Biophysical Chemistry for Life Scientists

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Interpretation of activity coefficients

As we noted earlier, deviations from ideal behavior in solutions arises from solute-solute interactions and from disruption of the solvent structure by the solute at sufficiently high solute concentrations. If the solvent remains essentially intact, then Roault's Law is most likely still applicable, namely $\ln a_A = \ln x_A$, $\gamma_A = 1$, except that $x_A = 1 - \overline{x}_B$, rather than $1 - x_B$. In other words, we use the true mole fraction of the solute (or the osmotic molality) rather then the stoichiometric mole fraction (stoichiometric molality). Or, we must take into account solute-solute

interactions, or dissociation of the solutes, and so on, before applying Roault's Law for the solvent. Of course, this means that for the solute, ln a_B = ln $\gamma_B x_B$, $\gamma_B \neq 1$, and RT ln γ_B is the extra free energy arising from the solute-solute interactions.

In the simple example that I have just outlined to illustrate the stacking of nucleic acid bases, I noted that ln $\gamma^m{}_B$ = m_1/m. Recall that I invoke the following simple equilibrium to describe the association process:

$$M_1 + M_1 \leftrightarrow M_2 \qquad K_2$$

monomer **dimer**

$$M_2 + M_1 \leftrightarrow M_3 \qquad K_3$$

$$M_3 + M_1 \leftrightarrow M_4 \qquad K_4$$

$$M_{n-1} + M_1 \leftrightarrow M_n \qquad K_n$$

According to this model,

$$\overline{m} = m_1 + m_2 + m_3 + m_4 + \ldots m_n$$

$$= m_1 + K_2 (m_1)^2 + K_2\, K_3 (m_1)^3 + \ldots\ K_2\, K_3 K_4 \ldots K_n (m_1)^n$$

$$m = m_1 + 2m_2 + 3m_3 + 4m_4 + \ldots\ nm_n$$

$$= m_1 + 2K_2 (m_1)^2 + 3K_2\, K_3 (m_1)^3 + \ldots$$

$$+ nK_2\ K_3 K_4 \ldots K_n (m_1)^n$$

From these two relationships, it follows that

$$d\overline{m}/dm_1 = m/m_1$$

but since $\phi = \overline{m}/m$,

or $\phi\, dm + m d\phi = d\overline{m} = (m/m_1) dm_1$

or $\phi\, d \ln m + d\phi = d \ln m_1$

and since $d \ln \gamma_B^m = (\phi - 1)\, d \ln m + d\phi$

it follows that $d \ln \gamma_B^m = d \ln m_1 - d \ln m = d \ln (m_1/m)$

or $\gamma_B^m = (m_1 / m)_B$!

In other words, for this simple association equilibrium, the activity coefficient is just the fraction of the solute existing as the monomer!

This is an important and general result. Of course, molecular aggregation constitutes only one (extreme) way of describing solute-solute interactions (an extreme situation that has led to complex formation, but the strength of the interaction is measured by the equilibrium constant).

How to deal with solute-solute interactions?

There are two ways to deal with solute-solute interactions:

(1) indirectly using the activity coefficient;

(2) explicitly by invoking an equilibrium to describe the interactions between the solute molecules.

Suppose you have a solute B that dimerizes in solution. If you didn't know this, and measure the chemical potential, you would express the result as

$$\mu_B(T) = \mu^\circ_B(T) + RT \ln a_B = \mu^\circ_B(T) + RT \ln \gamma_B^c c_B$$

and $\gamma_B^c \ll 1.$

Now, if you had taken explicit note of the dimerization, and if both the monomer (M) and dimer (D) actually forms Henry's Law solutions, then you can write

$$2\text{ M} \leftrightarrow \text{D}$$

and

$$\mu_M(T) = \mu^\circ_M(T) + RT \ln \gamma_M^c c_M \cong \mu^\circ_M(T) + RT \ln c_M$$

$$\mu_D(T) = \mu^\circ_D(T) + RT \ln \gamma_D^c c_D \cong \mu^\circ_D(T) + RT \ln c_D$$

where $\gamma_M^c, \gamma_D^c \approx 1$

Comparing the results for μ_B and μ_M, it is clear that

$$\gamma_B^c c_B = c_M$$

$$\text{or} \quad \gamma_B^c = c_M/c_B$$

the identical result obtained earlier.

Moreover, in discussing the dimerization, one can write the equilibrium constant as

$$K = a_D/a_M^2 = \gamma_D^c c_D/(\gamma_M^c)^2 c_M^2 \approx c_D/c_M^2$$

as $\gamma_D^c, \gamma_M^c \approx 1$ and there is no ambiquity.

It also follows that

$$\mu^\circ_D(T) - \mu^\circ_M(T) = - RT \ln K$$

Another example

Suppose the solute B in the above example participates in the following reaction:

$$B + X \leftrightarrow Y$$

Normally, one can simply write

$$K = a_Y/a_B\, a_X = \gamma_Y^c\, c_Y/(\gamma_B^c\, c_B\, \gamma_X^c\, c_X)$$

It would have been OK to assume that $\gamma_X^c, \gamma_Y^c \approx 1$, but because of the dimerization of B, $\gamma_B^c << 1$, i.e., γ_B^c deviates significantly from unity. So,

$$K = (c_Y/c_B\, c_X) \bullet (1/\gamma_B^c)$$

On the other hand, if one takes explicit account of the dimerization of B, one can also write

$$M + X \leftrightarrow Y$$

and $K = a_Y/a_M\, a_X = \gamma_Y^c\, c_Y/(\gamma_M^c\, c_M\, \gamma_X^c\, c_X)$

$$= c_Y/c_M\, c_X$$

since $\gamma_Y^c, \gamma_X^c, \gamma_M^c \approx 1$.

Comparing the two outcomes, it is clear that the results are identical, since $c_M = \gamma_M^c c_B$. So, if one knows what one is doing, there is no ambiguity.

γ_B can be derived from a knowledge of U (r), the potential energy of interaction between the solutes, assuming pairwise interactions

Recall $\mu_B(T) = \mu^\circ_B(T) + RT \ln a_B$

If the solute behaves ideally, i.e., satisfy Henry's Law (condition of dilute solutions), then

$$\mu_B^{ideal}(T) = \mu^\circ_B(T) + RT \ln c_B$$

If the solute is not behaving ideally,

$$\mu_B^{real}(T) = \mu^\circ_B(T) + RT \ln c_B + RT \ln \gamma_B^c$$

or $$\mu_B^{real}(T) - \mu_B^{ideal}(T) = RT \ln \gamma_B^c$$

So $RT \ln \gamma_B^c$ is merely the reversible work (maximum) that must be expended to take the solute solution from the ideal to the real situation. Since $\gamma_B^c < 1$

typically, this reversible work is negative, i.e., work can be extracted from the process. In light of this, it follows that

$$\mathrm{RT}\ \ln \mathrm{RT}\ \ln \gamma_B^{c} \approx (1/2)\, N_A\, c_B\, (1/\tilde{V}_{\mathrm{solution}})\, (1/1000) \bullet \int_0^{\infty} \rho(r)\, U\,(r)\, 4\, \pi r^2\, dr$$

where $\tilde{V}_{\mathrm{solution}}$ = volume of solution (in liters) containing 1 mole of solute;

$\rho(r)$ = radial distribution function giving the probability of finding another solute molecule at distance r and r + dr;

and $U(r)$ = potential energy of interaction between a pair of solute molecules.

So the problem reduces to knowing $\rho(r)$ and $U(r)$.