Compressions: Isothermal: Salt Solutions

In 1933 Gucker [1-3] reviewed attempts to measure the apparent isothermal molar compressions of salts in aqueous solution, these attempts dating back to the earliest reliable measurements by Rontgen and Schneider [4] in 1886 and 1887. Gucker showed [2] that for several aqueous salt solutions the apparent isothermal molar compression, $\phi(K_j)$, is a linear function of the square root of the salt concentration.

$$\phi(K_j) = \phi(K_j)^{\infty} + a \cdot c_j^{1/2} \quad (a)$$

This general equation holds for CaCl$_2$ (aq) at 60 Celsius. In general terms, $\phi(K_j)$ for salts is negative becoming less negative as the salt concentration increases. Gibson described an interesting approach which characterises salt solutions in terms of effective pressures, $p_c$, exerted by the salt on the solvent [5]. This effective pressure is expressed as a linear function of the product of salt and solvent concentrations. The constant of proportionality is characteristic of the salt. Leyendekkers based an analysis using the Tammann-Tait-Gibson (TTG) model, on the assertion that solutes, salts and organic solutes, exert an excess pressure on water in aqueous solution [6,7]. The TTG approach described by Leyendekkers is intuitively attractive but the analysis is based on an extra - thermodynamic assumption [8]. Calculation of an excess pressure requires an estimate of the volume of solute molecules, $\phi_j$ in solution. If this property is independent of solute molality $m_j$, the dependence of the volume of a solution (in 1 kg of water) on solute molality is described by the dependence of the 'partial molar volume' of water. The difference between $[V(aq; w_1 = 1 kg) - m_j \cdot \phi(Vj)]$ and $M^*_i \cdot V^*_i (\ell)$ is understood in terms of an effective pressure on the solvent. The assumptions underlying this calculation are not trivial. Furthermore from a thermodynamic viewpoint, the pressure is the same in every volume element of a solution [8].

Footnotes