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ION-SOLVENT INTERACTION PARAMETER BY e.m.f. METHOD

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Various expressions for activity coefficient computation are reviewed with particular reference to the recent work in dissociation equilibria study of oxalic acid by electromotive force measurements. The ion-solvent interaction parameter, B, measured through e. m. f. method, were found to be independent of the solution composition in dilute solutions.

Since the proposition[1] of the term 'activity coefficient', many attempts were made by many workers to derive correct expressions for it for accurate computation of stability constants and the associated thermodynamic functions of metal-complexes, acids, salts, etc. Most simple among these were given by Debye and Huckel[2] in the forms,

$$\log \gamma \pm = \tfrac{3}{3} A Z_+ Z_- \sqrt{\mu} \quad \ldots \quad (1)$$

$$\text{and,} \quad \log \gamma \pm = - \frac{A Z_+ Z_- \sqrt{\mu}}{1 + Ba^0 \sqrt{\mu}} \quad \ldots \quad (2)$$

Eq (1) is an approximate one applicable only in very dilute solution usually when $\mu < 10^{-3}$M while ey (2) can be applied upto $\mu \sim 10^{-2}$m. In eq (2), a° was referred as 'average effective diameter of the ion' although its exact physical significance probably cannot be expressed precisely. A and B are constants which depend on the nature of solvent and temperature. In the derivation of the above equations interactions of ions were only taken into account while ion-solvent interactions were ignored, which has considerable influence in more concentrated solutions. Harned et al[3] and Bates and his coworkers[4] used extensively eq (3) and (4) respectively for computation of activity coefficient in more concentrated solutions by adding additional terms β^* and β^0 respectively to account for the contribution due to ion-solvent interaction.

$$\log \gamma \pm = - A Z_+ Z_- \sqrt{\mu} + \beta^* \mu \quad \ldots \quad (3)$$

$$\log \gamma \pm = - \frac{A Z_+ Z_- \sqrt{\mu}}{1 + Ba^0 \sqrt{\mu}} + \beta^0 \mu \quad \ldots \quad (4)$$

Though eq (4) is claimed to obey upto $\mu = 1$, it suffers from some disadvantages due to having two arbitrary parameters, a^0 and β^0. Some workers[5] assigned the value of a^0 equal to the interionic distances found in crystalline solids. It should be noted that a crystalline solid is more or less a static one and the ions are free from the constraint of the surrounding solvent molecules. During e. m. f. measurements in solutions, the ions are solvated and remain in quasi-static condition. However, in the computation of activity coefficient, in many cases Bates and his coworkers chose the value of a^0 by trial to fit approximately well in the e. m. f. equation. It should be noted that the ion-solvent interaction parameter β^0 in eq (4) will thus depend on the value of a^0 taken. Hence the value of β^0 obtained through an approximate value of a^0 cannot be treated constant for a particular ion, because the value of a^0 may vary with the composition of the solution also.

Since the value of B with water as solvent is approximately 0.33×10^8 at 25°C and a^0 is of the order of 10^{-8}, Guggenheim[6–8] simplified eq (4) by proposing,

$$\log \gamma \pm = - \frac{A Z_+ Z_- \sqrt{\mu}}{1 + \sqrt{\mu}} + \beta_i \mu \quad \ldots \quad (5)$$

which has now only one unknown parameter, β_i. Prasad and coworkers have carried out studies on ionic interactions and ionic equilibria by e. m. f measurements by applying eq (5) to many electrolytes[9–14]. In the course of these studies, it was found that in dilute acid solution, β_i is additive and independent of the composition of ionic atmosphere[15–16].

The E° of the cell (C—1), studied by Harned and Ehlers[17] were recalculated with the help of eq (6)

$$H_2/HCl\ (M), AgCl/Ag \qquad (C-1)$$

$$E = E^\circ - \frac{2\ 30259RT}{F} \log M_H M_{Cl} - \frac{2.30259RT}{F} \log \gamma_H \gamma_{Cl} \quad \ldots \quad (6)$$

On application of eq (5) to eq (6), it resulted

$$E + \frac{2.30259RT}{F} \left(\log M - \frac{A \sqrt{\mu}}{1 + \sqrt{\mu}}\right) = E^\circ - \frac{2.30259RT}{F} .\beta\mu \quad (7)$$

where β stands for $(\beta_H + \beta_{Cl})$. When L. H. S. of eq (7)

was plotted against various values of μ, a straight line was obtained at each temperature. The value of β obtained from the slopes of these straight lines[16] are given in Table-I along with other β values for other ions.

Cell (C 2) and cell (C—3) were also studied to recalculate the thermodynamic functions associated with second step dissociation of oxalic acid at a number of temperatures

H_2/NaHOx (M_1), Na_2Ox (M_2), NaCl (M_3), AgCl/Ag ... (C—2)

H_2/K HOx (M_1), Na_2Ox (M_2), NaCl (M_3), AgCl/Ag ... (C—3)

In the above recalculation, it was assumed that β for pure HCl will remain same as in (i) a mixture of NaHOx, Na_2Ox and NaCl, and (ii) a mixture of KHOx, Na_2Ox and NaCl in dilute solution generally upto μ = 0.2. On the basis of this assumption the value for $(\beta_H + \beta_{OX} - \beta_{HOX})$ were found out[16] from cells (C—2) and (C—3) separately. However, the values were found same in both the cases, which supports the above assumption.

It was reported[18] that though an approximation in a° during application of eq (4) does not affect the equilibrium study having pK value above 3, it considerably affects, giving erratic result of thermodynamic functions in case of equilibrium having pK values below 3. The limitation, however, does not arise in the application of eq (5). pK_2 of sulphuric acid is nearly 2. Sharma and Prasad[19] determined pK_2 with the application of eq (5) in the e. m. f. equation and the values were found closely in agreement with those obtained by Nair and Nancollas[20] at each temperature. First dissociation constant of oxalic acid is also of the order of 10^{-2}. Recently[21] it was found out from 10° to 50°C at 5° interval by measuring the cells (C—4)

H_2/H_2Ox (M_1), NaCl (M_2), AgCl/Ag ... (C—4)

and using eq (5) for activity coefficient computation. The values of $(\beta_H + \beta_{HOX})$ are also recorded in Table-I.

TABLE-I

Temperature	$(\beta_H + \beta_{Cl})$	$(\beta_H + \beta_{OX} - \beta_{HOX})$	$(\beta_H + \beta_{HOX})$
0	0 464	0.637	—
5	0.456	0 611	—
10	0.444	0.593	1.12
15	0.460	0.616	1.09
20	0.480	0.630	1.11
25	0.490	0.663	1.10
30	0.476	0.634	1.02
35	0.466	0.622	0.86
40	0.467	0 610	0.64
45	0.469	0.612	0.48
50	0.459	0.592	0.35

It should be noted that the ratio $M_1 : M_2 : M_3$ in cells (C—2) and (C—3) were 4 : 2 : 3 and 1 : 5 : 2.5 respectively. As value for a° will certainly depend on the buffer ratio and its composition, value of β° obtained from the use of eq (4) should not come same for same ions. However, application of eq (5) resulted same values for β in both the cases. It appears, thus, the ion-solvent interaction parameter, β is independent of the buffer composition and the nature of surrounding ionic cloud in dilute solution, generally when $\mu \leqslant 0.1$.

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