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# DELAYED ADSORPTION AND DIFFUSION IN COLLOIDAL MEDIA

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The behavior of the diffusion coefficient of a solute which can be adsorbed by a colloid only after the colloid has aggregated to a certain size is deduced on the basis of a few assumptions. Some relations of such a mechanism to cell reactions are indicated.

A type of reaction plausible in cell behavior is one in which two or more substances may be released under a stimulus. This paper considers such a release with two substances one of which can aggregate into larger micelles and upon reaching an optimum size adsorbs the second substance, which we call the solute. After this initial adsorption we may consider either no further aggregation and adsorption or further aggregation with adsorption as being the possibilities of greatest interest. For our purposes the significant point is what effect these alternative possibilities have upon the diffusion coefficient of the solute. In addition, we indicate how this mechanism may be used to interpret certain reactions in a cell, e.g. reactions which begin at a certain rate, proceed at that rate for some time, and then fall to a minimum.

The aggregation of the colloid particles is assumed to take place in the following chain:

$$n_1 + n_1 \rightarrow n_2 ,$$
$$n_2 + n_1 \rightarrow n_3 ,$$

$$\cdot$$

$$\cdot \tag{1}$$

$$\cdot$$

$$n_{m-1} + n_1 \rightarrow n_m ,$$
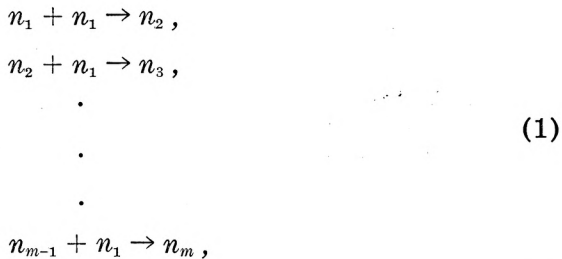
where n_m is the size at which adsorption of the solute occurs. This chain expresses the assumption that a higher aggregate is formed from the next lower by the adjoining of a simple micelle, in short there is no aggregation of higher aggregates with each other. We

shall consider first the mechanism which allows no aggregation after adsorption. The differential equations for this chain are

$$\frac{dn_1}{dt} = -k_1 n_1{}^2 - k_2 n_1 n_2 - \cdots - k_{m-1} n_1 n_{m-1},$$

$$\frac{dn_2}{dt} = \frac{k_1 n_1{}^2}{2} - k_2 n_1 n_2,$$

$$\cdot$$
$$\cdot$$
$$\cdot$$

$$\frac{dn_e}{dt} = k_{e-1} n_1 n_{e-1} - k_e n_1 n_e, \tag{2}$$

$$\cdot$$
$$\cdot$$
$$\cdot$$

$$\frac{dn_m}{dt} = k_{m-1} n_1 n_{m-1}.$$

On making the substitution $n_1 \, d \, t = d \, x$ these equations are transformed into the linear forms

$$\frac{dn_1}{dx} = -\sum_{i=1}^{m-1} k_i n_i,$$

$$\frac{dn_2}{dx} = \frac{k_1}{2} n_1 - k_2 n_2, \tag{3}$$

$$\cdot$$
$$\cdot$$

$$\frac{dn_r}{dx} = k_{m-1} n_{m-1}.$$

The characteristic equation of this set is

$$\begin{vmatrix} \lambda + k_1 & k_2 & k_3 & \cdots & k_{m-1} & 0 \\ -\dfrac{k_1}{2} & \lambda + k_2 & 0 & \cdots & & 0 \\ 0 & -k_2 & \lambda + k_3 & \cdots & & \\ \cdots & \cdots & \cdots & \cdots & -k_{m-1} & \lambda \end{vmatrix} = 0. \tag{4}$$

A simple relationship is found between the determinants of each or-

der. Consider for $m = 3$ we have

$$D_2(\lambda) = \begin{vmatrix} \lambda + k_1 & k_2 \\ -\dfrac{k_1}{2} & \lambda + k_2 \end{vmatrix}$$

observe that

$$D_3(\lambda) = (\lambda + k_3)D_2(\lambda) + \frac{k_1\,k_2\,k_3}{2},$$

and in general

$$D_e(\lambda) = (\lambda + k_e)D_{e-1}(\lambda) + \frac{k_1\,k_2\cdots k_e}{2}. \qquad (5)$$

Inasmuch as we shall not treat the general case, except to observe that the physical conclusions will probably not be much different for large values of m, we can state that in order to be physically meaningful the solutions of equation (3)

$$n_k = \sum_{j=1}^{m} c_{kj}\,e^{\lambda_j x} \qquad (6)$$

satisfy the boundary conditions at all values of time

$$\sum_{1}^{m} k\,n_k = n_0.$$

Since x and not time occurs in equation (6), we see that it is not necessary that the real part of the λ be negative. From the defining equation for x, we have $x \to x_0$, x_0 finite, $n_1 \to 0$, then $t(x) \to \infty$; thus an infinite time is required for all the n_1 to disappear even though the x_0 is finite.

All the information needed for our purpose can be had from a detailed treatment of the set for $m = 3$. That is there will be an aggregate of three colloid particles built up before adsorption of the solute occurs. The problem immediately suggested is the relative behavior of n_1 and n_2. This behavior can be obtained from the integral curves. Using the notation of L. R. Ford (1933),

$$\frac{dn_2}{dn_1} = \frac{-\dfrac{k_1}{2}\,n_1 + k_2\,n_2}{k_1\,n_1 + k_2\,n_2}, \qquad (7)$$

$$\varDelta = (k_1 + k_2)^2 - 6\,k_1\,k_2.$$

Since $k_1 + k_2 \neq 0$, the integral curves are not conics.

For

$$M_1: \quad n_2 = \mu_1\, n_1 \qquad M_2: \quad n_2 = \mu^2\, n_1$$

where

$$\mu_{1,2} = \frac{-(k_1 - k_2) \pm \sqrt{\varDelta}}{2\,k_2}, \tag{8}$$

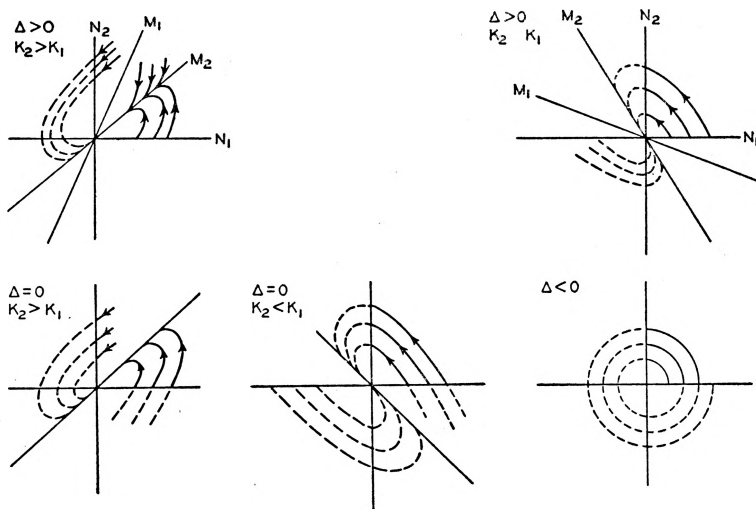the integral curves are shown in Figure 1.

FIGURE 1

These solutions are physically well-behaved in that all show that either n_1 disappears before n_2 or they disappear together. But the presence of n_2 after the disappearance of n_1, makes it impossible for all of n_2 to be transformed into n_3. Thus for the simple case of n_1, n_2, n_3, we can expect as a resultant state only n_3 or a mixture of n_2 and n_3. The first will result if $k_2 > k_1$ and $\varDelta \geqq 0$. The k's will be determined by the reaction, hence in a specific experiment we can examine the products present after sufficient time which will decide whether n_2 and n_3 or only n_3 remains.

An alternative treatment of the integral curves which is immediately applicable to the general case has been suggested in a letter by Dr. A. S. Householder. From the conditions, the integral curves in the n_2, n_1 plane are confined to the region bounded by the coordinate axes and the line $n_1 + 2n_2 = n_0$. Since $dn_1/dx < 0$ for any n_1 and n_2 not both zero, the integral curve can cross the n_2 axis ($n_1 = 0$). While for $n_2 = 0$, unless $n_1 = 0$ simultaneously, the integral curve is directed into the region. The scalar product of the vector with the

normal is $-3k_2 n_2$ which is always negative for $n_2 > 0$. Initially $n_2 = 0$ and $n_1 = n_0$, thus the curve begins at the intersection of the line $n_1 + 2n_2 = n_0$ and the n_1 axis; the integral curve is tangent to the line and directed upward from the n_1 axis. As n_2 builds up the integral curve turns inward away from the line $n_1 + 2n_2 = n_0$.

The general set is treated in the same manner. Here the integral curves are confined to the region bounded by the $m-1$ coordinate hyper-planes and the hyper-plane $\sum_1^{m-1} k\, n_k = n_0$. The integral curve can cross the hyper-plane $n_1 = 0$ for always $dn_1/dx < 0$. But when $n_k = 0$, $k \neq 1$, $dn_k/dx = k_{k-1}\, n_{k-1} > 0$ unless n_{k-1} is also 0; but if n_{k-1} is 0, $dn_{k-1}/dx, > 0$, etc., until we meet an $n_r \neq 0$. Hence if any n_k, $k \neq 1$, approaches zero the integral curve turns toward a region where the n_k is increasing. Finally the scalar product of the tangent and the outward normal is $-(m-1)k_{m-1}\, n_{m-1}$ which completes the proof that for a finite x, but an infinite t, n_1 vanishes in the general case; and although some of the other n's may vanish simultaneously with n_1, they cannot vanish ahead of n_1.

The solutions of the set satisfying the boundary conditions

$$n_1 + 2n_2 + 3n_3 = n_0,$$

and at $x = 0$, $n_1 = n_0$ where n_0 is the initial number of simple colloid particles, are

$$n_1 = \frac{n_0}{\lambda_1 - \lambda_2}\left[(\lambda_1 + k_1)\, e^{\lambda_2 x} - (\lambda_2 + k_1)\, e^{\lambda_1 x} \right],$$

$$n_2 = \frac{n_0 (\lambda_1 + k_1)(\lambda_2 + k_1)}{k_2 (\lambda_1 - \lambda_2)}\left[e^{\lambda_1 x} - e^{\lambda_2 x} \right],$$

$$n_3 = \frac{n_0}{3}\left[1 + \frac{3(\lambda_1 + k_1)(\lambda_2 + k_1)}{\lambda_1 (\lambda_1 - \lambda_2)}\, e^{\lambda_1 x} \right.$$
$$\left. - \frac{3(\lambda_1 + k_1)(\lambda_2 + k_1)}{\lambda_2 (\lambda_1 - \lambda_2)}\, e^{\lambda_2 x} \right],$$

(9)

where

$$\lambda_{1,2} = \frac{-(k_1 + k_2) \pm \sqrt{\Delta}}{2}.$$

The relation between x and t is $n_1\, d\, t = d\, x$

$$t = \int_0^x \frac{dx}{n_1}$$

where $x = 0$ when $t = 0$. Before the integration can be performed the upper limit must be fixed. Calling this upper limit x and recalling that we are concerned about the value of the time from the beginning of the reaction until the appearance of the first particle capable of adsorbing a solute particle, we have on introducing $n_3 = 1$ into (9) and calling the coefficients of exponentials α and β respectively

$$3/n_0 = 1 + \alpha\, e^{\lambda_1 x} - \beta\, e^{\lambda_2 x} . \tag{10}$$

This equation cannot be solved explicitly for x. Making the substitutions

$$y_1 = \alpha\, e^{\lambda_1 x} + 1 - 3/n_0 ,$$

$$y_2 = \beta\, e^{\lambda_2 x} ,$$

we can solve graphically if we have numerical values for α, β, and n_0. Taking $n_0 = 1000$, $k_2 = 4\, k_1 = 4\, k$ then $\Delta = k^2$, $\lambda_1 = -4\, k$, $\lambda_2 = -6\, k$ and we find $\alpha = -5.55$, $\beta = 3.75$. Substituting these values we have $x = 0.48/k$

$$\tau = \frac{2}{1000} \int_0^x \frac{e^{4kx}}{5 - 3\, e^{-2kx}}\, d\,x ,$$

where τ is the time required for the first n_3 to appear in the system. Integrating numerically by using Simpson's rule, we find

$$\tau = 48.18/1000\, k \quad \text{secs.} \tag{11}$$

Our analysis culminating in (11) can be summarized: when the aggregation takes place according to (3) with $m = 3$, at the end of $48.18/1000\, k$ secs. the particles capable of adsorbing solute particles appear in the system. Before their appearance, the other colloid particles would have negligible effect upon the diffusion coefficient of the solute. After their appearance, however, they would act to reduce the value of D according to J. Reiner's curve (1939). The effect is shown in Figure 2a. If the aggregation continues with the number of adsorbed solute particles a function of the surface area as in an
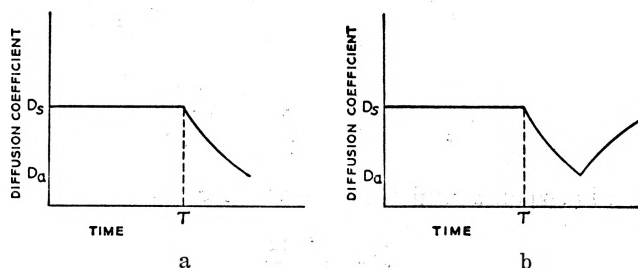

FIGURE 2

earlier paper (H. Branson, 1942), we would have the variation represented in Figure 2b.

In order for the mechanism to be applicable to cellular reactions, τ has to be in general small, except for some reactions where it may be of the order of a second. From physical considerations we see that k is a function of the diffusion coefficient and the radius of the aggregating particles; M. V. Smoluchowski (1918) found for a colloid solution $k = 4 \pi \tau D$. Introducing values given in that paper from Zsigmondy's experiments we have $k \sim 10^{-12}$ and $\tau \sim 10^{10}$ secs. Thus unless the diffusion coefficient within the cell is considerably larger than in solution, this reaction gives an inordinately long time for the beginning of the decrease in the diffusion coefficient. More plausible values of τ can be obtained by considering n_o to be much larger in (10). Raising n_o to 10^7 causes practically no change in x, and taking $r \sim 10^{-6}$ cm then for D of the order of 10^3, τ will be of the order of a hundredth of a second. This is not an unreasonable value of D for aggregations where the binding energy is large.

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