DEGREES OF DISSOCIATION AND HYDRATION NUMBERS OF SIX TETRA ALKYL AMMONIUM HALIDES AND NINETEEN 2 : 1 STRONG ELECTROLYTES IN AQUEOUS SOLUTIONS AT 25°C

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The actual ionic concentrations and hydration numbers of some tetra alkyl ammonium halides and 2 : 1 strong electrolytes in aqueous solutions at 25°C have been evaluated for the first time from the existing osmotic coefficient data.

It was recently demonstrated[1-3] that the non-ideal properties of strong electrolytes in dilute and concentrated aqueous solutions are due to incomplete dissociation[4] and hydration[5] as originally supposed[5] (see ref.[3] for more literature). The degrees of dissociation, α, and the hydration numbers, n_h, evaluated from the vapour pressure (or molal osmotic coefficient, φ) data were shown to explain quantitatively the concentration dependences of many properties of strong electrolytes like the e.m.f. of concentrtion cells[1a,1b,2,3], solution density[1e,2,3], equivalent conductivity[1a,1b,1e,3] and diffusion coefficient[1a,1e,3]. Thus, data on n_h and α for thirty five 1 : 1 electrolytes and fifteen multivalent electrolytes were made available for the first time in ref.[2] and ref.[3], respectively. This paper presents n_h and α data for six tetra alkyl ammonium halides (Table I) and nineteen 2 : 1 strong electrolytes (Table II) in aqueous solutions at 25°C, evaluated from the vapour pressure ratio (or the activity a_A), obtained from the φ data in refs[6,7],

$$(p_A/p_A^0) = a_A = n_A/(n_A + n_B) \qquad (1)$$

as described in ref.[2].

In the above equation, p_A and p_A^0 are the vapour pressures over the solution and solvent (A) respectively and n_A and n_B are the amounts in moles of "free" solvent (A) and solute (B), respectively. For a solution of molality m, $n_A = (55{\cdot}51 - mn_h)$, where 55·51 is the number of moles of water in 1 kg, and $n_B = [1 + (\nu - 1)\alpha]\, m$ is the total number of moles of solute.

The results are presented in Tables I and II. n_h is constant over the range of con-

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centrations for which α is presented in the Tables; and at higher concentrations (not discussed in this paper) it decreases. It can be seen that as for the other strong electrolytes[1-3], α decreases from the value of unity at infinite dilution to a constant minimum value, α_m, over a large range of concentrations. Also, the maximum degree of ionic association, $(1 - \alpha_m)$, is higher the lower the value of n_h and the higher the cationic valency. α_m for the halides increases in general in the order $I^- > Br^- > Cl^-$, except in Table I.

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TABLE I

Degrees of dissociation (α) and hydration numbers (n_h) of tetra alkyl ammonium halides in aqueous solutions at 25°C. The upper and lower limits of m between which $\alpha = \alpha_m = \text{const.}$ are denoted by asterisks

m	$(CH_3)_4NCl$	$(C_2H_5)_4NCl$	$(C_3H_7)_4NCl$	$(C_4H_9)_4NCl$	$(C_2H_5)_4NBr$	$(C_3H_7)_4NBr$
0·1	0·818	0·812	0·809	0·819	0·773	0·759
0·2	0·765	0·774	0·743	0·773	0·689	0·659
0·3	0·732	0·719	0·699	0·744	0·625	0·589
0·4	0·707	0·693	0·667	0·729	0·573	0·533
0·5	0·688	0·672	0·644	0·717	0·535	0·492
0·6	0·671	0·654	0·627	0·709	0·502	0·459
0·7	0·658	0·640	0·615	0·705*	0·475	0·432
0·8	0·646	0·630	0·604	0·702	0·449	0·410
0·9	0·637	0·620	0·599	0·703	0·428	0·393
1·0	0·631	0·611	0·596	0·705	0·408	0·381
1·2	0·618	0·613	0·591*	0·704*	0·379	0·366
1·4	0·611	0·613	0·590	—	0·355	0·359
1·6	0·606	0·610	0·593	—	0·335	0·356*
1·8	0·603*	0·606	0·590*	—	0·319	0·355
2·0	0·602	0·600*	—	—	0·304	0·358
2·5	0·602	0·591	—	—	0·275	0·355*
3·0	0·603	0·594	—	—	0·259*	—
3·5	0·603	0·598	—	—	0·256	—
4·0	0·602*	0·597*	—	—	0·257	—
4·5	—	—	—	—	0·259*	—
α_m[a]	0·603	0·596	0·591	0·704	0·258	0·356
n_h[a]	3·79	5·20	8·47	6·18	4·30	5·02

[a] $\Delta\alpha_m \leqq \pm 0{\cdot}005$ and $\Delta n_h \leqq \pm 0{\cdot}05$.

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TABLE II

Degrees of dissociation (α) and hydration numbers (n_h) of 2 : 1 strong 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	$MgCl_2$[c]	$MgBr_2$	MgI_2	$Mg(ClO_4)_2$	$Mg(NO_3)_2$	$MgAc_2$[b]	$CaCl_2$[c]	$CaBr_2$	CaI_2	$Ca(ClO_4)_2$	$Ca(NO_3)_2$	$SrCl_2$[c]
0·1	0·759	0·769	0·790	0·797*	0·755	0·681	0·753	0·759	0·779	0·784	0·729	0·750
0·2	0·749	0·760	0·782*	0·798	0·741	0·661	0·736	0·746	0·775	0·783*	0·707	0·731
0·3	0·740	0·757*	0·780	0·798	0·739*	0·650	0·728	0·740*	0·772*	0·783	0·694	0·720
0·4	0·739*	0·758	0·780	0·798	0·740	0·643	0·723*	0·740	0·774	0·785	0·687	0·717*
0·5	0·740	0·763	0·783	0·797*	0·742	0·639	0·725	0·742	0·778	0·788	0·682	0·717
0·6	0·741	0·760	0·780*	—	0·743	0·637*	0·725	0·743	0·775	0·787	0·679	0·715
0·7	0·738	0·756*	—	—	0·738*	0·636	0·723	0·742	0·773	0·784	0·674*	0·713
0·8	0·738	—	—	—	—	0·637	0·722	0·741	0·773*	0·781*	0·674	0·713
0·9	0·739	—	—	—	—	0·639	0·725	0·739*	—	—	0·672	0·715
1·0	0·740*	—	—	—	—	0·638	0·725	—	—	—	0·673	0·717
1·2	—	—	—	—	—	0·639	0·724*	—	—	—	0·676	0·717
1·4	—	—	—	—	—	0·638	—	—	—	—	0·678	0·715*
1·6	—	—	—	—	—	0·635*	—	—	—	—	0·678	—
1·8	—	—	—	—	—	—	—	—	—	—	0·674	—
2·0	—	—	—	—	—	—	—	—	—	—	0·672*	—
α_m[a]	0·740	0·759	0·781	0·798	0·740	0·637	0·724	0·741	0·774	0·785	0·675	0·715
n_h[a]	15·32	19·20	21·36	21·90	14·49	7·73	13·38	16·30	18·44	18·25	6·15	12·08
ref.[7]	13·7	17·0	19·0	—	—	—	12·0	14·6	17·0	—	—	10·7

TABLE II
(Continued)

m	$SrBr_2$	SrI_2	$Sr(ClO_4)_2$	$Sr(NO_3)_2$	$BaCl_2$[c]	$BaBr_2$	BaI_2	$Ba(ClO_4)_2$	$MnCl_2$	$FeCl_2$	$CoCl_2$
0·1	0·759	0·774	0·758	0·720	0·747	0·752	0·766	0·757	0·754	0·752	0·756
0·2	0·746	0·773*	0·751	0·686	0·720	0·736	0·759*	0·745	0·738	0·736	0·743
0·3	0·739	0·771	0·752*	0·665	0·711	0·728	0·758	0·739*	0·730	0·726	0·736
0·4	0·735	0·772	0·754	0·651	0·707	0·724*	0·759	0·738	0·728*	0·722*	0·734*
0·5	0·735*	0·773	0·757	0·639	0·704*	0·728	0·764	0·741	0·727	0·724	0·735
0·6	0·735	0·774	0·757	0·629	0·703	0·729	0·761	0·743	0·728	0·722	0·738
0·7	0·734	0·773	0·754	0·619	0·702	0·727	0·756*	0·741	0·727	0·722	0·738
0·8	0·734	0·774	0·751*	0·610	0·702	0·725	—	0·737*	0·726	0·721	0·734
0·9	0·736	0·773	—	0·603	0·702	0·727	—	—	0·726	0·723	0·737
1·0	0·736	0·770*	—	0·594	0·702	0·727	—	—	0·729*	0·724*	0·737
1·2	0·734*	—	—	0·582	0·703	0·726*	—	—	—	—	0·733*
1·4	—	—	—	0·573	0·704*	—	—	—	—	—	—
1·6	—	—	—	0·564	—	—	—	—	—	—	—
1·8	—	—	—	0·557	—	—	—	—	—	—	—
2·0	—	—	—	0·553	—	—	—	—	—	—	—
2·5	—	—	—	0·545	—	—	—	—	—	—	—
3·0	—	—	—	0·543*	—	—	—	—	—	—	—
3·5	—	—	—	0·543	—	—	—	—	—	—	—
4·0	—	—	—	0·543*	—	—	—	—	—	—	—
α_m[a]	0·735	0·772	0·754	0·543	0·703	0·726	0·759	0·740	0·727	0·722	0·735
n_h[a]	14·14	16·85	17·53	3·09	9·08	11·90	17·31	13·40	12·21	13·79	14·15
ref.[7]	12·7	15·5	—	—	7·7	10·7	15·0	—	11·0	12·0	13·0

[a] $\Delta\alpha_m \leqq \pm 0{\cdot}005$ and $\Delta n_h \leqq \pm 0{\cdot}05$; [b] Ac = acetate; [c] from ref.[3].

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