Acidity Function Calculations for Perchloric Acid

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A COMPARISON has recently been made[1] of the degrees of dissociation of perchloric acid obtained from Raman and nuclear magnetic resonance methods. While all the results agree up to a concentration of about 5 M, at higher concentrations however not only do the two methods give different results, but workers using the same technique obtain different results. It seemed appropriate, therefore, to attempt calculations aimed at detecting the first appearance of un-dissociated perchloric acid using acidity function (H_0) and water activity data. The H_0 data for the acid have recently been accurately redetermined and extended,[2] using a reliable set of structurally similar indicators.

A simple relationship between H_0 and water

activity for strong acids has been suggested by Bascombe and Bell,[3]

$$-H_0 - \log c + h \log a = \log f_B = A \cdot c \qquad (1)$$

where c is molarity of acid, h is the number of water molecules firmly hydrating the proton, a is water activity, f_B is the molar activity coefficient of free base used to measure H_0 and A is the salting-out coefficient.

For an acid dissociating to an extent α, Equation (1) would become,

$$-H_0 - \log \alpha c + h \log a = A \alpha c \qquad (2)$$

For weak acids α is small even at small values of c, and since values of A are about 0·1 (or less) the term $A \alpha c$ can be neglected. This means that
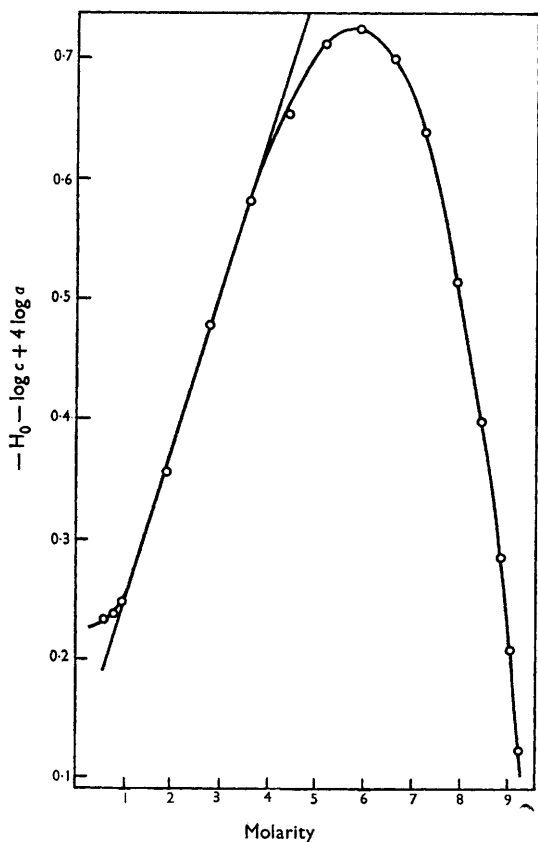
values of α may be calculated from the left-hand side of Equation (2), cf. iodic acid.[4] For strong acids the term $A \alpha c$ may not be negligible. If a constant value of h is assumed (4 in this case) then a graph of $-H_0 - \log c + 4 \log a$, ($\alpha = 1$), against c should be linear over the range of concentration where the acid is completely dissociated and when h remains constant. The gradient of the line should be equal to A in this range. The original calculations of Bascombe and Bell[3] gave a linear graph up to 8 M and with a gradient of 0·1.

Using the more accurate H_0 data[2] and the water activities of Robinson and Baker[5] the above function has been plotted and is shown in the Figure. The activity and concentration data were used to the third decimal place and the H_0 data to the second place of decimals. The graph is only linear between 1 M and 4 M (3·8) and with a gradient of 0·13. The maximum in the curve occurs at about 5·8 M.

It is interesting to consider the effects of incomplete dissociation and changes in h from the value of 4 upon the form of the graph. Incomplete dissociation ($\alpha < 1$) will cause the graph to deviate from linearity and in the direction observed. This occurs at about 4 M and it is interesting that the chlorine resonance measurements,[1] which appear to be more unequivocal than p.m.r. results, show the first appearance of undissociated acid at about this concentration.

The incomplete dissociation of the acid, however, is not sufficient alone to explain the maximum in the curve at about 6 M. If contributions from lower hydrates are becoming important at this concentration, i.e., values of h less than 4, then this would also cause the plotted function to behave in the way observed in the Figure. This shows the importance of the need to consider successive hydration equilibria[6] in quantitative calculations on the constitution of strong acid solutions. It is not possible to calculate values of α for perchloric acid using Equation (2) because of this.

The two points in the Figure at concentrations below 1 M are higher than the linear portion of the graph. This is probably not fortuitous since a value of $h > 4$ would cause this, cf., Wyatt's treatment[6] has $h = 5$ in the most dilute solutions.

Molarity

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