Compressions; Isentropic and Isothermal; Solutions: Limiting Estimates

The density of an aqueous solutions at defined T and p and solute molality \( m_j \) yields the apparent molar volume of solute \( j \), \( \phi(V_j) \). The dependence of \( \phi(V_j) \) on \( m_j \) can be extrapolated to yield the limiting (infinite dilution) property \( \phi(V_j)\infty \). The isothermal dependence of densities on pressure can be expressed in terms of an analogous infinite dilution apparent molar isothermal compression, \( \phi(K_{Tj})\infty \). Similarly the isentropic compressibilities of solutions are characterised by \( \phi(K_{Sj})\infty \) which is accessible via the density of a solution and the speed of sound in the solution. Nevertheless the isothermal property \( \phi(K_{Tj})\infty \) presents fewer conceptual problems in terms of understanding the properties of solutes and solvents which control volumetric properties. The challenge is to use \( \phi(K_{Sj};\text{def})\infty \) in order to obtain \( \phi(K_{Tj})\infty \). The linking relationship is the Desnoyers-Philip equation [1].

The apparent molar isothermal compression for solute \( j \) \( \phi(K_{Tj}) \) is related to the concentration \( c_j \) of solute using equation (a) where \( \phi(V_j) \) is the apparent molar volume of the solute.

\[
\phi(K_{Tj}) = [\kappa_T(aq) - \kappa_{\text{T1}}^{\ast}(\ell)] \cdot (c_j)^{-1} + \kappa_{\text{T1}}^{\ast}(\ell) \cdot \phi(V_j) \quad (a)
\]

The corresponding isentropic compression for solute \( j \), \( \phi(K_{Sj};\text{def}) \) is related to the concentration \( c_j \) using equation (b).

\[
\phi(K_{Sj};\text{def}) \equiv [\kappa_S(aq) - \kappa_{\text{S1}}^{\ast}(\ell)] \cdot (c_j)^{-1} + \kappa_{\text{S1}}^{\ast}(\ell) \cdot \phi(V_j) \quad (b)
\]

[We replace the symbol \( \equiv \) by the symbol \( = \) in the following account.]

By definition \( \delta(aq) = \kappa_T(aq) - \kappa_S(aq) \) \( \quad (c) \)

And \( \delta_1^{\ast}(\ell) = \kappa_{\text{T1}}^{\ast}(\ell) - \kappa_{\text{S1}}^{\ast}(\ell) \) \( \quad (d) \)

Hence \( \phi(K_{Tj}) \) and \( \phi(K_{Sj};\text{def}) \) are related by equation (e).

\[
\phi(K_{Tj}) - \phi(K_{Sj};\text{def}) = (c_j)^{-1} \cdot [\delta(aq) - \delta_1^{\ast}(\ell)] + \delta_1^{\ast}(\ell) \cdot \phi(V_j) \quad (e)
\]
The difference \( \phi(K_{\text{def}}) - \phi(K_{\text{cj}}) \) depends on the concentration of the solute \( c_j \). Further \( \delta(aq) - \delta'_i(\ell) \) is not zero. In fact,

\[
\delta(aq) - \delta'_i(\ell) = \{T \cdot [\alpha_p(aq)]^2 / \sigma(aq) - \{T \cdot [\alpha_{p_i}(\ell)]^2 / \sigma'_i(\ell)\}\}
\]  

(f)

Using the technique of adding and subtracting the same quantity, equation (f) is re-expressed as follows.

\[
\delta(aq) - \delta'_i(\ell) = \{\delta(aq)/[\alpha_p(aq)]^2 \cdot [\alpha_p(aq) + \alpha_{p_i}(\ell)] \cdot [\alpha_p(aq) - \alpha_{p_i}(\ell)] - \delta'_i(\ell) / \sigma(aq) \cdot [\sigma(aq) - \sigma'_i(\ell)]\}
\]  

(g)

The difference \( [\alpha_p(aq) - \alpha_{p_i}(\ell)] \) is related to \( \phi(E_{pj}) \) using equation (h).

\[
\phi(E_{pj}) = [\alpha_p(aq) - \alpha_{p_i}(\ell)] \cdot (c_j)^{-1} + \alpha_{p_i}(\ell) \cdot \phi(V_j)
\]  

(h)

Similarly, \( [\sigma(aq) - \sigma'_i(\ell)] \) is related to \( \phi(C_{pj}) \) using equation (i).

\[
\phi(C_{pj}) = [\sigma(aq) - \sigma'_i(\ell)] \cdot (c_j)^{-1} + \sigma'_i(\ell) \cdot \phi(V_j)
\]  

(i)

Using equations (g) - (i), we express equation (e) as follows.

\[
\phi(K_{\text{def}}) - \phi(K_{\text{cj}}) = [\delta(aq)/\alpha_p(aq)] \cdot \{1 + [\alpha_{p_i}(\ell)/\alpha_p(aq)]\} \cdot \phi(E_{pj}) - \delta'_i(\ell) / \sigma(aq) \cdot \phi(C_{pj}) + \delta'_i(\ell)
\]  

(j)

Equation (j) was obtained by Desnoyers and Philip [1] who showed that if \( \phi(K_{Tj})^\infty \) and \( \phi(K_{Sj}; \text{def})^\infty \) are the limiting (infinite dilution) apparent molar properties, the difference is given by equation (k).

\[
\phi(K_{Tj})^\infty - \phi(K_{Sj}; \text{def})^\infty = \delta'_i(\ell) \cdot \{[2 \cdot \phi(E_{pj})^\infty / \alpha_{p_i}(\ell)] - [\phi(C_{pj})^\infty / \sigma'_i(\ell)]\}
\]  

(k)

Using equation (b), \( \phi(K_{Sj}; \text{def}) \) is plotted as a function of \( c_j \) across a set of different solutions having different entropies.

Limit(\( c_j \rightarrow 0 \)) \( \phi(K_{Sj}; \text{def}) \) defines \( \phi(K_{Sj}; \text{def})^\infty \). Granted two limiting quantities, \( \phi(E_{pj})^\infty \) and \( \phi(C_{pj})^\infty \) are available for the
solution at the same T and p, equation (k) is used to calculate \( \phi(K_{Tj})^\infty \) using \( \phi(K_{Sj}; \text{def})^\infty \).

An alternative form of equation (j) refers to a solution, molality \( m_j \) [2].

\[
\phi(K_{Tj}) - \phi(K_{Sj}; \text{def}) = \\
\delta_i^j(\ell) \cdot \left\{ 2 \cdot \frac{\phi(E_{pj})}{\alpha_i^*(\ell)} - \frac{\phi(C_{pj})}{\sigma_i^*(\ell)} \right\} \\
+ \left[ \rho_i^*(\ell) \cdot m_j \cdot \left( \frac{\phi(E_{pj})}{\alpha_i^*(\ell)} \right)^2 \right] \cdot \left\{ 1 + \rho_i^*(\ell) \cdot m_j \cdot \frac{\phi(C_{pj})}{\sigma_i^*(\ell)} \right\}^{-1}
\]

The fact that \( \phi(K_{Tj})^\infty \) can be obtained from \( \phi(K_{Sj}; \text{def})^\infty \)

indicates the importance of the Desnoyers-Philip equation. Bernal and Van Hook [3] used the Desnoyers-Philip equation to calculate \( \phi(K_{Tj})^\infty \) for glucose(aq), sucrose(aq) and fructose(aq) at 348 K.

Similarly Hedwig et. al. used the Desnoyers –Philip equation to obtain estimates of \( \phi(K_{Tj})^\infty \) for glycyl dipeptides (aq) at 298 K [4].

Footnotes