Topic 2990

Volumes; Neutral Solutes; Limiting Partial Molar Volumes

A given aqueous solution at temperature $T$ and pressure $p$ contains solute $j$, having molality $m_j$. The chemical potential of solute $j$, $\mu_j (aq)$ is related to $m_j$ using equation (a).

\[
\mu_j (aq; T; p) = \mu_j^0 (aq; T; p^0) + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m^0) + \int_{p^0}^p V_j^\infty (aq; T) \cdot dp \quad (a)
\]

But $V_j (aq; T; p) = \frac{\partial \mu_j}{\partial p} \quad (b)$

Also $\mu_j^0 (aq; T; p^0)$ is, by definition, independent of pressure. From equation (a),

\[
V_j (aq; T; p) = V_j^\infty (aq; T; p) + R \cdot T \cdot \frac{\partial \ln(\gamma_j)}{\partial p} \quad (c)
\]

In equation (c), there is no term explicitly in terms of molality $m_j$.

From the definition of $\gamma_j$, limit$(m_j \to 0)V_j (aq; T; p) = V_j^\infty (aq; T; p) \quad (d)$

$V_j^\infty (aq; T; p)$ is the limiting partial molar volume of solute $j$ in aqueous solution at temperature $T$ and pressure $p$. In other words $V_j^\infty (aq; T; p)$ is the partial moar volume of solute $j$ in the (ideal) solution where there are no solute-solute interactions and characterises solute-water interactions.

Because $\gamma_j$ tends to unity as $m_j$ tends to zero, $\gamma_j$ is sometimes called an asymmetric activity coefficient [1]. [Contrast rational activity coefficients where $f_1 \to 1$ as $x_1 \to 1$.]

At the risk of being repetitive we distinguish between the two possible reference states for substance $j$ such as urea. One reference state is the pure solid chemical substance $j$ at ambient pressure and 298.2 K. Another reference state is the ideal solution where $m_j = 1 \text{ mol kg}^{-1}$ at ambient pressure and 298.2 K. The properties of urea in the two states, pure solid and solution standard state are clearly quite different. Indeed, we can compare $V_j^\infty (aq; 298.2 \text{ K}; \text{ambient} p)$ and $V_j^\infty (s; 298.2 \text{ K}; \text{ambient} p)$. We can also compare, for example, $V_j^\infty (j = \text{urea}; \text{sln};$
298.2 K; ambient p) in a range of solvents [2]. These points are also nicely illustrated by the volumetric properties of water [3,]. At 298.2 K and ambient pressure $V_1^*(\ell; \text{H}_2\text{O})$ is 18.07 cm$^3$ mol$^{-1}$ but for water as a solute in three solvents $V^\infty(\text{H}_2\text{O}; \text{sln})=18.47 (\text{MeOH}), 14.42 (\text{EtOH})$ and 17.00 (THF) cm$^3$ mol$^{-1}$ [4]. There is, of course, no reason why we should expect anything different. A water molecule in liquid water is surrounded by many millions of other water molecules. But a water molecule at infinite dilution in solvent ethanol is surrounded by many millions of ethanol molecules [5,6].

In the analysis of experimental results, we may express the composition of the solution in terms of mole fraction of solute $x_j$. Then

$$\mu_j(aq; T ; p)$$

$$= \mu_j^0(aq; T ; p^0; x - \text{scale}) + R \cdot T \cdot \ln(x_j \cdot f_j^*) + \int_{p^0}^p \frac{\partial}{\partial p} \left( f_j^{\infty}(aq; T) \right) \; dp \quad (e)$$

But mole fraction $x_j$ is independent of pressure.

$$V_j(aq; T ; p) = V_j^{\infty}(aq; T ; p) + R \cdot T \cdot \left( \frac{\partial \ln(f_j^*)}{\partial p} \right)_T \quad (f)$$

From the definition of $f_j^* $, $\lim(x_j \to 0) V_j(aq; T ; p) = V_j^{\infty}(aq; T ; p)$ \quad (g)

The limiting value of $V_j(aq; T ; p)$ is identical on the molality and mole fraction scales. If we use the concentration scale a problem arises in that the concentration of solute $j$, $c_j$ is dependent on pressure because the volume of the solution is pressure dependent.

**Footnote**


[2] For $j =$ urea at 298.2 K and ambient pressure, $V_j^{\infty}(\text{sln})/\text{cm}^3 \text{ mol}^{-1} = 44.24$ (water), 36.97 (methanol), 40.75 (ethanol) and 41.86 (DMSO).

[3] $V_j^{\infty}(298.15 \text{ K}; j=\text{water}) = 18.57 \text{ cm}^3 \text{ mol}^{-1}$ (solvent = octan-1-ol)

and 31.3 cm$^3$ mol$^{-1}$ (solvent = CCl$_4$); P. Berti, S. Cabani and V. Mollica, Fluid Phase Equilib., 1987,32, 1.


\[ V^\ast (\ell;C_6H_{14}) = 131.61 \text{ cm}^3 \text{ mol}^{-1}, \text{but} \]

\[ V^\infty (C_6H_{14}; \text{sln; solvent }=C_{16}H_{34}) = 130.2 \text{ cm}^3 \text{ mol}^{-1} \text{ at } 298 \text{ K and ambient pressure.} \]

In this context the limiting enthalpies of solution water in monohydric alcohols depend on the alcohol at 298.2 K; (S.-O. Nilsson, J. Chem. Thermodyn., 1986, 18, 1115).

[6] The partial molar volumes of fullerene in solution is 401 cm$^3$ mol$^{-1}$ in cis-decalin and 389 cm$^3$ mol$^{-1}$ in 1,2-dichlorobenzene both values being significantly less than the predicted volume of the pure liquid C$_{60}$; (P. Ruelle, A. Farina-Cuendet and U. W. Kesselring, J. Chem. Soc. Chem. Commun., 1995, 1161).