Dissociation of Strong Acids in Aqueous Solutions

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The dissociation of strong acids has been considered as the interaction between the acids (HA) and water (W). The equilibrium constant (K) expression of that interaction, rearranged in the form $\log (a_{\pm}{}^2/a_W{}^2) = y = \log K + \log a_{HA}/a_W$, has been used to determine K. Plotting of experimental data as $y = f(a_W)$ leads to the appearance of an inflexion point where the quotient a_{HA}/a_W can be substituted by the ratio of total concentrations of acid and water at the inflexion point. The values for the dissociation constants of H_2SO_4, HBr, HI, $HClO_4$, HCl, and HNO_3 are 34.96 (first dissociation constant) 23.63, 15.28, 12.30, 8.39, and 2.82 respectively.

Interesting work on the development of a novel approach to the determination of thermodynamic equilibrium constants has been carried out in our laboratory during the last decade.[1–3] The method does not demand any extrapolation of the apparent equilibrium constant values to infinite dilution and it leads to the thermodynamic dissociation constants using the analytical concentrations of the reacting species which are far from dilute solutions.

In this paper the dissociation of an acid (HA) as the interaction between the acid and water [equation (1)] is studied. The corresponding equilibrium constant is defined by equation (2), where a is the chemical activity of various species

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad (1)$$

$$K = \frac{a_H a_A}{a_{HA} a_W} \qquad (2)$$

denoted by the subscripts. For the sake of simplicity, H represents H_3O^+ and W represents H_2O. The standard state of the activities of ions and undissociated acid molecules is their infinite dilution in the aqueous solution. However, the standard state of water activity is pure water. The concentration scale of the species is mol dm^{-3}.

The species involved in equilibrium (1) are hydrated but this is omitted in the presentation of the dissociation process. The water concentrations in the acid solutions, as considered in this paper, are sufficiently high, more than 0.8 on the mol fraction concentration scale. As a consequence, we may suppose that the hydrates formed are not changed in these solutions and that there is an excess of water molecules which make the interaction presented by equation (1) possible.

Experimental data on the acid and water activities, plotted as $y = f(a_W)$ according to equation (3), exhibit a sigmoid

$$\ln\frac{a_H a_A}{a_W{}^2} = y = \ln K + \ln\frac{a_{HA}}{a_W} \qquad (3)$$

curve having an inflexion point. The appearance of this characteristic point led us to make use of the zero value of the second derivative of equation (3) at the inflexion point and to try to substitute the ratio a_{HA}/a_W with more convenient quantities. This problem is under consideration in the present paper.

The differentiation of equation (3), considering it as $y = f(a_W)$ and when $a_{HA} = F(a_W)$, leads to equation (4). It contains

$$\frac{dy}{da_{HA}} = \frac{d\ln a_{HA}}{da_W} - \frac{1}{a_W} \qquad (4)$$

the expression $d\ln a_{HA}/da_W$ which can be evaluated from the Gibbs–Duhem equation (5). Since a_H, a_A, and a_{HA} are

$$c_{HA}d\ln a_{HA} - c_W d\ln a_W + c_H d\ln a_H + c_A d\ln a_A = 0 \qquad (5)$$

functions of a_W, $dy/da_W = d\ln a_H a_A/da_W - 2/a_W$, and $c_H = c_A$, equation (6) can be obtained to give the value we require.

$$\frac{d\ln a_{HA}}{da_W} = -\frac{c_W}{c_{HA}}\cdot\frac{1}{a_W} - \frac{c_H}{c_{HA}}\left(\frac{dy}{da_W} + \frac{2}{a_W}\right) \qquad (6)$$

Here, c denotes stoicheiometric concentration expressed in mol dm^{-3}. Equations (4)—(6) and the mass-balance equations (7) and (8) lead to equation (9) (tot. = total). When the

$$c_{W(tot.)} = c_W + c_H \qquad (7)$$

$$c_{HA(tot.)} = c_{HA} + c_H \qquad (8)$$

$$\frac{dy}{da_W} = -\frac{c_{W(tot.)} + c_{HA(tot.)}}{c_{HA(tot.)}}\cdot\frac{1}{a_W} \qquad (9)$$

second derivative of equation (9) is equalized with zero, to fulfil the condition for the inflexion point, and then rearranged, equation (10) is obtained. Here, the superscript zero denotes that these values are obtained from the second derivative expression equalized with zero.

$$d\ln\frac{c^0_{W(tot.)} + c^0_{HA(tot.)}}{c^0_{HA(tot.)}} = d\ln a^0_W \qquad (10)$$

$$d\ln\frac{c^0_{W(tot.)} + c^0_{HA(tot.)}}{c^0_{W(tot.)}} = d\ln a^0_{HA} \qquad (11)$$

Following the same pattern as in equations (3)—(10), we differentiate equation (3) but this time considering it as $y = f(a_{HA})$ and when $a_W = F(a_{HA})$. Equation (11) is thus obtained.

Equations (10) and (11) determine the a_W and a_{HA} values at the inflexion point of the sigmoid curve lying in the space (y, a_{HA}, a_W). For different acids a family of sigmoid curves is obtained whose inflexion points also form a curve in the same co-ordinate system. It allows the integration of equations (10) and (11) and by a further rearrangement we obtain equation (12), where P represents an integration constant. For its

$$\ln\frac{a^0_{HA}}{a^0_W} = \ln\frac{c^0_{HA(tot.)}}{c^0_{W(tot.)}} + P \qquad (12)$$

$$\ln\frac{c^{0*}_{HA}}{c^{0*}_W} = \ln\frac{c^{0*}_{HA(tot.)}}{c^{0*}_{W(tot.)}} + P \qquad (13)$$

evaluation we assume that the dissociation process becomes ideal (represented by *) when the chemical activities of the species involved in equilibrium (1) are equal to their stoicheiometric concentrations. When $a^0_{\mathrm{HA}} = c^{0*}_{\mathrm{HA}}$ and $a^0_{\mathrm{W}} = c^{0*}_{\mathrm{W}}$, then equation (12) changes to equation (13), determining the integration constant P.

Differentiating equation (3), setting activities equal to concentrations on the mol fraction scale and introducing the mass-balance equation, $x_{\mathrm{HA}} + x_{\mathrm{W}} + 2x_{\mathrm{H}} = 1$, where x denotes the mol fraction concentration, it is found that $c^{0*}_{\mathrm{HA}} = c^{0*}_{\mathrm{W}}$. This has also been concluded elsewhere.[3] This gives the equality $c^{0*}_{\mathrm{HA(tot.)}} = c^{0*}_{\mathrm{W(tot.)}}$, leading to the zero value of the integration constant P in equation (13). Therefore, the final equation (14) determines the quotient $a^0_{\mathrm{HA}}/a^0_{\mathrm{W}}$ by means of the ratio of the total concentrations of acid and water at the inflexion point. Introducing equation (14) and

$$\frac{a^0_{\mathrm{HA}}}{a^0_{\mathrm{W}}} = \frac{c^0_{\mathrm{HA(tot.)}}}{c^0_{\mathrm{W(tot.)}}} \qquad (14)$$

the ordinate value of the inflexion point in equation (3), the thermodynamic dissociation constant can be calculated.

Results and Discussion

To illustrate the method described in equations (3)—(14) the experimental data on the activities of strong acids and water, over the whole range of acid concentrations, were taken from the literature.[4] The squares of the mean ion activities ($a_\pm$) were used to substitute the $a_{\mathrm{H}}a_{\mathrm{A}}$ product. The water activities,[4] on the mol fraction scale and denoted as b_{W} in this paper, were recalculated to the molarity scale, a_{W}, by the relation $a_{\mathrm{W}} = 55.34b_{\mathrm{W}}$. These experimental data were plotted as ln $(a_\pm^2/a_{\mathrm{W}}^2) = y = \mathrm{f}(a_{\mathrm{W}})$, according to equation (3). The obtained signoid curves are shown in the Figure.

In the case of sulphuric acid the available mean ion activities data are given as $a_\pm^3 = a_{\mathrm{H}}^2a_{\mathrm{SO_4}}$. Thus, equation (3), applied to the double dissociation of sulphuric acid, has to be plotted as ln $(a_\pm^3/a_{\mathrm{W}}^3) = \mathrm{f}(a_{\mathrm{W}})$. The overall equilibrium constant obtained from the inflexion point and the second dissociation constant ($K_a = 0.01$) of sulphuric acid taken from the literature[5] led to the first step dissociation constant (K) of sulphuric acid shown in the Table.

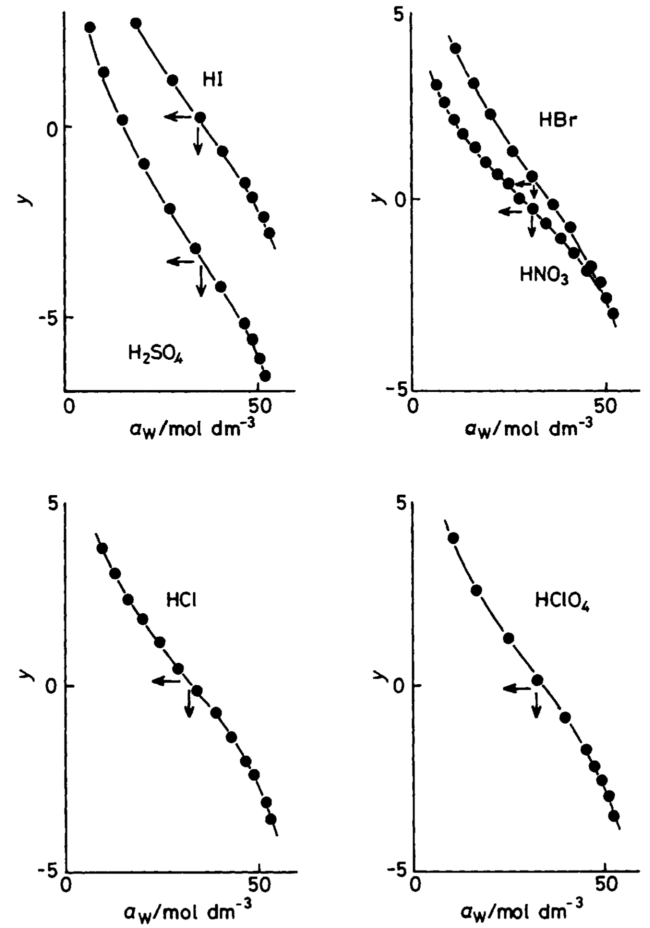

Figure. The presentation of literature data[4] according to equation (3); $y = \ln(a_\pm^2/a_{\mathrm{W}}^2)$. The arrows show the co-ordinates of inflexion points

Table. Values of the dissociation constant K defined by equation (2). The literature K_a values have been chosen to cover the range of pub lished data ($K_a = a_{\mathrm{H}}a_{\mathrm{A}}/a_{\mathrm{HA}}$); $T = 298$ K

	y_0	$c^0_{\mathrm{HA(tot.)}}$/ mol dm^{-3}	$c^0_{\mathrm{W(tot.)}}$/ mol dm^{-3}	K	log K_a	
					This work	Lit. values
H_2SO_4	−3.13	5.14	43.90	34.96 [a]	3.29	2.0,[b] 3.1,[c] 3.59 [d]
HBr	0.46	5.81	47.28	23.63	3.12	2.1—4.7,[e] 9 [f]
HI	0.23	5.03	45.37	15.28	2.93	9.5 [f]
$HClO_4$	0.15	5.01	43.67	12.30	2.83	1.58,[g] 2.4—3.1 [h]
HCl	0.12	6.41	48.36	8.39	2.67	1.0—2.6,[e] 7 [f]
HNO_3	−0.25	8.10	41.10	2.82	2.19	1.44,[i] 3.78 [j]

[a] The first dissociation constant. [b] N. Bailey, A. Carrington, K. A. K. Lot, and M. C. R. Symons, *J. Chem. Soc.*, 1960, 290. [c] G. Schwarzenbach, *Z. Phys. Chem.*, 1936, **176**, 133. [d] P. A. H. Wyatt, *Trans. Faraday Soc.*, 1960, **54**, 490. [e] E. Högfeldt, *J. Inorg. Nucl. Chem.*, 1961, **17**, 302. [f] These log K_a values[8] are in fact log $K_{a(4)}$, and give log K_a values of 3.8 (HBr), 4.3 (HI), and 1.8 (HCl) using the equation $K_{a(4)} = K_a \cdot a_{\mathrm{W}}^3$. [g] K. Heinzinger and R. E. Weston, *J. Chem. Phys.*, 1965, **42**, 272. [h] W. Kangro, *Z. Phys. Chem.* (*Frankfurt am Main*), 1962, **32**, 273. [i] G. C. Hood and C. A. Reily, *J. Chem. Phys.*, 1960, **32**, 127. [j] E. Högfeldt, *Acta Chem. Scand.*, 1963, **17**, 785.

In order to compare our K values, defined by equation (2), with the published values of acidity constants expressed as $K_a = a_{\mathrm{H}}a_{\mathrm{A}}/a_{\mathrm{HA}}$, the equation $K_a = 55.34K$ was used. The experimental data presented by equation (3) were fitted by means of the third degree polynomial, using the least-squares procedure. The mean square error (99% confidence error limit), recalculated to introduce the error of the operation $K = 10^{\log K}$, did not exceed 10%.

The Figure shows that sigmoid curves exist predominantly between 0.2 and 1 of the water activities, given on the mol fraction scale. In the same water activity region the water concentrations, given on the mol fraction concentration scale, are between 0.8 and 1. The total water and acid concentrations at the inflexion point (Table) demonstrate that the total water concentrations are approximately eight or more times greater than the total acid concentrations in the vicinity of the inflexion point. As a consequence, one could expect that there are sufficient water molecules to hydrate oxonium ions since anions and the unionized acid molecules usually hydrate very poorly.[5–7]

This paper communicates a novel approach to an old and difficult problem. It had been emphasized long ago that the extrapolation of the apparent equilibrium constant to zero ionic strength is subjected to grave uncertainties. However, alternative methods for more certain determinations have not been offered. In the case of our method the activities of the species in the acid rich solutions are used without the extrapolation of the values of apparent dissociation constant to infinite dilution. The dissociation constants obtained by our procedure are as trustworthy as the activities found in the literature[4] which represent the quantities needed to evaluate y in equation (3). However, this problem does not influence the general validity of the method presented in equations (3)—(14).

The methods based on the use of thermodynamic data, contrary to the spectroscopic techniques, lead to much greater values of the dissociation constants (*cf.* K_a values for HBr, HI, and HCl in ref. 8). This could be explained, perhaps, if we assume that the dissociation process is described by $HA + 4H_2O \rightleftharpoons H_9O_4^+ + A^-$. Then the resulting $K_{a(4)}$ value can be calculated from our K_a value (Table) as $K_{a(4)} = K_a a_W^3$ (here, $a_W = 55.34$). In this way the log $K_{a(4)}$ values obtained for HBr, HI, and HCl are 8.3 (9), 8.2 (9.5), and 7.9 (7), respectively (literature values[8] in parentheses). The $K_{a(4)}$ values calculated for these three acids approach the literature values to some extent. It could be presumed from this that the dissociation of acids occurs through the formation of $H_9O_4^+$ ions. However, this prediction has to be confirmed by additional experimental data.

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