Activity of Solvents: Classic Analysis

Thermodynamics underpins a classic topic in physical chemistry concerning the depression of freezing point, $\Delta T_f$ of a liquid by added solute [1,2]. We note the superscript ‘id’ in equation (a) relating the activity of a solvent in an ideal solution, molality $m_j$.

$$\ln(a_i)^{id} = -M_1 \cdot m_j = -M_1 \cdot n_i / n_i^0 \cdot M_1 = -n_j / n_j^0$$

(a)

If the properties of a given aqueous solution are determined to a significant extent by solute-solute interactions, a determined molar mass for a given solute will be in error. Otherwise an observed depression is not a function of solute-solute interactions. Glasstone [2] comments that the ratio $\Delta T_f / m_j$ decreases with increasing concentration of solute, emphasising that a simple analysis is only valid for dilute solutions. Nevertheless the general idea is that the depression for a given $m_j$ is not a function of the hydration of a solute. Barrow [3] noted that the ratio $\Delta T_f / m_j$ for mannitol(aq) in very dilute solutions [4] is effectively constant. A similar opinion is advanced by Adam [5] who nevertheless comments on the importance of the condition ’dilute solution’ in a determination of the molar mass of a given solute.

In summary, classic physical chemistry emphasises the importance of the superscript ‘id’ in equation (a). For very dilute solutions in a given solvent $\ln(a_i)$ is linear function of $m_j$, leading to description of such properties as ‘depression of freezing point’ and ‘elevation of boiling point’ under the heading ‘colligative properties. Only the molality of solute $m_j$ is important; solute-solute interactions and hydration characteristics of solutes apparently play no part in determining these colligative properties.

The key to these statements is provided by the Gibbs-Duhem equation. For a solution prepared using 1 kg of water ($\lambda$) and $m_j$ moles of a simple solute $j$, the Gibbs energy is given by equation (b).

$$G(aq) = (1/M_j) \cdot \mu_i(aq) + m_j \cdot \mu_j(aq)$$

(b)

Then,

$$G(aq) = (1/M_j) \cdot [\mu_i^*(\lambda) - \phi \cdot R \cdot T \cdot M_1 \cdot m_j]$$

$$+ m_j \cdot [\mu_j^0(aq;id;m_j = 1) + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m^0)]$$

(c)
According to the Gibbs - Duhem Equation, the chemical potentials of solvent and solute are linked. At fixed $T$ and $p$,

$$n_1 \cdot d\mu_1 (aq) + n_j \cdot d\mu_j (aq) = 0 \quad (d)$$

Or, $$(1/M_1) \cdot d[\mu^*_i (\lambda) - \phi \cdot R \cdot T \cdot M_i \cdot m_j]$$

$$+ m_j \cdot d[\mu_j^0 (aq; id; m_j = 1) + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m^0)] = 0 \quad (e)$$

Or, 

$$-d(\phi \cdot m_j) + m_j \cdot d\ln(m_j \cdot \gamma_j / m^0) = 0 \quad (f)$$

Or, 

$$-\phi \cdot dm_j - m_j \cdot d\phi + m_j \cdot d[\ln(m_j) + \ln(\gamma_j) - \ln(m^0)] = 0 \quad (g)$$

Hence, 

$$\phi - 1 = \frac{dm_j}{m_j} + d\phi = d\ln(\gamma_j) \quad (h)$$

The latter equation forms the basis of the oft-quoted statement that if the thermodynamic properties of a solute are ideal then so are the properties of the solvent. Similarly if the thermodynamic properties of the solute are ideal then so are the properties of the solvent.

From equation (h), 

$$\phi = 1 + \frac{1}{m_j} \cdot \int_{m_j}^{m_j^{(j)}} m_j \cdot d\ln(\gamma_j) \quad (i)$$

The importance of equation (i) emerges from the idea that $\gamma_j$ describes the impact of solute-solute interactions on the properties of a given solution. If we can formulate an equation for $\ln(\gamma_j)$ in terms of the properties of the solution, we obtain $\phi$ from equation (i). If the properties of a real solution containing a neutral solute are not ideal, both $\gamma_j$ and $\phi$ are linked functions of the solute molality. Pitzer [6] suggests equations (j) and (k) for $\ln(\gamma_j)$ and $\phi$ in terms of solute molalities using two parameters, $\lambda$ and $\mu$.

$$\ln(\gamma_j) = 2 \cdot \lambda \cdot m_j + 3 \cdot \mu \cdot (m_j)^2 \quad (j)$$

$$\phi - 1 = \lambda \cdot m_j + 2 \cdot \mu \cdot (m_j)^2 \quad (k)$$

For example in the case of mannitol(aq) and butan-1-ol(aq), Pitzer [6] suggests the following equations for $\ln(\gamma_j)$.

For mannitol(aq) 

$$\ln(\gamma_j) = -0.040 \cdot m_j \quad (l)$$

For butan-1-ol(aq) 

$$\ln(\gamma_j) = -0.38 \cdot m_j + 0.51 \cdot (m_j)^2 \quad (m)$$

Guggenheim[7] using the mole fraction scale suggests equation (n) where $A$ and $B$ are characteristic of the solute.
\[ 1 - \phi = A \cdot x_j + B \cdot (x_j)^2 \]  

Prigogine and Defay [1] comment that the non-ideal properties of solutions can be understood in terms of the different molecular sizes of solute and solvent. A similar comment is made by Robinson and Stokes [8] who use a parameter describing the ratio of molar volumes of solute and solvent. The extent to which the properties of a solution differ from ideal can often be traced to a variety of causes including solvation, molecular size and shape.

**Footnotes**


