

# Recombination and scavenging of a randomly walking excess electron in solution

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## Abstract

We consider a geminate reaction between A and B reactants affected by the bulk reaction between B and scavengers C. The exact solution of the problem obtained for randomly walking B reactant (excess electron) and diffusing scavengers C is compared with the superposition approximation commonly used to interpret experimental data. The difference is shown to be great enough to lead to qualitatively incorrect description of the experiment even at small concentration of scavengers. In particular, it is shown that the superposition approximation can decrease essentially the rate and the ultimate probability of geminate recombination in the presence of scavengers.

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## 1. Introduction

The problem of recombination kinetics and product yield investigation in the reaction



of isolated geminate (spatially correlated) pairs [1–4] produced from a ‘parent’ molecule in the presence of the competing bulk reaction, e.g.,



with acceptor C is known in the literature as a ‘scavenger problem’ [5–10].

A conventional approach to the problem is based on the phenomenological theory that relies on the incorporation of a constant decay rate of a bulk reaction with acceptors (a scavengers term) into the equation for the survival probability of an isolated pair of radicals [5–9] or on a more consistent many-particle theory which uses a superposition decoupling of three-particle correlation in the reduced distribution function [10]. However, it has been shown that

the use of the superposition decoupling in the derivation of kinetic equations for a wide class of reactions is incorrect, it was criticized in a number of works [11–13].

At the same time, recently the exactly solvable many-particle model for the ‘scavenger problem’ was suggested to take into account the mobility of all reactants [14]. This model allows us to obtain exact kinetic equations for a general type of mobility of A and C reactants and the Coulomb interaction in a geminate pair [15]. The most essential assumption of the model is that B particle of geminate pair reacting with scavengers C moves by infinitely large jumps (the hopping mechanism [16–18]). The hopping mechanism has been used more than once for describing the scavenging of an excess electron moving by random walks in solutions [19,20]. In Letter [21] the scavenger problem was reconsidered in terms of the exactly solvable many-particle model [14]. However, in that Letter we have deliberately simplified the microscopic model, considering C reactant moving by infinitely large jumps too, so as to concentrate attention on the main demerit of approximate theories. This demerit is of general physical nature and consist in neglecting space time correlations in the evolution of geminate pair (A + B) and free pairs (B + C). We have found that taking account of this correlation can change considerably the rate of

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geminate product accumulation kinetics even at low concentration of scavengers. The goal of this Letter is to consider a more realistic situation of diffusion motion of acceptors in liquid solutions and to compare the results obtained commonly used approximate theory and exactly solvable model of the ‘scavenger problem’.

## 2. Superposition approximation and exactly solvable model

Commonly  $\mathcal{P}_B(t)$  (survival probability of B reactant) and  $\mathcal{P}_P(t)$  (accumulation kinetics of geminate reaction products) are experimentally measured quantities. In addition, recently, a new method for the determination of the bulk reaction rate constant has been proposed which is based on direct experimental measurements of the formation rate of geminate recombination products in the presence of bulk scavengers  $\dot{\mathcal{P}}_P(t)$  [22].

The superposition approximation [10] refines the phenomenological theory in view of the non-stationary stage of the bulk kinetics. As a result, the accumulation kinetics of geminate reaction products is obtained by integrating the product of the bulk reaction kinetics  $N(t)$  and a pure geminate reaction rate  $K_g(t)$ :

$$\mathcal{P}_P(t) \simeq \mathcal{P}_P^{\text{sp}}(t) \equiv \int_0^t d\tau K_g(\tau)N(\tau), \quad (3)$$

while survival probability of B reactant is expressed as the product of bulk and geminate kinetics:

$$\mathcal{P}_B(t) \simeq \mathcal{P}_B^{\text{sp}}(t) \equiv N(t)\Omega(t), \quad (4)$$

Note that the superposition approximation actually substantiates the validity of papers [23,24] wherein formulae (3) and (4) were introduced intuitively.

The survival probability of geminate pairs in the absence of a competing bulk reaction is defined by the expression:

$$\Omega(t) = 1 - \int_0^t d\tau K_g(\tau) \quad (5)$$

In the general case the bulk reaction kinetics may be expressed as [3,4]:

$$N(t) = \exp \left\{ -[C] \int_0^t d\tau K(\tau) \right\}, \quad (6)$$

where  $K(t)$  is a time dependent rate constant of the decay on acceptors. The stationary rate constant  $k$  is determined from  $K(t)$  in the following way:

$$k = \lim_{t \rightarrow \infty} K(t) \quad (7)$$

Thus in the superposition approximation the experimentally measured quantities are readily expressed in a simple way in terms of pure geminate and bulk reactions kinetics. This indicates that, in fact, the superposition approximation considers these reactions as proceeding independently.

The results of the exactly solvable model of the ‘scavenger problem’ formulated by the authors in Ref. [14] can be used for exact description of many-particle problem. Assuming the hopping motion of B reactant with the mean

residence time  $\tau_B$  between the jumps, this model gives the recipe for calculating the quantities measured:

$$\mathcal{P}_P(t) = \int_0^t d\tau K_g(\tau)\tilde{N}(\tau), \quad (8)$$

$$\mathcal{P}_B(t) = \tilde{\Omega}(t)\tilde{N}(t)e^{-t/\tau_B} + \frac{1}{\tau_B} \int_0^t d\tau \tilde{N}(t-\tau)e^{-(t-\tau)/\tau_B}\mathcal{P}_B(\tau), \quad (9)$$

where  $\tilde{\Omega}(t)$  is the survival probability of a geminate pair in the case of immobile B particle, and  $\tilde{N}(t)$  is the exact many-particle survival probability of immobile B reactant surrounded by bulk acceptors (‘target problem’ [25,26]). The bulk kinetics  $N(t)$  (6) goes to it with  $\tau_B \rightarrow \infty$ .

In this limit of immobile B particle recipes (8) and (9) are reduced to

$$\mathcal{P}_P(t) = \int_0^t d\tau \tilde{K}_g(\tau)\tilde{N}(\tau), \quad \mathcal{P}_B(t) = \tilde{N}(t)\tilde{\Omega}(t), \quad (10)$$

$$\tau_B \rightarrow \infty$$

Comparison of (10) with (3) and (4) shows that at  $\tau_B = \infty$  the superposition approximation coincides with the exact solution of the problem. Thus, for immobile B there are no time correlations between geminate and bulk reactions in the given model at any concentration of acceptors.

## 3. Microscopic model of the ‘scavenger problem’

In further investigations we use the simplest microscopic model of the reacting system. Let us take that uncharged A reactant moves by continual diffusion with the diffusion coefficient  $D_A$ , while the motion of B reactant is described by the model of infinite jumps with the mean frequency  $\tau_B^{-1}$  (the so-called two-scale migration [27]).

We shall describe a geminate reaction by the model of isotropic ‘black’ sphere of the radius  $R_{AB}$  [28]. The ‘black’ sphere model excludes re-contacts of reactants and, consequently, related time correlations in the system. Starting with the initial distance  $r_0$ , we easily obtain that at  $r_0 > R_{AB}$  the geminate reaction rate in the absence of bulk acceptors is of the form:

$$K_g(t, r_0) = \tilde{K}_g(t, r_0)e^{-t/\tau_B};$$

$$\tilde{K}_g(t, r_0) = \frac{R_{AB}}{r_0} \sqrt{\frac{\tilde{\tau}_g}{4\pi t^3}} \exp\left(-\frac{\tilde{\tau}_g}{4t}\right) \quad (11)$$

where  $\tilde{\tau}_g = (r_0 - R_{AB})^2/D_A$  is the characteristic decay time of the geminate pair, and  $\tilde{K}_g$  is the geminate reaction rate for the case of immobile B reactant. Further, quantities related to the problem with immobile B particle will be marked by a wavy line.

By analogy with  $\tilde{\tau}_g$  we introduce the characteristic decay time of the geminate pair  $\tau_g$  for two-scale migration defining it as the characteristic decay time of the function  $K_g(t, r_0)$ . It has been calculated in Letter [21]:

$$\tau_g = \frac{3}{2}\tau_B \left( \sqrt{9 + 4\tilde{\tau}_g/\tau_B} - 3 \right) \approx 3\sqrt{\tilde{\tau}_g\tau_B}, \quad \tau_B \ll \tilde{\tau}_g \quad (12)$$

The use of (11) in (5) with the subsequent integration gives the expression for the survival probability:

$$\Omega(t, r_0) = 1 - \frac{R_{AB}}{2r_0} \left[ e^{-\sqrt{\eta}} \operatorname{erfc} \left( \sqrt{\frac{\tilde{\tau}_g}{4t}} - \sqrt{\frac{t}{\tau_B}} \right) + e^{\sqrt{\eta}} \operatorname{erfc} \left( \sqrt{\frac{\tilde{\tau}_g}{4t}} + \sqrt{\frac{t}{\tau_B}} \right) \right] \quad (13)$$

where the parameter  $\eta = \tilde{\tau}_g/\tau_B$  is introduced to define the ratio between  $\tilde{\tau}_g$  and B reactant residence time in the pair. Since the geminate reaction is arrested immediately after the first jump of B reactant, the depth of the reaction course depends noticeably on the parameter  $\eta$ :

$$\Omega(\infty, r_0) \equiv \Omega_\infty(r_0) = 1 - \frac{R_{AB}}{r_0} \exp(-\sqrt{\eta}), \quad (14)$$

Only in the limit  $\eta \rightarrow 0$  it is equal to the diffusion escape probability. In this limiting case of immobile B ( $\tau_B \rightarrow \infty$ ) expression (13) is easily seen to turn into the well-known diffusion result [3]:

$$\lim_{\tau_B \rightarrow \infty} \Omega(t, r_0) \equiv \tilde{\Omega}(t, r_0) = 1 - \frac{R_{AB}}{r_0} \operatorname{erfc} \left( \sqrt{\frac{\tilde{\tau}_g}{4t}} \right) \quad (15)$$

When calculating the bulk reaction kinetics, we assume that C reactants move by continual diffusion with the diffusion coefficient  $D_C$ , while B reactant (excess electron) moves by infinite jumps with the mean time  $\tau_B$  between them. During this interval between jumps the bulk reaction develops due to acceptors diffusion to the immobile electron (kinetics  $\tilde{N}(t)$ ), while a regular very large electron jump changes the acceptors surroundings in uncorrelated way and the process is repeated anew forming after all a two-scale bulk kinetics  $N(t)$ .

The model of a ‘black’ ball of radius  $R_{BC}$  (a ‘black’ sphere with penetration) where the reaction proceeds instantaneously is used for further calculations. (We neglect the intrinsic volume of reactants referring to long-range reactions). In this case the initial non-stationary stage of the kinetics turns into a point (‘instantaneous quenching’ [29]), and  $\tilde{N}(t)$  proceeds as a well-known Smoluchowski kinetics [28]:

$$\tilde{N}(t) = \exp \left[ -[C] \left( V + \tilde{k}t + 2\sqrt{\frac{3}{\pi}} V \tilde{k}t \right) \right], \quad (16)$$

$$\tilde{k} = 4\pi R_{BC} D_C,$$

where  $V = \frac{4\pi}{3} R_{BC}^3$  is the reaction zone volume. The dimensionless parameter  $\xi = [C]V$  (the density parameter) can be introduced which is equal to the average number of acceptors in the reaction zone of the volume  $V$ .

Kinetics (16) consists of three co-factors. The first co-factor,  $e^{-\xi}$ , defines the depth of the initial non-stationary stage, and is the probability that no acceptors can be found in the reaction volume at the initial instant of time. The second co-factor describes the exponential decay with a diffusion rate constant  $\tilde{k}$  and the last is the diffusion non-

stationary correction. In this Letter we will use the binary approximation of the bulk kinetics [30], which allows us to expand the non-stationary part of kinetics over acceptor concentration  $[C]$  with the accuracy of linear term:

$$\tilde{N}(t) \approx e^{-[C]\tilde{k}t} \left[ 1 - \xi - 2\sqrt{\frac{3}{\pi}} \xi [C] \tilde{k}t \right] \quad (17)$$

The validity condition of formula (17) defines the binary time interval  $[C]\tilde{k}t \ll \xi^{-1}$  where time dependent observable values will be considered.

The exact many-particle bulk kinetics is described by integral equation (9) for  $\tilde{\Omega}(t) \equiv 1$ . A regular method of binary approximation obtaining for the solution of this equation is described in [15]. Using the result of this work we get

$$N(t) \approx e^{-[C]kt} \left[ 1 - \xi - 2f(t/\tau_B) \sqrt{\frac{3}{\pi}} \xi [C] \tilde{k}t \right] \quad (18)$$

In contrast to the case of diffusion mobilities of both reactants, the stationary rate constant of the bulk two-scale reaction is

$$k = \tilde{k} + \frac{V}{\tau_B} + \sqrt{3\tilde{k} \frac{V}{\tau_B}}, \quad (19)$$

and  $f(\tau)$  is a function decreasing from unity to zero:

$$f(\tau) = \frac{1}{2} \left[ e^{-\tau} + \left( \sqrt{\frac{\pi}{4\tau}} + \sqrt{\pi\tau} \right) \operatorname{erf}(\sqrt{\tau}) - \sqrt{\pi\tau} \right] \quad (20)$$

At  $t \gg \tau_B$  it goes to asymptotic  $f(\tau) \approx \sqrt{(\pi/\tau)}/4$ , and the non-stationary part of bulk kinetics becomes time independent.

The stationary rate constant (19) is equal to the sum of diffusion rate constant  $\tilde{k}$  (16), the hopping rate constant  $V/\tau_B$  [16–18] and the interference term which results from the intricate character of the reactants approach. The existence of this term is the distinguishing feature of stationary rate constant (19) of the two-scale bulk reaction. It has been obtained already in [27]. The second feature as follows from our result (18) is a decrease of the non-stationary part of kinetics in compare with (17) due to a fast decreasing function  $f(t/\tau_B)$ .

#### 4. Comparison of results

We begin the examination of the time correlation influence with the kinetics of geminate reaction product accumulation analysis. Comparison between (3) and (8) shows that in the general case of mobile B the exact rate of geminate reaction products formation  $\dot{\mathcal{P}}_p(t) = K_g(t)\tilde{N}(t)$  cannot be expressed only in terms of the kinetics of geminate and bulk reactions. It is the product of geminate reaction rate  $K_g(t)$  and the above mentioned probability  $\tilde{N}(t)$  formed solely during the residence time of B particle in a geminate pair before it jumps into the bulk. Thus here the use of pure bulk reaction kinetics  $N(t)$  is physically unjustified.

To analyze errors brought about by the superposition approximation at arbitrary mobility of B reactants, we use our calculations for the microscopic model chosen. Comparison with binary formulae (17) and (18) shows that the bulk reaction kinetics  $N(t)$  differs from  $\tilde{N}(t)$  by the exponential multiplier over the difference between  $k$  and  $\tilde{k}$ , while the second power factor appears due to non-stationary parts of kinetics (17) and (18):

$$\frac{N(t)}{\tilde{N}(t)} = \exp \left[ -(\xi + \sqrt{3\xi\beta})\tau \right] \left[ \frac{1 - \xi - f(\tau)\tilde{n}(\tau)}{1 - \xi - \tilde{n}(\tau)} \right] \quad (21)$$

Here  $\beta = [C]\tilde{k}\tau_B$  and  $\tau = t/\tau_B$  are the rate of the diffusion reaction with immobile B reactant and time in  $\tau_B$  units, respectively. We introduce the notation for diffusion non-stationary part of kinetics (16) and (17):  $\tilde{n}(\tau) = 2\sqrt{3\xi\beta\tau}/\pi$ . Accordingly, the accumulation rate  $\dot{\mathcal{P}}_P^{\text{sp}}(t)$  of geminate reaction products predicted by superposition approximation (3) differs from the exact result in the same way. So the superposition approximation can essentially reduce the accumulation rate of geminate reaction products.

The behaviour of relative deviation  $\Delta_{\text{Pdot}} = 1 - \dot{\mathcal{P}}_P^{\text{sp}}/\dot{\mathcal{P}}_P = 1 - N(t)/\tilde{N}(t)$  of geminate reaction rate  $\dot{\mathcal{P}}_P(t, r_0)$  as compared to the results of the superposition approximation  $\dot{\mathcal{P}}_P^{\text{sp}}(t, r_0)$  is shown in Fig. 1. It is easy to see that the deviation is very large even at the very beginning of the binary time interval equal  $\tau \ll (\xi\beta)^{-1} \approx 300$ . The second power factor of (21) slightly decreases the deviation as compared to the Markovian exponential part of kinetics designated in Fig. 1 by line 1. Nevertheless the deviation remains greater than that for the corresponding value for the model of hopping motion of acceptors  $\Delta_{\text{Pdot}} = 1 - \exp(-\xi\tau)$  [21] denoted here by line 3.

To find the accumulation kinetics  $\mathcal{P}_P(t)$  of geminate reaction products, use formulae (8), (11) and (18). We have

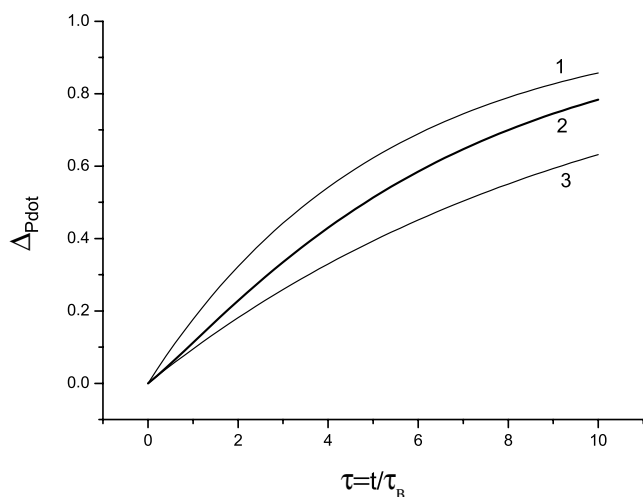


Fig. 1. The relative deviation  $\Delta_{\text{Pdot}} = 1 - \dot{\mathcal{P}}_P^{\text{sp}}/\dot{\mathcal{P}}_P$  (line 2), and for the Markovian parts of kinetics  $\Delta_{\text{Pdot}} = 1 - \dot{\mathcal{P}}_P^{\text{(m)sp}}/\dot{\mathcal{P}}_P^{\text{(m)}}$  (line 1). Line 3 is  $\Delta_{\text{Pdot}}$  for the model of the hopping motion of acceptors [21]. Parameters:  $\xi = 0.1$ ,  $D_C\tau_B/R_{\text{BC}}^2 = 0.1$ .

$$\mathcal{P}_P(t, r_0) = (1 - \xi)\mathcal{P}_P^{\text{(m)}}(t, r_0) - \mathcal{P}_P^{\text{(n)}}(t, r_0), \quad (22)$$

where  $\mathcal{P}_P^{\text{(m)}}$  is the contribution of the Markovian (exponential) term of (17) calculated in the previous Letter [21]:

$$\mathcal{P}_P^{\text{(m)}}(t, r_0) = \frac{R_{\text{AB}}}{r_0} \varphi(\eta, \beta + 1, \tau), \quad (23)$$

The function  $\varphi(\eta, x, \tau)$  is defined by the following expression:

$$\varphi(\eta, x, \tau) = \frac{1}{2} \left\{ e^{-\sqrt{\eta x}} \operatorname{erfc} \left( \sqrt{\frac{\eta}{4\tau}} - \sqrt{x\tau} \right) + e^{\sqrt{\eta x}} \operatorname{erfc} \left( \sqrt{\frac{\eta}{4\tau}} + \sqrt{x\tau} \right) \right\}, \quad (24)$$

which, in accordance with the physical meaning of the product accumulation kinetics, is a monotonically increasing function that attains its steady-state value at rather long times:

$$\varphi(\eta, x, \infty) = \exp(-\sqrt{\eta x}), \quad (25)$$

The value  $\mathcal{P}_P^{\text{(n)}}(t, r_0)$  is determined by diffusion non-Markovian part of kinetics (18) and equals:

$$\mathcal{P}_P^{\text{(n)}}(t, r_0) = \frac{R_{\text{AB}}}{r_0} \frac{\sqrt{3}}{\pi} \sqrt{\xi\eta\beta} \int_0^{(\beta+1)\tau} \frac{dx}{x} \times \exp \left( -x - \frac{\eta(\beta+1)}{4x} \right), \quad (26)$$

This integral comes to the Bessel function in the limit  $t \rightarrow \infty$ . In this limit we can rewrite (22) in the analytical form using Eq. (25):

$$\mathcal{P}_P(\infty, r_0) = \frac{R_{\text{AB}}}{r_0} \left[ (1 - \xi)e^{-\sqrt{\eta(\beta+1)}} - \frac{2\sqrt{3}}{\pi} \sqrt{\xi\eta\beta} K_0 \left( \sqrt{\eta(\beta+1)} \right) \right], \quad (27)$$

where  $K_0(x)$  is a modified Bessel function of zero order.

The expression for the accumulation kinetics of geminate reaction products in the superposition approximation is deduced by substituting (11) and (18) into Eq. (3) and integrating

$$\dot{\mathcal{P}}_P^{\text{sp}}(t, r_0) = (1 - \xi)\dot{\mathcal{P}}_P^{\text{(m)sp}}(t, r_0) - \dot{\mathcal{P}}_P^{\text{(n)sp}}(t, r_0), \quad (28)$$

where the Markovian part of the kinetics equals:

$$\dot{\mathcal{P}}_P^{\text{(m)sp}}(t, r_0) = \frac{R_{\text{AB}}}{r_0} \varphi(\eta, \gamma + 1, \tau) \quad (29)$$

The introduced parameter  $\gamma = [C]k\tau_B$  is the bulk reaction rate in  $\tau_B$  units. Using (19), it can be rewritten as  $\gamma = \beta + \xi + \sqrt{3\xi\beta}$ .

The non-Markovian part of the kinetics is defined by the integral:

$$\dot{\mathcal{P}}_P^{\text{(n)sp}}(t, r_0) = \frac{R_{\text{AB}}}{r_0} \frac{\sqrt{3}}{\pi} \sqrt{\xi\eta\beta} \int_0^{(\gamma+1)\tau} \frac{dx}{x} \times \exp \left( -x - \frac{\eta(\gamma+1)}{4x} \right) f \left( \frac{x}{\gamma+1} \right), \quad (30)$$

In contrast to (26), this integral is not taken analytically even in a stationary limit  $\tau \rightarrow \infty$ .

The behaviour of the relative deviation  $\Delta_P = 1 - \mathcal{P}_P^{\text{sp}}/\mathcal{P}_P$  of accumulation kinetics (22) as compared to the results of the superposition approximation (28) is presented in Fig. 2. As follows from the figure  $\Delta_P$  (line 2) and its Markovian version  $\Delta_P^{(m)} = 1 - \mathcal{P}_P^{(m)\text{sp}}/\mathcal{P}_P^{(m)}$  (line 1) grow up with  $\tau$  and tend rapidly to stationary values. The non-Markovian part of the kinetics decreases the relative deviation, however, as in Fig. 1, it remains larger than that for the model of the hopping motion of scavengers (line 3).

The ratio between (28) and (22) at large  $\tau$  and small  $\xi$  is recast as

$$\frac{\mathcal{P}_P^{\text{sp}}(\infty, r_0)}{\mathcal{P}_P(\infty, r_0)} = \exp \left[ -\frac{\xi}{2} \sqrt{\frac{\eta}{\beta+1}} \left( 1 + \sqrt{\frac{3\beta}{\xi}} \right) \right] \Theta, \quad \xi \ll 1 \quad (31)$$

The first exponential factor in Eq. (31) is defined by the ratio between Markovian contributions (29) and (23), while  $\Theta$  specifies the relation of the non-Markovian parts of the geminate product:

$$\Theta = \frac{1 - \xi - \mathcal{P}_P^{(n)\text{sp}}(\infty, r_0)/\mathcal{P}_P^{(m)\text{sp}}(\infty, r_0)}{1 - \xi - \mathcal{P}_P^{(n)}(\infty, r_0)/\mathcal{P}_P^{(m)}(\infty, r_0)} \quad (32)$$

From (31) it follows that even at small  $\xi$  the result of the superposition approximation can decrease essentially the ultimate probability of geminate recombination in the presence of scavengers in comparison with the exact solution if  $\eta$  is large enough.

The relative deviation  $\Delta_P^s = 1 - \mathcal{P}_P^{\text{sp}}(\infty, r_0)/\mathcal{P}_P(\infty, r_0)$  as a function of the parameter  $\eta$  is shown in Fig. 3. It is easy to see that taking in account the non-Markovian part of the deviation defined by the factor  $\Theta$  in Eq. (31) decreases noticeably the values of  $\Delta_P^s$  (line 2) in comparison with the

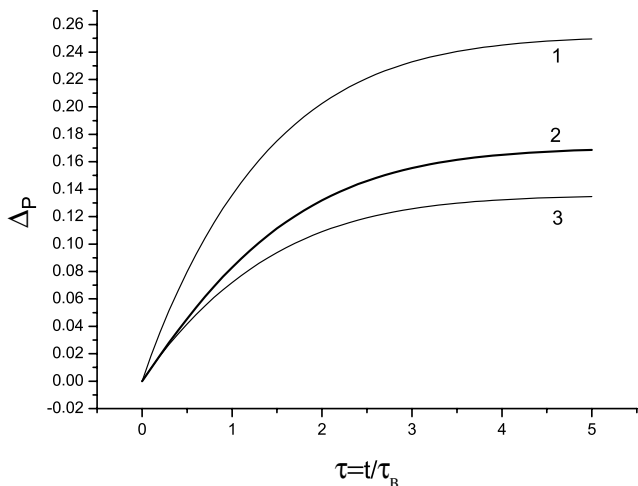


Fig. 2. The relative deviation  $\Delta_P = 1 - \mathcal{P}_P^{\text{sp}}(t, r_0)/\mathcal{P}_P(t, r_0)$  (line 2), and for the Markovian parts of kinetics  $\Delta_P^{(m)}$  (line 1). Line 3 is  $\Delta_P$  for the model of the hopping motion of scavengers [21]. Parameters:  $\xi = 0.1$ ,  $\eta = 10$ ,  $R_{AB}/r_0 = 0.95$ ,  $D_C\tau_B/R_{BC}^2 = 0.1$ .

pure Markovian part (line 1) including only the first exponential part of relation. The corresponding deviation for the hopping acceptors motion (line 3) lies everywhere below.

To calculate the survival probability of  $\mathcal{P}_B(t)$  of B reactant, we solve Eq. (9) by a conventional method of the Laplace transformation using expressions (15) and (17) for  $\tilde{\Omega}(t, r_0)$  and  $\tilde{N}(t)$ . This equation has a many-particle character. The right binary approximation in the limit of ultrafast geminate reaction has to turn into the product of the escape probability and the bulk kinetics:  $\mathcal{P}_B(t, r_0) = \Omega_\infty(r_0)N(t)$  [15]. Taking into account this requirement, we obtain the representation:

$$\mathcal{P}_B(t, r_0) = (1 - \xi)\mathcal{P}_B^{(m)}(t, r_0) - \mathcal{P}_B^{(n)}(t, r_0), \quad (33)$$

where the Markovian part of the kinetics can be represented as

$$\mathcal{P}_B^{(m)}(t, r_0) = e^{-[C]kt} \left[ 1 - \frac{R_{AB}}{r_0} \varphi(\eta, \lambda, \tau) \right] \quad (34)$$

This result coincides with the corresponding result of [21] except the parameter  $\lambda = 1 - \xi - \sqrt{3\xi\beta}$ . At large  $t$  the last expression tends to the following:

$$\begin{aligned} \mathcal{P}_B^{(m)}(t, r_0) &\simeq e^{-[C]kt} \left[ 1 - \frac{R_{AB}}{r_0} e^{-\sqrt{\lambda}\eta} \right] \\ &= e^{-[C]kt} \Omega_\infty^{\text{eff}}(r_0), \quad t \gg \tau_B \end{aligned} \quad (35)$$

It should be noted that, as shown in [21],  $\Omega_\infty^{\text{eff}}(r_0)$  cannot be interpreted as the escape probability of some effective geminate reaction which is independent of the bulk reaction. This value contains the correlation corrections that make it smaller than the escape probability of the pure geminate reaction  $\Omega_\infty(r_0)$  (13). Therefore the attempt to interpret (35) in terms of the logic of superposition approximation (4) is not justified.

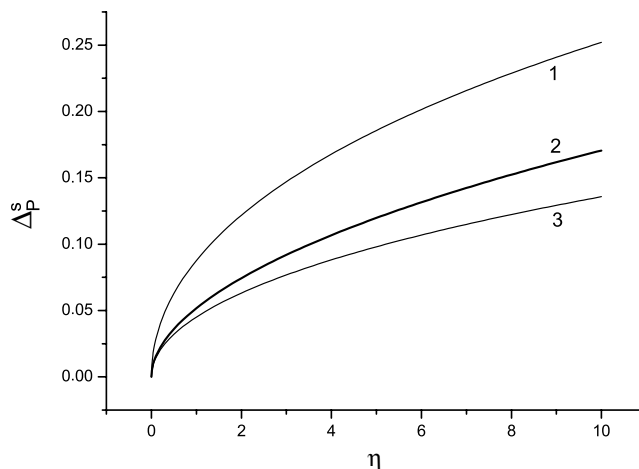


Fig. 3. The relative deviation  $\Delta_P^s = 1 - \mathcal{P}_P^{\text{sp}}(\infty, r_0)/\mathcal{P}_P(\infty, r_0)$  defined by Eqs. (31) and (32) (line 2) and their Markovian part (line 1) versus  $\eta = \tilde{\tau}_g/\tau_B$ . Line 3 is the  $\Delta_P^s$  for the model of the hopping motion of scavengers [21]. Parameters:  $\xi = 0.1$ ,  $D_C\tau_B/R_{BC}^2 = 0.1$ .



The non-Markovian part of the kinetics can be represented as

$$\mathcal{P}_B^{(n)}(t, r_0) = e^{-[C]kt} [\phi(\eta, \lambda, \tau) + A(\eta, \lambda, \tau) + B(\eta, \lambda, \tau)] \quad (36)$$

The introduced functions are:

$$\phi = \frac{R_{AB}}{2r_0} \sqrt{\frac{3\xi\beta}{\lambda}} \left[ e^{-\sqrt{\eta\lambda}} \operatorname{erfc}\left(\sqrt{\frac{\eta}{4\tau}} - \sqrt{\lambda\tau}\right) - e^{\sqrt{\eta\lambda}} \operatorname{erfc}\left(\sqrt{\frac{\eta}{4\tau}} + \sqrt{\lambda\tau}\right) \right] \quad (37)$$

$$A = \int_0^\tau d\tau' e^{-\lambda\tau'} \frac{d}{d\tau'} \left( [\tilde{\Omega}(\tau', r_0) - 1] \tilde{n}(\tau') \right) \quad (38)$$

$$B = \int_0^\tau d\tau' e^{-\lambda\tau'} \left[ \delta(\tau') - \tilde{K}_g(\tau', r_0) \right] f(\tau - \tau') \tilde{n}(\tau - \tau'), \quad (39)$$

where  $\delta(\tau)$  – is the Dirac delta-function.

The corresponding result of superposition approximation  $\mathcal{P}_B^{\text{sp}}(t, r_0)$  is described by Eqs. (4), (13) and (18). It is interesting to compare  $\mathcal{P}_B$  and  $\mathcal{P}_B^{\text{sp}}$  at large times when B reactant leaves a geminate pair for the bulk. In this case the expressions for these kinetics are simplified:

$$\frac{\mathcal{P}_B^{\text{sp}}(t, r_0)}{\mathcal{P}_B(t, r_0)} \simeq \frac{\Omega_\infty}{\Omega_\infty^{\text{eff}}} \left( 1 - \frac{R_{AB}}{r_0} \frac{(e^{-\sqrt{\lambda\eta}} - J(\lambda\eta)) \sqrt{3\xi\beta/\lambda}}{(1 - \xi - \sqrt{3\xi\beta}/2) \Omega_\infty^{\text{eff}}} \right)^{-1}, \quad (40)$$

$t \gg \tau_B$

where  $\Omega_\infty$  is the escape probability defined by Eq. (14) and  $J(x)$  is the following quadrature:

$$J(x) = \frac{2}{\sqrt{\pi}} \int_0^\infty dy \sqrt{y} \exp(-y) \operatorname{erfc}\left(\sqrt{\frac{x}{4y}}\right) \quad (41)$$

It is easy to see that in Eq. (40) the factor  $\Omega_\infty/\Omega_\infty^{\text{eff}}$  is defined by the ratio between the Markovian parts of  $\mathcal{P}_B^{\text{sp}}$  and  $\mathcal{P}_B$ , while the multiplier between the brackets is the relation of the non-Markovian parts of the kinetics.

Fig. 4 shows the dependence of the relative deviation  $\Delta_B^s = 1 - \mathcal{P}_B^{\text{sp}}(\infty, r_0)/\mathcal{P}_B(\infty, r_0)$  vs parameter  $\eta$ . It is readily observed that  $\Delta_B^s$  is always negative. Underestimating

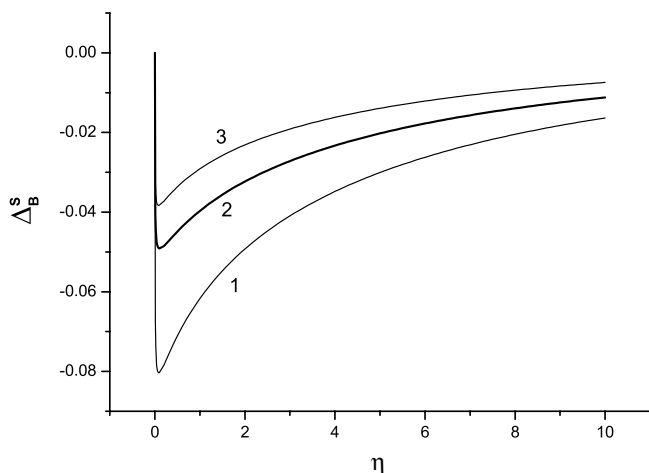


Fig. 4. The relative deviation  $\Delta_B^s = 1 - \mathcal{P}_B^{\text{sp}}(\infty, r_0)/\mathcal{P}_B(\infty, r_0)$  defined by Eqs. (33) and (40) (line 2) and their Markovian part (line 1) versus  $\eta = \tilde{\tau}_g/\tau_B$ . Line 3 is  $\Delta_B^s$  for the model of the hopping motion of acceptors [21]. Parameters:  $\xi = 0.1$ ,  $D_C \tau_B/R_{BC}^2 = 0.1$ .

the rate of geminate reaction, the superposition approximation thus overestimates the probability of reactant B to survive and escape into the bulk. The largest relative deviations are observed for small  $\eta$  when the contribution of geminate reaction to the total kinetics  $\mathcal{P}_B(t)$  is the most substantial.

## 5. Conclusion

Thus, the present Letter indicates that the role of time correlations in the course of reactions (1) and (2) can be rather significant. The influence of correlations increases with increasing mobility of particle B and results in the fact that the reaction rate in geminate channel  $\mathcal{P}_p(t)$  stops to be proportional to the bulk kinetics  $N(t)$ . According to (8) the rate is equal to the product of the geminate reaction rate  $K_g(t)$  and the kinetics  $\tilde{N}(t)$  forming during the lifetime of B reactant in a geminate pair:  $\mathcal{P}_p(t) = K_g(t)\tilde{N}(t)$ . As a result, according to (21), the reaction rate in the geminate channel differs strongly from the prediction following from the superposition approximation:  $\mathcal{P}_p^{\text{sp}}(t) = K_g(t)N(t)$ . This, in turn, leads to the fact that the superposition approximation substantially underestimates the yield of geminate reaction products in the cases where the bulk reaction courses deeply during the lifetime of geminate pair. These distinctions are more pronounced in the case of diffusion motion of acceptors rather than for the hopping model examined in [21].

Such pronounced distinctions in a theoretical description of the values observed should have a strong effect on the interpretation of experimental data. Indeed, a characteristic time of geminate reaction  $\tau_g$  can be determined by a standard method from the experimental dependence of the scavenging yield on the concentration of scavengers [3]. The superposition approximation provides a recipe for calculating  $\tau_g$  in terms of the ratio between the linear slope  $\alpha$  of the experimental curve and the rate constant  $k$  of the bulk reaction of excess electron with the scavengers ( $\tau_g^{\text{sp}} \sim \alpha/k$ ) whereas the result of the exact solution is  $k/\tilde{k}$  times greater:  $\tau_g \sim \alpha/\tilde{k}$ . As follows from (19), the value of rate constant ratio can be large enough:  $k/\tilde{k} = 1 + a + \sqrt{3a}$  where  $a = R_{BC}^2/(3D_C\tau_B)$ . Thus, in liquid hydrocarbons where the mobility of the excess electron substantially exceeds that of the acceptors, the constant  $k$  is determined mainly by electron mobility. Indeed, using both the lifetime of the excess electron in the localized state in cyclohexane  $\tau_B \sim 10^{-10}$  s [19] and the typical values  $R_{BC} = 10 \text{ \AA}$  and  $D_C = 10^{-5} \text{ cm}^2/\text{s}$  we get  $k/\tilde{k} \approx 7.5$ . Note that this value is almost twice greater than the corresponding ratio  $k/\tilde{k}$  for the hopping motion of acceptors.

For the same reason one should be rather careful in performing experiments in which an attempt is made to determine the bulk kinetics  $N(t)$  from the measured fluorescence rate in the presence of scavengers  $\mathcal{P}_p(t)$  and of the pure geminate reaction  $K_g(t)$  [22]. Indeed, according to the recipe of the superposition approximation (3)  $\mathcal{P}_p^{\text{sp}}(t)/K_g(t) = N(t)$ , whereas in reality the rate constant  $\tilde{k}$

of the determinate resulting kinetics  $\tilde{N}(t)$  can be by order of magnitude lower than that of the bulk reaction. Actually, the jump of the excess electron is finite and can be substantially smaller than the size of the geminate pair. In these cases the difference in theoretical description will be smaller too. Nevertheless the influence of correlations can be considerable, particularly, on the formation of such a sensitive value as  $\mathcal{P}_p(t)$ .

Finally, it is worth noting that our microscopic model neglects the Coulomb interaction in a geminate pair and considers the case of the photodetachment process of excess electron generation in solution. However, our results can be readily applied to the description of charged geminate pairs in water-like solutions for which the Onzager radius  $|r_c| \leq 10$ . As follows from [31,32], in this case it will suffice to perform the following substitution:

$$\tilde{\tau}_g \rightarrow \tilde{\tau}_g^c = \frac{r_c^2}{4D_A} \left[ \coth\left(\frac{r_c}{2r_0}\right) - \coth\left(\frac{r_c}{2R_{AB}}\right) \right]^2, \quad (42)$$

$$\frac{R_{AB}}{r_0} \rightarrow \frac{r_{\text{eff}}(R_{AB})}{r_{\text{eff}}(r_0)}, \quad r_{\text{eff}}(r) = \frac{|r_c|}{1 - \exp(-|r_c|/r)}, \quad (43)$$

because in highly polar solvents the survival probability of charged geminate pairs  $\tilde{Q}^c(t, r_0)$  is kinetically identical to the corresponding value  $\tilde{Q}(t, r_0)$  (15) without Coulomb interaction.

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