THE JOURNAL OF CHEMICAL PHYSICS VOLUME 59, NUMBER 4 15 AUGUST 1973

Hydrodynamic effect in diffusion-controlled reaction*

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(Received 29 March 1973)

A calculation is presented for the effect of the hydrodynamic interaction on the diffusion-controlled rate coefficient for particles that coalesce by diffusion under the influence of an interaction potential. The hydrodynamic effect is found to make a substantial reduction in the rate compared to the Debye model which includes only the effects of diffusion and the forces between the reacting particles. For the case where the particles are hard spheres the reduction is 46%. For ionic species the reduction varies between 25% and 60% depending on the extent of attraction or repulsion.

I. INTRODUCTION

The first theory of diffusion-controlled reaction rates for coagulation of colloidal particles in electrolytic solution is due to Smoluchowski.[1] This theory was generalized by Debye[2] who took into account the effect of potential forces between the particles and also applied the theory to reactions between ions and solute molecules. Some years ago, Friedman[3] pointed out that there is a hydrodynamic interaction between the reacting particles which on the average hinders their mutual approach by diffusional Brownian motion and hence tends to reduce the reaction rate. Friedman estimated, on the basis of an approximate theory, a reduction of the rate constant by about 15%. Due to the uncertainties in the theory this is not a very significant effect. In this article we treat the hydrodynamic interaction from a somewhat different, and we believe more consistent, point of view. It is shown that the hydrodynamic effect is much larger than expected by Friedman, and that the reduction in the rate constant can be of the order of 50% or more. Hence the hydrodynamic effect contributes a significant correction to the conventional Smoluchowski–Debye theory.

II. THE HYDRODYNAMIC THEORY

The hydrodynamic interaction between Brownian particles immersed in a fluid comes about because each particle in its mean motion creates a systematic flow pattern which tends to drag along the other particles. The flow of the surrounding fluid for a single spherical particle was first calculated by Stokes. As is well known, the fluid exerts a friction force

$$\mathbf{F} = -\zeta \mathbf{u} = -6\pi\eta a \mathbf{u} \quad , \tag{2.1}$$

where ζ is the friction constant, η the shear viscosity of the fluid, "a" the radius of the particle, and $\mathbf{u}$ the velocity of the particle with respect to the fluid. The flow of the fluid is given by

$$\mathbf{v}(\mathbf{r}) = \mathsf{A}(\mathbf{r}) \cdot \mathbf{u} \tag{2.2}$$

with the Stokes tensor

$$\mathsf{A}(\mathbf{r}) = \left(\frac{a}{4r}\right)\left[\left(3+\frac{a^2}{r^2}\right)\mathsf{I} + 3\left(1-\frac{a^2}{r^2}\right)\frac{\mathbf{rr}}{r^2}\right] \quad , \tag{2.3}$$

where it is assumed that the particle is at the origin at the chosen time. At large distances this can be approximated by

$$\mathbf{v}(\mathbf{r}) = \zeta\, \mathsf{T}(\mathbf{r}) \cdot \mathbf{u} \quad , \tag{2.4}$$

where

$$\mathsf{T}(\mathbf{r}) = \frac{1}{8\pi\eta r}\left[\mathsf{I} + \frac{\mathbf{rr}}{r^2}\right] \tag{2.5}$$

is the Oseen tensor which can be regarded as the Green's solution to the linearized time-independent Navier–Stokes equation. When several particles, say n, are present the speed of a selected particle must be measured with respect to the flow caused by the other particles. For the frictional force on the jth particle one finds, in the linear approximation,

$$\mathbf{F}_j = -\sum_{k=1}^{n} \boldsymbol{\zeta}_{jk} \cdot \mathbf{u}_k \quad , \tag{2.6}$$

where $\boldsymbol{\zeta}_{jk}$ is the inverse of the $3n \times 3n$ matrix $\zeta_j^{-1}\delta_{jk}\mathsf{I} + \mathsf{T}_{jk}$ and $\mathsf{T}_{jk} = \mathsf{T}(\mathbf{r}_{jk})(1-\delta_{jk})$.

It has been shown by Zwanzig[4] that the net frictional force in Eq. (2.6) leads to a Fokker–Planck equation for the distribution $P(\mathbf{r}_1, \ldots, \mathbf{r}_n, t)$ in the $3n$-dimensional coordinate space of n Brownian particles. Zwanzig considers only the case of identical particles, but his derivation is easily generalized to a variety of species. One finds the following Fokker–Planck equation

$$\partial P/\partial t = \sum_{j,k} \nabla_j \cdot \mathbf{D}_{jk} \circ \nabla_k P(\mathbf{r}^n, t) - \sum_j \nabla_j \cdot [\mathbf{A}_j P(\mathbf{r}^n, t)] \quad , \tag{2.7}$$

where the diffusion tensor D_{jk} is given by

$$\mathsf{D}_{jk} = k_B T[\zeta_j^{-1}\delta_{jk}\mathsf{I} + \mathsf{T}_{jk}] \tag{2.8}$$

and the streaming term $\mathbf{A}_j$ is related to the additional direct interaction and/or external forces $\mathbf{g}_k$ which may be present, by

$$\mathbf{A}_j = (k_B T)^{-1}\sum_k \mathsf{D}_{jk}\cdot\mathbf{g}_k \ . \tag{2.9}$$

Since on the average the Brownian particles are far apart, the Fokker–Planck Eq. (2.7) can be solved approximately by superposition of two-body correlations. The reduced equation for a typical pair can be written

$$\begin{aligned}\partial P(\mathbf{r}_1, \mathbf{r}_2, t)/\partial t = \{ & D_1\nabla_1\cdot[\nabla_1 + \beta(\nabla_1 U)]P \\ & + D_2\nabla_2\cdot[\nabla_2 + \beta(\nabla_2 U)]P \\ & + k_B T\,\nabla_1\cdot\mathsf{T}_{12}\cdot[\nabla_2 + \beta(\nabla_2 U)]P \\ & + k_B T\,\nabla_2\cdot\mathsf{T}_{12}\cdot[\nabla_1 + \beta(\nabla_1 U)]P\} \ ,\end{aligned} \tag{2.10}$$

where $\beta = (k_B T)^{-1}$ and $U(\mathbf{r}_1, \mathbf{r}_2)$ is the potential from which the additional forces $\mathbf{g}_{1,2}$ are derived.

III. SOLUTION TO THE TWO PARTICLE PROBLEM

We consider the case $U(\mathbf{r}_1, \mathbf{r}_2) = U(|\mathbf{r}_1 - \mathbf{r}_2|)$ and restrict attention to solutions of Eq. (2.10) that depend only on the relative coordinates $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. For such solutions Eq. (2.10) may be written in the form

$$\partial P(\mathbf{r}, t)/\partial t = -\nabla\cdot\mathbf{j}(\mathbf{r}, t) \ , \tag{3.1}$$

where the flux $\mathbf{j}(\mathbf{r}, t)$ is defined by

$$\mathbf{j}(\mathbf{r}, t) = -[(D_1 + D_2)\mathsf{I} - 2k_B T\mathsf{T}(\mathbf{r})]\cdot[\nabla P(\mathbf{r}, t) + \beta(\nabla U)P(\mathbf{r}, t)] . \tag{3.2}$$

We seek the steady-state rate at which particles coalesce and make the usual assumption that reaction occurs as soon as the particles touch. For stationary solutions $P(\mathbf{r}, t) = P(\mathbf{r})$, Eq. (3.1) becomes $\nabla\cdot\mathbf{j}(\mathbf{r}) = 0$ with

$$\mathbf{j}(\mathbf{r}) = -[(D_1 + D_2)\mathsf{I} - 2k_B T\mathsf{T}(\mathbf{r})]\cdot[\nabla P(\mathbf{r}) + \beta(\nabla U)P(\mathbf{r})] \ . \tag{3.3}$$

These equations must be solved subject to the boundary condition $P = 0$ when $|\mathbf{r}| = (a_1 + a_2)$ where a_1 and a_2 are the radii of the two particles, and the boundary condition that $P(\mathbf{r})$ tends to $n_1 n_2 \exp[-\beta U(r)]$ as $r \to \infty$ where n_1 and n_2 are the mean number densities of the two species.

With the assumption of spherical symmetry one easily integrates $\nabla\cdot\mathbf{j}(\mathbf{r}) = 0$ and finds for the radial current density j_r,

$$j_r = -[J/(4\pi r^2)] \ . \tag{3.4}$$

Since $P(\mathbf{r}) = P(r)$ it follows from Eqs. (3.3) and (3.4) that

$$dP/dr + \beta(dU/dr)P = J/[4\pi(D_1 + D_2)]r(r - l) \ , \tag{3.5}$$

where

$$l = 3a_1 a_2/(a_1 + a_2) \ . \tag{3.6}$$

In obtaining Eq. (3.5) use has been made of the fact that D_1 equals $(k_B T/\zeta_1)$ or $[k_B T/(6\pi\eta a_1)]$ according to Stokes' law; an analogous expression holds for the second particle.

Integration of Eq. (3.5) leads to the solution for $P(r)$

$$\exp[\beta U(r)]P(r) = n_1 n_2 - [J/4\pi(D_1 + D_2)] \times \int_r^\infty \exp[\beta U(s)][s(s - l)]^{-1} ds \ . \tag{3.7}$$

An explicit expression for the flux J follows from use of the boundary condition $P(a_1 + a_2) = 0$,

$$J = [n_1 n_2 4\pi(D_1 + D_2)/K(\infty)] \ , \tag{3.8}$$

where

$$K(r) = \int_{(a_1+a_2)}^{r} \exp[\beta U(s)][s(s - l)]^{-1} ds \ . \tag{3.9}$$

If Eq. (3.8) is employed to eliminate the flux in Eq. (3.7) one obtains the following expression for $P(r)$:

$$P(r) = \exp[-\beta U(r)]\, n_1 n_2 [K(r)/K(\infty)] . \tag{3.10}$$

The principal result of our analysis is the exact expression for the flux J presented in Eq. (3.8) for the model of particles coagulating by diffusion under the joint influence of the potential $U(r)$ and the hydrodynamic interaction. The flux one finds corresponds to a rate coefficient

$$k = [(4\pi)(D_1 + D_2)/K(\infty)] \ . \tag{3.11}$$

This can be put in the form

$$k = 4\pi(D_1 + D_2)(a_1 + a_2)/F(\alpha), \tag{3.12}$$

where

$$F(\alpha) = (a_1 + a_2)K(\infty) = \int_0^1 \exp\{\beta U[(a_1 + a_2)/y]\} \times (1 - \alpha y)^{-1} dy \tag{3.13}$$

with

$$\alpha = l/(a_1 + a_2) = 3a_1 a_2/(a_1 + a_2)^2 \ . \tag{3.14}$$

In the next section we compare this result for the rate coefficient of diffusion-controlled reactions to previous theories.

IV. DISCUSSION OF THE RESULT

The limit $U = 0$ and $l = 0$ in Eqs. (3.8), (3.9) corresponds to Smoluchowski's model of rigid sphere diffusion so that

$$k_s = 4\pi(D_1 + D_2)(a_1 + a_2) \ . \tag{4.1}$$

If we set $U=0$ in our result we find the effect of the hydrodynamic interaction on the rate coefficient to be

$$k_H = -\alpha[\ln(1-\alpha)]^{-1}k_s . \tag{4.2}$$

The dimensionless parameter α takes its maximum value $(\frac{3}{4})$ for particles of equal size $a_1 = a_2$ in which case $k_H = 0.54 k_s$.

The Debye model of spheres diffusing under the influence of the potential U but in the absence of a hydrodynamic interaction is recovered by putting $\alpha = 0$ in Eq. (3.13),

$$k_D = 4\pi(D_1+D_2)(a_1+a_2)/F(0). \tag{4.3}$$

Hence we find that our result is related to Debye's result by

$$k = [F(0)/F(\alpha)]k_D . \tag{4.4}$$

Here one sees immediately that in the limit of strong attraction $k \approx k_D$ whereas in the limit of strong repulsion $k \approx (1-\alpha)k_D$. In the latter limit, for equal size particles, $k \approx (\frac{1}{4})k_D$.

In order to compare our result with that of Friedman we expand $K(\infty)$ to linear terms in l;

$$k_L = 4\pi(D_1+D_2)\left\{\int_{(a_1+a_2)}^{\infty} \exp[\beta U(s)]s^{-2}[1+(l/s)]ds\right\}^{-1} \tag{4.5}$$

which is identical in form to Friedman's approximate result except that he obtains $(l/2)$ in place of l in Eq. (4.5). The difference between the linear approximation Eq. (4.5) and the exact result will be nonnegligible for values of the parameters of interest. For example for equal size particles when $U=0$ one obtains $[k_H/k_s] = 0.54$ while the linear approximation Eq. (4.5) yields $[k_L/k_s] = 0.73$. The difference between the appearance of a factor of l instead of $(l/2)$ in the linear approximation Eq. (4.5) is also significant. For equal size particles when $U=0$ one obtains, with the factor $(l/2)$ the result $[k_L/k_s] = 0.84$ instead of 0.73.

For ionic systems the appropriate form of the potential is $U(r) = [q_1q_2/r\epsilon]$. For this potential our result may be expressed as

$$k/k_s = \left[\int_0^1 \exp(xy)(1-\alpha y)^{-1}dy\right]^{-1}, \tag{4.6}$$

where $x = [q_1q_2\beta/\epsilon(a_1+a_2)]$ with ϵ the dielectric constant of the solution. The Debye result is $[k_D/k_s] = x(e^x-1)^{-1}$ and the linear approximation result[3] is

$$k_L/k_s = x\{(e^x-1)+\alpha[e^x(1-x^{-1})+x^{-1}]\}^{-1}. \tag{4.7}$$

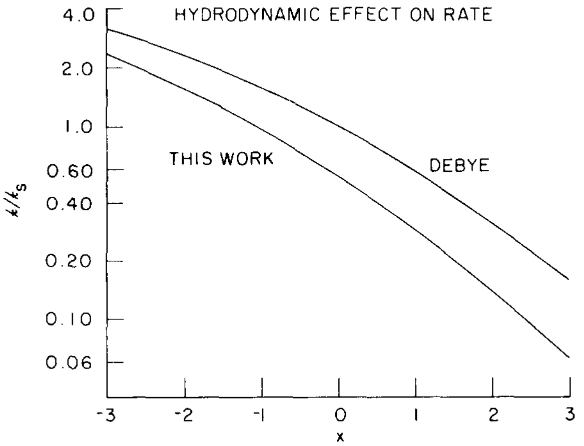

FIG. 1. Effect of Coulomb interaction on the rate coefficient for diffusion controlled reactions. The ordinate is the ratio of rate coefficient to the Smoluchowski result k_s, Eq. (4.1). The abscissa is $x = [q_1q_2\beta/\epsilon(a_1+a_2)]$; $x=1$ is a typical value for two sodium atoms at a separation of 7 Å. The upper curve is the Debye model and the lower curve is the result of the work reported here including the effects of the hydrodynamic interaction according to Eq. (4.6) with $\alpha = (3/4)$.

In Fig. 1 the result of our theory is plotted as $[k/k_s]$ versus x for the case of a Coulomb potential, Eq. (4.6), and equal size particles, $\alpha = (\frac{3}{4})$. For purposes of comparison the curve of $[k_D/k_s]$ has been added. Friedman found[3] that the effect of the hydrodynamic interaction was to reduce the rate coefficient from the Debye value by about 15% over the entire range of x covered in Fig. 1. He concluded that the possibility of finding experimental evidence for the hydrodynamic effect was remote. Our results indicate a much larger reduction in the rate coefficient and a greater variation of this reduction over the relevant range of x. For example when the attraction is greatest, $x=-3.0$, the reduction is 25% and when the repulsion is greatest, $x=3.0$, the reduction is 60%. For neutral species, where $U(r)=0$, the reduction is 46%. Thus our calculation indicates that the hydrodynamic effect may be experimentally important. However one word of caution must be added. This and similar hydrodynamic models are based on the use of Oseen's tensor which is only an accurate description for incompressible fluids within the linear theory when the solute particles are widely separated [cf. Eqs. (2.3) and (2.4)]. For repulsive interactions $U(r)$ there is substantial contribution to the integral $F(\alpha)$, Eq. (3.13), from small values of the interparticle distance, but for attractive interaction the main contribution is from large values of the distance.

ACKNOWLEDGMENT

We thank Professor James Kinsey for assistance in producing Fig. 1.

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*Supported in part by the National Science Foundation.

[1] M. von Smoluchowski, Phys. Z. **17**, 557 (1916); Phys. Z. **17**, 585 (1916); Z. Phys. Chem. (Leipz.) **92**, 129 (1917); see also S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

[2] P. Debye, Trans. Electrochem. Soc. **82**, 265 (1942).

[3] H. L. Friedman, J. Phys. Chem. **70**, 3931 (1966).

[4] R. Zwanzig, Adv. Chem. Phys. **15**, 325 (1969).