

DEGREES OF DISSOCIATION AND HYDRATION NUMBERS OF TWENTY SIX STRONG ELECTROLYTES IN AQUEOUS SOLUTIONS AT 25 °C

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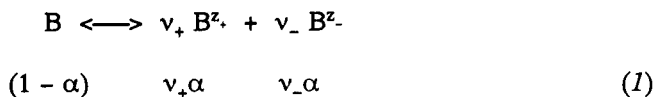
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This paper brings further results on the degrees of dissociation (α) and hydration numbers (n_h) of strong electrolytes in aqueous solutions at 25 °C, evaluated for the first time from osmotic coefficients (ϕ). Presented here are also the equations for the non-ideality parameters, ϕ and γ_{\pm} (the mean molal ionic activity coefficient), in terms of α and n_h .

Researches on the properties of strong electrolytes in aqueous solutions have lead¹⁻⁴ to the conclusion that incomplete dissociation⁵ and hydration are the main causes of non-ideality as supposed earlier⁶. This conclusion is in accord with the increasing number of publications on ionic association; cf. the literature cited in ref.³. However, the existing theories of non-ideality are mostly based on the assumption of complete dissociation⁷⁻⁹.

It was demonstrated^{1,3,4} that the values of α and n_h evaluated from the data on vapour pressures enable the quantitative interpretation of many other equilibrium properties of solutions. The values of n_h obtained were found¹⁻³ to be close to those used by the authors in ref.⁸ to get best-fits of their equation for γ_{\pm} based on the idea of complete dissociation. Also, it was shown³ that the equivalent conductivity of dilute solutions decreases linearly with the degree of association ($1 - \alpha$), and that the Debye, Hückel and Onsager's limiting law is an asymptotic law for complete dissociation at infinite dilution. The molal volumes of solutions were also accounted for in terms of α and $(1 - \alpha)$ as in the case of weak electrolytes^{1,3,4}.

Thus, for one mole of an electrolyte B composed of ν_+ cations B^{z_+} of charge z_+ and ν_- anions B^{z_-} of charge z_- , the following association/dissociation equilibrium,



holds, where $\nu_+ z_+ = -\nu_- z_-$. Thereby, the actual number of moles of solute in the solution = $[1 + (\nu - 1)\alpha] = i$, the van't Hoff's factor, where $\nu_+ + \nu_- = \nu$. At infinite dilution, B dissociates completely and hence $\alpha = 1$ and $i = \nu$, whereas for $m > 0$, $\alpha < 1$ and $i < \nu$.

Both α and n_h can be evaluated by the method described in ref.¹, from the data on vapour pressures. The ratio of the vapour pressure (p_A) over a solution of molality m to that (p_A^0) over the pure solvent (A), was found to be equal to the mole fraction N_{Af} of "free" solvent:

$$p_A/p_A^0 = N_{Af} = n_{Af}/(n_{Af} + n_B). \quad (2)$$

In the above equation, $n_{Af} = (55.51 - m n_h)$ is the number of moles of "free" water, and $n_B = i m$ is the number of moles of solute in the solution. (Note that Eq. (2) is a modified form of Raoult's law which incorporates the effects of hydration and incomplete dissociation on the vapour pressure.) The above vapour pressure ratio, defined^{7,8} as the solvent activity a_A , was calculated from the tables of data on ϕ in ref.⁸, using the relation⁸

$$\ln a_A = -\nu m \phi / 55.51. \quad (3)$$

It follows from Eqs (2) and (3) that the non-ideality parameter ϕ defined by Eq. (3) stands for

$$\phi = -(55.51/\nu m) \ln N_{Af} \quad (4)$$

on the basis of the idea of incomplete dissociation and hydration. On the other hand, the equations for ϕ based on the assumption of complete dissociation are quite complicated, e.g., see ref.⁸.

With the knowledge of the "ionic molality", αm , which was hitherto inaccessible (cf. the "elusive" single ionic activity⁹), the e.m.f.s, ΔE of concentration cells were shown¹ to be equal to

$$\Delta E = -(\delta_A \nu R T / n F) \ln [(\alpha m / n_{Af}) / (\alpha m / n_{Af})^0], \quad (5)$$

where δ_A is a constant and $n = \nu_+ z_+ = -\nu_- z_-$; δ_A was obtained from the slopes of the linear graphs of ΔE vs $\ln (\alpha m / n_{Af})$ (see e.g., Fig. 3 for HCl, NaCl and KBr in ref.¹). Since δ_A was found to be < 1 , it implies a decrease of e.m.f., due probably to the solute-solvent (polarization) interaction, e.g. see ref.¹⁰ and the literature cited therein. When the ratio $(\alpha m / n_{Af})$ is equal to the ratio $(\alpha m / n_{Af})^0$ of the solution in the reference cell, the value of $\Delta E = 0$.

As the data on ΔE are stored⁸ in the form of values of γ_{\pm} which is defined by the equation^{7,8}

$$\Delta E = -(\nu R T / n F) \ln m \gamma_{\pm}, \quad (6)$$

TABLE I
 Degrees of dissociation (α) and hydration numbers (n_h) of strong electrolytes in aqueous solutions at 25 °C. The upper and lower limits of m between which $\alpha = \alpha_m = \text{const.}$ are denoted by asterisks. The last row gives the values of δ_A

m	H ₂ SO ₄	(NH ₄) ₂ SO ₄	Li ₂ SO ₄	Nafor ^a	Naac ^{a,b}	Napro ^a	Nabut ^c	Na ₂ SO ₄	Na ₂ CrO ₄
0.1	0.507	0.647	0.716	0.856	0.864	0.868	0.859	0.681	0.708
0.2	0.476	0.590	0.666	0.836	0.847	0.854	0.840	0.613	0.656
0.3	0.462	0.551	0.637	0.827	0.843	0.850	0.834*	0.563	0.615
0.4	-	0.522	0.619	0.823	0.839*	0.849*	0.831	0.526	0.588
0.5	0.442	0.500	0.603	0.821	0.838	0.848	0.831	0.496	0.564
0.6	-	0.482	0.594	0.819*	0.837	0.848	0.833	0.470	0.545
0.7	0.438*	0.465	0.585	0.817	0.840	0.848	0.835	0.447	0.527
0.8	-	0.453	0.578	0.817	0.841	0.847	0.831*	0.426	0.510
0.9	-	0.441	0.573	0.819	0.839	0.847	-	0.407	0.495
1.0	0.439	0.429	0.568	0.818	0.837*	0.848	-	0.388	0.481
1.2	-	0.411	0.563	0.818	-	0.850	-	0.358	0.455
1.4	-	0.399	0.559	0.817	-	0.848*	-	0.334	0.437
1.5	0.438*	-	-	-	-	-	-	-	-
1.6	-	0.387	0.557	0.817	-	-	-	0.314	0.421
1.8	-	0.379	0.552*	0.817	-	-	-	0.297	0.409
2.0	-	0.372	0.551	0.816	-	-	-	0.283	0.402
2.5	-	0.360	0.553	0.818	-	-	-	0.262	0.396
3.0	-	0.356*	0.551*	0.817*	-	-	-	0.252*	0.389*
3.5	-	0.356	-	-	-	-	-	0.250	0.389
4.0	-	0.356*	-	-	-	-	-	0.253*	0.390*
4.5	-	-	-	-	-	-	-	-	-
5.0	-	-	-	-	-	-	-	-	-
α_m^c	0.438	0.356	0.552	0.817	0.839	0.848	0.833	0.252	0.389
n_h	8.27	2.71	6.35	2.67	5.54	6.74	9.38	5.20	7.25
δ_A	0.699	0.722	0.812	0.930	0.953	0.971	0.971	0.804	0.832

TABLE I
(Continued)

<i>m</i>	Na ₂ S ₂ O ₃	Na ₂ fum ^a	Na ₂ mal ^a	K ₂ C ₂ O ₄	K ₃ Fe(CN) ₆	CoCl ₂ ^d	CoBr ₂	CoI ₂	Co(NO ₃) ₂	NiCl ₂
0.1	0.697	0.700	0.646	0.700	0.624	0.756	0.766	0.785	0.755	0.755
0.2	0.640	0.666	0.598	0.645	0.570	0.743	0.758*	0.775*	0.739	0.739
0.3	0.599	0.643	0.569	0.606	0.541	0.736*	0.755	0.779	0.733*	0.732*
0.4	0.571	0.625	0.553	0.581	0.524	0.734	0.756	0.776	0.730	0.729
0.5	0.546	0.616	0.543	0.562	0.510	0.735	0.759	0.781	0.732	0.732
0.6	0.526	0.616	0.526	0.545	0.498	0.738	0.758	0.781	0.734	0.732
0.7	0.509	0.613*	0.535	0.530	0.490	0.738	0.756*	0.775*	0.733	0.731
0.8	0.490	0.613	0.533	0.517	0.485*	0.734	-	-	0.733	0.730
0.9	0.475	0.613	0.529	0.503	0.484	0.737	-	-	0.735	0.731
1.0	0.462	0.613*	0.526	0.491	0.484	0.737	-	-	0.736	0.732*
1.2	0.441	-	0.525	0.473	0.485	0.733*	-	-	0.734*	-
1.4	0.429	-	0.523*	0.460	0.484*	-	-	-	-	-
1.5	-	-	-	-	-	-	-	-	-	-
1.6	0.416	-	0.523	0.452	-	-	-	-	-	-
1.8	0.407	-	0.523	0.444	-	-	-	-	-	-
2.0	0.399	-	0.523*	0.438	-	-	-	-	-	-
2.5	0.392*	-	-	0.432*	-	-	-	-	-	-
3.0	0.390	-	-	0.435	-	-	-	-	-	-
3.5	0.392*	-	-	0.432*	-	-	-	-	-	-
4.0	-	-	-	-	-	-	-	-	-	-
4.5	-	-	-	-	-	-	-	-	-	-
5.0	-	-	-	-	-	-	-	-	-	-
α _m ^c	0.392	0.614	0.523	0.433	0.484	0.735	0.757	0.778	0.734	0.731
r _b ^a	6.13	9.28	5.68	4.90	8.44	14.15	18.37	21.97	12.46	14.61
δ _A	0.796	0.823	0.757	0.778	0.706	0.921	0.926	0.964	0.895	0.911

TABLE I
(Continued)

<i>m</i>	CuCl ₂	Cu(NO ₃) ₂	ZnCl ₂	Zn(ClO ₄) ₂	Zn(NO ₃) ₂	Al ₂ (SO ₄) ₃	Cr ₂ (SO ₄) ₃	Ga(ClO ₄) ₃	ThCl ₄
0.1	0.748	0.746	0.761	0.790*	0.765	0.234	0.234	0.752	0.615
0.2	0.726	0.725	0.749	0.789	0.752	0.161	0.187	0.724*	0.604*
0.3	0.713*	0.716*	0.735	0.788	0.747	0.124	0.165	0.725	0.612
0.4	0.710	0.712	0.719	0.790	0.743*	0.112*	0.155	0.727	0.612
0.5	0.712	0.714	0.702	0.790	0.746	0.113	0.150*	0.723*	0.603*
0.6	0.714	0.714	0.687	0.789*	0.746	0.111*	0.151	-	-
0.7	0.715	0.714	0.670	-	0.745	-	0.150*	-	-
0.8	0.712	0.714	0.650	-	0.746	-	-	-	-
0.9	0.711*	0.715	0.631	-	0.746	-	-	-	-
1.0	-	0.715*	0.614	-	0.743*	-	-	-	-
1.2	-	-	0.576	-	-	-	-	-	-
1.4	-	-	0.544	-	-	-	-	-	-
1.5	-	-	-	-	-	-	-	-	-
1.6	-	-	0.523	-	-	-	-	-	-
1.8	-	-	0.509	-	-	-	-	-	-
2.0	-	-	0.499	-	-	-	-	-	-
2.5	-	-	0.484	-	-	-	-	-	-
3.0	-	-	0.477*	-	-	-	-	-	-
3.5	-	-	0.473	-	-	-	-	-	-
4.0	-	-	0.471	-	-	-	-	-	-
4.5	-	-	0.477	-	-	-	-	-	-
5.0	-	-	0.476*	-	-	-	-	-	-
α_m^c	0.712	0.714	0.475	0.789	0.745	0.112	0.150	0.725	0.608
n_h^b	9.79	11.80	5.41	21.88	13.51	44.16	36.74	35.35	34.93
δ_A^d	0.862	0.881	0.865	0.955	0.912	0.535	0.490	0.944	0.810

^a for formate, ac acetate, pro propionate, but butyrate, fum fumarate and mal maleate; ^b from ref.¹; ^c S.D. $\sigma_m < \pm 0.005$, $n_h < \pm 0.05$, $\delta_A < \pm 0.005$; ^d from ref.².

δ_A can be obtained directly as the slope of the linear plot of $\ln m \gamma_{\pm}$ vs $\ln (\alpha m / n_{Af})$. In Eq. (6), the product $m \gamma_{\pm}$ is defined⁷ as the mean ionic activity a_{\pm} ; and $\Delta E = 0$ corresponds to $a_{\pm} = 1$. On comparing Eqs (5) and (6), one finds that γ_{\pm} stands for

$$\gamma_{\pm} = (1/m) ((\alpha m / n_{Af}) / (\alpha m / n_{Af})^0)^{\delta_A} \quad (7)$$

in terms of α and n_{Af} . As in the case of ϕ , the equations⁸ for γ_{\pm} based on the idea of complete dissociation are quite complex.

The values of α , n_h and δ_A for several strong electrolytes, evaluated from the ϕ and γ_{\pm} data in ref.⁸ by the method described before¹, are presented in Table I. As in the case of the data for seventy five strong electrolytes published earlier¹⁻³, α decreases from the value of unity at infinite dilution to a constant minimum value α_m over a considerable range of concentrations (marked by asterisks in Table I). The values of n_h and δ_A are constant in the range of concentrations for which the data are presented. These were calculated by linear regression using the method of least squares; the correlation coefficients obtained were above 0.999. The state of electrolytes in solutions of concentrations higher than those presented in Table I here and in the Tables elsewhere¹⁻³, have yet to be investigated.

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