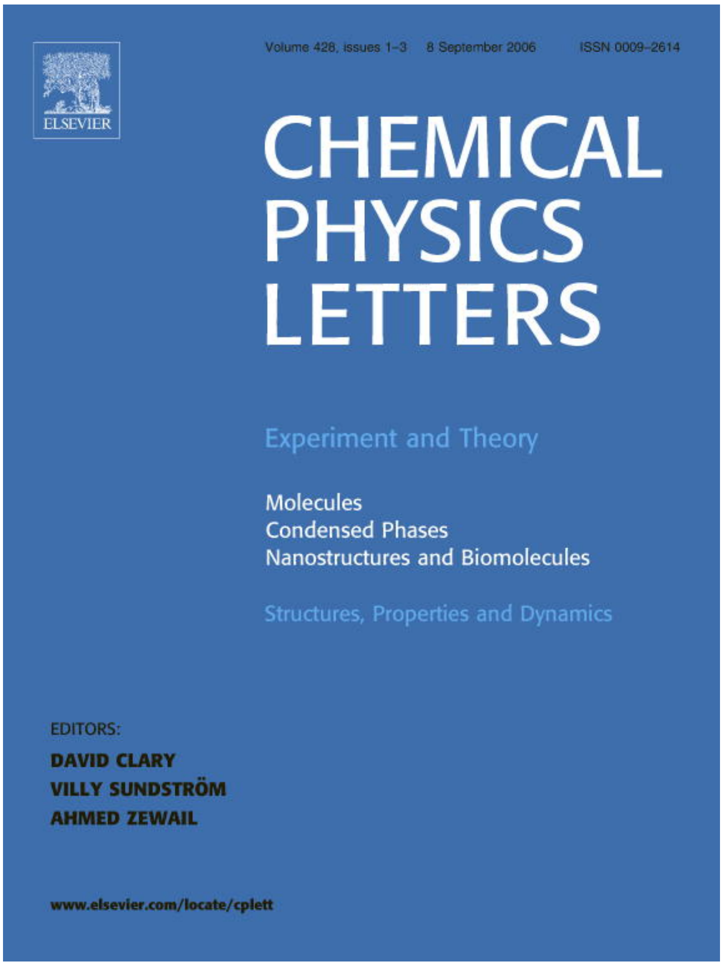
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Geminate recombination in the presence of scavengers: Breakdown of the superposition approximation

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Abstract

For a 'scavenger problem' known in the literature the exact many-particle solutions obtained by the authors for recombination of excess electron in solution are compared with the approximations commonly used to interpret experimental data. Distinctions related to an important role of time correlations are analyzed. The differences are shown to be great enough to lead to qualitatively incorrect description of the experiment. In particular, it is shown that the superposition approximation can decrease essentially the ultimate probability of geminate recombination in the presence of scavengers. This, in turn, may give rise to considerable errors in the determination of geminate pair parameters.

1. Introduction

After thermalization in a chemically inert solvent, A and B radicals produced from a 'parent' molecule form geminate (spatially correlated) pairs [1–6]. The subsequent reaction

$$A + B \rightarrow P \tag{1}$$

is divided into two stages: geminate and bulk recombinations. Geminate reaction proceeds between spatially correlated radicals formed from one and the same parent molecule. As a rule, this takes several nanoseconds [7,8]. Bulk reaction is recombination of radicals that left initial geminate pairs to find themselves in the bulk. At small concentration of such pairs this stage differs essentially from a geminate one in the time scale, and is commonly observed on the times from micro to milliseconds. Ignoring this stage enables one to treat reaction (1) as recombination of isolated geminate pairs [9–11].

Under the above conditions, the simplest bulk reaction competing with a geminate one is possible on addition of uniformly distributed C acceptors of one (say B) type of radicals to the solution. Usually C reactants are in excess (as compared to Bs), thus their concentration remains almost unchanged,

$$B + C \rightarrow C + D. \tag{2}$$

The problem of calculating the decay kinetics of A or B reactants (or the formation kinetics of P or D products of geminate (1) or bulk (2) reactions, respectively), and the dependence of P product yield on C acceptors concentration in such a two stage reaction is known in the literature as the 'scavenger problem' [12–16].

A conventional phenomenological theory relies on the incorporation of a constant decay rate on acceptors (a scavenging term) into the equation for the survival probability of an isolated geminate pair of radicals [12–16], thus it gives the results depending solely on a relative mobility of B and C reactants. Similar situation also takes place in a more consistent many-particle theory developed later on and based on the superposition decoupling of three-particle correlations in hierarchies for the partial distribution functions [17]. However, even in the binary approach the use of the superposition decoupling in a many-particle derivation of kinetic equations for some reactions proved to be

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incorrect and was criticized [18–20]. So the goal of this contribution is to study the ‘scavenger problem’ using the exactly solvable many-particle model [21] with allowance for the mobility of all reactants.

The exactly solvable many-particle model describes the processes of recombination and scavenging of excess electron moving by random walk in solution. The most essential assumption of the model is the supposition that the mean step length of randomly walking electron (B reactant) is infinitely large (the hopping motion). Just this assumption made it possible to obtain exact kinetic equations for the general case of randomly walking A and C reactants and with allowance for the Coulomb interaction in a geminate pair. However, in this Letter we deliberately simplify the microscopic model so as to concentrate attention on the main demerit of approximate theories. This demerit is of general physical nature independent of the type of acceptors motion, and determined solely by the presence of stationary rate constant of electron capture. So we ignore deliberately non-stationarity effects responsible for additional correlations in the system, and focus our attention on the simplest case where B reactant decays on acceptors at a constant rate. When applied to reactions with acceptors moving by diffusion, the exponential kinetics is often employed as a useful approximation neglecting the non-stationary part of diffusion rate constant. However, strictly speaking, the bulk reaction developing exponentially in time corresponds to the microscopic model involving the hopping motion of B and C reactants and the reacting ‘black’ spheres. Just this model will be the subject of our investigation. Since the Coulomb interaction in a geminate pair is not considered, such a model can be used to describe the photodetachment processes of excess electron generation in solution.

2. Conventional theory and superposition approximation

Commonly, $\mathscr{P}_{\mathrm{B}}(t)$ – B reactant decay kinetics and $\mathscr{P}_{\mathrm{P}}(t)$ – accumulation kinetics of geminate reaction products are the experimentally measured quantities. Besides, 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 $\dot{\mathscr{P}}_{\mathrm{P}}(t)$ [22].

A conventional theory [12–16] introduces a constant decay rate on acceptors [C]k into microscopic equations of a geminate pair, therefore, the influence of a competing bulk reaction is defined only by this parameter that is the product of the acceptor concentration [C] and stationary rate constant k of B particles decay on these acceptors. Thus, we have the recipe for the calculation of the experimentally measured quantities:

$$\mathscr{P}_{\mathrm{P}}(t) \simeq \mathscr{P}_{\mathrm{P}}^{\mathrm{ct}}(t) \equiv \int_0^t \mathrm{d}\tau K_{\mathrm{g}}(\tau)\exp(-[\mathrm{C}]k\tau) \tag{3}$$

$$\mathscr{P}_{\mathrm{B}}(t) \simeq \mathscr{P}_{\mathrm{B}}^{\mathrm{ct}}(t) \equiv \Omega(t)\exp(-[\mathrm{C}]kt) \tag{4}$$

As usual, geminate reaction rate in the absence of acceptors $K_{\mathrm{g}}(t)$ is expressed in terms of the elementary rate $w_{\mathrm{AB}}(\vec{r})$:

$$K_{\mathrm{g}}(t) = \int \mathrm{d}\vec{r}' \int \mathrm{d}\vec{r}\, w_{\mathrm{AB}}(\vec{r}) G_{\mathrm{AB}}(\vec{r},t|\vec{r}',0) P(\vec{r}') \tag{5}$$

where $P(\vec{r}')$ is the initial distribution of reactants in geminate pairs, and $G_{\mathrm{AB}}(\vec{r},t|\vec{r}',0)$ is the probability density to find A and B reactants at the relative distance $\vec{r}$ at the instant of time t if at the initial moment $t=0$ they were at the distance $\vec{r}'$ (the Green function). It obeys the equation

$$\partial_t G_{\mathrm{AB}}(\vec{r},t|\vec{r}',0) = [\widehat{\mathscr{L}}_{\mathrm{AB}} - w_{\mathrm{AB}}(\vec{r})] G_{\mathrm{AB}}(\vec{r},t|\vec{r}',0) \tag{6}$$

with the initial condition $G_{\mathrm{AB}}(\vec{r},0|\vec{r}',0) = \delta(\vec{r}-\vec{r}')$. In Eq. (6) $\widehat{\mathscr{L}}_{\mathrm{AB}}$ is the integral operator defining Markovian random walks of A and B in relative coordinates of the pair AB. The survival probability of geminate pairs in the absence of a competing bulk reaction is defined by the expression

$$\Omega(t) = 1 - \int_0^t \mathrm{d}\tau K_{\mathrm{g}}(\tau) \tag{7}$$

The superposition approximation [17] adjusts the phenomenological theory in view of the non-stationarity 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 and a pure geminate reaction rate:

$$\mathscr{P}_{\mathrm{P}}(t) \simeq \mathscr{P}_{\mathrm{P}}^{\mathrm{sp}}(t) \equiv \int_0^t \mathrm{d}\tau K_{\mathrm{g}}(\tau) N(\tau), \tag{8}$$

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

$$\mathscr{P}_{\mathrm{B}}(t) \simeq \mathscr{P}_{\mathrm{B}}^{\mathrm{sp}}(t) \equiv N(t)\Omega(t), \tag{9}$$

Note that, the superposition approximation actually substantiates the validity of papers [23,24] wherein formulae (8) and (9) were introduced intuitively.

In the general case the bulk reaction kinetics may be expressed as [10,11]

$$N(t) = \exp\left\{-[\mathrm{C}]\int_0^t \mathrm{d}\tau K(\tau)\right\} \tag{10}$$

In the absence of initial correlations between reactants the rate constant of the bulk reaction is

$$K(t) = \int \mathrm{d}\vec{r}' \int \mathrm{d}\vec{r}\, w_{\mathrm{BC}}(\vec{r}) G_{\mathrm{BC}}(\vec{r},t|\vec{r}',0) \tag{11}$$

The stationary rate constant of the decay on acceptors k appearing in formulae (3) and (4) is determined from (11)

$$k = \lim_{t\to\infty} K(t) \tag{12}$$

The Green function $G_{\mathrm{BC}}(\vec{r},t|\vec{r}',0)$ of the pair BC is defined by the equation

$$\partial_t G_{\mathrm{BC}}(\vec{r},t|\vec{r}',0) = [\widehat{\mathscr{L}}_{\mathrm{BC}} - w_{\mathrm{BC}}(\vec{r})] G_{\mathrm{BC}}(\vec{r},t|\vec{r}',0) \tag{13}$$

with the initial condition $G_{\mathrm{BC}}(\vec{r},0|\vec{r}',0) = \delta(\vec{r}-\vec{r}')$. Just as in Eq. (6), $\widehat{\mathscr{L}}_{\mathrm{BC}}$ is the integral operator describing the translational motion of reactants in relative coordinates of the reaction pair, and the bulk reaction between B and C reactants is specified by the elementary rate $w_{BC}(\vec{r})$ that depends on their relative position.

Thus in both theories the experimentally measured quantities are expressed in a simple way in terms of pure geminate and bulk reactions kinetics. This indicates that, in fact, both a conventional theory and the superposition approximation consider these reactions proceed independently.

3. Microscopic model of the 'scavenger problem'

For further investigation we choose the simplest microscopic model of the reacting system. Let us take that A reactant moves by continual diffusion, while the motion of B reactant is described by the model of infinite jumps with the mean frequency τ_B^{-1} (the so-called two-scale migration [25])

$$\widehat{\mathscr{L}}_{AB} = D_A \nabla^2_{\vec{r}} - \tau_B^{-1}\widehat{I} \tag{14}$$

Here $\widehat{I}$ is a unit operator.

We shall describe a geminate reaction by the model of isotropic 'black' sphere of the radius R_{AB} [26]. The 'black' sphere model excludes re-contacts of reactants and, consequently, related time correlations in the system. Starting with the initial distance $r_0(P(\vec{r}) = \delta(\vec{r} - \vec{r_0}))$, we easily obtain that at $r_0 > R_{AB}$ the geminate reaction rate in the absence of bulk acceptors is defined as

$$K_g(t, r_0) = \widetilde{K}_g(t, r_0)\mathrm{e}^{-t/\tau_B}; \quad \widetilde{K}_g(t, r_0) = \frac{R_{AB}}{r_0}\sqrt{\frac{\tilde{\tau}_g}{4\pi t^3}}\exp\left(-\frac{\tilde{\tau}_g}{4t}\right) \tag{15}$$

where $\tilde{\tau}_g = (r_0 - R_{AB})^2/D_A$ is the characteristic decay time of the geminate pair, and $\widetilde{K}_g$ 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 τ_g for the case of the two-scale migration defining it as the characteristic decay time of the function $K_g(t, r_0)$. Obviously, it is proportional to the maximum of this function $\tau_g = \lambda t_m$. The proportionality coefficient λ is determined from the coincidence condition of τ_g and $\tilde{\tau}_g$ at $\tau_B \to \infty$. It is easily seen that $\lambda = 6$. So for τ_g

$$\tau_g = \frac{3}{2}\tau_B\left(\sqrt{9 + 4\tilde{\tau}_g/\tau_B} - 3\right) \approx 3\sqrt{\tilde{\tau}_g\tau_B}, \quad \tau_B \ll \tilde{\tau}_g \tag{16}$$

The use of (15) in (7) with the subsequent integration gives the expression for the survival probability:

$$\Omega(t, r_0) = 1 - \frac{R_{AB}}{2r_0}\left[\mathrm{e}^{-\sqrt{\eta}}\mathrm{erfc}\left(\sqrt{\frac{\tilde{\tau}_g}{4t}} - \sqrt{\frac{t}{\tau_B}}\right) + \mathrm{e}^{\sqrt{\eta}}\mathrm{erfc}\left(\sqrt{\frac{\tilde{\tau}_g}{4t}} + \sqrt{\frac{t}{\tau_B}}\right)\right] \tag{17}$$

Here the parameter $\eta = \tilde{\tau}_g/\tau_B$ is introduced which defines 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 η

$$\Omega(\infty, r_0) \equiv \Omega_\infty(r_0) = 1 - \frac{R_{AB}}{r_0}\exp\left(-\sqrt{\eta}\right), \tag{18}$$

Only in the limit $\eta \to 0$ it is equal to the diffusion escape probability. In this limiting case of immobile B ($\tau_B \to \infty$) expression (17) is easily seen to turn into the well-known diffusion result [10]

$$\lim_{\tau_B \to \infty} \Omega(t, r_0) \equiv \widetilde{\Omega}(t, r_0) = 1 - \frac{R_{AB}}{r_0}\mathrm{erfc}\left(\sqrt{\frac{\tilde{\tau}_g}{4t}}\right) \tag{19}$$

When calculating the bulk reaction kinetics, we shall take that C reactants (just as B) move by jumps of infinite length:

$$\widehat{\mathscr{L}}_{BC} = -(\tau_B^{-1} + \tau_C^{-1})\widehat{I} \tag{20}$$

The choice of this model of motion excludes re-contacts determined by the kinematics of reactants approach thus reducing the value of time correlations in the system.

The model involving jumps of infinite length describes the so-called hopping mechanism of reactions. Physically, it is realized when a reactant reaches the reaction zone in a single jump. In this case the rate constant is equal to the product of the frequency of jumps and the reaction volume. Being an obvious alternative to the diffusion mechanism, the hopping mechanism was first proposed in papers [27,28] to describe luminescence impurity quenching experiments in solid solutions. For the liquid phase reaction it is developed in papers [29,30], and was first found experimentally in excess electron capture reactions in non-polar liquids [31].

The model of a 'black' ball of the radius R_{BC} where the reaction proceeds instantaneously is the analog of a 'black' sphere for the hopping mechanism. (Here we neglect the intrinsic volume of reactants and refer to long-range reactions.) In this case the non-stationary stage of the kinetics turns into a point ('instantaneous quenching' [32]), and the bulk reaction proceeds exponentially. Calculations with $\widehat{\mathscr{L}}_{BC}$ in form of (20) yield

$$N(t) = \exp\left[-\xi - \xi\left(\tau_B^{-1} + \tau_C^{-1}\right)t\right], \tag{21}$$

where the dimensionless parameter $\xi = [\mathrm{C}]V$ (the density parameter) appears that is equal to the average number of acceptors in the reaction zone of the volume $V = \frac{4\pi}{3}R_{BC}^3$. Kinetics (21) consists of two co-factors. The first co-factor, $\mathrm{e}^{-\xi}$, defines the depth of a 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 constant rate equal to the product of the total frequency of jumps $\tau_B^{-1} + \tau_C^{-1}$ and the average number ξ of acceptors entering the reaction zone.

Passing to experimentally measured quantities of the 'scavenger problem', note that for both approximate theories we can easily derive

$$\mathscr{P}_{\mathrm{P}}^{\mathrm{sp}}(t) = \mathrm{e}^{-\xi}\mathscr{P}_{\mathrm{P}}^{\mathrm{ct}}(t), \quad \mathscr{P}_{\mathrm{B}}^{\mathrm{sp}}(t) = \mathrm{e}^{-\xi}\mathscr{P}_{\mathrm{B}}^{\mathrm{ct}}(t), \tag{22}$$

The above relations show that in the microscopic model chosen a phenomenological theory (3) and (4) becomes kinetically identical to the result of the superposition approximation (8) and (9).

The explicit expression for the accumulation kinetics of geminate reaction product in the superposition approximation is deduced by substitution of (15), (21) in Eq. (8) and integration

$$\mathscr{P}_{\mathrm{P}}^{\mathrm{sp}}(t, r_0) = \frac{R_{\mathrm{AB}}}{r_0}\mathrm{e}^{-\xi}\varphi(\eta, \gamma + 1, \tau), \tag{23}$$

where $\gamma = \xi(\tau_{\mathrm{B}}/\tau_{\mathrm{C}} + 1)$ and $\tau = t/\tau_{\mathrm{B}}$ are the bulk reaction rate and time in τ_{B} units, respectively. Formula (23) involves the function $\varphi(\eta, x, \tau)$

$$\begin{aligned}\varphi(\eta, x, \tau) = \frac{1}{2}\Bigg\{ & \mathrm{e}^{-\sqrt{\eta x}}\mathrm{erfc}\left(\sqrt{\frac{\eta}{4\tau}} - \sqrt{x\tau}\right) \\ & + \mathrm{e}^{\sqrt{\eta x}}\mathrm{erfc}\left(\sqrt{\frac{\eta}{4\tau}} + \sqrt{x\tau}\right)\Bigg\},\end{aligned} \tag{24}$$

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

$$\varphi(\eta, x, \tau \to \infty) = \varphi_{\infty}(\eta, x) = \exp(-\sqrt{\eta x}), \tag{25}$$

this gives the expression for the ultimate probability of geminate reaction in the presence of bulk acceptors

$$\mathscr{P}_{\mathrm{P}}^{\mathrm{sp}}(t \to \infty, r_0) = \frac{R_{\mathrm{AB}}}{r_0}\mathrm{e}^{-\xi}\exp(-\sqrt{\eta(\gamma + 1)}) \tag{26}$$

Comparison between (26) and (18) shows that the presence of bulk acceptors leads to an additive increase in geminate pair decay rate. This agrees completely with the independence of geminate and bulk reactions mentioned above.

4. The exactly solvable model

The simplicity of the above microscopic description of a reacting system makes it possible to exactly solve a many-particle problem using the results of the exactly solvable model of the 'scavenger problem' formulated by the authors in Ref. [21]. Assuming the hopping motion of B reactant, this model gives the recipe for the calculation of the quantities measured:

$$\mathscr{P}_{\mathrm{P}}(t) = \int_0^t \mathrm{d}\tau K_{\mathrm{g}}(\tau)\widetilde{N}(\tau), \tag{27}$$

$$\begin{aligned}\mathscr{P}_{\mathrm{B}}(t) = {} & \widetilde{\Omega}(t)\widetilde{N}(t)\mathrm{e}^{-t/\tau_{\mathrm{B}}} \\ & + \frac{1}{\tau_{\mathrm{B}}}\int_0^t \mathrm{d}\tau \widetilde{N}(t - \tau)\mathrm{e}^{-(t-\tau)/\tau_{\mathrm{B}}}\mathscr{P}_{\mathrm{B}}(\tau),\end{aligned} \tag{28}$$

where $K_{\mathrm{g}}(t)$ is the pure geminate reaction rate defined in (5), (15), $\widetilde{\Omega}(t)$ is defined in (19), $\widetilde{N}(t)$ is the exact many-particle survival probability of immobile B reactant surrounded by bulk acceptors. The kinetics $N(t)$ (21) goes to it with $\tau_{\mathrm{B}} \to \infty$.

In this limit of immobile B particle recipes (27) and (28) are reduced to:

$$\mathscr{P}_{\mathrm{P}}(t) = \int_0^t \mathrm{d}\tau \widetilde{K}_{\mathrm{g}}(\tau)\widetilde{N}(\tau); \quad \mathscr{P}_{\mathrm{B}}(t) = \widetilde{N}(t)\widetilde{\Omega}(t) \tag{29}$$

Comparison of (29) with (8) and (9) shows that at $\tau_{\mathrm{B}} = \infty$ the superposition approximation coincides with the exact solution of the problem. Thus for immobile B time correlations between geminate and bulk reactions are absent in the given model at any concentration of acceptors.

We begin the examination of the time correlation influence with the accumulation kinetics analysis of geminate recombination products. Comparison between (27) and (8) shows that in the general case of mobile B the rate of geminate reaction products formation $\dot{\mathscr{P}}_{\mathrm{P}}(t) = K_{\mathrm{g}}(t)\widetilde{N}(t)$ cannot be expressed only in terms of the kinetics of geminate and bulk reactions. It is the product of geminate reaction rate $K_{\mathrm{g}}(t)$ and the above probability $\widetilde{N}(t)$ 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 make calculations for the microscopic model chosen. The many-particle kinetics $\widetilde{N}(t)$ is

$$\widetilde{N}(t) = \exp\left(-\xi - \xi\frac{t}{\tau_{\mathrm{C}}}\right) \tag{30}$$

Comparison with a binary formula (21) shows that the bulk reaction kinetics $N(t)$ differs from $\widetilde{N}(t)$ by the exponential multiplier:

$$N(t) = \exp\left(-\xi\frac{t}{\tau_{\mathrm{B}}}\right)\widetilde{N}(t) \tag{31}$$

Accordingly, the accumulation rate $\dot{\mathscr{P}}_{\mathrm{P}}^{\mathrm{sp}}(t)$ of geminate reaction products predicted by the superposition approximation differs from the exact result in the same way. So the superposition approximation can reduce essentially the accumulation rate of geminate reaction products.

To find the explicit form of the exact many-particle accumulation kinetics $\mathscr{P}_{\mathrm{P}}(t)$ of geminate reaction products, use formulae (27), (15) and (30). We have

$$\mathscr{P}_{\mathrm{P}}(t, r_0) = \frac{R_{\mathrm{AB}}}{r_0}\mathrm{e}^{-\xi}\varphi(\eta, v + 1, \tau), \tag{32}$$

The introduced dimensionless parameter $v = \xi\tau_{\mathrm{B}}/\tau_{\mathrm{C}}$ has the meaning of the bulk reaction rate with immobile B reactant in units of τ_{B}. It follows from its definition that the parameter γ from (23) tends to v with τ_{B} tending to ∞. The function $\varphi(\eta, x, \tau)$ is defined by formula (24). As expression (23) for $\mathscr{P}_{\mathrm{P}}^{\mathrm{sp}}$ coincides with (32) up to the substitution of v for γ, the ultimate probability of geminate reaction can be obtained from Eq. (26)

$$\mathscr{P}_{\mathrm{P}}(t\to\infty,r_0)=\frac{R_{\mathrm{AB}}}{r_0}\mathrm{e}^{-\xi}\exp(-\sqrt{\eta(\nu+1)}) \tag{33}$$

The ratio of (26) and (33) at small ξ is recast as

$$\frac{\mathscr{P}^{\mathrm{sp}}_{\mathrm{P}}(t\to\infty,r_0)}{\mathscr{P}_{\mathrm{P}}(t\to\infty,r_0)}=\exp\left(-\frac{\xi}{2}\sqrt{\frac{\eta}{\nu+1}}\right),\quad \xi\ll 1 \tag{34}$$

From this it follows that even at small ξ the result of the superposition approximation differs considerably from the exact solution if η is rather large.

The behaviour of the accumulation kinetics $\mathscr{P}_{\mathrm{P}}(t,r_0)$ and the rate $\dot{\mathscr{P}}_{\mathrm{P}}(t,r_0)$ of the geminate reaction products accumulation as compared to the results of the superposition approximation $\mathscr{P}^{\mathrm{sp}}_{\mathrm{P}}(t,r_0)$ and $\dot{\mathscr{P}}^{\mathrm{sp}}_{\mathrm{P}}(t,r_0)$ is given in Figs. 1 and 2. The superposition approximation decreases noticeably the ultimate probability of the geminate reaction in the presence of scavengers, and, according to (31), overestimates the decay of $\dot{\mathscr{P}}^{\mathrm{sp}}_{\mathrm{P}}(t,r_0)$ as compared to the exact solution denoted by lines with circles.

Before passing to the decay kinetics $\mathscr{P}_{\mathrm{B}}(t)$ of B reactant, note that no radical distinctions should be expected, at least, at low concentrations of acceptors. This is because for the rather fast motion of B, when correlations are essential, the contribution of geminate reaction into complete kinetics is insignificant. To calculate the explicit form of the exact many-particle kinetics of B reactant, we solve (28) by a conventional method of the Laplace transformation using expressions (19) and (30) for $\widetilde{\Omega}(t,r_0)$ and $\widetilde{N}(t)$. This gives

$$\mathscr{P}_{\mathrm{B}}(t,r_0)=N_{\mathrm{B}}(t)\left[1-\frac{R_{\mathrm{AB}}}{r_0}\varphi(\eta,\mathrm{e}^{-\xi},\tau)\right] \tag{35}$$

Here $N_{\mathrm{B}}(t)$ is the many-particle kinetics of the bulk reaction representable as:

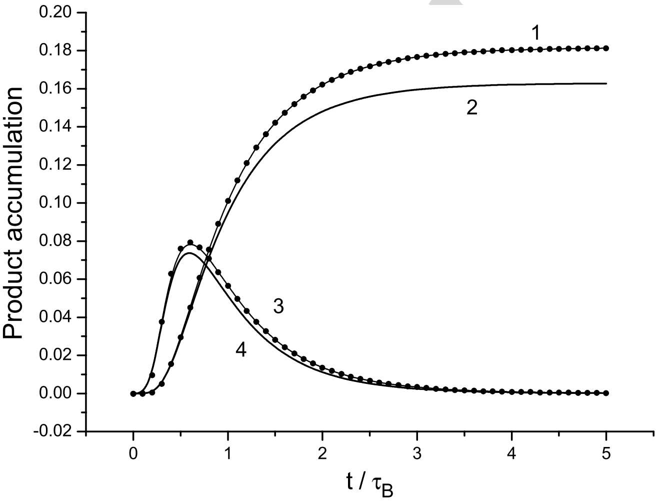

Fig. 1. The accumulation kinetics $\mathscr{P}_{\mathrm{P}}(t)$, $\mathscr{P}^{\mathrm{sp}}_{\mathrm{P}}(t)$ – (1, 2) and accumulation rate $\dot{\mathscr{P}}_{\mathrm{P}}(t)$, $\dot{\mathscr{P}}^{\mathrm{sp}}_{\mathrm{P}}(t)$ – (3, 4) of geminate reaction products in the presence of scavengers. $\xi=0.1$, $\eta=5$, $R_{\mathrm{AB}}/r_0=0.95$, $\tau_{\mathrm{B}}/\tau_{\mathrm{C}}=0.1$.

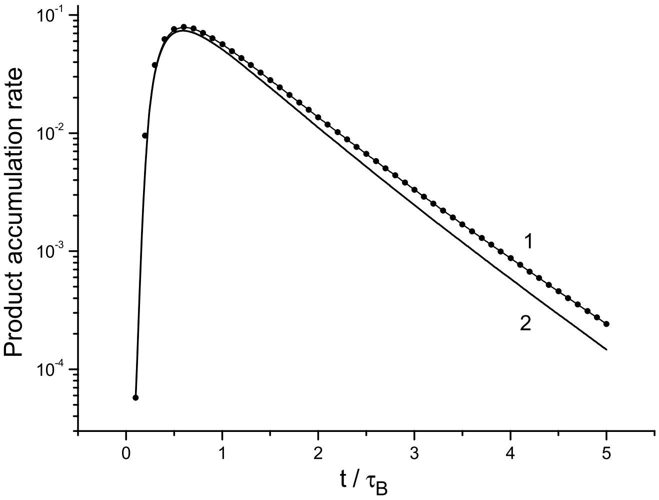

Fig. 2. The exact product accumulation rate $\dot{\mathscr{P}}_{\mathrm{P}}(t)$ – 1, and superposition approximation $\dot{\mathscr{P}}^{\mathrm{sp}}_{\mathrm{P}}(t)$ – 2. Parameters are the same as in Fig. 1.

$$\begin{aligned}N_{\mathrm{B}}(t)&=\exp\left(-\xi-\xi\frac{t}{\tau_{\mathrm{C}}}-(1-\mathrm{e}^{-\xi})\frac{t}{\tau_{\mathrm{B}}}\right)\\&\equiv\widetilde{N}(t)N_0(t)\end{aligned} \tag{36}$$

The bulk reaction kinetics is defined by two independent processes. The first process described by $\widetilde{N}(t)$ (30) is the reaction between mobile acceptors and immobile B particle, while the second one, $N_0(t)$, defines the reaction of mobile B particle with the ensemble of immobile acceptors. A regular very large jump of B reactant changes the environment of acceptors in an uncorrelated way, thus the rate of the second process is equal to the product of the frequency of jumps $1/\tau_{\mathrm{B}}$ and the many-particle probability of acceptors entering the reaction zone, $1-\mathrm{e}^{-\xi}$. At small parameters ξ expansion (36) gives the formula of a binary kinetics (21) depending on a relative mobility of B and C reactants.

It is easy to see that the structure of expression (35) coincides with the structure defined by superposition approximation recipe (8). Following the superposition approximation logic, the second co-factor may be considered to be the survival probability $\Omega^{\mathrm{eff}}(t,r_0)$ of some effective geminate pair making allowance for correlations with the bulk reaction. However, it is readily seen that the presence of acceptors results in the acceleration of the kinetics $\Omega^{\mathrm{eff}}(t,r_0)$ as compared to pure geminate kinetics $\Omega(t,r_0)$. This means that in a hypothetical effective pair geminate recombination proceeds at a higher rate. Unlike (15), in such a pair the reaction rate may be represented as $K^{\mathrm{eff}}_{\mathrm{g}}(t,r_0)=K_{\mathrm{g}}(t,r_0)/N_0(t)$.

This is paradoxical: taking account of time correlations with the competing bulk reaction accelerates the reaction in the effective geminate pair, though it seems obvious that this reaction must be retarded due to the additional decay channel in the effective acceptor surroundings. However, the paradox arises from the superposition approximation logic. The attempt to treat the exact kinet-

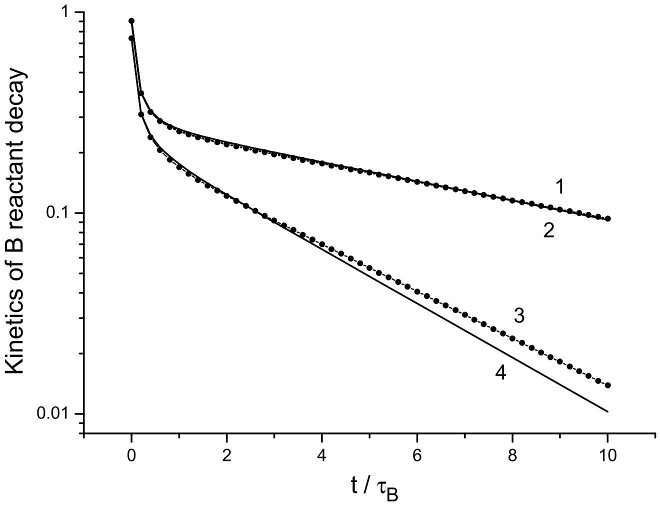

Fig. 3. The exact kinetics $\mathscr{P}_B(t)$ – (1, 3) and superposition approximation $\mathscr{P}_B^{sp}(t)$ – (2, 4) for different values of ξ: $\xi = 0.1$ – (1, 2); $\xi = 0.3$ – (3, 4). Other parameters: $\eta = 0.1$, $R_{AB}/r_0 = 0.95$, $\tau_B/\tau_C = 0.1$.

ics $\mathscr{P}_B(t, r_0)$ as the product of the bulk kinetics and some independent effective geminate kinetics is physically unjustified. The dependence of $K_g^{eff}(t, r_0)$ on the reaction kinetics $N_0(t)$ suggests that geminate and bulk reactions are correlated in time. That is why the attempt to represent them as two independent processes leads to a physical contradiction. Note that adequate description follows from the derivation of kinetic equations of the 'scavenger problem' based on the application of the concepts of a general kinetic theory to the exactly solvable many-particle problem [33].

The behaviour of the kinetics $\mathscr{P}_B(t, r_0)$ and $\mathscr{P}_B^{sp}(t, r_0)$ is given in Fig. 3 for two values of the density parameter ξ. Note that relative deviations at small values of ξ (curves 1 and 2) are not as great as for geminate reaction product accumulation. However, they are proportional to the density parameter, and thus can be measured in the framework of the binary approach. The increased distinctions beyond the limits of the binary interval (curves 3 and 4) are due to the many-particle nature of the kinetics $N_B(t)$ (36).

5. Conclusion

Evidently, considerable distinctions in the theoretical treatment of the measured quantities are to affect the experimental data interpretation. In a classical variant [10] the experiment is run as follows: the dependence of the scavenging yield $F = 1 - \mathscr{P}_P(t \to \infty)$ on the concentration [C] of bulk acceptors is measured with the subsequent determination of the geminate pair kinetics $\Omega(t)$ from the measured concentration dependence $F(\alpha[C])$. Here α is the experimentally measured constant depending on the properties of the solvent and acceptors. Commonly, the formula (3) of the conventional theory is employed assuming that the scavenging yield is the Laplace transform of geminate reaction kinetics:

$$1 - \mathscr{P}_P^{ct}(t \to \infty) = [C]k \int_0^\infty dt\,\Omega(t) e^{-[C]kt} \approx F(\alpha[C]) \qquad (37)$$

The inverse Laplace transformation of (37) with $[C]k$ as a transformation variable gives the geminate kinetics $\Omega\left(\frac{k}{\alpha}t\right)$. Its characteristic decay time is determined from the ratio $\tau_g \sim \alpha/k$, with the bulk reaction rate constant value k taken from independent experiments on a pure bulk reaction. However, it follows from the exact solution (27) that even if the 'instantaneous quenching' effect is neglected, formula (37) can still be reproduced but with an essential distinction: instead of the bulk reaction rate $[C]k = \xi(1/\tau_C + 1/\tau_B)$ the role of the Laplace variable will be played by the bulk reaction rate with immobile B reactant: $[C]\tilde{k} = \xi/\tau_C$ that can be essentially less than $[C]k$. Thus the value τ_g found by formula (37) is $k/\tilde{k}$ times less than it actually is. Since for our model, according to (16), $\tau_g \approx 3\sqrt{\tilde{\tau}_g \tau_B} = 3(r_0 - R_{AB})/\sqrt{D_A \tau_B}$, the value of the initial distance in the geminate pair decreases similarly.

Another part of experimental works is concerned with the rate constant of the bulk reaction of a geminate partner decay on acceptors. In particular, Letter [22] suggests an ingenious method of excluding a pure geminate kinetics from the geminate reaction channel based on formula (8) of the superposition decoupling: $\dot{\mathscr{P}}_P^{sp}(t) = K_g(t)N(t)$. It is seen from this formula that the bulk kinetics $N(t)$ may be obtained by dividing the experimentally measured fluorescence rate $\dot{\mathscr{P}}_P^{sp}(t)$ of geminate reaction products in the presence of acceptors by the fluorescence rate $K_g(t)$ of pure geminate reaction products. However, as follows from the exact solution (27), the kinetics $\widetilde{N}(t)$ thus obtained is not the bulk kinetics and can differ considerably from it. For example, for equally mobile B and C reactants in our model, such an experiment will give the rate constant twice less than the bulk reaction rate constant found.

In conclusion, it should be noted that a rather simple microscopic model considered in this contribution does not pretend to the detailed description of actual experimental situations involving more realistic organization of mobility, reactivity and force interaction of reactants. So it gives no detailed answers but just poses an actual problem of a consistent many-particle derivation of the 'scavenger problem' equations valid for reactants mobility of arbitrary type. This will be the subject of the subsequent publications.

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