Dissociation of Perchloric Acid measured by Raman and N.m.r. Spectrometry

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RAMAN measurements of the dissociation of perchloric acid at 25—35° have been made recently in three laboratories.[1-3] There is unanimous agreement, contrary to previously published evidence by the Raman photographic method[4] and by proton magnetic resonance,[5,6] that perchloric acid is completely dissociated in aqueous solution up to at least 8M. Above 8M there are discrepancies between the values of the degree of dissociation (α) reported by the three groups.[1-3] the results of two of these groups[1,2] are shown in the Figure; the third group[3] found complete dissociation up to 12M. The measurements made in this laboratory[2] have been confirmed by further measurements shown in the Figure, and by additional measurements on the 631 cm.$^{-1}$ and 462 cm.$^{-1}$ lines which, although of lower accuracy because their specific intensities are lower, are in overall agreement.

In an attempt to resolve the large discrepancy shown in the Figure between the n.m.r. data[5,6] and the Raman measurements up to 8M, new proton resonance measurements have been made using an AEI RS 2 spectrometer operating at 60 Mc./sec. Susceptibility corrections were applied.

The proton magnetic resonance method of determining α is based on measurements of the chemical

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[1] K. Heinzinger and R. E. Weston, *J. Chem. Phys.*, 1965, **42**, 272.
[2] A. K. Covington, M. J. Tait, and W. F. K. Wynne-Jones, *Proc. Roy. Soc.*, 1965, *A*,**286**, 235.
[3] E. L. Glasner and T. F. Young, unpublished; quoted by Heinzinger and Weston (ref. 1).
[4] O. Redlich, E. K. Holt, and J. Bigeleisen, *J. Amer. Chem. Soc.*, 1944, **66**, 13.
[5] G. C. Hood, O. Redlich, and C. A. Reilly, *J. Chem. Phys.*, 1954, **22**, 2067.
[6] G. C. Hood and C. A. Reilly, *J. Chem. Phys.*, 1960, **32**, 127.

shift as a function of concentration. The observed shift relative to water (s) is a concentration-weighted average[7] of the shifts arising from the proton in the hydronium ion (s_1) and the undissociated acid (s_2)

$s = s_1\alpha p + \frac{1}{3}[s_2(1 - \alpha)p]$ where $p = 3x/(2 - x)$ and x is the stoicheiometric mole fraction of the acid. s_2 was determined[5,6] from measurements on the anhydrous acid, a procedure which is open to criticism, but α is relatively insensitive to the value chosen for s_2. This is not so for s_1 to which α is extremely sensitive. Measurements proved to be possible down to 0·05M, much lower than previously reported,[5,6] and hence s_1 can be evaluated accurately. The value (9·14 p.p.m.) is lower than that used by Hood, Redlich, and Reilly[5] (9·17 p.p.m.) or Hood and Reilly[6] (10·30 p.p.m.). The latter work contains errors in the calculation of p for the six lowest concentrations and hence the incorrect limiting slope was drawn. When this mistake is corrected, results from the two determinations are in excellent agreement with Hindman's smoothed values[8] and the present work. α-Values recalculated using the lower s_1 (and $s_2 = 5{\cdot}46$ p.p.m.) indicate complete dissociation up to 6M but above this value are lower (by 10% at 11M) than the lowest Raman values.

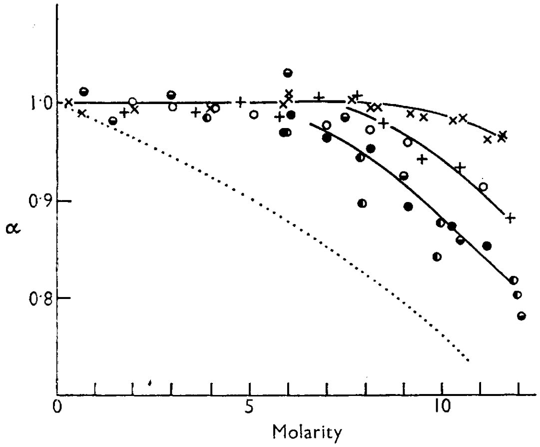

FIGURE. *Degree of dissociation of Perchloric Acid. Raman measurements:*—+ *Heinzinger and Weston*[1] *at* 33°, × *Covington, Tait, and Wynne-Jones*[2] *at* 25°, *plus some additional measurements.*

N.m.r. measurements at 25°:------ *Hood and Reilly*[6] (*original data*), ◐ *Hood, Redlich, and Reilly*[5] (*recalculated*), ◒ *Hood and Reilly*[6] (*recalculated*), ● *this work* (*proton resonance*), ○ *this work* (*chlorine resonance*).

It has been suggested[1] that ^{35}Cl resonance should be more unequivocal than proton m.r. measurements, being less susceptible to hydrogen-bonding and anion effects.[10] Previously reported values[9] are of insufficient accuracy to test this. Using a substitution method with the most concentrated (11·2M) solution as reference, the relative chlorine resonance shifts (s_r) have been redetermined at 5 Mc./sec. α-Values were calculated from the equation

$$s_r = s_0(1 - \alpha)$$

where[9] s_0 (the shift of the anhydrous acid) = 40 ± 3 p.p.m., and by taking $\alpha = 1$ in the most dilute solution studied (2M). The results confirm Heinzinger and Weston's suggestion[1] and lie close to their Raman results, although this may be accidental. There is an uncertainty of about ±1% in all the chlorine resonance points arising from scatter in the measurements at 2M. The uncertainty in the s_0 value leads to a maximum error of ±1% in the most concentrated solution.

Proton and chlorine n.m.r. studies and Raman measurements show that perchloric acid is completely dissociated up to 6—8M. At higher concentrations, chlorine resonance and Raman measurements indicate dissociation greater than 91% at 12M but differences in the Raman determination due to instrumental factors remain to be resolved. Proton resonance furnishes low values for the dissociation, probably arising from changes in the hydronium ion chemical shift with concentration.

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[7] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, 1953, **21**, 1688.
[8] J. C. Hindman, *J. Chem. Phys.*, 1962, **36**, 1000.
[9] Y. Masuda and T. Kanda, *J. Phys. Soc. Japan*, 1954, **9**, 82.
[10] A. J. Kresge, *J. Chem. Phys.*, 1963, **39**, 1360.