16.2: Diffusion to Capture with Interactions

What if the association is influenced by an additional potential for A-B interactions? Following our earlier discussion for diffusion in a potential, the potential U_{AB} results in an additional contribution to the flux:

$$J_U = -\frac{D_A C_A}{k_B T}\frac{\partial U_{AB}}{\partial r}$$

So the total flux of A incident on B from normal diffusion J_{diff} and the interaction potential J_U is

$$J_{A\to B} = -D_A\left[\frac{\partial C_A}{\partial r} + \frac{C_A}{k_B T}\frac{\partial U_{AB}}{\partial r}\right]$$

To solve this we make use of a mathematical manipulation commonly used in solving the Smoluchowski equation in which we rewrite the quantity in brackets as

$$J_{A\to B} = -D_A\left[e^{U_{AB}/k_B T}\frac{d\left[C_A e^{U_{AB}/k_B T}\right]}{dr}\right] \tag{16.2.1}$$

Substitute this into the expression for the rate of collisions of A with B:

$$\begin{aligned}\frac{dn_{A\to B}}{dt} &= A_B J_{A\to B}\\ &= 4\pi R_B^2 J_{A\to B}\end{aligned}$$

Separate variables and integrate from the surface of the sphere to $r=\infty$ using the boundary conditions: $C(R_B)=0, C(\infty)=C_A$:

$$\left(\frac{dn_{A\to B}}{dt}\right)\underbrace{\int_{R_B}^{\infty} e^{U_{AB}/k_B T}\frac{dr}{r^2}}_{(R^*)^{-1}} = 4\pi D_A\underbrace{\int_0^{C_A} d\left[C_A e^{U_{AB}/k_B T}\right]}_{C_A} \tag{16.2.2}$$

Note that integral on the right is just the bulk concentration of A. The integral on the right has units of inverse distance, and we can write this in terms of the variable R*:

$$(R^*)^{-1} = \int_{R_B}^{\infty} e^{U_{AB}/k_B T} r^{-2} dr$$

Note that when no potential is present, then $U_{AB} \to 0$, and $R^* = R_B$. Therefore R* is an effective encounter distance which accounts for the added influence of the interaction potential, and we can express it in terms of f, a correction factor the normal encounter radius: $R^* = f R_B$. For attractive interactions $R^* > R_B$ and f >1, and vice versa.[1]

Returning to eq. (16.2.2), we see that the rate of collisions of A with B is

$$\frac{dn_{A\to B}}{dt} = 4\pi D_A R_B^* C_A$$

As before, if we account for the total number of collisions for two diffusing molecules A and B:

$$\begin{aligned}\frac{dn_{TOT}}{dt} &= J_{A\to B} A_{AB} C_B\\ &= k_a C_A C_B\\ k_a &= 4\pi(D_A + D_B) R_{AB}^*\\ R_{AB}^* &= R_A^* + R_B^*\end{aligned}$$

Example: Electrostatic potential[2]

Let's calculate the form of the where the interaction is the Coulomb potential.[3]

$$U_{AB}(r) = \frac{z_A z_B e^2}{4\pi\epsilon r} = k_B T\frac{\ell_B}{r}$$

where the Bjerrum length is $\ell_B = z_A z_B e^2/(4\pi\epsilon k_B T)$. Then

$$\begin{aligned}(R^*_{AB})^{-1} &= \int_{R_{AB}}^{\infty} e^{U_{AB}/k_B T} \frac{dr}{r^2} \\ &= \ell_B^{-1}\left[\exp(\ell_B/R_{AB} - 1\right]\end{aligned}$$

and

$$R^*_{AB} = \ell_B (e^{\ell_B/R_{AB} - 1})^{-1}$$

For $\ell_B \gg R_{AB}, R^*_{AB} \to R_{AB}$. For $\ell_B = R_{AB}, R^*_{AB} = 0.58 R_{AB}$ if the charges have the same sign (repel), or $R^*_{AB} = 1.58 R_{AB}$ if they are opposite charges (attract).

$$4\pi r^2 J_{A\to B} = \frac{4\pi D_A \left[C_A(\infty) e^{U_{AB}(\infty)/k_B T} - C_A(R_0) e^{U_{AB}(R_0)/k_B T}\right]}{\int_{R_0}^{\infty} r^{-2} e^{U_{AB}(r)/k_B T} dr}$$

$C_A(\infty)$ is the bulk concentration of A. For the perfectly absorbing sphere, the concentration of A at the boundary with B, $C_A(R_0)=0$. For a homogeneous solution we also assume that the interaction potential at long range $U_{AB}(\infty) = 0$.

1. A more general form for the flux, in which the boundary condition at the surface of the sphere CA(R0) is non-zero, for instance when there is an additional chemical reaction on contact, is
2. See also J. I. Steinfeld, Chemical Kinetics and Dynamics, 2nd ed. (Prentice Hall, Upper Saddle River, N.J., 1998), 4.2-4.4.
3. See M. Vijayakumar, K.-Y. Wong, G. Schreiber, A. R. Fersht, A. Szabo and H.-X. Zhou, Electrostatic enhancement of diffusion-controlled protein-protein association: comparison of theory and experiment on barnase and barstar, J. Mol. Biol. 278 (5), 1015-1024 (1998).