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Foot (1/15) Legend (p. 6)
Table I (p. 7) Fig. 1

**BULK AND SURFACE HYDRATION NUMBERS AND DEGREES OF DISSOCIATION
OF NaCl IN AQUEOUS SOLUTIONS AT 25°C FOR ALL CONCENTRATIONS**

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Abstract:

The interpretation of the equilibrium properties (osmotic coefficients) of solutions of strong electrolytes in terms of hydration and incomplete dissociation, has now been extended to the whole range of concentrations from 0 to saturation. Osmotic pressure, a bulk property is characterized by a bulk hydration number and vapour pressure, a surface property, by a surface hydration number. Supporting data are provided for NaCl. The simple quantitative mathematical relations obtained here replace the complicated expressions based on the assumption of complete dissociation.

The equation^{1a,b} for the osmotic pressure π_{OS} ,

$$\pi_{OS} = iRT/V_{Afb} = iRTmd_A/(1-mW_b) = vm\phi d_A RT \quad \dots(1)$$

where $i [= 1+(v-1)\alpha]$ is the van't Hoff factor, α is the degree of dissociation, v is the number of ions into which one mole of solute (B) dissociates, V_{Afb} is the volume of 'free' (f) solvent (A) in the bulk (b) per mole of B, m is the molality, d_A is the density of A, W_b is the mass in kg. of $n_b (= 55.51W_b)$ moles of water engaged as hydration by one mole of B, 55.51 is the number of moles of water in 1 kg and ϕ is the molal osmotic coefficient (non-ideality parameter), was shown¹ to be valid for a large range of concentrations for many electrolytes (e.g., 0 to 4m NaCl).

The equation^{1a,b} for the vapour pressure ratio (p_A/p_A^0) [defined² as the solvent activity $a_A = \exp(-vm\phi/55.51)$],

$$a_A = N_{Afs} = (55.51-mn_s)/(55.51-mn_s+im) \quad \dots(2)$$

where N_{Afs} is the mole fraction of 'free' solvent (at the surface (s) of solution) and n_s is the number of moles of water engaged as hydration by one mole of B (at the vapour/solution interface), was demonstrated^{1a,b} to be valid for many (over 100) strong electrolytes over a large range of concentrations (e.g., 0 to 4m NaCl). [Note: in ref.^{1a,b} (cf: the literature therein), although it was observed that Eqs (1) and (2) for the surface and bulk properties gave nearly the same degrees of dissociation but differing hydration numbers, it was not realized that they were both correct.]

On combining Eqs.(1) and (2), one finds that the concentration dependence of ϕ is given by the equation,

$$\phi = i/v(1-mW_b) = -(55.51/vm)\ln N_{AfS} \quad \dots(3)$$

In this paper, it is demonstrated that Eq.(3) is in fact valid for all concentrations from zero up to saturation: By combining Eqs.(1) and (2) in the form,

$$im = -(55.51-mn_b)\ln a_A = [(1-a_A)/a_A](55.51-mn_s) \quad \dots(4a)$$

and eliminating im , one obtains the ratio R_{Af} ,

$$R_{Af} = [-a_A \ln a_A / (1-a_A)] = (55.51-mn_s) / (55.51-mn_b) \quad \dots(4b)$$

which depends on n_s and n_b , but not on i . R_{Af} can be calculated using the available a_A or ϕ data (in the term in the middle in the above equation), and it represents the ratio of the number of moles of 'free' water in the surface to that in the bulk. For aqueous solutions of NaCl at 25°C, the values of R_{Af} calculated from the ϕ data in ref.³ (see column 2, Table I) are tabulated in column 4, Table I. A computer linear (best-fit) plot of the ratio $(55.51-mn_s)/R_{Af}$ vs m (see Fig.1) gives $n_s = 3.348$ and $n_b = 2.457$ (n_b is the -ve slope of the line in Fig.1), S.E.: 0.001.

The values of the degrees of dissociation, α ($= i-1$), calculated from Eqs (2) and (1) by using the above values of n_s and n_b respectively, are presented in columns 5 and 6 of Table I. The near identity (+0.001) of these values can be noted. It can be seen that α reduces from the value of unity at $m = 0$ to

a minimum at about $m = 1.4$ and then rises again.

The third column in Table I gives the values of ϕ, cal $[(i/v(1-mW_b))]$ obtained by using in Eq. (1) the α values in column 5 calculated from Eq. (2). It can be seen that the maximum difference ($\phi, \text{lit} - \phi, \text{cal}$) is only $+0.001$ over the entire concentration range.

Thus, it is for the first time that the concentration dependence of ϕ has been quantitatively explained from zero to saturation. In this context, attention is drawn^{1c} to the complicated expressions²⁻⁴ for the concentration dependence of ϕ based on the idea of complete dissociation, which moreover are not valid up to saturation. E.g., see equation (7) for $\text{NaCl}(\text{aq})$ in the review⁴.

The above results have now enabled the extension of the quantitative expressions^{1a,b} for the activity coefficients and the molal volumes (or densities) of solutions to the entire concentration range⁵.

Finally, it is pointed out here that recently experimental evidence has been obtained⁶ for the first time by X-ray diffraction studies for the existence of ion pairs in aqueous saturated solutions of alkali halides. These findings have been supported by molecular dynamic simulations⁷.

References

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Caption for Figures:

Figure 1:

The linear dependence of the ratio, $(55.51 - mn_s)/R_{Af}$ on molality m for aqueous solutions of NaCl at 25 °C from zero to saturation (6.144m); cf: Eq. (4b). R_{Af} was calculated using the ϕ -data from ref.3. $n_s = 3.348$, (-Slope =) $n_b = 2.457$ (S.E.: 0.001) and intercept = 55.51 (S.E.: 0.008).

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Table I. Degrees of dissociation (α) at various molalities (m) (6.144m: satd. soln.) for aqueous solutions of NaCl at 25°C. Also presented are the values of R_{Af} (cf: Eq.(4)) and the comparison of $\phi(\text{cal})$ with $\phi(\text{lit})^3$.

m	$\phi(\text{lit})$	$\phi(\text{cal})$	R_{Af}	$\alpha(\text{Eq.2})$	$\alpha(\text{Eq.1})$
0.000	1.000	1.000	1.00000	1.000	1.000
0.001	0.988	0.988	0.99998	0.976	0.976
0.002	0.984	0.984	0.99996	0.968	0.968
0.005	0.976	0.976	0.99991	0.952	0.952
0.010	0.968	0.968	0.99983	0.935	0.935
0.020	0.959	0.959	0.99965	0.916	0.916
0.050	0.944	0.944	0.99915	0.884	0.884
0.100	0.933	0.933	0.99832	0.858	0.858
0.200	0.924	0.924	0.99667	0.832	0.832
0.300	0.921	0.921	0.99503	0.818	0.818
0.400	0.920	0.920	0.99339	0.808	0.807
0.500	0.921	0.921	0.99173	0.801	0.801
0.600	0.923	0.923	0.99006	0.797	0.797
0.700	0.926	0.926	0.98837	0.795	0.795
0.800	0.929	0.929	0.98667	0.792	0.792
0.900	0.932	0.932	0.98497	0.790	0.790
1.000	0.936	0.936	0.98323	0.789	0.789
1.200	0.944	0.944	0.97973	0.788	0.788
1.400	0.953	0.953	0.97616	0.788	0.788
1.600	0.962	0.962	0.97253	0.787	0.788
1.800	0.973	0.973	0.96878	0.791	0.791
2.000	0.984	0.984	0.96497	0.793	0.794
2.500	1.013	1.013	0.95507	0.801	0.802
3.000	1.045	1.045	0.94459	0.812	0.812
3.500	1.080	1.080	0.93345	0.826	0.825
4.000	1.116	1.116	0.92174	0.837	0.837
4.500	1.153	1.153	0.90944	0.847	0.847
5.000	1.191	1.192	0.89656	0.856	0.855
5.500	1.231	1.231	0.88298	0.863	0.863
6.000	1.270	1.270	0.86900	0.865	0.865
6.144	1.281	1.280	0.86491	0.864	0.865

$(55.51 - m m_s) / R_{Af}$

