Topic800

Compressions: Isentropic: Neutral Solutes

Granted that $\phi(K_{Sj}; \text{def})$ has been measured for solutions containing neutral solutes (at defined $T$ and $p$), interesting patterns emerge for the dependences of $\phi(K_{Sj}; \text{def})$ on molality $m_j$ and on solute $j$. Further these dependences are readily extrapolated (geometrically) to infinite dilution to yield estimates of $\phi(K_{Sj}; \text{def})^\infty$. These comments apply to solutions of neutral solutes in both aqueous and non-aqueous solutions; e.g. solutions in propylene carbonate [1] and aqueous solutions of carbohydrates [2].

For dilute solutions of neutral solutes $\phi(K_{Sj}; \text{def})$ is often approximately a linear function of the molality $m_j$.

Thus $\phi(K_{Sj}; \text{def}) = \phi(K_{Sj}; \text{def})^\infty + b_{KS} \cdot (m_j / m^0)$  (a)

For aqueous solutions containing ureas, acetamides and $\alpha,\omega$-alkanediols, the slope $b_{KS}$ is positive. For dextrose(aq), sucrose(aq), urea(aq) and thiourea(aq) $\phi(K_{Sj}; \text{def})^\infty$ is negative. In contrast $\phi(K_{Sj}; \text{def})^\infty$ is positive for dioxan(aq) and acetamide(aq). In other words $\phi(K_{Sj}; \text{def})^\infty$ is characteristic of the solute [3,4]. Group additivity schemes are discussed for $\phi(K_{Sj}; \text{def})^\infty$ with respect to glycylpeptides(aq) [5], amino acids(aq) [6-8] and alcohols [9-11]. With increase in temperature $\phi(K_{Sj}; \text{def})^\infty$ for amino acids(aq) [8] and glycyldipeptides(aq) [12,13] increases. Particularly interesting in terms of solute-water interactions is the study reported by Galema et al [14, 15] who comment on the calculation of $K_{Sj}(\text{aq}; \text{def})$ for solute-j using equation (b).

$K_{Sj}(\text{aq}; \text{def}) = \phi(K_{Sj}; \text{def}) + m_j \cdot \left[ \partial \phi(K_{Sj}; \text{def}) / \partial m_j \right]_{T,p}$  (b)

This study confirmed the importance of the stereochemistry of carbohydrates on their hydration. A clear contrast is drawn between those solutes where the hydrophilic groups match and mismatch into the three dimensionally hydrogen - bonded structure of liquid water. With increase in solute concentration, the dependence of $K_{Sj}(\text{aq}; \text{def})$ on composition is non-linear [16]. For amines(aq) $K_{Sj}(\text{aq}; \text{def})$ passes through minima [16].

Chalikian discusses the isentropic compression of a wide range of solutes with reference to group contributions [17], the discussion being extended to proteins [18] and oligopeptides[19].

Footnotes