Volume; Partial and Apparent Molar

In descriptions of the volumetric properties of solutions, two terms are extensively used. We refer to the partial molar volume of solute $j$ in, for example, an aqueous solution $V_j(aq)$ and the corresponding apparent molar volume $\phi(V_j)$. Here we explore how these terms are related. We consider an aqueous solution prepared using water, 1 kg, and $m_j$ moles of solute $j$. The volume of this solution at temperature $T$ and pressure $p$ is given by equation (a).

$$V(aq; w_1 = 1 \text{ kg}) = (1/M_j) \cdot V_j(aq) + m_j \cdot V_j(aq) \quad (a)$$

The chemical potential of solvent, water, in the aqueous solution $\mu_1(aq)$ is related to the molality $m_j$ using equation (b) where $\mu_1^*(\ell)$ is the chemical potential of pure water ($\ell$), molar mass $M_1$, at the same $T$ and $p$.

$$\mu_1(aq) = \mu_1^*(\ell) - \phi \cdot R \cdot T \cdot M_1 \cdot m_j \quad (b)$$

Here practical osmotic coefficient $\phi$ is defined by equation (c).

$$\lim_{m_j \rightarrow 0} \phi = 1 \quad \text{at all } T \text{ and } p \quad (c)$$

But

$$V_1(aq) = \left[ \partial \mu_1(aq) / \partial p \right]_T \quad (d)$$

Then

$$V_j(aq; w_1 = 1 \text{ kg}) = V_j^*(\ell) - R \cdot T \cdot M_1 \cdot m_j \cdot (\partial \phi / \partial p)_T \quad (e)$$

For the solute, the chemical potential $\mu_j(aq)$ is related to the molality of solute $m_j$ using equation (f) where pressure $p$ is close to the standard pressure.

$$\mu_j(aq) = \mu_j^0(aq) + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m_j^0) \quad (f)$$

where

$$\lim_{m_j \rightarrow 0} \gamma_j = 1 \quad \text{at all } T \text{ and } p \quad (g)$$

Then

$$V_j(aq) = V_j^0(aq) + R \cdot T \cdot \left[ \partial \ln(\gamma_j) / \partial p \right]_T \quad (h)$$

Limit

$$V_j(aq) = V_j^0(aq) = V_j^\infty(aq) \quad (i)$$

Combination of equations (a), (e) and (h) yields equation (j).

$$V(aq; w_1 = 1 \text{ kg}) = \left[ V_j^*(\ell) - R \cdot T \cdot M_1 \cdot m_j \cdot (\partial \phi / \partial p)_T \right] + m_j \cdot \left[ V_j^\infty(aq) + R \cdot T \cdot \left[ \partial \ln(\gamma_j) / \partial p \right]_T \right] \quad (j)$$

An important point emerges if we re-arrange equation (j).
\[ V(\text{aq}; w_1 = 1 \text{ kg}) = \left(1/M_j\right) \cdot V_j^* (\ell) + m_j \cdot \{V_j^*(\text{aq}) + R \cdot T \cdot [\partial \ln(\gamma_j)/\partial p]_T - R \cdot T \cdot (\partial \phi/\partial p)_T \} \quad (k) \]

Equation (k) has an interesting form in that the brackets \{\ldots\} contain \(V_j^*(\text{aq})\) and terms describing the extent to which the volumetric properties of the solution are not ideal in a thermodynamic sense. It is therefore convenient to define an apparent molar volume of solute \(j\), \(\phi(V_j)\) using equation (l).

\[ \phi(V_j) = V_j^*(\text{aq}) + R \cdot T \cdot [\partial \ln(\gamma_j)/\partial p]_T - R \cdot T \cdot (\partial \phi/\partial p)_T \quad (l) \]

Then \(\lim(m_j \to 0) \phi(V_j) = V_j^*(\text{aq}) \quad (m)\)

Therefore we obtain equation (n).

\[ V(\text{aq}; w_1 = 1 \text{ kg}) = \left(1/M_j\right) \cdot V_j^* (\ell) + m_j \cdot \phi(V_j) \quad (n) \]

Interest in equation (n) arises from the fact that for a given solution \(V(\text{aq})\) can be measured \{using the density \(\rho(\text{aq})\)\} and hence knowing \(V_j^*(\ell), \phi(V_j)\) is obtained. If we measure \(\phi(V_j)\) as a function of \(m_j\), equation (m) indicates how one obtains \(V_j^*(\text{aq})\). Moreover the difference \([\phi(V_j) - V_j^*(\text{aq})]\) signals the role of solute-solute interactions.

**Footnotes**

[1] \[ R \cdot T \cdot \left[ \frac{\partial \phi}{\partial p} \right] = [J K^{-1} \text{ mol}^{-1}] \cdot [K] \cdot \left[ \frac{1}{[N m^{-2}]} \right] = [m^3 \text{ mol}^{-1}] \]

[2] \[ R \cdot T \cdot \left[ \frac{\partial \ln(\gamma_j)}{\partial p} \right] = [J K^{-1} \text{ mol}^{-1}] \cdot [K] \cdot \left[ \frac{1}{[N m^{-2}]} \right] = [N m \text{ mol}^{-1}] \cdot \left[ \frac{1}{[N m^{-2}]} \right] = [m^3 \text{ mol}^{-1}] \]