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DIFFUSION AS A FUNCTION OF AGGREGATION IN COLLOIDAL MEDIA

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With the assumption that adsorption is a simple function of surface area, an analytical treatment is given for the dependence of the diffusion coefficient of an adsorbable solute upon the degree of aggregation of the adsorbing colloid. A simple relation is deduced after introducing some approximations. Some implications of the final diffusion equation are given.

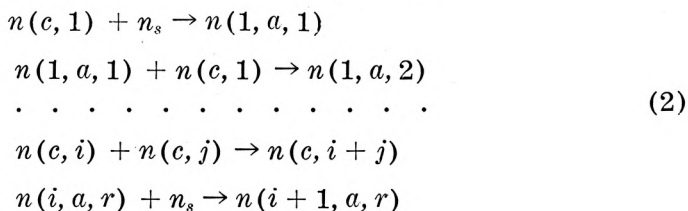
The effects which colloids may have upon diffusion have been discussed qualitatively by N. Rashevsky (1938) and the specific problem of the adsorption of a diffusing solute by a single type of colloid has been treated by J. M. Reiner (1939). This note reports an investigation of a general phenomenon in a colloidal medium: with the assumption that adsorption is a simple function of surface area what could we expect to be the effect upon the diffusion coefficient of an adsorbable solute of the continued aggregation of the adsorbing colloid. This discussion proceeds under some plausible assumptions which simplify the analysis. The results are finally related to certain membrane phenomena of the cell.

The system we consider has initially simple, colloid particles and solute particles. The primordial colloid particles coalesce giving larger particles of uniform surface, uniformly distributed. If the initial number of simple colloid particles is designated by N_c and the initial number of neutral solute by N_s , the relationships which must always be met are

$$\begin{aligned} N_s &= n_s + \sum_{l=1}^r \sum_{k=1}^m l n(l, a, k) \\ N_c &= \sum_{l=1}^r \sum_{k=1}^m k [n(c, k) + n(l, a, k)] , \end{aligned} \tag{1}$$

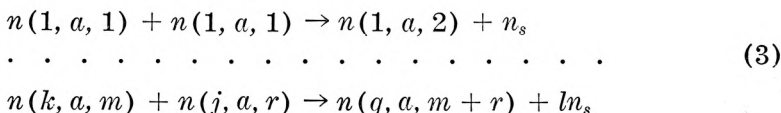
where $n(l, a, k)$ designates the number of k -th-aggregated colloid particles with l adsorbed solute particles, $n(c, k)$ is the k -th-aggregated colloid particles having no adsorbed solute particles, and n_s is the number of solute particles not adsorbed. The types of possible re-

actions taking place in the system may be written



provided $i + 1 \leq r^{2/3}$. This condition is explained below. The first three reactions express the general assumption that a solute particle may be adsorbed by a single colloid particle but that the aggregate cannot adsorb another solute particle until the surface is at least twice the surface of the single colloid particle. Any other reaction of agglomeration is possible in the system so long as it does not violate this principle.

Nevertheless two particles having such a number of adsorbed particles that the complex formed by their agglomeration would have more than the allowed number of adsorbed solute particles were they all retained, can still agglomerate with the release of solute particles. This is expressed by adding to (2)



where $(m + r)^{2/3} - 1 < q \leq (m + r)^{2/3}$, $k + j = q + l$.

For simplicity the reactions are assumed to be irreversible. With these assumptions the maximum number of adsorbed particles is easily deduced. If we let v_1 , r_1 , and s_1 represent the volume, radius and surface of a single colloid particle and v_k , r_k , and s_k the same for an aggregate of k particles, we have

$$v_k = \frac{4}{3} \pi r_k^3 ; s_k = 4 \pi r_k^2$$

$$v_k = k v_1$$

since the k aggregate to form a spherical cluster, $k r_1^3 = r_k^3$ thereupon $s_k = 4 \pi k^{2/3} r_1^2 = k^{2/3} s_1$. The maximum number of adsorbed solute particles on an aggregate of k colloid particles is

$$l = k^{2/3} \quad \text{if } k \text{ is an integer,}$$

$$k^{2/3} - 1 < l < k^{2/3} \quad \text{if } k \text{ is not an integer,}$$

which we have already used in (2) and (3).

Some hint as to possible numerical values for the maximum number of colloidal particles which may aggregate before flocculation can be taken from the specification of the range of colloidal particle size, the diameters ranging from 10^{-7} to 10^{-5} cm. Assuming that our primordial colloid particle has the smaller diameter and the largest the larger, we have the maximum for $m \approx 10^6$ and the maximum for $r \approx 10^4$.

The solute particles are taken as uncharged so Fick's law for the transport of solute is

$$J = J_s + \sum_{l=1}^r \sum_{k=1}^m J(l, a, k), \quad (4)$$

in which J is the number of solute particles passing through unit surface in unit time whether as simple solute or in aggregate. The l , k , r , and m are the same as in (1). The $J(l, a, k)$ may be written

$$J(l, a, k) = -D(l, a, k) \text{ grad } n(l, a, k). \quad (5)$$

Introducing (5) into (4) with the corresponding forms for J_s and $J(l, a, k)$ and with the dependence of n_s and $n(l, a, k)$ on the positional coordinates expressed through N_s , we have

$$-D \text{ grad } N_s = -D_s \text{ grad } n_s - \sum_{l=1}^r \sum_{k=1}^m D(l, a, k) \text{ grad } n(l, a, k)$$

or

$$D = D_s \frac{\partial n_s}{\partial N_s} + \sum_{l=1}^r \sum_{k=1}^m D(l, a, k) \frac{\partial n(l, a, k)}{\partial N_s}. \quad (6)$$

D is the effective diffusion coefficient of the solute. Using (1) this becomes

$$D = D_s \left[1 - \sum_{l=1}^r \sum_{k=1}^m l \frac{\partial n(l, a, k)}{\partial N_s} \right] + \sum_{l=1}^r \sum_{k=1}^m D(l, a, k) \frac{\partial n(l, a, k)}{\partial N_s}. \quad (7)$$

Inasmuch as the adsorbed solute particles do not appreciably affect the bulk of the colloid aggregates we may take $D(l, a, k) = D(c, k)$ for all values of k . Furthermore on the basis of Einstein's law of diffusion the diffusion coefficient of an aggregate of h colloid particles is related to that of an aggregate of one solute particle and one solute particle by

$$D(c, h) = \frac{D(c, 1)}{h^{2/3}}. \quad (8)$$

These substitutions simplify (6). There remains, however, the rather complex double summations. We can approximate them through

$$\sum_{l=1}^r \sum_{k=1}^m l n(l, a, k) \approx \beta(p) n(r, a, p) \quad (9)$$

$$\sum_{l=1}^r \sum_{k=1}^m n(l, a, k) \approx \alpha(p) n(r, a, p). \quad (10)$$

Without reference to the coefficients or to the first and last symbols in the parentheses we see that the $n(l, a, k)$ are merely the number of particles of each size group in the system. The mechanism here described places all the particles initially in $n(1, a, 1)$, thus initially (10) could be replaced by $n(1, a, 1)$. As time goes on, other $n(l, a, k)$'s will arise but the most unlikely distribution, one perfectly flat, would lead to a multiplicative factor equal to the number of particle sizes. For any other distribution the factor for any p would be in general a function of p but less than p . The factor $\beta(p)$ would behave in the same manner, although the numerical value would be different from that of $\alpha(p)$. We can relieve ourselves from too much specificity by putting

$$\alpha(p) = p^a, a < 1; \beta(p) = p^b, b \leq 1.$$

On closer inspection, (10) is seen to be equivalent to replacing the size-distribution curve by a rectangle of height $n(r, a, p)$ and width $\alpha(p)$. In (9) we replace the three dimensional distribution by a solid of cross-sectional area $\beta(p)$ and height $n(r, a, p)$. It is of interest to observe that p will be a function of time, for the distribution curve of particle size will move towards the maximum size with increasing time. Instead of the variation of $n(r, a, p)$ with time we think it best to keep p , which we shall call the degree of aggregation, as the independent variable.

If $N_s > N_c$ then practically all the N_c will be used as $n(1, a, 1)$ before the formation of any higher associated particles. This permits the division of the problem into two sections, the initial aggregation to form $n(1, a, 1)$ and the subsequent reactions to form higher aggregates. This first is essentially J. M. Reiner's problem. Both are contained in our analysis as we see upon introducing the approximations and the relations

$$n(l, a, p) \approx \frac{n(1, a, 1)}{p} = \frac{N_c}{p} \quad \text{and} \quad N_c = \varepsilon N_s, \quad \varepsilon < 1,$$

whence

$$\begin{aligned}
 D &= D_s \left[1 - p^a \frac{\partial n(l, a, p)}{\partial N_s} \right] + \frac{D(1, a, 1)}{p(2/3 - b)} \frac{\partial n(l, a, p)}{\partial N_s} \\
 &= D_s \left[1 - \frac{\varepsilon}{p(1 - a)} \right] + \frac{\varepsilon D(1, a, 1)}{p(5/3 - b)}.
 \end{aligned}
 \tag{11}$$

In terms of time, (11) holds from t_1 to t_m where $(t_1 - t_0)$ would be the time required for all N_c to become $n(1, a, 1)$ and $t_m - t_1$ would be the time for the formation of maximum size. For $t_0 \leq t \leq t_1$ Reiner's (3) holds

$$D = D_s \left[1 - \frac{\partial n(1, a, 1)}{\partial N_s} \right] + D(1, a, 1) \frac{\partial n(1, a, 1)}{\partial N_s},$$

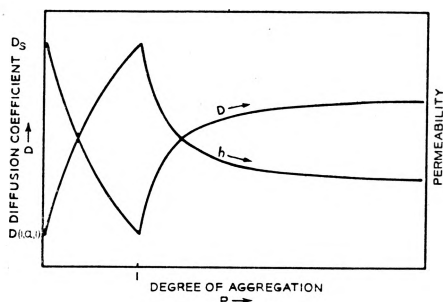


FIGURE 1

which is observed to be the same as our (11) with $p = 1$. Represented graphically these equations join exactly at $p = 1$ as is shown in Figure 1.

The removal of the assumption that $N_s > N_c$ and the precise sequential reactions do not influence the shape of the curve. This would not contradict (3) so long as the binding energy of colloid for colloid is not considerably greater than that of colloid for solute. It may cause a smoother transition at the minimum and a raising of the minimum so that D does not reach $D(1, a, 1)$. Furthermore we need not limit the number of adsorbed particles to one for the surface area of a simple colloid particle. If we would consider the number of adsorbed particles per cm^2 , then the resulting curve for the variation of the diffusion coefficient would probably have the same shape. We may also weaken the requirement that the agglomeration gives spherical particles by introducing a shape factor γ , so that

$$s_k = \gamma k^{2/3} s_1, \quad k^{1/3} > \gamma \geq 1.$$

The shape factor will be a function of k , the number of particles in

the complex. With our assumptions the inclusion of this factor would raise the maximum for 1 with a given k to $\gamma k^{2/3} - 1 < l \leq \gamma k^{2/3}$ but would cause no change in the other equations.

E. L. MacBain's data on the diffusion coefficient of long chain sulfonic acids, C_{10} to C_{14} , exhibit a minimum at dilute solution followed by a rise at higher concentrations. The curve is similar to Figure 1 but the data do not seem susceptible to interpretation by our mechanism. These experiments are instructive, however, in calling our attention to the fact that the D - p curve in Figure 1 could be transferred into a D -concentration curve. Since the aggregation is directly proportional to the concentrations by measuring the diffusion coefficient of various concentrations of N_s and N_c a test of the mechanism outlined here could be carried through so long as the degree of aggregation does not vary appreciably during an experimental determination.

If the reaction takes place within a cell we may take $N_s = q_s t$ and $N_c = q_c t$ where the q 's are the average rates of production of the solute and the adsorbing particle within the cell. In (11) ε would be q_c/q_s . For sufficiently rapid aggregation the action of this mechanism within a cell may give a purely physical interpretation of certain trigger mechanisms and other aspects of cellular behavior.

The rather simple extension that the presence of n_s primes the release of n_c in spurts gives a sinusoidal curve for the variation of the diffusion coefficient.

Finally the view that the diffusion solute lowers the permeability of the cell membrane to another diffusing substance admits a variation of the membrane permeability, h , inverse to that of D in Figure 1.

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