E2-06 Testing a new theory on concentrated electrolyte solutions using activity coefficients and corresponding permittivity functions

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The properties of electrolye solutions at low concentrations can be theoretically predicted using the Debye Huckel theory. However, at high concentrations, a different model (quasi lattice) is required as the basis of the theory. Recently, in high concentrated solutions, the presence of a quasi lattice has been shown by X-ray analysis.

Combination of charge cloud model and quasi lattice model using a new partition function yields an equation:

$$RT\ln f = (1 - d)\ kc^{1/2} + d\ \gamma\ c^{1/8}$$

where k is the Debye Huckel constant, c the concentration of electrolyte and d the ratio (c/c_s), c_s the molar salt concentration of solid salt, γ a constant.

The above equation satisfies the activity data up to salt concentrations over 4 mol dm^{-3} which is better than the agreement with improved versions of Debye Huckel equation. Further it gives good agreement with theoretically predicted minimum activity coefficients with those of experimental data.

Normally the single permittivity value of the solvent is used in the above equation for all concentrations of electrolyte. However, as it is more appropriate to use permittivity values of electrolyte solutions themselves, we have used the functions recently published to calculate these values. When these values are used in our equation, better agreement with activity coefficients is observed. However, at extreme high concentrations deviations from experimental data are observed. This could be attributed to an inadequacy of water molecules to solvate ions at high concentrations.