Apparent Molar Ionic Products of Water in Aqueous Potassium Nitrate Solutions and Calibration of the Glass Electrode as a Wide-range Proton Concentration Probe

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Precise values of the apparent molar ionic (stoicheiometric) products of water in KNO_3 solutions have been determined in the temperature range 15—45 °C and over a range of ionic strengths 0·060—0·180M by means of a glass, silver–silver chloride electrode system calibrated as a proton concentration probe. The results are extrapolated to infinite dilution and compared with values previously reported in aqueous KCl solutions. The accuracy and precision of the results were found to be limited by the reproducibility of the Beckman ' Research ' meter used confirming that, properly calibrated, such electrode systems can replace the hydrogen electrode without undue loss of accuracy. Proton dissociation constants for the 2-hydroxyethylammonium ion are also reported for 0·060M-KNO_3 solutions and the use of this reagent as a calibrant in glass-electrode work is suggested.

SINCE no previous determination of the apparent ionic products of water in KNO_3 solutions over the required range of temperature and ionic strength has been made, the stoicheiometric values reported here were determined as a necessary preliminary to a study of the ionisation of some 4-substituted catechols under the same conditions.[1] The constants were determined potentiometrically by a titration method. Glass electrodes were used in these determinations in order to maintain the conditions used in the catechol investigation.[1] Throughout these determinations the pcH scale was employed, where pcH $= -\log_{10}[H^+]$, and square brackets have the usual meaning of concentrations in mol l^{-1}. A direct method of calibration of the glass electrode in terms of the pcH scale was used for the following reasons: (i) calibrations relying on buffers such as that suggested by McBryde [2,3] are limited to the accuracy of the buffers; (ii) when titrating very weak acids of the catechol type log K_w is required to a high degree of precision; and (iii) the electrodes can usually be calibrated from the known initial $[H^+]$, thus obviating transfer from calibrating to titration media.

EXPERIMENTAL

Hydrogen-ion concentrations were measured with a Beckman ' Research pH-Meter ' reproducible to 0·001 pcH unit in conjunction with a cell consisting of a glass electrode

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[1] R. F. Jameson and M. F. Wilson, following paper.
[2] W. A. E. McBryde, *Analyst.*, 1969, **94**, 337.
[3] W. A. E. McBryde, *Analyst.*, 1971, **96**, 1147.

and ' Wilhelm '-type reference half-cell with J-shaped liquid junction designed by Forsling *et al.*[4] The cell may be represented as in (1), where X has the range of values 0·060—0·180.

$$\begin{array}{c|c|c|c|cc} & \mathrm{KNO_3} & \mathrm{KNO_3} & \mathrm{KNO_3} & & \\ & (1{\cdot}99\,\mathrm{M}) & (2{\cdot}00\,\mathrm{M}) & [(X-Y)\mathrm{M}] & & \\ \mathrm{Ag(s)}, & & & & \mathrm{G.E.} & (1) \\ \mathrm{AgCl(s)} & & & & & \\ & \mathrm{KCl} & & \mathrm{HNO_3} & & \\ & (0{\cdot}01\,\mathrm{M}) & & (Y\mathrm{M}) & & \end{array}$$

The pH meter and test solution were earthed to a single point to prevent the introduction of an earth loop. The cell incorporated a Teflon stirrer and inlet tube for oxygen-free nitrogen gas which was used to saturate the cell solution. A solution of vanadium(II) ions and a pre-saturator solution of KNO_3 also immersed in the thermostat-bath were used to treat nitrogen gas before bubbling through the cell. The use of an oil-bath prevented interference from outside electrical effects and protected the electrodes from the effect of light; at all times accuracy of temperature control was better than $\pm 0{\cdot}01$ °C. Fluctuations in room temperature were also found slightly to affect the measurements, and so room temperature was maintained at $24{\cdot}0 \pm 0{\cdot}5$ °C. Because the electrode system was standardized internally from the known initial $[H^+]$ in the solutions to be titrated (thus avoiding transference of electrodes from one solution to another after standardization) the buffer-adjustment control on the meter was sealed and not used. This has the added advantage over the usual methods of calibration *via* buffers, that this control is too coarse in most commercial pH meters.

Treatment of the Glass Electrodes.—Several makes of electrode were tried with final selection of the wide-range Beckman AS7LB as the most reproducible. However the reproducibility was limited to about 15 titrations and indeed some new ones had to be rejected. Initial tests revealed that good reproducibility between titrations was only obtainable if the electrodes were subjected to careful pre-treatment and storage between experiments. A set of four glass electrodes was used and for a series of titrations the electrodes were used consecutively; they were stored in a thermostatted water-bath in solutions having the same initial concentrations of ions as present at the beginning of a titration. Electrodes were allowed to soak at the correct temperature for 12 h before use, and were calibrated as detailed below. Drifting during titrations was considered non-existent since at no time was a difference in reading observed on returning to a low pH as a check after each titration.

Preparation of Silver–Silver Chloride Electrodes.—Electrodes were prepared by the electrolytic method using a modification of the method due to MacInnes and Parker.[5] Platinum grids, obtained from Johnson-Matthey, were *ca.* 1 cm^2 in area and attached to platinum wire which was sealed into B10 soda-glass cones. It was arranged that the electrodes could be rotated during electroplating, thus stirring the catholyte and, by preventing electroplating shadows, resulting in smooth deposits. The grids were alkali-cleaned, anodised in concentrated nitric acid, and then thoroughly rinsed in flowing conductivity water before silver plating. The cyanide-free silver plating solution was of potassium argentocyanide (30 g l^{-1}) and was carefully filtered before use. The anodes were platinum rods which were surrounded by Whatman filter tubes to prevent contamination of the solution. The current density was 0·8 mA cm^{-2} and plating was continued for 10 h. After being soaked overnight in ammonia solution, the electrodes were rinsed for 48 h in flowing conductivity water. Finally the grids were chloridized for 3 h in 0·10M-HCl solution, current density 1 mA cm^{-2}, and then rinsed for 24 h in flowing conductivity water. Electrodes were ' plum coloured ' but turned brown on storage in M/20-KCl solution in darkness. The e.m.f.'s of electrodes made in this way were stable and reproducible to better than 0·02 mV (measured in M/20-KCl by means of a Pye Universal Precision Potentiometer).

Preparation of Materials.—Volumetric solutions of nitric acid were made up in carbonate-free deionized water from B.D.H. ampoules and independently standardized with AnalaR sodium carbonate which was prepared by Vogel's method.[6] Nitric acid solutions were standardised with potassium hydroxide as titrant, prepared by Vogel's electrolytic method.[6] AnalaR potassium nitrate was used to adjust the ionic strength of the solutions. 2-Aminoethanol (B.D.H.) was twice distilled under reduced pressure (19 mmHg) and the distillate of b.p. 75—76 °C was collected; the purity as determined by titration was 99·98%.

RESULTS

Calibration of the Glass Electrodes.—Calibration at low and high pcH was carried out by titrating strong acid with strong base of known concentrations. A previous investigation by Gorton and Jameson,[7] confirmed in the present work, involved the titration of acetic acid with strong base with the use of data of Harned and Owen.[8] This revealed that in the pcH range 2—7 glass electrodes of the type used in this work obey the Nernst relation, and that therefore for solutions for which the activity coefficients are kept sensibly constant the meter reading is proportional to $-\log\,[H^+]$, and it was thus only necessary to confirm this linearity and the slope in the higher pcH range *ca.* 8—11·5.

This was achieved by titration of solutions of protonated 2-aminoethanol with strong base in various ionic strength backgrounds of KNO_3. Reliable experimental data for the ionisation of 2-aminoethanol have been published by Bates and Pinching[9] who studied the ionisation at various temperatures and ionic strengths using a Harned cell. From these data values of the dissociation constants of protonated 2-aminoethanol at an ionic strength of 0·060M were calculated by use of revised values of the Debye–Hückel constants A and B.[10] For each volume of potassium hydroxide added in a titration, a value of pcH was calculated by use of the values of the dissociation constant of 2-hydroxyethylammonium ion calculated as above. The calculated pcH values were then compared with the experimentally deter-

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[4] W. Forsling, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, 1952, **6**, 901.

[5] D. A. MacInnes and K. J. Parker, *J. Amer. Chem. Soc.*, 1915, **37**, 1445.

[6] A. I. Vogel, ' A Textbook of Quantitative Inorganic Analysis,' Longmans, London, 1961.

[7] J. E. Gorton and R. F. Jameson, *J. Chem. Soc.* (*A*), 1968, 2615.

[8] H. S. Harned and B. B. Owen, ' The Physical Chemistry of Electrolytic Solutions,' Reinhold, New York, 2nd edn., 1950, p. 523.

[9] R. G. Bates and G. D. Pinching, *J. Res. Nat. Bur. Stand.* 1951, **46**, 349.

[10] R. A. Robinson and R. H. Stokes, ' Electrolytic Solutions,' Butterworths, London, 2nd edn., 1959.

mined or apparent values and the difference between them, ΔpcH, was calculated. The small, but constant, value of ΔpcH was ascribed to the fact that no background electrolyte was employed in the work of Bates and Pinching; thus it is in principle possible, by using this as a further correction, to calculate accurate pK values for the dissociation of protonated 2-aminoethanol in KNO_3 solutions. This was done for the 0·060M-KNO_3 solutions by use of the programme LETAGROPVRID[11] and values are shown in Table 1 together with those calculated from the experimental data of Bates and Pinching.[9] At very low ionic strengths a fairly large error due to changes in activities was observed, but this was readily allowed for in making use of the calibration data to check linearity of the glass electrode.

TABLE 1

Dissociation constants of protonated ethanolamine at an ionic strength of 0·060M

t/°C	pK[a]	pK[b]
15	9·764 ± 0·001 *	9·779
25	9·477 ± 0·001	9·471
35	9·201 ± 0·001	9·181
45	8·951 ± 0·001	8·912

* Standard deviations.

[a] This work, molar scale, KNO_3. [b] Bates and Pinching, molal scale, no background salt.

Investigation of Liquid Junction Potential.—The liquid junction potential associated with the 'Wilhelm' reference half-cell has been investigated by Biedermann and Sillén.[12] These workers found that when the bridge solution and the test solution contained appreciably different concentrations of hydrogen and hydroxyl ions, *i.e.*, at the low and high regions of the pcH scale respectively, it was not possible to eliminate the junction potential since the mobilities of these ions are very high. In this case the value of E_j, the liquid junction potential of the cell, was determined experimentally as a function of the test solution composition. Experimental E_j values were in good agreement with values calculated by use of a form of Henderson's equation.[13]

In this work, because the concentration of background electrolyte in the test solution varied in the range 0·060—0·180M compared with the concentration of the bridge solution which was 2·00M-KNO_3, the junction potential was expected to be significantly large but constant throughout most of the pcH range. The variation of E_j was investigated by titration of strong base against strong acid in the appropriate background electrolyte concentration with the Wilhelm reference half-cell. The stoicheiometric concentration of hydrogen ions was calculated for each volume of base added and hence the term $2{\cdot}303RT/F \log_{10} [H^+]$. Plots of e.m.f. against $-\log_{10} [H^+]$ were made and deviations from linearity were observed at the low and high ends of the pcH scale; the investigation showed that in the range $2{\cdot}2 < \text{pcH} < 11{\cdot}8$ the variations in the total liquid junction potential were negligible. An estimate of the absolute value of E_j was not attempted in this work, but since it was constant in the range of pcH under investigation no such estimate was required.

Determination of the Apparent Ionic Products of Water.—For that part of the pcH range in which the Nernst relation is obeyed and where E_j is constant, the expression for the e.m.f. of the cell can be written as (2), where E_0' is specific

$$E = E_0' - 2{\cdot}303RT/F \log_{10} (a_{H^+}) \qquad (2)$$

for the particular ionic medium and salt bridge (E_j = constant) combination. Hence, on the acid side, the pH-meter reading Q_1 is related to the concentration of hydrogen ions by expression (3), where $f_\pm$ is the mean ionic activity

$$Q_1 = -\log_{10} f_\pm [H^+] + c \qquad (3)$$

coefficient (appropriate for these solutions) and c is a constant. Similarly the meter reading on the base side, Q_2, is given by expression (4). From these equations K_w is given by equation (5), it being assumed that $f_\pm$ is constant

$$Q_2 = -\log_{10} f_\pm \cdot \frac{K_w}{[OH^-]} + c \qquad (4)$$

$$-\log_{10} K_w = Q_2 - Q_1 + \text{pcH} + \text{pcOH} \qquad (5)$$

over the entire range. Determinations of pK_w were made by titrating solutions of nitric acid with potassium hydroxide at the correct ionic strength. Five pairs of values of meter readings Q_1 and Q_2 were selected from that part of the pcH range where the Nernst relation was obeyed, and for the calculation of pK_w the 25 possible permutations of Q_1 and pcH with Q_2 and pcOH were made by substitution into equation (5). The values of pK_w are summarised in Table 2.

TABLE 2

Apparent molar ionic products of water together with standard deviations measured in an ionic medium of KNO_3

Ionic strength/ M	pK_w at indicated temperatures			
	15 °C	25 °C	35 °C	45 °C
0·060	14·159 ±0·002	13·809 ±0·002	13·491 ±0·002	13·203 ±0·002
0·100	14·132 ±0·002	13·778 ±0·002	13·457 ±0·002	13·168 ±0·002
0·140	14·116 ±0·002	13·753 ±0·002	13·441 ±0·002	13·154 ±0·004
0·180	14·101 ±0·003	13·749 ±0·002	13·423 ±0·002	13·138 ±0·003

DISCUSSION

No previous systematic determination of the ionic products of water in dilute aqueous KNO_3 solutions has been made (although Harned and his co-workers[8] studied the ionisation in various media, their work excluded the use of KNO_3 as an electrolyte), but for a single determination of the constant in 0·100M-KNO_3 and at 25 °C by Eilbeck *et al.*[14] (their value of 13·780 is in very good agreement with ours). Our results are compared with values determined by Harned and Hamer[15] (in aqueous KCl) in the Figure by plotting the values together and extrapolating them to infinite dilution. (The molal

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[11] N. Ingri and L. G. Sillén, *Arkiv Kemi*, 1964, **23**, 97.

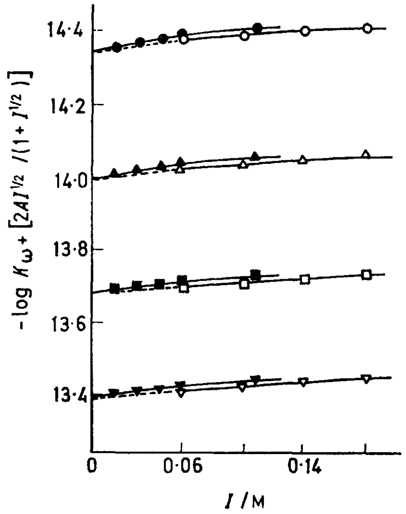
[12] G. Biedermann and L. G. Sillén, *Arkiv Kemi*, 1953, **5**, 425.

[13] P. Henderson, *Z. phys. Chem.*, 1908, **63**, 325.

[14] W. J. Eilbeck, F. Holmes, G. G. Phillips, and A. E. Underhill, *J. Chem. Soc.* (*A*), 1967, 1161.

[15] H. S. Harned and W. J. Hamer, *J. Amer. Chem. Soc.*, 1933, **55**, 2194.

ionic products of water, $m_{\mathrm{H}}m_{\mathrm{OH}}$, in aqueous KCl were calculated from Harned and Hamer's results and hence the log product log $m_{\mathrm{H}}m_{\mathrm{OH}}$. The figure, in which A is the Debye–Hückel constant and I the ionic strength, is one form of Debye–Hückel type extrapolation which may be applied to results of this kind.) An extrapolation similar to this was made by Harned and Hamer [15] to obtain values of K_{w} at infinite dilution. The Figure shows that our values extrapolate well; although, using the glass electrode, we could not determine values of pK_{w} at ionic strengths less than 0·060M, the trend of the results indicates that the intercepts will be in good agreement with those determined by Harned and Hamer using a hydrogen electrode.



Extrapolation of pK_{w} values to $I \rightarrow 0$ at: 15 (○), 25 (△), 35 (□), and 45 °C (▽). Open symbols refer to present work in KNO_3 and filled symbols to the work of Harned and Hamer in KCl (ref. 15)

It is also noteworthy that our work shows that, with care, the limit of precision (standard deviation) of the glass electrode used as a proton concentration probe is equal to the reproducibility of the Beckman Research pH meter. This seems to be in agreement with the more recent work of Henry *et al.*[16] who show that the precision can even *equal* that of the hydrogen electrode if more sophisticated apparatus is employed to measure the e.m.f.

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[16] R. P. Henry, J. E. Prue, F. J. C. Rossotti, and R. J. Whewell, *Chem. Comm.*, 1971, 868.