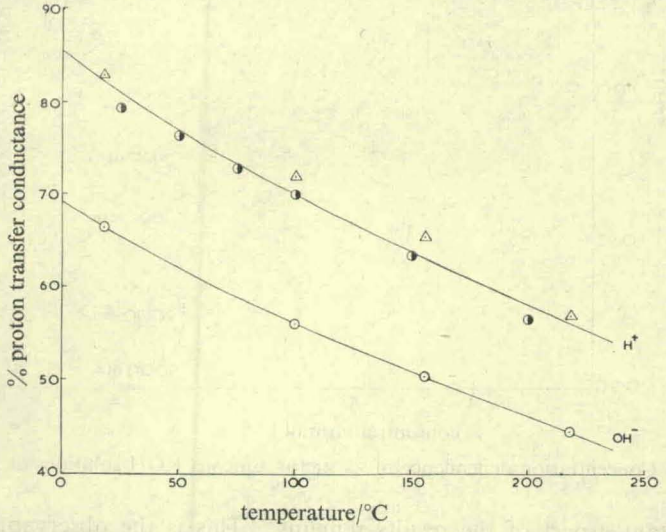

FIG. 7.—Temperature dependence of the percentage contribution of the proton transfer mechanism to the conductance of hydrogen and hydroxyl ions at very low concentrations in water. ◑, from data for KCl and HCl at 0.01 molal, ref. (3). △, from data for NaCl and HCl at infinite dilution, ref. (31). ○, from data for NaOH and NaCl at infinite dilution, ref. (31).

entirely compatible, and introduce a systematic error of some 15 %. However, the difference between the hydrodynamic mobilities of the H^+ and OH^- only amounts to about 4 % if assumptions (*a*) and (*b*) are valid. If on the other hand the 15 % difference is real, this implies that the proton transfer mechanism occurs more readily when there is an excess of protons in the solution. It suggests that although the proton transfer mechanism is of the same form for H^+ and OH^- conductance, there are differences [18] which require further elucidation.

Further explanation of fig. 4 is now appropriate. The ordinate values were calculated as for fig. 7, except that the conductance data were taken from the Landolt-Börnstein tables.[25] Fig. 4 therefore assumes that the transport numbers of the hydroxyl ion in KOH, NaOH and LiOH, and the hydrogen ion in HCl, are independent of concentration, and that all pairs of electrolytes involved in the calculation (i.e., HCl and KCl, KOH and KCl etc.), are equally associated at the same concentration. This throws doubt upon these ordinate values, and fig. 4 therefore only has semi-quantitative significance. However, the transference number studies of Lengyel *et al.*[32] on concentrated solutions of HCl, NaOH and KOH, lend support to the assumption, because they indicate that the transference numbers change by less than 5 % over the concentration ranges used in fig. 4. Thus, whilst the absolute values of the percentages quoted in fig. 4 may be subject to criticism, the relative trends shown should be significant because the errors involved in the approximations will be systematic.

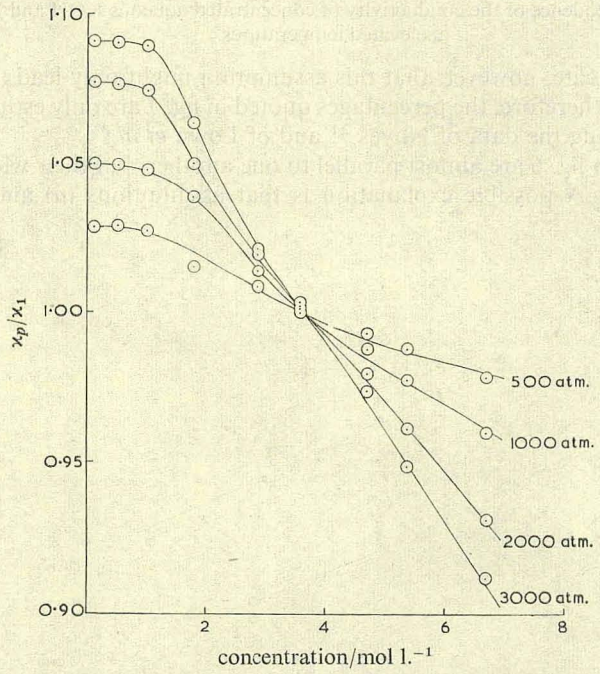

FIG. 8.—Concentration dependence of $\varkappa_p/\varkappa_1$ for aqueous KOH solutions at 25°.

One important aspect of the results remains. This is the observation that the pressure dependence of the conductance is almost independent of concentration up to about 1 molal. Fig. 8 exemplifies the behaviour for KOH at 25°C. Similar plots were obtained for NaOH and LiOH, except that in the latter case κ_p/κ_1 did

not pass through unity, (although extrapolation of the data indicated that this might have occurred at about 10 or 11 molal if it had not been prevented by prior saturation of the solution).

Now the effect of pressure on the concentration dependence of the equivalent conductance in very dilute solutions is predicted by the Debye-Hückel-Onsager theory. Hamann [14] pointed out that the limiting Onsager slope decreases by more than 10 % over the range 1-3000 atm at 25°C. This was calculated using data for the pressure dependence of the viscosity and dielectric constant of water. Thus, according to the Onsager theory, κ_{2000}/κ_1 should increase by about 0.2 % over the range 0-0.01 molal, while the present results indicate that κ_p/κ_1 is almost independent of concentration even up to about 1 molal. It therefore appears that in considering $(\kappa_p/\kappa_1) = f(\text{concentration})$, rather than $\kappa = f(\text{concentration})$ at constant pressure, those effects which normally result in failure of the Debye-Hückel-Onsager limiting law at concentrations above about 0.01 molal are to some extent masked. This does not imply that it is only ionic interactions which determine the effect of concentration on κ_p/κ_1 to 1 molal, otherwise κ_{2000}/κ_1 might increase by several percent, whereas in fact it decreases by less than 0.3 %. It is possible, however, that in the range 0.1-1 molal, there is some cancellation between the effects of ionic interactions and other, short-range forces (e.g., hydration effects) on the effect of concentration in the pressure dependence of ionic conductance. When the concentration has been increased to about 2 molal, however, these ion-solvent effects become particularly important and κ_p/κ_1 then decreases markedly with concentration.

The conductance of dilute aqueous strong acids increases with pressure,[3, 14] but with increasing concentration we can predict that the increase of conductance with pressure should diminish, and at sufficiently high concentrations the conductance should decrease with pressure provided that saturation does not occur first. Indeed we have observed such a reversal in behaviour of $\kappa = f(P)$ for aqueous solutions of orthophosphoric acid at 25°.[33] We therefore conclude, as indicated in fig. 4, that the proton transfer mechanism of conductance of hydrogen and hydroxyl ions in dilute aqueous solutions of acids and bases is gradually erased as the concentration is increased above about 1 molal, and that the conductance of these ions occurs increasingly by the hydrodynamic mechanism.

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