INTERPRETATION OF PROPERTIES OF AQUEOUS ELECTROLYTE SOLUTIONS IN TERMS OF HYDRATION AND INCOMPLETE DISSOCIATION

Rajalakshmi HEYROVSKÁ

Na Šťáhlavce 6, 160 00 Prague 6

The existing data on the vapour pressures, densities and e.m.f.s of concentration cells of dilute and concentrated aqueous solutions of strong electrolytes have been interpreted in terms of hydration and incomplete dissociation. Hydration numbers and degrees of dissociation have been presented for several 1 : 1 strong electrolytes at 25°C. Thus the actual ionic concentrations of strong acids, bases and salts, hitherto inaccessible, have now been made available.

Association of ions of many multivalent and some univalent strong electrolytes in solvents of low dielectric constant as well as in water has been recognized; but that of ions of simple 1 : 1 strong electrolytes like sodium chloride in water is considered negligible[1-5]. However, recent preliminary work[6] on the properties of over fifty univalent and multivalent strong electrolytes in aqueous solutions has shown that, in all cases, the degree of dissociation, α, decreases from unity at infinite dilution to a constant minimum value, α_m, over a considerable range of concentrations. Thus, in general, electrolytes in solutions exist in association–dissociation equilibrium with their ions as originally supposed[7-9], as a result of interionic attraction and repulsion between ions of unlike and like charges, respectively, depending on the dielectric constants of the solvents. Two simple proofs are given here by accounting for the volumes of solutions and for the e.m.f.s of concentration cells of dilute as well as concentrated solutions of 1 : 1 electrolytes in terms of the degrees of dissociation and hydration numbers, n_h, derived from vapour pressures. α and n_h data are tabulated for thirty-five 1 : 1 electrolytes in aqueous solutions at 25°C. Similar tables are being prepared for multivalent electrolytes.

Degree of Dissociation and Hydration Number from Vapour Pressure

The Raoult's law[10] of dependence of vapour pressure on the mole fraction of solvent (A), modified by Callendar (see ref.[11]) for the hydration of solutes, is given by the equation

$$\left(p_A/p_A^0\right) = n_A/(n_A + n_B), \qquad (1)$$

where p_A and p_A^0 are the vapour pressures over the solution and pure solvent and n_A and n_B are the amounts in moles of "free" solvent and solute (B), respectively. In a solution of molality m, $n_A = (55.51 - mn_h)$, where 55.51 is the amount of water in moles in $1\,000$ g. The ratio p_A/p_A^0, which is termed[12] the activity, a_A, of the solvent, can be obtained[1] from the molal osmotic coefficient, φ, as $a_A = \exp\,.$ $.\,(-vm\varphi/55.51)$, where v is the total number of ions into which one mole of electrolyte decomposes.

When a fraction α of one mole of an electrolyte dissociates into v ions, the total number of moles of solute in a solution of molality m is $n_B = [1 + (v - 1)\,\alpha]\,m$, where $[1 + (v - 1)\,\alpha] = i$ is the van't Hoff's factor[7-9]. Eq. (1) can now be tested by re-writing it in the form,

$$p_A/(p_A^0 - p_A) = a_A/(1 - a_A) = n_A/n_B = (55.51 - mn_h)/im \qquad (2)$$

and by using the available φ data[1]. Fig. 1 shows the dependence of $mp_A/(p_A^0 - p_A)$ on m for aqueous solutions of two simple electrolytes, NaCl and KBr ($v = 2$, $\alpha \leq 1$, $i = 1 + \alpha$) compared with that of sucrose, a non-electrolyte ($v = 1$, $\alpha = 0$, $i = 1$). It can be seen that the graphs are linear over a wide range of molalities (m) ((about) 0 to 2, sucrose; 1·8 to 4, NaCl; 1·8 to 4·5, KBr) implying the constancy of i and n_h in this region. (The region of higher concentrations beyond the linearity will be discussed in another paper.) The constants, i_m and n_h, evaluated from the intercept $(55.51/i_m)$ and slope (n_h/i_m) are 0.999 and 5.01 (refs[1,11]: $n_h = 5$), respectively, for sucrose. The values of $\alpha_m(= i_m - 1)$ and n_h obtained similarly for thirty-five 1 : 1 electrolytes are given in Table I. For comparison, the hydration numbers in[1] are also presented in the same table. The main observation from these results is that the maximum degree of ionic association $(1 - \alpha_m)$ increases as the hydration number
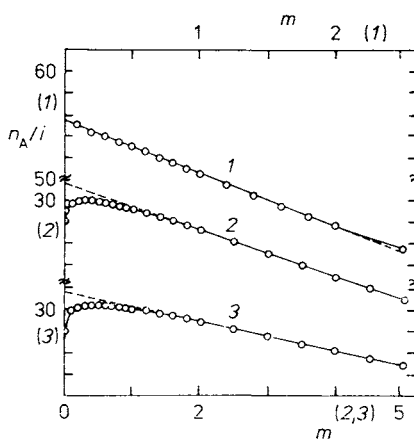

Fig. 1

Dependence of n_A/i ($\equiv mp_A/(p_A^0 - p_A)$) on m for aqueous solutions at 25°C: *1* sucrose; *2* NaCl; *3* KBr

TABLE I

Degrees of dissociation (α) and hydration numbers (n_h) of strong $1:1$ electrolytes in aqueous solutions at 25°C. The upper and lower limits of m between which $\alpha = \alpha_m = $ const. are denoted by asterisks

m	HCl	HBr	HI	HClO$_4$	HNO$_3$	LiOH	NaOH	KOH	CsOH	LiCl	LiBr	LiI
0·1	0·864	0·870	0·875	0·870	0·867	0·837	0·838	0·870	0·865	0·859	0·863	0·878
0·2	0·846	0·856	0·874	0·854	0·844	0·798	0·826	0·835	0·840	0·840	0·842	0·880*
0·3	0·837	0·849*	0·871*	0·843	0·833	0·771	0·822	0·821	0·822*	0·833	0·834	0·880
0·4	0·835	0·849	0·870	0·834	0·827	0·751	0·818	0·813	0·820	0·831	0·826	0·882
0·5	0·834*	0·850	0·870	0·829	0·822	0·736	0·813	0·812	0·822	0·828*	0·821	0·880
0·6	0·833	0·848	0·871	0·826	0·820*	0·721	0·809	0·810*	0·821	0·828	0·817*	0·878*
0·7	0·832	0·850	0·871	0·823	0·820	0·712	0·804	0·810	0·823	0·828	0·815	—
0·8	0·832	0·848	0·870*	0·821*	0·819	0·703	0·799	0·811	0·821	0·828	0·816	—
0·9	0·833	0·848	—	0·818	0·819	0·696	0·794	0·809	0·821	0·828	0·816	—
1·0	0·834	0·850*	—	0·818	0·820	0·691*	0·791	0·808	0·820*	0·829	0·815	—
1·2	0·833*	—	—	0·818	0·820	0·691	0·786	0·809	—	0·828	0·819	—
1·4	—	—	—	0·820	0·819	0·691	0·781	0·811	—	0·829	0·817	—
1·6	—	—	—	0·820*	0·818	0·693	0·775	0·811	—	0·827*	0·814*	—
1·8	—	—	—	—	0·819	0·691	0·768	0·808*	—	—	—	—
2·0	—	—	—	—	0·821	0·691	0·764*	—	—	—	—	—
2·5	—	—	—	—	0·821	0·689*	0·762	—	—	—	—	—
3·0	—	—	—	—	0·818*	—	0·757	—	—	—	—	—
3·5	—	—	—	—	—	—	0·753	—	—	—	—	—
4·0	—	—	—	—	—	—	0·761	—	—	—	—	—
4·5	—	—	—	—	—	—	0·766	—	—	—	—	—
5·0	—	—	—	—	—	—	0·761*	—	—	—	—	—
$\alpha_m{}^a$	0·833	0·849	0·871	0·819	0·819	0·691	0·761	0·809	0·822	0·828	0·816	0·880
$n_h{}^a$	7·44	8·53	10·07	7·93	4·82	1·78	4·51	6·39	6·59	6·54	7·74	8·46
ref.[1]	8·0	8·6	10·6	7·4	—	—	—	—	—	7·1	7·6	9·0

TABLE I
(Continued)

m	LiClO$_4$	LiNO$_3$	LiAc^b	NaCl	NaBr	NaI	NaClO$_4$	NaAc^b	NaCNS	KF	KCl	KBr
0·1	0·877	0·861	0·859	0·854	0·856	0·862	0·855	0·864	0·864	0·850	0·849	0·851
0·2	0·868*	0·840	0·834	0·831	0·833	0·844	0·830	0·847	0·849	0·818	0·817	0·822
0·3	0·866	0·834	0·825	0·815	0·821	0·835	0·815	0·843	0·841	0·800	0·798	0·806
0·4	0·868	0·830*	0·818	0·802	0·811	0·833*	0·804	0·839*	0·837*	0·788	0·786	0·793
0·5	0·868	0·830	0·815	0·794	0·807	0·832	0·795	0·838	0·837	0·780	0·775	0·784
0·6	0·868	0·830	0·813	0·788	0·802	0·831	0·788	0·837	0·837	0·772	0·769	0·779
0·7	0·867	0·829	0·812*	0·784	0·800	0·831	0·785	0·840	0·837	0·768	0·762	0·774
0·8	0·869	0·828	0·812	0·780	0·797	0·832	0·782	0·841	0·836	0·766	0·757	0·771
0·9	0·869	0·829	0·810	0·776	0·797	0·832	0·779	0·839	0·836	0·761	0·753	0·768
1·0	0·865*	0·831	0·810	0·773	0·794	0·832	0·776	0·837*	0·837	0·761	0·748	0·765
1·2	—	0·831	0·811	0·767	0·789*	0·831	0·771	—	0·836	0·759	0·743	0·761
1·4	—	0·829	0·812	0·761	0·790	0·832	0·769	—	0·836	0·757	0·737	0·759
1·6	—	0·828*	0·812	0·761	0·790	0·833	0·768	—	0·837	0·756	0·733	0·755*
1·8	—	—	0·812	0·759*	0·791	0·832	0·767	—	0·838	0·755*	0·732	0·754
2·0	—	—	0·810*	0·758	0·793	0·830	0·764	—	0·836*	0·753	0·730*	0·754
2·5	—	—	—	0·758	0·792*	0·829	0·762*	—	—	0·751	0·728	0·755
3·0	—	—	—	0·758	—	0·833*	0·759	—	—	0·752	0·728	0·755
3·5	—	—	—	0·759	—	—	0·759	—	—	0·752	0·727	0·754
4·0	—	—	—	0·757*	—	—	0·759	—	—	0·755*	0·729	0·754
4·5	—	—	—	—	—	—	0·761	—	—	—	0·730*	0·755
5·0	—	—	—	—	—	—	0·761	—	—	—	—	0·753*
5·5	—	—	—	—	—	—	0·760	—	—	—	—	—
6·0	—	—	—	—	—	—	0·760*	—	—	—	—	—
α_m^a	0·867	0·829	0·811	0·758	0·791	0·831	0·760	0·839	0·837	0·753	0·728	0·754
n_h^a	8·14	5·45	4·19	3·81	4·47	5·12	2·42	5·54	3·80	3·90	2·29	2·37
ref.[1]	8·7	—	—	3·5	4·2	5·5	2·1	—	—	—	1·9	2·1

TABLE I
(Continued)

m	KI	KAc[b]	KCNS	RbCl	RbBr	RbI	RbAc[b]	CsCl	CsBr	CsAc[b]	NH_4Cl
0·1	0·858	0·869	0·851	0·842	0·841	0·839	0·868	0·831	0·831	0·872	0·851
0·2	0·832	0·853	0·819	0·806	0·804	0·802	0·853	0·787	0·786	0·858	0·820
0·3	0·819	0·849	0·803	0·784	0·785	0·782	0·849*	0·760	0·755	0·853	0·803
0·4	0·811	0·845*	0·794	0·770	0·772	0·767	0·847	0·736	0·734	0·854	0·790
0·5	0·805	0·847	0·786	0·758	0·761	0·756	0·848	0·721	0·715	0·856	0·783
0·6	0·801	0·846	0·782	0·750	0·754	0·749	0·848	0·707	0·705	0·858	0·775
0·7	0·797	0·846	0·779	0·744	0·747	0·739	0·849	0·698	0·694	0·858	0·770
0·8	0·797	0·847	0·777	0·740	0·740	0·734	0·848	0·690	0·685	0·857	0·767
0·9	0·795	0·847	0·774	0·734	0·735	0·729	0·849	0·684	0·678	0·856*	0·764
1·0	0·793	0·846	0·772	0·729	0·732	0·723	0·847	0·679	0·671	0·854	0·763
1·2	0·791*	0·846	0·766	0·723	0·724	0·717	0·848*	0·670	0·663	0·855	0·758
1·4	0·790	0·846*	0·761	0·719	0·720	0·710	—	0·669	0·655	0·854*	0·756*
1·6	0·790	—	0·758	0·714	0·716	0·707	—	0·657	0·649	—	0·755
1·8	0·791	—	0·756*	0·712	0·714	0·704	—	0·654	0·646	—	0·755
2·0	0·792	—	0·755	0·709	0·714	0·705	—	0·656	0·644	—	0·754
2·5	0·792	—	0·754	0·705*	0·710	0·701*	—	0·651*	0·642*	—	0·755
3·0	0·789*	—	0·755	0·704	0·705*	0·699	—	0·650	0·640	—	0·753
3·5	—	—	0·756	0·704	0·704	0·701	—	0·651	0·640	—	0·756
4·0	—	—	0·755	0·706	0·705	0·702	—	0·651	0·642	—	0·755
4·5	—	—	0·756	0·703	0·704	0·702	—	0·653	0·641	—	0·753*
5·0	—	—	0·754*	0·705*	0·706*	0·700*	—	0·651	0·641*	—	—
5·5	—	—	—	—	—	—	—	0·651	—	—	—
6·0	—	—	—	—	—	—	—	0·650*	—	—	—
α_m^a	0·790	0·846	0·755	0·704	0·705	0·701	0·848	0·651	0·641	0·855	0·755
n_h^a	2·66	6·04	1·38	2·13	1·79	1·89	6·31	1·97	1·79	6·28	1·85
ref.[1]	2·5			1·2	0·9	0·6					

^{a} $\Delta\alpha_m \leqq \pm 0.002$ and $\Delta n_h \leqq \pm 0.02$ for all, but $\sim \pm 0.005$ and $\sim \pm 0.05$ for NaOH; ^{b} Ac = acetate.

decreases. In the preliminary investigations[6a−d] the use of equation

$$vm\varphi \simeq 55 \cdot 51 (n_B/n_A) \qquad (3)$$

which is the limiting form of Eq. (1) for $n_B \ll n_A$ (cf.[13]), resulted in lower hydration numbers but almost the same α_m values as in Table I.

The constancy of α_m in the linear region shows that the ions associate only to a certain maximum degree in the given solvent, here water. The dimensionless ratio K defined by

$$K = \alpha_m^2/(1 - \alpha_m) = K_c/c , \qquad (4)$$

where K_c is the molar dissociation constant for a 1 : 1 electrolyte and c is the molar concentration, is a constant in this range of concentrations. Similar results were obtained for multivalent electrolytes[6d,e]. Of the listed electrolytes in Table I, HI has the highest K of 5·88 and CsBr has the lowest of 1·14, while for NaCl, $K = 2·37$. In the literature, the linear increase at moderately high concentrations in aqueous solutions of K_c with c for a weak electrolyte such as 2,4-dinitrophenol[2] as well as for a strong electrolyte like copper sulphate (Bjerrum's result discussed similarly in ref.[14]) suggests that $\alpha = \alpha_m$, a constant for these cases also. The dissociation constant, K_{ds}, defined as $[\alpha^2/(1 - \alpha)] (m/n_A)$ has been shown[6c] to be equal to exp. $.[-(F/RT)(\psi_+ - \psi_-)]$, where ψ_+ and ψ_- are the Lange's (inner) potentials of the ions in the solution. The existing theories of ion association[1−5] do not predict the constancy of α observed here.

Assuming n_h to be independent of concentration (as, e.g., in ref.[1]) from $m = 0$ to m corresponding to the end of linearity in Fig. 1, the values of $\alpha(= i - 1)$ at various concentrations were calculated from Eq. (2). These are given in Table I. It can be seen from Table I that, e.g., a solution of HCl of molality 0·1 contains a total of 0·1864 moles of solute (n_B) comprising of 0·0864 mole each of H^+ and Cl^- ions and 0·0136 mole of HCl in the undissociated (or "ion pair") form. That the α and n_h values derived above from the vapour pressure data can explain the properties of electrolyte solutions, is demonstrated below in the next part of this paper.

Correlation of α with the Molal Volumes and Densities of Solutions

The volume V at temperature T of a solution of molality m and the solution density d are related by $V = (1\ 000 + mM_B)/d$, where M_B is the molecular weight of solute B. In the case of strong electrolytes, the concentration dependences of V and d are usually interpreted[3,15−17] by parametrical equations containing fractional powers of m based on the idea of complete dissociation. On the other hand, it is demonstrated here that V depends on α as originally observed by Heydweiller[18] despite his (in-

correct) use of the Arrhenius conductivity ratio for α. (A more exact relation between α and conductivity is discussed in[6a,c] and it is currently being refined.)

Let V_B^0 be the volume per mole of the electrolyte and $V_A^0 = 1\,000/d_0$ be the volume of 1 000 g of water before they are mixed, where d_0 is the density of water at temperature T. The total volume of the ingredients before the solution is prepared $= V_A^0 + mV_B^0$. Let $(V_+ + V_- \pm \delta V)$ be the effective sum of the volumes per mole of the ions in the solution, where V_+ and V_- are the volumes per mole of the cation and anion and $\pm \delta V$ is the sum of the volume changes caused by dissociation and interactions of the ions in the given medium[17,19,20]. The effective volume V_B of the i moles of solute in the solution is directly dependent on α as

$$V_B = (1 - \alpha) V_B^0 + \alpha(V_+ + V_- \pm \delta V) = V_B^0 - \alpha[V_B^0 - (V_+ + V_- \pm \delta V)]. \quad (5)$$

Therefore, V, the sum of the volumes of the solvent and solute, is given by the equation

$$V = V_A + mV_B = V_A + mV_B^0 - \alpha m[V_B^0 - (V_+ + V_- \pm \delta V)], \quad (6)$$

where V_A is the volume of 1 000 g of water in the solution. The difference, $V_A - V_A^0$, is a measure of the volume change, if any, brought about by the hydration of the solute.

Fig. 2 shows the linear dependence of $(V - mV_B^0)$ on the ionic molality, αm, for NaCl and KBr, where V was calculated from the tables[16] for the c/m ratio as $V = = 1\,000m/c$ and the values of V_B^0 (= 26·8 and 42·9 cm³/mole for NaCl and KBr, respectively) were taken from ref.[20]. The linear relation holds for molalities from 0 to about 1·4 for NaCl and 0·8 for KBr. Least square evaluations of the intercepts show that $V_A = V_A^0(\pm 0.04 \text{ cm}^3)$ and thereby, that the solvent water does not suffer any appreciable volume change due to hydration of the solute. This implies that hydration of the solute is probably similar to adsorption[6b,21]. The slopes of the straight lines give the contraction in volume represented by the term in the square brackets in Eq. (6), from which the values of $(V_+ + V_- \pm \delta V)$ were found to be 16·35 and 32·94 cm³/mole for NaCl and KBr, respectively. These are comparable with the values of Φ_v^0 (apparent molal volume at infinite dilution) reported in the literature: 16·6 (refs[16,20]) and 16·3 (ref.[19]) for NaCl and 33·6 (ref.[19]) and 33·7 (refs[16,20]) for KBr. From Fig. 2 one infers that the undissociated electrolyte (or associated ion pair) has the same volume V_B^0 in the solution as in the solid state and that V_A^0, V_B^0 and $(V_+ + V_- \pm \delta V)$ are independent of concentration in the region of validity of linearity.

The volumes, V_{calc}, and densities, d_{calc}, of the solutions calculated from Eq. (6) using the above slopes and intercepts, are compared with the actual volumes, V, and densities, d, in Table II. Their close agreement $[V_{calc} = V(\pm 0.04 \text{ cm}^3)$ and

TABLE II

Comparison of actual and calculated volumes V (cm^3) and densities d (g/cm^3) of aqueous solutions of NaCl and KBr at 25°C

m	NaCl				KBr			
	V	V_{calc}[a]	d	d_{calc}[b]	V	V_{calc}[a]	d	d_{calc}[b]
0·0	1 003·01	1 003·05	0·99700	0·99696	1 003·01	1 003·02	0·99700	0·99699
0·0064[c]	1 003·13	1 003·16	0·99825	0·99822	—	—	—	—
0·0256[c]	1 003·48	1 003·49	0·99802	0·99801	—	—	—	—
0·0576[c]	1 004·07	1 004·06	0·99930	0·99931	—	—	—	—
0·1024[c]	1 004·90	1 004·88	1·00108	1·00110	—	—	—	—
0·1	1 004·85	1 004·84	1·00099	1·00100	1 006·49	1 006·46	1·00538	1·00541
0·2	1 006·70	1 006·67	1·00496	1·00499	1 009·98	1 009·96	1·01369	1·01371
0·3	1 008·56	1 008·53	1·00890	1·00893	1 013·48	1 013·48	1·02192	1·02193
0·4	1 010·43	1 010·42	1·01281	1·01282	1 017·02	1 017·02	1·03009	1·03007
0·5	1 012·30	1 012·30	1·01672	1·01672	1 020·54	1 020·57	1·03818	1·03815
0·6	1 014·18	1 014·19	1·02059	1·02058	1 024·09	1 024·11	1·04621	1·04618
0·7	1 016·06	1 016·07	1·02446	1·02445	1 027·65	1 027·65	1·05416	1·05416
0·8	1 017·96	1 017·97	1·02829	1·02828	1 031·23	1 031·20	1·06205	1·06207
0·9	1 019·86	1 019·87	1·03210	1·03209	—	—	—	—
1·0	1 021·76	1 021·77	1·03590	1·03589	·	·	—	—
1·2	1 025·60	1 025·59	1·04342	1·04343	—	—	—	—
1·4	1 029·46	1 029·44	1·05086	1·05088	·	—	—	—

[a] V_{calc}: Eq. (6); [b] $d_{calc} = (1\,000 + mM_B)/V_{calc}$. [c] For 0·0064, 0·0256, 0·0576, and 0·1024 mol/kg solutions of NaCl, $\alpha = 0·947, 0·907, 0·877$, and $0·854$, respectively; obtained by using n_h and φ (ref.[1]) in Eq. (2).
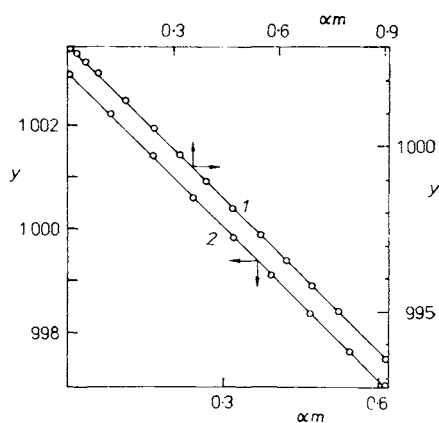

FIG. 2

Linear dependence of y ($\equiv (V - mV_B^0)$, cm^3) on ionic molality, αm, for aqueous solutions at 25°C, 1 NaCl; 2 KBr (full lines — least squares fit)

$d_{calc} = d(\pm 0{\cdot}00004 \text{ g/cm}^3)]$ proves that the electrolytes are incompletely dissociated in aqueous solutions. Similar results were obtained in the cases of KCl and KI. It is pointed out here that the volumes of solutions of weak electrolytes like acetic acid have also been interpreted[16,17] by an equation similar to Eq. (6). In the preliminary work[6d], a simpler expression for V_B (without $\pm \delta V$) was used; however, inclusion of $\pm \delta V$ can explain the reported[16,17] negative values of Φ_v^0. (At higher concentrations, the linear relations demonstrated in Fig. 2 do not hold: e.g., $(V - V_{calc})$ is about 0·5 and 1·5 cm³ for 2 molal solutions of NaCl and KBr respectively, but this will be discussed in a different paper.)

Correlation of α and n_h with the e.m.f. of Concentration Cells

The measured e.m.f., ΔE $(= E - E^0)$ of a concentration cell without transport is related to $\log (p_A/p_A^0)$ through the Gibbs–Duhem requirement[1]

$$-55{\cdot}51RT\,\mathrm{d}\ln p_A = mF\,\mathrm{d}E\,,\qquad(7)$$

where F is the Faraday constant. ΔE is used[1,12,16] for the exact evaluation of the molal activity coefficient γ (or the non-ideality correction factor), say for a 1 : 1 electrolyte, from the relation

$$\Delta E + (2RT/F)\ln m = (-2RT/F)\ln \gamma\,,\qquad(8)$$

where $(-2RT/F)\ln m$ is the supposed ideal e.m.f. corresponding to complete dissociation at any molality m. However, in agreement with the idea of partial dissociation, it is found here that ΔE is directly proportional to the logarithm of the number
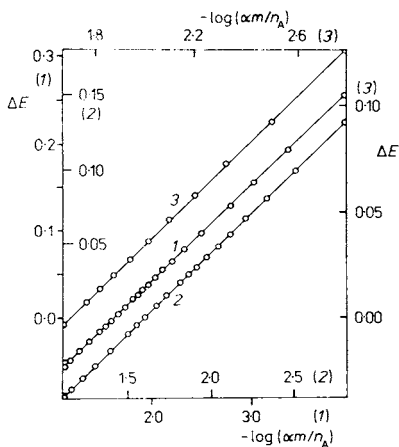

Fig. 3

Linear dependence of ΔE (V) on $-\log$ . . $(\alpha m/n_A)$ for aqueous solutions at 25°C, 1 NaCl; 2 KBr; 3 HCl (full lines — least squares fit)

of moles of ions per mole of "free" solvent. Fig. 3 shows the linear relation between ΔE (back-calculated from γ data[1] as $\Delta E = -0.1183 \log m\gamma$) and $-\log (\alpha m/n_A)$ for solutions of NaCl $(m = 0.0064$ to $4)$, KBr $(m = 0.1$ to $4.5)$ and HCl $(m = 0.1$ to $1.2)$ in aqueous solutions at 25°C. Thus, ΔE depends both on α and n_h (since $n_A = = 55.51 - mn_h$). The least square slopes were found to be 0.113, 0.108, and 0.115 V for NaCl, KBr and HCl, respectively. Hence, ΔE is given by the equation

$$\Delta E = -\delta_A (2RT/F) \ln \left[(\alpha m/n_A)/(\alpha m/n_A)^0 \right], \qquad (9)$$

where $(\alpha m/n_A)^0$ pertains to the reference solution or electrode at E^0 (for which $m\gamma = 1$), and δ_A is a constant. For NaCl, KBr and HCl δ_A has the values 0.953, 0.915, and 0.970, respectively. The preliminary results[6b,c] show that the slopes and hence δ_A depend appreciably on the valency of the ions; e.g., $\delta_A \simeq 0.85$ for 2 : 1 electrolytes. It is tentatively interpreted as a factor by which the actual e.m.f. is reduced by the polarization effect of the solvent[22].

With reference to Fig. 3, line 3 for HCl, since ΔE (the ordinate) is directly proportional to pH $(= -\log m\gamma)^1$, the relation between the "true molality of the hydrogen ions", αm, and pH is given by

$$pH - (pH)^0 = -\delta_A \log \left[(\alpha m/n_A)/(\alpha m/n_A)^0 \right], \qquad (10)$$

where $(pH)^0$ refers to the reference solution. E.g., for 0.1 molal HCl solution at 25°C, $\alpha m = 0.0864$ (Table I) and pH $(= -\log m\gamma) = 1.099$.

For very dilute solutions, since $(\alpha m/n_A)$ is proportional to αc, Eq. (9) reduces to the E vs $\log \alpha c$ linear relation proposed by Nernst[23].

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