The Degrees of Dissociation of Methanesulphonic Acid from Acidity Function Data

By J. G. DAWBER

(*Department of Chemistry, North Staffordshire College of Technology, Stoke-on-Trent*)

THE degrees of dissociation of methanesulphonic acid in aqueous solution, obtained by different methods, have recently been compared.[1,2] While the values obtained by Raman spectroscopy[1] and proton magnetic resonance[2] are compatible, those calculated[3] from measurements of the Hammett acidity function, H_0,[4] are completely at variance with the spectroscopic values (see Figure 1). The values calculated from the H_0 data were based on Bascombe and Bell's[5] theory for the hydration of the proton to $H(H_2O)_4^+$. The question arises, therefore, whether the H_0 results[3] are at fault or whether the simple hydration treatment for the proton[5] is invalid. Some acidity function calculations for the perchloric acid–water system[6,7] have demonstrated the deficiencies of such elementary hydration treatments.[5,8] A more realistic approach to the problem of proton hydration would seem to be that given by Wyatt[9] which involves several successive hydration equilibria.

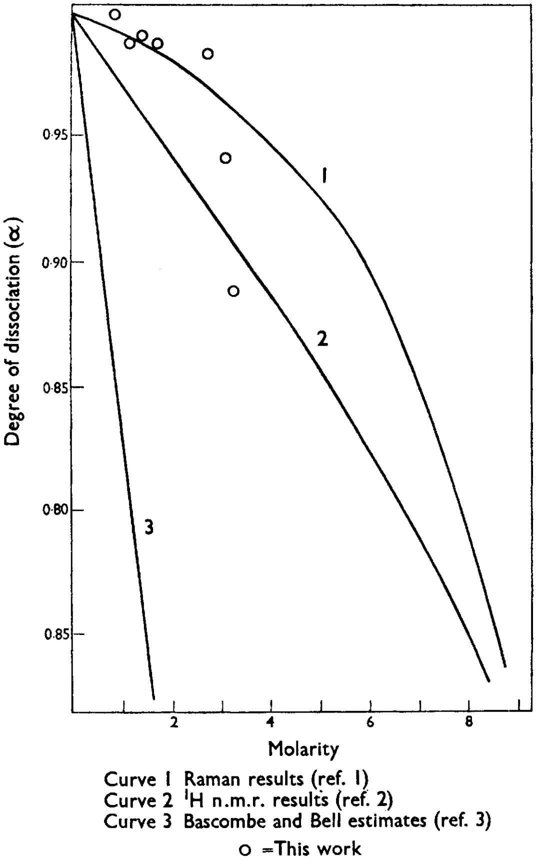

FIGURE 1. *Degrees of dissociation.*

By modifying Wyatt's treatment to include incomplete dissociation of the acid, an equation has been derived[7] which allows calculations of the degrees of dissociation (α) to be made from acidity function data and activities of water (a) in the solutions. This equation may be written

$$\frac{1}{\alpha} = \left(\frac{1-a}{aF}\right)\frac{1}{\text{antilog}[-(H_0 + A\alpha c + k)]} - 1{\cdot}0$$

where $F = (1 + 20a + 150a^2 + 500a^3 + 625a^4)$, c is the molarity of acid, A is the Setschenov salting-out coefficient, and k is a constant. The values of A and k may be obtained from a graph[7] of $-\left\{\log\frac{(1-a)}{2aF} + H_0\right\}$ against c, when the gradient gives the value of A and the intercept gives the value of k.

Such a graph for the methanesulphonic acid–water system has been plotted in Figure 2. The experimental H_0 data are those of Bascombe and Bell.[3] The water activities were obtained by a Gibbs–Duhem calculation and graphical integration from the mean molal activity coefficients for methanesulphonic acid.[10] One value of water activity was needed for this calculation and it was assumed to be 0·9966 at a molality of 0·1. This is the value for hydrochloric acid at the same molality calculated from the osmotic coefficient.[11] This assumption is probably reasonable in view of the similarities of the two systems.[10] Unfortunately the mean molal activity coefficients for methane sulphonic acid only extend up to 4 molal acid (about 3·3 molar),[10] which limits the range for

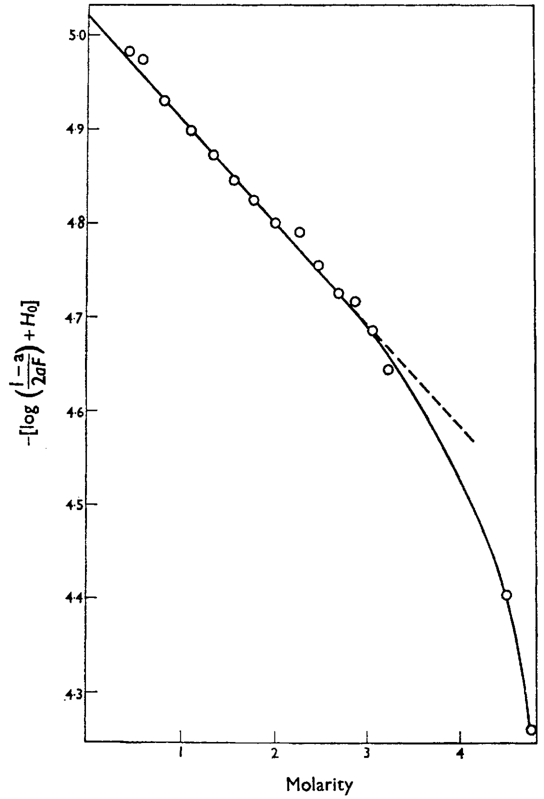

FIGURE 2. *Determination of* A *and* k.

which the calculations of the present work could be carried out.

The slope of the graph in Figure 2 gave a value for A of $-0{\cdot}109$. This is a reasonable value for a Setschenov coefficient, and a negative value is not uncommon especially where large anions and organic ions are concerned.[12] The intercept of the graph gave a value of k of 5·02 (*cf.*, 4·98 for perchloric acid[7]).

Using these values for A and k, values of α were calculated using the above equation, and these are compared with the other published values in Figure 1. The calculated values of this work are in reasonable accord with the spectroscopic values,[1,2] but do not allow a decision to be made between the two sets of results, which are probably limited by the accuracy of the water activities used in the calculations. However, the theory[7] based on the Wyatt's treatment[9] of proton hydration has given results for α which are compatible with the spectroscopic values.[1,2] On the other hand the Bascombe and Bell[3] estimates for α calculated from the same H_0 data but based on a simple hydration treatment[5] are seen to be far too low.

This would seem to suggest that while the experimental H_0 results for methanesulphonic acid[3] are correct, the simple model for the hydration of the proton[5] to $H(H_2O)_4^+$ is unacceptable for this acid.

(*Received, October 27th*, 1967; *Com.* 1161.)

---

[1] J. H. R. Clarke and L. A. Woodward, *Trans. Faraday Soc.*, 1966, **62**, 2226.

[2] A. K. Covington and T. H. Lilley, *Trans. Faraday Soc.*, 1967, **63**, 1749.

[3] K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1959, 1096.

[4] L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721; L. P. Hammett and M. A. Paul, *ibid.*, 1934, **56**, 827.

[5] K. N. Bascombe and R. P. Bell, *Discuss. Faraday Soc.*, 1957, **24**, 158.

[6] J. G. Dawber, *Chem. Comm.*, 1966, 3.

[7] J. G. Dawber, *J. Chem. Soc.* (*A*), 1966, 1056.

[8] E. Högfeldt, *Acta Chem. Scand.*, 1960, **14**, 1627; L. Leifer and E. Högfeldt, Proceedings of the First Australian Conference on Electrochemistry, Pergamon Press Ltd., London, 1967, p. 107.

[9] P. A. H. Wyatt, *Discuss. Faraday Soc.*, 1957, **24**, 162; M. Ojeda and P. A. H. Wyatt, *J. Phys. Chem.*, 1964, **68**, 1857.

[10] H. P. Gregor, M. Rothenberg, and N. Fine, *J. Phys. Chem.*, 1963, **67**, 1110.

[11] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1955, p. 468.

[12] F. A. Long and W. F. McDevit, *Chem. Rev.*, 1952, **51**, 119.