Activity of Aqueous Solutions

A given aqueous solution is prepared using 1 kg of water ($\lambda$), molar mass $M_1$, and $m_j$ moles of solute at temperature $T$ and pressure $p$ (which is close to the standard pressure $p^0$). At fixed $T$ and $p$, the activity of water $a_1(\text{aq})$ is related to the chemical potential of water in the aqueous solution using equation (a) where $\mu^*_1(\lambda)$ is the chemical potential of water ($\lambda$) at the same $T$ and $p$.

$$\mu_1(\text{aq}) = \mu^*_1(\lambda) + R \cdot T \cdot \ln(a_1) \quad \text{(a)}$$

Further equation (b) relates $\mu_1(\text{aq})$ to the molality of a simple solute, $m_j$ (e.g. urea) where $R$ is the gas constant ($= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

$$\mu_1(\text{aq}) = \mu^*_1(\lambda) - \phi \cdot R \cdot T \cdot M_1 \cdot m_j \quad \text{(b)}$$

Here $m_j$ is the molality of solute $j$ and $\phi$ is the practical osmotic coefficient. If the thermodynamic properties of the aqueous solution are ideal (i.e. no solute-solute interactions) the practical osmotic coefficient is unity.

At fixed $T$ and $p$, limit ($m_j \to 0$)$\phi = 1.0$ \hspace{1cm} \text{(c)}

Hence, $\mu_1(\text{aq}; \text{id}) = \mu^*_1(\lambda) - R \cdot T \cdot M_1 \cdot m_j \quad \text{(d)}$

Therefore in the case of an ideal solution, addition of a solute, molality $m_j$, stabilises the solvent; i.e. lowers the chemical potential of the solvent.

In the event that solute $j$ is a salt which forms with complete dissociation $\nu$ ions for each mole of salt in solution, $\mu_1(\text{aq})$ is given by equation (e).

$$\mu_1(\text{aq}) = \mu^*_1(\lambda) - \nu \cdot \phi \cdot R \cdot T \cdot M_1 \cdot m_j \quad \text{(e)}$$

We consider an aqueous solution containing a simple neutral solute $j$. In order to understand the properties of this solution, we need to consider water-solute interactions and solute $j$ – solute $j$ interactions. Solute-solute interactions determine the extent to which the properties of a given solution differ from those of the corresponding solution having thermodynamic properties which are ideal [1].

The extent to which the thermodynamic properties of solutions are not ideal also reflects in part the role of water-solute interactions. For example the extent to which urea-urea interactions differ from ethanol-ethanol interactions in
aqueous solutions reflects the different hydration characteristics of urea and ethanol.

Comparison of equations (a) and (b) yields the following important equation relating activity of solvent, water, and the molality of simple neutral solute $j$.

Thus, $\ln(a_{i,j}) = -\phi \cdot M_i \cdot m_j$  \hspace{1cm} (f)

The minus signs in equations (b) and (f) are extremely significant. If the thermodynamic properties of the solutions are ideal, $\phi$ is unity.

Then, $\ln(a_{i,j})^{\text{id}} = -M_i \cdot m_j = -M_i \cdot n_j / n_i^0 \cdot M_i = -n_j / n_i^0 \hspace{1cm} (g)$

Here $n_i^0$ is the amount of solvent, water, molar mass $M_i$; $n_j$ is the amount of solute $j$. Therefore a plot of $\ln(a_{i,j})^{\text{id}}$ against molality $m_j$ is linear with slope $-M_i$. Furthermore the plots for a range of neutral solutes will be superimposable. In other words $\ln(a_{i,j})^{\text{id}}$ is related to the ratio of amounts of solute to solvent. By adding a solute to a fixed amount of (solvent) water ($\lambda$) we lower the activity of water ($\lambda$), (i.e. the chemical potential of water, $\mu(aq)$ in an aqueous solution) and stabilise the solvent.

The chemical potential of solute $j$ in an aqueous solution $\mu_{j(aq)}$ is related to the molality of solute $m_j$ using equation (h) where $\mu_{j(aq)}^0$ is the chemical potential of solute $j$ in an aqueous solution, molality $m_j = 1$ mol kg$^{-1}$ and $\gamma_i = 1$ at all T and p, (taken as close to the standard pressure $p^0$).

$$\mu_{j(aq)} = \mu_{j(aq)}^0 + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m_j^0) \hspace{1cm} (h)$$

By definition, at all T and p $\lim (m_j \to 0) \gamma_j \to 1 \hspace{1cm} (i)$

The role of water activity in determining enzyme activity is an important consideration [2].

**Footnotes**
