Expansions: Isobaric: Apparent Molar: Neutral Solutes

For many aqueous solutions at ambient pressure and temperature, the dependence of \( \phi(E_{pj}) \) on molality of a neutral solute \( j \), \( m_j \) is accounted for by an equation having the following general form. [The reason for choosing the molality scale is again the fact that \( m_j \) is independent of \( T \) and \( p \) but concentration \( c_j \) is not.]

\[
\phi(E_{pj}) = a_1 + a_2 \cdot (m_j / m^0) + a_3 \cdot (m_j / m^0)^2 + a_4 \cdot (m_j / m^0)^3 + \ldots \quad (a)
\]

At low molalities, the linear term is dominant. Granted therefore that equation (a) accounts for the observed pattern, we need a quantitative description which accounts for this pattern. There are advantages in linking directly the apparent property \( \phi(E_{pj}) \) and the partial molar property \( E_{pj}(aq) \).

For an aqueous solution at fixed temperature and pressure,

\[
E_{pj}(aq) = m_j \left( \frac{\partial \phi(E_{pj})}{\partial m_j} \right) + \phi(E_{pj}) \quad (b)
\]

Hence the partial molar isobaric expansion of solute \( j \) can be calculated from the apparent molar isobaric expansion and its dependence on molality, \( m_j \). Hence if equation (a) satisfactorily describes the observed dependence of \( \phi(E_{pj}) \) on \( m_j \),

\[
E_{pj}(aq) = a_1 + 2 \cdot a_2 \cdot (m_j / m^0) + 3 \cdot a_3 \cdot (m_j / m^0)^2 + \ldots \quad (c)
\]

Therefore,

\[
\lim (m_j \to 0)E_{pj}(aq) = \lim (m_j \to 0)\phi(E_{pj})(aq) = E_{pj}^\infty(aq) = \phi(E_{pj})^\infty \quad (d)
\]

Consequently the parameter \( a_1 \) in equations (a) and (b) is the limiting partial molar isobaric expansion of solute \( j \).

For dilute solutions, equation (c) takes the following simple form.

\[
E_{pj}(aq) = E_{pj}^\infty(aq) + R \cdot S_{pj} \cdot (m_j / m^0) \quad (e)
\]

In these terms we can identify the basis of the parameter \( a_2 \) in equations (a) and (c).

Desrosiers et al [1] used a quadratic (cf. equation (a)) to express the dependence of \( \phi(E_{pj}) \) at 298 K on molality of urea in aqueous solutions;

\[
\phi(E_{pj}) = 0.07 \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}, \text{ coefficient } a_2 \text{ being positive and coefficient } a_3 \text{ being negative.}
\]
The majority of published information concerns the dependence on temperature of \( \phi(V_j) \). A survey \([2]\) based on a dilatometric study of 15 non-electrolytes in aqueous solution indicates that \([d\phi(V_j)\phi / dT] \) is less than \([dV_j^\phi(\ell) / dT]\) for the pure liquid substance \(j\); the second derivative \([d^2\phi(V_j)\phi / dT^2] \) is positive. However for hydrophilic solutes \([d\phi(V_j)\phi / dT] \) is larger than \([dV_j^\phi(\ell) / dT] \) and \([d^2\phi(V_j)\phi / dT^2] \) is negative \([3]\). A similar pattern is observed for sucrose and urea for which \([d^2\phi(V_j)\phi / dT^2] \) is negative. Indeed Hepler \([4]\) classified solutes in aqueous solutions as either structure-breaking (negative) or structure forming (positive) on the basis of the sign for \([d^2\phi(V_j)\phi / dT^2] \). The dependence of \( \phi(V_j) \) on temperature for both glycine and alanine in NaCl(aq) is small \([5]\), for monosaccharides(aq) \( E_{p\phi}(aq) \) is positive.

**Footnotes**