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The Steric Factor in the Time-Dependent Diffusion-Controlled Reactions

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A simple analytic approximation for the time-dependent rate constant in the diffusion-controlled reactions between particles with isotropic reactivity and axially symmetric active site has been derived. It is shown that in the general case the definition of the effective steric factor depends on time and the size of active site.

Introduction

It is well-known that in many diffusion-controlled reactions only a restricted region of the reaction surface constitutes the "active site" where these reactions occur. Because of their importance, especially in biophysics,^{2,3} these kinds of reactions have been widely investigated.⁴⁻¹² One is an important class reactions between species of kind A and B where the species A are chemically asymmetric and the B species have isotropic reactivity.^{4,5} Herein we restrict our treatment this very type of reactions.

To describe the apparent reduction of the rate constant for the steady-state case the effective steric factor (ESF) $f_s \leq 1$ is introduced by the relation

$$k_s = k_{sm} f_s \quad (1)$$

where $k_{sm} = 4\pi DR$ is the Smoluchowski steady-state rate constant for species A and B which have a spherically symmetric reactivity; $R = R_A + R_B$ is the radius of the reaction sphere, and $D = D_A + D_B$ is the relative translational diffusion coefficient.¹³

In the steady state, the problem is to calculate the total diffusive flux into the reaction sphere and represent it in the form (1) to extract the desired ESF. However, in the time-dependent case it is unclear as to how the ESF may be introduced. Previous theoretical studies have not considered the time-dependent case nor the validity of the steady-state approximation. The object of the present paper is to investigate this problem in the absence of rotational diffusion.

Statement of the Problem and General Solution

Let us consider a particle of kind A with axially symmetric active site $\partial\Omega_0$ and inert site $\partial\Omega_1$ on the reaction surface $\partial\Omega = \partial\Omega_0 \cup \partial\Omega_1$. We introduce the spherical coordinate system such that

$$\partial\Omega_0 = \{r = R, 0 \leq \theta \leq \theta_0, 0 \leq \varphi < 2\pi\};$$

$$\partial\Omega_1 = \{r = R, \theta_0 < \theta \leq \pi, 0 \leq \varphi < 2\pi\}$$

It is convenient to treat the corresponding mixed boundary-value problem¹⁴ in dimensionless form

$$\frac{\partial n}{\partial \tau} - \nabla^2_{\xi} n = 0, \quad (\xi > 1) \times (\tau > 0) \quad (2)$$

$$n|_{\tau=0} = 0, \quad \xi \geq 1 \quad (3)$$

$$n|_{\partial\Omega_0} = 1, \quad \frac{\partial n}{\partial \xi}|_{\partial\Omega_1} = 0, \quad \tau > 0 \quad (4)$$

$$n|_{\xi \rightarrow \infty} < \infty, \quad \tau > 0 \quad (5)$$

where $n(\xi, \tau) = 1 - n_B(\xi, \tau)/n_0$, $\xi = r/R$, $\tau = t/t_D$, and $t_D = R^2/D$;

$n_B(\xi, \tau)$ and n_0 are the local and initial (bulk) concentrations of the B particles, respectively.

Utilizing the Laplace transformation in τ , one can rewrite the problem (2-5) as follows:

$$\nabla^2_{\xi} \bar{n} - s\bar{n} = 0, \quad \xi > 1 \quad (6)$$

$$\bar{n}|_{\partial\Omega_0} = 1/s, \quad \frac{d\bar{n}}{d\xi}|_{\partial\Omega_1} = 0 \quad (7)$$

$$|\bar{n}|_{\xi \rightarrow \infty} < \infty \quad (8)$$

where $\bar{n}(\xi; s) = \int_0^\infty n(\xi, \tau) \exp(-s\tau) d\tau$ and s is the Laplace transform variable.

One readily finds that the solution of eq 6 satisfying the boundary condition (8) is

$$\bar{n}(\xi; s) = \sum_{l=0}^{\infty} \tilde{A}_l(s) \left(\frac{\pi}{2s^{1/2}\xi} \right)^{1/2} K_{l+1/2}(s^{1/2}\xi) P_l(\mu) \quad (9)$$

where $(\pi/2z)^{1/2} K_{l+1/2}(z)$ are appropriate modified spherical Bessel functions, $P_l(\mu)$ are the Legendre polynomials, and $\mu = \cos \theta$ and $\tilde{A}_l(s)$ are unknown constants to be determined from the mixed boundary conditions (7).

Substitution of eq 9 into the boundary conditions (7) yields the pair of dual series relations (DSR)¹⁴

$$\sum_{l=0}^{\infty} \tilde{A}_l(s) P_l(\mu) = 1/s \quad \text{in } \partial\Omega_0 \quad (10)$$

$$\sum_{l=0}^{\infty} [l - s^{1/2} g_l(s)] \tilde{A}_l(s) P_l(\mu) = 0 \quad \text{in } \partial\Omega_1 \quad (11)$$

Here

$$\tilde{A}_l(s) = \tilde{A}_l(s) \left(\frac{\pi}{2s^{1/2}} \right)^{1/2} K_{l+1/2}(s^{1/2})$$

and

$$g_l(s) = K_{l+3/2}(s^{1/2})/K_{l+1/2}(s^{1/2})$$

It is convenient to represent these DSR in the form

$$\sum_{l=0}^{\infty} \frac{1 - q_l(s)}{l + 1/2} X_l(s) P_l(\mu) = 1/s \quad \text{in } \partial\Omega_0 \quad (12)$$

$$\sum_{l=0}^{\infty} X_l(s) P_l(\mu) = 0 \quad \text{in } \partial\Omega_1 \quad (13)$$

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where

$$q_l(s) = \frac{1 + 2w_l(s)}{2[1 + l + w_l(s)]}; \quad w_l(s) = s^{1/2}g_l(s) - (2l + 1)$$

and $X_l(s)$ are new unknown coefficients which are defined by

$$X_l(s) = [l + 1 + w_l(s)]A_l(s)$$

The dimensionless total flux of particles B through the reaction surface in Laplace space $\bar{k}_*(s)$ is calculated by

$$\bar{k}_*(s) = \frac{\bar{k}(s)}{k_{sm}} = -\frac{1}{2} \int_{-1}^1 d\xi \bar{n}(\xi; s) \big|_{\partial\Omega_0} d\mu \quad (14)$$

Thus the desired flux is

$$\bar{k}_*(s) = X_0(s) \quad (15)$$

Therefore, the original problem has been reduced to the determination of $X_0(s)$.

It may be shown¹⁵ that the solution of the DSR $X_l(s; \theta_0)$ satisfies the following infinite set of linear equations

$$X_l - \sum_{p=0}^{\infty} M_{lp}(s; \theta_0) X_p = b_l(s; \theta_0), \quad l \geq 0 \quad (16)$$

Here

$$M_{lp}(s; \theta_0) = \frac{2l+1}{2p+1} q_p(s) Q_{lp}(\theta_0)$$

$$Q_{lp}(\theta_0) = \frac{1}{\pi} \left\{ \frac{\sin[(l+p+1)\theta_0]}{l+p+1} + \frac{\sin[(l-p)\theta_0]}{l-p} (1 - \delta_{lp}) + \theta_0 \delta_{lp} \right\}; \quad b_l(s; \theta_0) = \frac{2l+1}{2s} Q_{l0}(\theta_0)$$

and δ_{lp} is the Kronecker delta.

Approximate Solutions

The system (16) may be solved by iteration and the zeroth-order approximation is

$$\bar{k}_*^{(0)}(s; \theta_0) = \frac{1}{s} f_s^{(0)}(\theta_0) \quad (17)$$

where

$$f_s^{(0)}(\theta_0) = \frac{1}{2\pi} (\theta_0 + \sin \theta_0) \quad (18)$$

is the zeroth-order approximation for the steady-state ESF which works well for $\theta_0 \ll 1$.¹⁶

It is obvious that $f_s^{(0)}(\theta_0)$ does not uniformly approximate the ESF in $[0, \pi]$, so let us derive the first-order approximation

$$\bar{k}_*^{(1)}(s; \theta_0) = \frac{(1 + s^{1/2})f_s^{(1)}}{s[1 + s^{1/2}(1 - f_s^{(1)})]} \quad (19)$$

where

$$f_s^{(1)}(\theta_0) = \frac{f_s^{(0)}}{1 - f_s^{(0)}} \quad (20)$$

is the first-order approximation for the steady-state ESF. One can see that $f_s^{(1)}(\theta_0)$ yields correct results for both limiting cases $\theta_0 \rightarrow 0$ and $\theta_0 \rightarrow \pi$ and approximates sufficiently well the exact ESF in the whole segment $[0, \pi]$.¹⁵

In the original space formula (19) gives

$$k_*^{(1)}(\tau; \theta_0) = f_s^{(1)} \left\{ 1 + \frac{f_s^{(1)}}{1 - f_s^{(1)}} \exp[\tau(1 - f_s^{(1)})^2] \operatorname{erfc} \left(\frac{\tau^{1/2}}{1 - f_s^{(1)}} \right) \right\} \quad (21)$$

The ESF in the Time-Dependent Case

If we introduce the value

$$h(\theta_0) = \frac{f_s^{(1)}}{1 - f_s^{(1)}} = \frac{f_s^{(0)}}{1 - 2f_s^{(0)}} \quad (22)$$

we can rewrite eq 21 in the form

$$k_*^{(1)}(\tau; h) = \frac{h}{1+h} \{ 1 + h \exp[(1+h)^2 \tau] \operatorname{erfc}[(1+h)\tau^{1/2}] \} \quad (23)$$

One readily verifies that eq 23 is the relevant rate constant for the effective local concentration $n_{\text{eff}}(\xi; \tau)$ of B that obeys the boundary-value problem

$$\frac{\partial n_{\text{eff}}}{\partial \tau} - \nabla^2_{\xi} n_{\text{eff}} = 0, \quad (\xi > 1) \times (\tau > 0) \quad (24)$$

$$n_{\text{eff}}|_{\tau=0} = n_0, \quad \xi \geq 1 \quad (25)$$

$$\left(h n_{\text{eff}} - \frac{\partial n_{\text{eff}}}{\partial \xi} \right) \bigg|_{\partial\Omega} = 0, \quad \tau > 0 \quad (26)$$

$$n_{\text{eff}}|_{\xi \rightarrow \infty} < \infty, \quad \tau > 0 \quad (27)$$

The solution of the problem (24–27) is

$$n_{\text{eff}}/n_0 = 1 - \frac{1}{\xi} \left(\frac{h}{1+h} \right) \left\{ \operatorname{erfc} \left(\frac{\xi-1}{2\tau^{1/2}} \right) - \exp[(1+h)(\xi-1)] \exp[(1+h)^2 \tau] \operatorname{erfc} \left[\frac{\xi-1}{2\tau^{1/2}} + (1+h)\tau^{1/2} \right] \right\} \quad (28)$$

Thus, we find a spherically symmetric boundary-value problem of third kind that describes the reaction between effectively chemically isotropic particles and corresponds to the original mixed boundary-value problem (2–5).

Numerical calculation shows¹⁵ that $f_s^{(1)}(\theta_0)$ is a lower bound of the exact ESF $f_s(\theta_0)$. If we assume that this property holds in the time-dependent case, eq 23 allows us to evaluate the highest reduction of the rate constant due to the chemical asymmetry of species A.

Let us define the characteristic relaxation time $t_r(\theta_0)$ by the root of the equation

$$k^{(1)}(t, \theta_0) = 2k_s^{(1)}(\theta_0) \quad (29)$$

One sees from eq 23 that eq 29 has the solution only when $\theta_0 \in [\theta^*, \pi]$, where θ^* is the root of the equation $f_s^{(0)}(\theta_0) = 1/3$, i.e., $\theta^* \approx 0.373\pi$. Hence, in chosen approximation the transition effects are not important when $\theta_0 \in [0, \theta^*]$.

It follows from above that for the case of small θ_0 , which is of interest in biophysical problems,^{2,3} only the steady-state problem needs to be considered as the time-dependent effects can be ignored. One can give a physical interpretation of this as follows. It is clear that the region of nonzero gradient of the local concentration n_B is small for small θ_0 . So the characteristic relaxation time decreases since it is determined by the time of depletion of the excess of B particles in order to reach the steady state in this region.

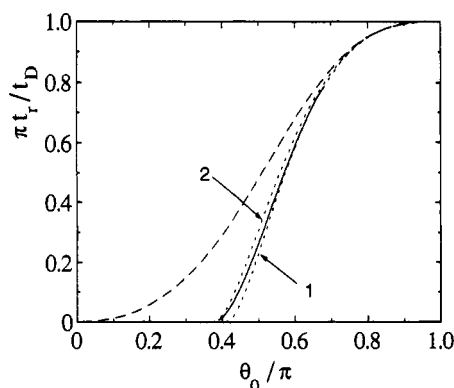


Figure 1. The dependence t_r and its two-sided bound on the angular size of the active site θ_0 . The solid curve is the relaxation time calculated from eq 29, dotted curves correspond to the lower (curve 1) and upper (curve 2) bounds governed by inequality (30), and the dashed curve is the relaxation time governed by eq 32.

With the aid of well-known inequalities for the error function, one readily shows that for $t_r(\theta_0)$ the following two-sided inequality holds

$$\psi(\theta_0; \pi/2) < t_r(\theta_0) \leq \psi(\theta_0; 1) \quad (30)$$

where

$$\psi(\theta_0; z) = \frac{t_D}{\pi} [f_s^{(1)}(1 + h^{-2}z)]^2$$

Note that the upper bound holds when $\theta_0 \in [\theta_0^*, \pi]$, and the lower bound holds when $\theta_0 \in [0, \theta_0^*]$, where $\theta_0^* \approx 0.409\pi$ is the root of the equation $f_s^{(0)}(\theta_0) = 1/[2 + (2/\pi)^{1/2}]$. The dependences t_r and its two-sided bound on θ_0 are shown in Figure 1. One can see from Figure 1 that the chemical asymmetry of reactants leads to a decrease of the transition period.

Evidently that when $0.8 \gtrsim \theta_0 \geq \pi$ the rate constant may be accurately evaluated for all $t > 0$ using the eq

$$k^{(1)}(t; \theta_0) = 4\pi D R_{\text{eff}}(\theta_0) \left[1 + \frac{R_{\text{eff}}(\theta_0)}{(\pi D t)^{1/2}} \right] \quad (31)$$

and $t_r(\theta_0)$ is given by the equation

$$t_r(\theta_0) = R_{\text{eff}}^2(\theta_0) / \pi D \quad (32)$$

In eqs 31 and 32

$$R_{\text{eff}}(\theta_0) = R f_s^{(1)}(\theta_0) \quad (33)$$

Hence, for a reaction sphere with a sufficiently large active site the ESF may be introduced in the form of a renormalization parameter of the reaction radius in both time-dependent and steady-state cases. It is important that eq 31 makes sense also for $0 \leq \theta_0 \leq 0.8$, but as the long time asymptotics of $k^{(1)}(t; \theta_0)$.

In case of the reaction $A + B \rightarrow P$ the usual form of rate expression for the particles' B bulk concentration is¹⁷

$$-\frac{d[B]}{dt} = k_{\text{Sm}} k_*(t; \theta_0) [A]_0 [B] \quad (34)$$

Therefore using eq 31, the long time dependence (for all $\theta_0 \in$

$[0, \pi]$) of the minority species B is obtained

$$[B](t) \propto \exp \left[-4\pi D R_{\text{eff}} [A]_0 \left(1 + \frac{2R_{\text{eff}}}{(\pi D t)^{1/2}} \right) t \right] \quad (35)$$

Note that eq 35 may be used for experimental verification of formula 31.

Conclusions

The results obtained here hold for the first-order approximation of the time-dependent rate constant and work well at least for almost reflecting ($\theta_0 \rightarrow 0$) or almost perfectly absorbing ($\theta_0 \rightarrow \pi$) reaction spheres. Nevertheless, it seems reasonable that eq 23 approximates $k(t; \theta_0)$ well for all permissible θ_0 if one takes $h(\theta_0)$ in the form

$$h(\theta_0) = \frac{f_s(\theta_0)}{1 - f_s(\theta_0)}$$

In general, the ESF for the time-dependent case may be introduced in terms of an effective second-order rate constant $h(\theta_0)$ in the relevant effective radiation boundary condition (26).

The ESF as a renormalization parameter under the reaction radius may be introduced in the following cases: (a) for all permissible angles θ_0 at long time values and in the steady state and (b) for the almost perfectly absorbing reaction sphere ($\theta_0 \rightarrow \pi$) at all time values. It should be noted that the method used in this work may be applied to a wide variety of problems in diffusion-limited reactions between asymmetric particles. For example, it may be applied to the time-dependent models of Schmitz and Schurr¹⁸ and of Solc and Stockmayer.¹⁹

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