Diffusion-Controlled Reactions Involving a Reactant with Two Reaction Sites: Evaluation of the Utility of Wilemski-Fixman Closure Approximation

Jesik Uhm, Jinuk Lee, Changsun Eun, and Sangyoub Lee[*]

Department of Chemistry, Seoul National University, Seoul 151-747, Korea. [*]*E-mail: sangyoub@snu.ac.kr*
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By using two different computer simulation methods, of which one produces exact results while the other is based on the Wilemski-Fixman closure approximation, we evaluate the utility of closure approximation in calculating the rates of diffusion-controlled reactions involving a reactant with multiple reaction sites. We find that errors in the estimates of steady-state rate constants due to closure approximation are not so large. We thus propose an approximate analytic expression for the rate constant based on the closure approximation.

Key Words : Diffusion-controlled reaction, Reactant with multiple reaction sites, Wilemski-Fixman closure approximation

Introduction

Diffusion-controlled reactions involving a reactant with multiple reaction sites are frequently observed in biological systems. An example that has attracted much attention is the kinetics of binding of ligands to receptors on cell surfaces.[1-4] In previous theoretical works, the receptors have been modeled as small circular patches that are randomly distributed on a sphere. For this simplified model problem, Zwanzig and Szabo obtained an approximate analytic solution based on an effective medium treatment.[4]

On the other hand, Samson and Deutch (SD) considered the diffusion-controlled rate into a pair of reacting sinks, and derived an exact expression for the steady-state rate constant.[5] Recently, Strieder *et al*. generalized the SD result for the case involving partially absorbing sinks,[6] while Traytak considered the steady-state competition among perfectly absorbing sinks distributed uniformly in a spherical region.[7]

For the model problem of Samson and Deutch, only the steady-state kinetics has been studied. In this problem, the coarse-graining approaches such as the effective medium treatment of Zwanzig and Szabo[4] and the renormalization group method of Traytak,[7] cannot be applied. In this work, we will consider the time-dependent kinetics for the SD model problem. An approximate but potentially useful approach is that based on the Wilemski-Fixman closure approximation.[8,9] The closure approximation is expected to provide a general theoretical framework that may also be applied to more complicated model problems involving a reactant with many reaction sites that are arranged in an arbitrary manner. Even with the closure approximation, however, we need to introduce additional mathematical approximations to obtain analytic rate expressions. There-fore, before going further, it is desirable to evaluate the accuracy of the closure approximation alone.

We do this by using two different computer simulation methods, of which one produces exact results while the other is based on the Wilemski-Fixman closure approximation. In the next section, we present brief overviews of these simulation methods. We then discuss the results for the double sink problem. We find that errors in the rate constant estimates due to closure approximation are not so large. We thus propose an approximate analytic expression for the rate constant based on the closure approximation.

Computer Simulation Methods

Exact simulation method. We want to calculate the bimolecular rate constant for a diffusion-controlled, irreversible reaction, A+B $\rightarrow$ Product(s). Because we are interested in evaluating the magnitude of errors in using the closure approximation, we will consider a model system as simple as possible. The reactant A consists of two spheres of diameter σ that are separated by d, while the reactant B is a simple sphere of diameter σ. The reaction occurs immediately when the center of B comes within the distance
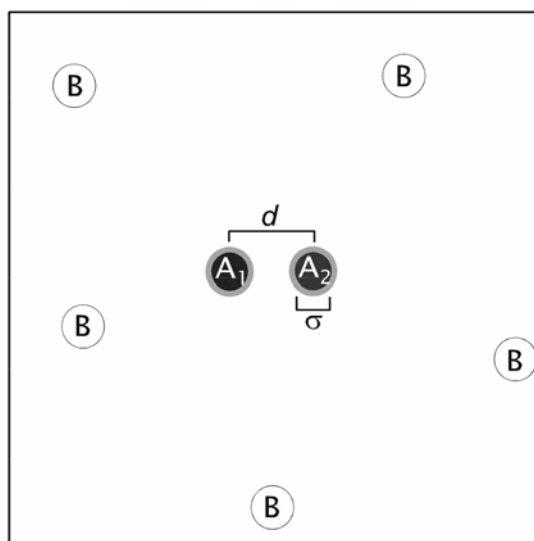

Figure 1. Schematic representation of the simulation system for calculating the survival probability of the central reactant A with two reaction sites.

$\sigma + \Delta r$ of either sphere of A.

To avoid any complication associated with the many-particle effects, we will assume that the reactant concentrations are very low. Then a straightforward computer simulation method for calculating the time-dependent rate coefficient is first to calculate the survival probability of the reactant A fixed at the center of simulation box. Many particles of B, which are mutually non-interacting, are placed in the simulation box, and each of the B reacts independently with the central A. It was shown by Szabo that for such a target problem, the rate coefficient is exactly the same as the irreversible rate coefficient at infinite dilution.[10] For a target problem, the survival probability $Y_A(t)$ is related to the rate coefficient as

$$Y_A(t) = \exp[-C_B \int dt k(t)], \qquad (1)$$

where C_B is the concentration of B particles.

The simulation system is depicted in Figure 1. The length of an edge of the cubic simulation box is 40σ, and the periodic boundary condition is imposed. We vary the distance between the two spheres of A molecule from 0 to 10σ. At $t = 0$, 100 particles of reactant B are randomly placed around the central A, and then survival probability is calculated as a function of time. Because the simulation box has a finite size and the periodic boundary condition is used, a B particle initially placed in the central box may have a chance to react with an A molecule in the image box at long times. However, such a many-particle effect may be negligible in the present simulation condition until the survival probability decays less than 10^{-3}. We are using a large enough simulation box with appropriate B particle concentration. If C_B is too small, the many particle effect comes into play. On the other hand, if C_B is too large, the survival probability decays too fast to obtain the value of $k(t)$ at long times.

Simulation method based on the closure approximation. In previous works, we presented efficient computer simulation methods for calculating the time-dependent rate coefficient for diffusion-influenced bimolecular reactions.[2-5] The methods were based on the closure approximation. It was shown that when the reactants are distributed in equilibrium at $t = 0$, the Laplace transform $\hat{k}(s)$ of the time-dependent rate coefficient $k(t)$ can be calculated from the following formula:

$$\hat{k}(s)/k_0 = s^{-1}[1 + k_R \hat{P}_{ret}(s)]^{-1}, \qquad (2)$$

where s is the Laplace transform variable. k_R is the reaction probability per unit time in the reaction zone, k_0 and is the initial value of the rate constant given by

$$k_0 \equiv k(0) = k_R V_{rx}, \qquad (3)$$

$$V_{rx} = \int d\Lambda S(\Lambda)g(\Lambda). \qquad (4)$$

Λ denotes the relative configurational coordinates for a pair
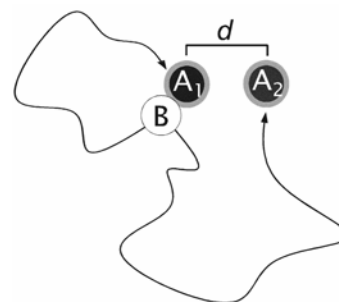

Figure 2. Schematic representation of the simulation method for calculating the time-dependent rate coefficient based on the closure approximation.

of reactants A and B. The sink function $S(\Lambda)$ has the value of unity only within the reaction zone and vanishes elsewhere. $g(\Lambda)$ is the equilibrium pair correlation function for the reactant pair. Note that if $g(\Lambda) = 1$, V_{rx} is the volume of the reaction zone. The key dynamic quantity in Eq. (2) is the *returning probability* $P_{ret}(t)$, which represents the probability that a pair of reactant molecules located in the reaction zone at $t = 0$ will be found again in the reaction zone at a later time t under the condition that the reaction is absent.[14] We can calculate this returning probability, as depicted in Figure 2, from Brownian dynamics (BD) trajectories in a straightforward manner. Once $P_{ret}(t)$ is obtained as a function of time, the Laplace transformation of $P_{ret}(t)$ and the inverse Laplace transformation of Eq. (2) can be carried out numerically by using the IMSL subroutines.[15] In the fully diffusion-controlled limit ($k_R \to \infty$), the steady-state rate constant k_{SS} can be calculated from the following expression:

$$k_{SS} = V_{rx}[\int_0^\infty dt P_{ret}(t)]^{-1}. \qquad (5)$$

Results and Discussion

Hereafter, we call the exact simulation method described in the previous section as BD Method 1, while the simulation method relying on the closure approximation as BD Method 2. In Figure 3, we compare the survival probability calculated with the approximate time-dependent rate coefficient obtained by BD Method 2 with the exact one calculated by BD Method 1.

Later, we will show that when the width of the sinks becomes zero ($\Delta r \to 0$) the rate coefficient obtained with the closure approximation is exact when the distance d between the two spherical reaction sinks of A is zero or very large, as evidenced also by Figure 3. The largest errors in the rate coefficient values evaluated with the closure approximation occur when d has the intermediate values. For the two cases with $d/\sigma = 0$ and 10, the slight discrepancy between the different BD simulation results is due to statistical errors of the simulation results.

As mentioned in the introduction, Samson and Deutch derived an exact expression for the steady-state rate constant for the double sink problem under consideration:
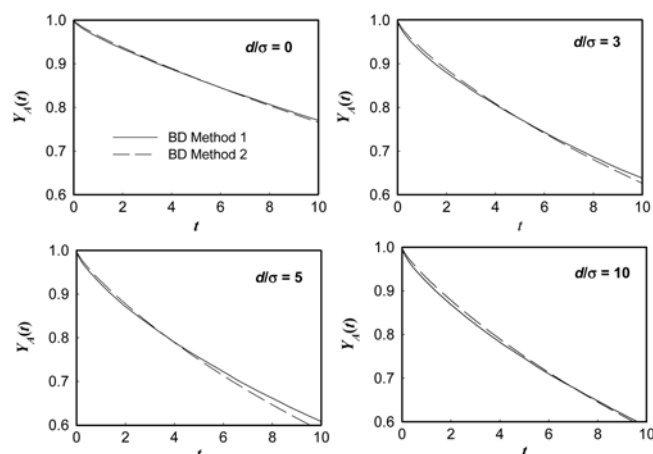
Figure 3. Comparison of the survival probabilities calculated from different BD methods. The solid curves represent the exact results obtained from BD Method 1, while the dashed curves are the approximate results from BD Method 2.
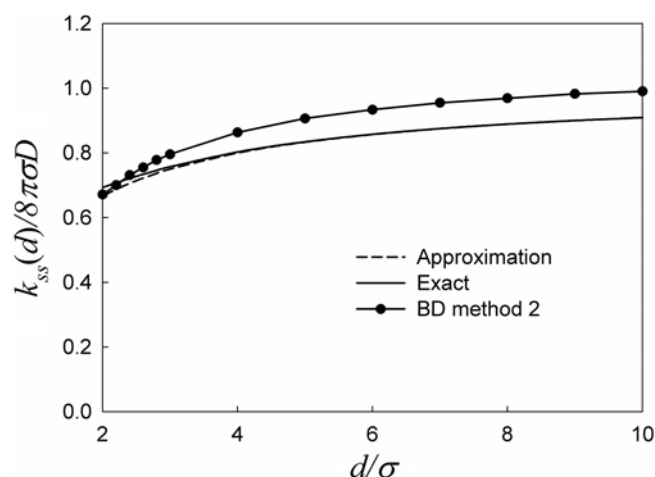

Figure 4. Comparison of the steady-state rate constants calculated as a function of the distance d between the two reaction sites of A. The solid curve represents the exact results calculated from Eq. (6). Filled circles are the results obtained from BD Method 2. The dashed curves are calculated from the approximate analytic expression given in Eq. (33).

$$\frac{k_{SS}(d)}{8\pi\sigma D} \equiv \frac{k(\infty;d)}{8\pi\sigma D} = 1 - \sum_{m=2}^{\infty} (-1)^m \frac{\sinh\mu_0}{\sinh m\mu_0}, \qquad (6)$$

where $\mu_0 = d/(2\sigma)$. In Figure 4, we compare the approximate steady-state rate constant calculated from Eq. (5) with that obtained in Eq. (6). We see that the rate constant values evaluated with the closure approximation tend to overestimate the true values when d has the intermediate values. However, even in the worst case, the error is about 10%.

Approximate Analytic Rate Expressions

Formal rate expression based on the closure approximation. Let us consider a reaction system containing an A molecule with two spherical reaction sinks and N_B molecules

of B. To describe the reaction kinetics systematically, we introduce a set of hierarchical kinetic equations describing the reaction-diffusion process of molecules A and B. The lowest-order equation in the hierarchy is given by

$$\frac{\partial}{\partial t}\psi_A(\mathbf{r}_A^{(2)}, t) = L_A(\mathbf{r}_A^{(2)})\psi_A(\mathbf{r}_A^{(2)}, t) -$$

$$\sum_{j=1}^{N_B} \int d\mathbf{r}_B S_{AB}(\mathbf{r}_A^{(2)}, \mathbf{r}_B)\psi_{AB_j}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, t). \qquad (7)$$

$\psi_A(\mathbf{r}_A^{(2)}, t)$ is the probability density that A has not reacted by time t, with the reaction sinks located at $\mathbf{r}_A^{(2)} = (\mathbf{r}_1, \mathbf{r}_2)$. The first term on the right side of Eq. (7) represents the change due to random thermal motion of the molecule A. $L_A(\mathbf{r}_A^{(2)})$ denotes the appropriate evolution operator whose explicit expression will be given later. The second term arises due to the reaction between A and B. $\psi_{AB_j}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, t)$ is the joint probability density that A is still active by time t, with the sinks located at $\mathbf{r}_A^{(2)}$, and that the jth B molecule B_j is located at r_B. The sink function $S_{AB}(\mathbf{r}_A^{(2)}, \mathbf{r}_B)$ denotes the reaction rate at the reactant configuration $(\mathbf{r}_A^{(2)}, \mathbf{r}_B)$. To make the problem analytically tractable, we assume a sink function of the form,

$$S_{AB}(\mathbf{r}_A^{(2)}, \mathbf{r}_B) = \kappa_1 S_1(\mathbf{r}_B - \mathbf{r}_1) + \kappa_2 S_2(\mathbf{r}_B - \mathbf{r}_2). \qquad (8)$$

κ_1 and κ_2 are inherent rate parameters with the two reaction sinks of A.

The evolution equation governing the two-particle distribution function is given by

$$\frac{\partial}{\partial t}\psi_{AB_j}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, t) = L_{AB}(\mathbf{r}_A^{(2)}, \mathbf{r}_B)\psi_{AB_j}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, t)$$

$$- S_{AB}(\mathbf{r}_A^{(2)}, \mathbf{r}_B)\psi_{AB_j}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, t)$$

$$- \sum_{k=1, k\neq j}^{N_B} \int d\mathbf{r}_B' S_{AB}(\mathbf{r}_A^{(2)}, \mathbf{r}_B')\psi_{AB_jB_k}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, \mathbf{r}_B', t), \quad (9)$$

Equation (9) for $\psi_{AB_j}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, t)$ involves the three-particle distribution functions, $\psi_{ABB'}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, \mathbf{r}_B', t)$, whose time evolution is governed by the higher order kinetic equations. In fact, the set of kinetic equations governing the time evolution of the distribution functions forms an infinite hierarchy. To truncate the hierarchy, we employ the superposition approximation (SA). First, we introduce the nonequilibrium pair correlation function $\rho_{AB}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, t)$ defined by

$$\sum_{j=1}^{N_B} \psi_{AB_j}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, t) = C_B Y_A(t)\rho_{AB}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, t) \qquad (10)$$

where C_B is the bulk number density of B and $Y_A(t)$ is the survival probability of A at time t that is given by

$$Y_A(t) = \int d\mathbf{r}_A^{(2)} \psi_A(\mathbf{r}_A^{(2)}, t), \qquad (11)$$

Then, the three-particle distribution function $\psi_{AB_jB_K}(\mathbf{r}_A^{(2)}, \mathbf{r}_B,$

r_B', t) is approximated by

$$\sum_{k=1,\,k\neq j}^{N_B} \psi_{AB_jB_k}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, \mathbf{r}_B', t) =$$

$$C_B^2 Y_A(t)\rho_{AB}(\mathbf{r}_A^{(2)}, \mathbf{r}_B, t)\rho_{AB}(\mathbf{r}_A^{(2)}, \mathbf{r}_B', t). \tag{12}$$

It is known that the SA, represented by Eq. (12), gives a solution that coincides with the exact one for an irreversible target problem, which involves an immobile reactant A surrounded by many non-interacting B's. Otherwise, the SA would be valid when the reactant concentrations are small.

By integrating Eq. (7), a kinetic equation for the survival probability $Y_A(t)$ can be obtained as

$$\frac{d}{dt}Y_A(t) = -k(t)C_B Y_A(t) \tag{13}$$

where the time-dependent rate coefficient $k(t)$ is given by

$$k(t) = \int d\Lambda S_{AB}(\Lambda)\rho_{AB}(\Lambda, t) \tag{14}$$

with Λ denotes the position vector of B relative to the two reaction sinks of A.

By substituting Eqs. (10)-(12) into Eq. (9), an evolution equation for the pair correlation function $\rho_{AB}(\mathbf{r}, t)$ can be obtained as

$$\frac{\partial}{\partial t}\rho_{AB}(\Lambda, t) = L_{AB}(\Lambda)\rho_{AB}(\Lambda, t) - S_{AB}(\Lambda)\rho_{AB}(\Lambda, t), \tag{15}$$

We now assume that the reactants are initially in the equilibrium configuration [*i.e.*, $\rho_{AB}(\Lambda, 0) = g_{AB}(\Lambda)$]. Then, Laplace transformation of Eq. (15) yields the following perturbative solution:

$$\hat{\rho}_{AB}(\Lambda, s) = s^{-1}g_{AB}(\Lambda) - s^{-1}\int d\Lambda_0 [\hat{G}_{AB}(\Lambda, s|\Lambda_0)$$

$$\times\ S_{AB}(\Lambda_0)g_{AB}(\Lambda_0)] + s^{-1}\int d\Lambda_1 [\hat{G}_{AB}(\Lambda, s|\Lambda_1)S_{AB}(\Lambda_1)$$

$$\times\ \int d\Lambda_0 \hat{G}_{AB}(\Lambda_1, s|\Lambda_0)S_{AB}(\Lambda_0)g_{AB}(\Lambda_0)]$$

$$-\cdots \tag{16}$$

Introducing the propagator $G_{AB}(\Lambda, t|\Lambda_0)$ *in the absence of reaction*,

$$G_{AB}(\Lambda, t|\Lambda_0) = e^{tL_{AB}(A)}\delta(\Lambda - \Lambda_0). \tag{17}$$

and by employing the Wilemski-Fixman closure approximation, Eq. (16) can be solved to give a Laplace transform expression for $\rho_{AB}(\Lambda, t)$. Then putting the result into Eq. (14), we obtain the Laplace transform expression for $k(t)$ as

$$\hat{k}(s) = \frac{k_0}{s[1 + (\hat{D}(s)/k_0)]} \tag{18}$$

k_0 is the *equilibrium* rate constant that would be observed if the diffusion of the B molecules onto A occurs infinitely fast:

$$k_0 = \int d\Lambda S_{AB}(\Lambda)g_{AB}(\Lambda). \tag{19}$$

The key dynamic function $D(t)$, called the sink-sink correlation function, is defined by

$$D(t) = \int d\Lambda S_{AB}(\Lambda)\int d\Lambda_0 G_{AB}(\Lambda, t|\Lambda_0)S_{AB}(\Lambda_0)g_{AB}(\Lambda_0). \tag{20}$$

Let us now assume that the reaction sinks of the reactant A are identical and non-overlapping. With $H(r)$ denoting the Heaviside step function, the reaction sink function is assumed to be given by

$$S_{AB}(\Lambda) = k_R[S_1(\mathbf{r}_B - \mathbf{r}_1) + S_2(\mathbf{r}_B - \mathbf{r}_2)]$$

$$S_1(\mathbf{r}_B - \mathbf{r}_1) = H(|\mathbf{r}_B - \mathbf{r}_1| - \sigma)(\sigma + \Delta r - |\mathbf{r}_B - \mathbf{r}_1|) \tag{21}$$

$$S_2(\mathbf{r}_B - \mathbf{r}_2) = H(|\mathbf{r}_B - \mathbf{r}_2| - \sigma)(\sigma + \Delta r - |\mathbf{r}_B - \mathbf{r}_2|).$$

That is, the reaction sinks are spherical shells of thickness Δr that are centered at $\mathbf{r}_1$ and $\mathbf{r}_2$. To obtain an analytic solution, we also assume that there is no interaction potential between the reactants except the excluded volume interactions. Hence

$$g_{AB}(\Lambda)\begin{cases} = 0 \ \text{if}\ |\mathbf{r}_B - \mathbf{r}_1| < \sigma\ \text{or}\ |\mathbf{r}_B - \mathbf{r}_2| < \sigma \\ = 1 \ \text{otherwise} \end{cases} \tag{22}$$

With Eqs. (21) and (22), we have

$$k_0 = k_R V_{rx};\ V_{rx} = 2(4\pi\sigma^2\Delta r), \tag{23}$$

$$D(r)/k_0 = (k_R/2)\sum_{i=1}^{2}\sum_{j=1}^{2}P_{ij}(t), \tag{24}$$

$$P_{ij}(t) = \int d\mathbf{r}_B S_i(|\mathbf{r}_B - \mathbf{r}_i|)\langle G(\mathbf{r}_B, t|\mathbf{r}_{B0})\rangle_j. \tag{25}$$

$$\langle G(\mathbf{r}_B, t|\mathbf{r}_{B0})\rangle_j = \frac{\int d\mathbf{r}_{B0} G(\mathbf{r}_B, t|\mathbf{r}_{B0})S_j(|\mathbf{r}_{B0} - \mathbf{r}_j|)g_{AB}(\mathbf{r}_{B0})}{\int d\mathbf{r}_{B0}S_j(|\mathbf{r}_{B0} - \mathbf{r}_j|)g_{AB}(\mathbf{r}_{B0})}. \tag{26}$$

Note that the quantity $\langle G(\mathbf{r}_B, t|\mathbf{r}_{B0})\rangle_j$ in Eq. (26) represents the probability that the B particle is found at $\mathbf{r}_B$ at time t, given that it was somewhere within the reaction sink around $\mathbf{r}_j$ at $t = 0$. Therefore, $P_{ii}(t)$ is the returning probability that the B particle, starting from the reaction zone around $\mathbf{r}_i$ at $t = 0$, will be found again within the same reaction zone at time t. On the other hand, $P_{ij}(t)$ is the transition probability that the B particle, starting from the reaction zone around $\mathbf{r}_j$ at $t = 0$, will move to the reaction zone around $\mathbf{r}_i$ at time t.

Approximate expression for $P_{ij}(t)$. In calculating $\langle G(\mathbf{r}_B, t|\mathbf{r}_{B0})\rangle_j$, we now neglect the presence of the ith sink, its excluded volume as well as the boundary condition imposed on it. This approximation is expected to be valid only when the distance between the sinks is large. Denoting the radial distance of the B particle from the center of the jth sink by r, we then have

$$\langle \hat{G}(\mathbf{r}_B, s|\mathbf{r}_{B0})\rangle_j \cong \frac{1}{4\pi D(1 + \sigma\alpha)}\cdot\frac{e^{-\alpha(r-\sigma)}}{r}, \tag{27}$$

where $\alpha = (S/D)^{1/2}$.

With this approximation, we have

$$\hat{P}_{jj}(s) \cong \int dr\, 4\pi r^2 S_j(r)\, \langle \hat{G}(r,s|r_0) \rangle_j$$
$$\cong (4\pi\sigma^2\Delta r)/[4\pi\sigma D(1+\sigma\alpha)] . \tag{28}$$

$$\hat{P}_{ij}(s) \cong \int d\mathbf{r}_B S_i(|\mathbf{r}_B - \mathbf{r}_i|)\langle \hat{G}(|\mathbf{r}_B - \mathbf{r}_j|,s|\mathbf{r}_0)\rangle_j$$

$$\cong (4\pi\sigma^2\Delta r)\frac{e^{-\alpha(d-\sigma)}}{4\pi Dd(1+\sigma\alpha)} \cdot \frac{\sinh(\sigma\alpha)}{\sigma\alpha} \tag{29}$$

Time-dependent rate coefficient for absorption into double sinks. With the approximations given by Eqs. (28) and (29), we finally obtain

$$\hat{k}(s) = \frac{k_0}{s\{1+k_R[\hat{P}_{11}(s)+\hat{P}_{12}(s)]\}} , \tag{30}$$

where $k_0 = (8\pi\sigma^2\Delta r)k_R$. When the distance between the two sinks becomes large, $\hat{P}_{12}(s) \to 0$ and we have

$$\hat{k}(s) = 2\frac{(4\pi\sigma^2\Delta r)k_R}{s[1+k_R\hat{P}_{11}(s)]} . \tag{31}$$

This tells that the two reaction sinks work independently, as it should. On the other hand, it is well known that the Wilemski-Fixman approximation gives the exact result for a single delta-function sink case. Hence, when $\Delta r \to 0$, the Wilemski-Fixman approximation produces the exact results in the two opposite limits ($d \to 0$ and $d \to \infty$).

In the diffusion-controlled case, that is, when the inherent reaction rate is infinitely fast with $k_R \to \infty$, we have

$$\hat{k}(s) = \frac{8\pi\sigma D(1+\sigma\alpha)}{s\left[1+\dfrac{\sigma}{d}e^{-\alpha(d-\sigma)}\dfrac{\sinh(\sigma\alpha)}{\sigma\alpha}\right]} . \tag{32}$$

In the steady-state approached as $t \to \infty$, Eq. (32) further reduces to

$$k_{ss} = k(t \to \infty) = 2(4\pi\sigma D)[1+(\sigma/d)]^{-1} . \tag{33}$$

Equation (33) was first obtained by Deutch *et al.*[16] In Figure 4, we have also displayed the steady-state rate constants calculated from Eq. (33). We see that the approximation given by Eq. (33) is very close to the exact result for $d > 2\sigma$. Even in the worst case, in which the two

sinks are at contact ($d = 2\sigma$), the error is less than 4%. However, this agreement appears to result from cancellation of errors, that is, due to the use of Wilemski-Fixman closure approximation and the approximation made for $P_{ij}(t)$.

Conclusion

We have examined the utility of Wilemski-Fixman closure approximation in calculating the rates of diffusion-controlled reactions involving a reactant with multiple reaction sites. For a simple model problem involving two spherical sinks, we have found that the error in the estimates of steady-state rate constants due to the closure approximation is about 10% in the worst case. Therefore, for the two-sink problem, we have derived an approximate analytic expression for the time-dependent rate coefficient based on the closure approximation. We have obtained a quite accurate rate expression. The errors are most severe for the steady-state rate constants, but even in this case the largest error is less than 4% owing to the cancellation of errors.

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