Activity of Water: One Neutral Solute

Classical accounts of the physical chemical properties of solutions concentrate attention on the properties of solutes. Many experiments set out to determine activity coefficients $\gamma_j$ for solutes in solution; (see also mean activity coefficients $\gamma_\pm$ for salts). Information concerning solvent activity is obtained by exploiting the Gibbs-Duhem equation which (at fixed $T$ and $p$) links the properties of solute and solvent. However recent technological developments allow the activity of water in an aqueous solution to be measured [1].

The classic analysis of colligative properties of solutions by van’t Hoff and others in the 19th Century is successful for dilute solutions. The importance of solute-solute interactions was generally recognised very early on in the 20th Century. However the role of solute-solvent interactions was perhaps underplayed.

We develop a model for a given solution prepared by dissolving $n_j$ moles of neutral solute $j$, molar mass $M_j$, in $n_1^0$ moles of water ($\lambda$), molar mass $M_1$. The molality of solute as prepared is given by equation (a).

$$m_j^{(\text{prepared})} = n_j / n_1^0 \cdot M_1$$  \hspace{1cm} (a)

Then $\ln(a_j;\text{prepared})^{id}$ is given by equation (b).

$$\ln(a_j)^{id} = -M_1 \cdot m_j = -n_j / n_1^0$$  \hspace{1cm} (b)

However in another description of the solution under investigation each mole of solute $j$ is strongly hydrated by $h$ moles of water. The mass of solvent water, $w_1$ is given by equation (c).

$$w_1 = [n_1^0 - h \cdot n_j] \cdot M_1$$  \hspace{1cm} (c)

Hence the molality of hydrated solute is given by equation (d).

$$m_j^{(\text{hydrated solute})} = n_j / [n_1^0 - h \cdot n_j] \cdot M_1$$  \hspace{1cm} (d)

In effect the molality of the solute increases because there is less ‘solvent water’

By analogy with equation (b), $\ln(a_j;\text{hyd}) = -n_j / (n_1^0 - h \cdot n_j)$ \hspace{1cm} (e)

Therefore for a range of solutions containing different solutes but prepared using the same amount of solute, the activities are a function of the different extents of hydration of the solutes. With increase in $h$, $\ln(a_j;\text{hyd})$ decreases
(i.e. becomes more negative) indicative of increasing stabilisation of the water in the system by virtue of solute-water hydration interaction.

In a real solution, the properties of a solute are not ideal because there exist solute-solute communication by virtue of the fact that each solute molecule is ‘aware’ that some of the solvent has been ‘removed’ by solute hydration. The amount of solvent ‘available’ to each molecule has been depleted by hydration of all solutes in solution. In other words a Gibbs-Duhem communication operates in the solution.

**Hydration of Hydrophilic Solutes; Scatchard Model**

The model of an aqueous solution described in conjunction with equation (a) is used to obtain the ratio, \( \frac{n_i^0}{n_j} \); equation (f).

\[
\text{Then, } \quad \frac{n_i^0}{n_j} = \frac{1kG}{M_i} \cdot \frac{M_j}{w_j} \quad (f)
\]

Thus \( \frac{n_i^0}{n_j} \) describes the solution as prepared using \( n_j \) and \( n_i^0 \) moles of solutes and solvent respectively. We assert that by virtue of solute hydration an amount of water is removed from the ‘solvent’. In solution the mole fraction of (solvent) water is \( x_i \), the mole fraction of hydrated solute is \( x_j \).

Then, \( x_i + x_j = 1 \) \( (g) \)

The mole fraction ratio \( \frac{x_w}{x_j} \) is given by equation (h).

\[
\frac{x_w}{x_j} = \frac{x_w}{1 - x_w} \quad (h)
\]

Equation (h) forms the basis of a treatment described by Scatchard [2] in 1921, nearly a century ago. The model proposed by Scatchard [2] was based on a model for water (\( \lambda \)), described as a mixture of hydrols; monohydrols and polymerised water. Scatchard discusses hydration of solutes although not all solutes in a given solution are seen as hydrated; i.e. the solution contains various hydrates. In fact a given solute may be hydrated to varying degrees; i.e. a given solution contains various hydrates. However Scatchard envisaged [2] that one hydrate may be dominant. We note the date when the model was proposed by Scatchard [2]. The concept of hydrogen bonding in aqueous solutions has its origin in a paper published by Latimer and Roedbush in 1920 [3]; see also [4]; i.e. the previous year to publications by Scatchard [2].
Scatchard [2] invoked an assumption called the ‘semi-ideal’ assumption in which mole fraction $x_w$ in equation (h) is replaced by the activity of the solvent, water $a_w$.

Hence, from equation (h),

$$\frac{x_w}{x_j} = \frac{a_w}{1 - a_w}$$  \hspace{1cm} (i)

The difference between amounts of water defined by equations (f) and (i) yields the ‘average degree of hydration’, $h$ of solute $j$.

Then,

$$h = \frac{(1.0/0.0180)}{m_j} - \frac{a_w}{1 - a_w}$$  \hspace{1cm} (j)

Equation (j) is Scatchard’s equation. If one can measure $a_w$ for an aqueous solution molality $m_j$ we obtain the ‘average degree of hydration’ for solute $j$.

Scatchard using vapour pressure data obtained an estimate of $h$ for sucrose at 30 Celsius. In the case of a solution containing 34 g of sucrose in 100 g water ($\lambda$), $h$ equals 4.46, decreasing with increase in the ‘strength’ of the solution.

The term ‘semi-ideal’ proposed by Scatchard emerges from the identification of solvent activity with mole fraction of depleted solvent. In summary Scatchard [2] obtained a property $h$ but there is no indication of the stability of the hydrate.

Stokes and Robinson [5] extended the Scatchard analysis using a chemical equilibrium involving solute hydrates. The hydration of a given solute is described by a set of equilibrium constants describing $i$-hydration steps. For solute S,

$$S_{i-1} + H_2O \leftrightarrow S_i \hspace{1cm} (i = 1,2,\ldots,n)$$  \hspace{1cm} (k)

Each step is described by an equilibrium constant, $K_i$. So for a solute hydrated by 3 water molecules there are 3 equilibrium constants. Stokes and Robinson [5] set $n$ equal to 11 for sucrose. However in this case Stokes and Robinson [5] simplify the analysis by assuming that the equilibrium constants for all hydration steps are equal. The resulting equations are as follows.

$$\frac{(1/M_1)}{m_j} = \frac{a_w}{1 - a_w} + \frac{\sigma}{\Sigma}$$  \hspace{1cm} (\lambda)

where

$$\sigma = K \cdot a_w + \ldots + K \cdot (a_w)^n$$  \hspace{1cm} (m)

and

$$\Sigma = 1 + K \cdot a_w + \ldots + (K \cdot a_w)^n$$  \hspace{1cm} (n)
Equation $\lambda$ is interesting because for a given solute, the dependence of $a_w$ on $m$ yields two interesting parameters, $n$ and $K$, describing hydration of a given solute $j$. The equilibrium constants defined above are dimensionless.

Stokes and Robinson [5] describe a method of data analysis but modern computer-based methods should lighten the arithmetic drudgery. For sucrose(aq) at 298.15 K, Stokes and Robinson estimate that $n = 11$ and $K = 0.994$. For glucose(aq) $n = 6$ with $K = 0.786$. Finally we note that the composition of the solutions should be expressed in molalities; i.e. each solution made up by weight. If this is not done, conversion of concentrations to molalities is required. Possibly the literature will yield the required densities of the solutions. The worst approximation sets the density of the solutions at the density of water $\lambda$ at the same temperature.

**Footnotes**

[1] Water Activity Meter, Decagon Devices Inc. WA 99163, USA.