THE STRUCTURE OF CONCENTRATED ELECTROLYTE SOLUTIONS (PART 1) THEORETICAL PROCEDURE TO PREDICT THE ELECTROLYTE CONCENTRATION OF A SOLUTION WHEN ITS ACTIVITY COEFFICIENT IS MINIMUM

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The mean activity coefficient of a salt in aqueous medium decreases with increasing concentration and reaches a minimum value and then increase, often exceeding unity.

This variation of the activity coefficients could be explained up to very high concentrations on a hybrid model[1] comprising of Debye Huckel Charge Cloud and Extended Lattice models.

The hybrid model yields an equation of the form $RT\ln f_{\pm} = 1^*BC - (1-1^*)\, kC^{\frac{1}{2}}$ Where $f_{\pm}$, c,k,B and I* are the mean activity coefficient salt concentration, Debye Huckel limiting law constant. Lattice model constant and the partition function respectively. The partition function (1)* involved in joining the two models uses no adjustable parameters unlike previous attempts of other workers.

The above equation for the mean activity coefficient predicts a value for the salt concentration (C_{min}) at which the activity coefficient is minimum. This is found to be independent of parameters of charge cloud and lattice models and is found to be a function of molar salt concentration of solid salt (C_s) and the concentration of salt ($C_{1.0}$) when its activity coefficient is unity, as shown by the equation.

$$5C_{min}^{1/6} + M\, C_{min}^{1/3} - 3C_s^{1/3} = 0$$

where M is a constant involving C_s and $C_{1.0}$ only)

Some of the results of the predicted C_{min} values with their corresponding observed values are given below.

Salt	Observed C_{min}	Predicted C_{min}	$C_{1.0}/C_{min}$
LiCl	0.45	0.432	5.09
NaCl	1.00	0.972	4.92
$MgCl_2$	0.37	0.356	5.01
$AlCl_3$	0.25	0.253	5.02
KF	1.10	1.11	4.94

The radio $C_{1.0}/C_{min}$ is found to be a constant irrespective of the salt and valencies of the ions

References:

Wijayanayake R.H. & Griffith T.R. (1980)
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