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# Concentration dependence of fluorescence quenching by ionic reactants

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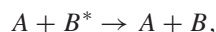
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## Abstract

Fluorescence quenching for ionic reactants when the quenchers are nondilute is studied theoretically. The fluorophore and quenchers are assumed to interact by Coulomb potential. It has been shown that for oppositely charged ions with large Onsager length the positive deviation from the linear Stern–Volmer law is negligibly small. Our results are in good agreement with available experimental data on the luminescence quenching of the ions  $W_6I_{14}^{2-}$  by bipyridinium ions.

## 1. Introduction

Fluorescence quenching in solution is a simple example of diffusion-controlled reaction of the pseudo first-order



where  $A$  is a quencher,  $B$  and  $B^*$  are the ground and an excited state of the fluorophore [1]. Hereafter we assume that both species have spherically symmetric reactivity. Since the quencher concentration  $c$  is a constant, we can consider quenchers as sinks of infinite capacity.

It is well-known that the lifetime  $\tau$  of an excited fluorophore in solution containing quenchers obeys the relation [1, 2]

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_c, \quad (1)$$

where  $\tau_0$  is the intrinsic lifetime of the fluorophore in the absence of quenchers and  $k_c$  is the rate coefficient for quenching. Thus the intrinsic lifetime of the fluorophore is shortened due to the presence of quenchers. To calculate  $k_c$  it is convenient to assume that fluorophore reactants diffuse towards immobile sinks with a relative diffusion coefficient. For instance, in the case

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of uncharged reactants and fully diffusion-controlled quenching at very low concentrations of quenchers, one can use the Smoluchowski steady-state rate coefficient [3]

$$k_S = 4\pi DR, \quad (2)$$

where  $D = D_A + D_B$ ,  $D_A$  and  $D_B$  are the diffusion coefficients of quencher and fluorophore, respectively;  $R$  is the encounter distance. Thus in this case ignoring the time-dependent effects we have the classical linear Stern–Volmer law [4, 2, 5]

$$\frac{I_0}{I(c)} = 1 + k_S c \tau_0, \quad (3)$$

where  $I_0$  and  $I(c)$  are the fluorescence intensity in the absence and in the presence of quenchers, respectively.

However, at higher quencher concentrations the problem of concentration effects naturally arises, and we cannot find the value of  $k_c$  by simply multiplying  $k_S$  by the quencher concentration  $c$ . In the case of uncharged reactants, Felderhof and Deutch [6], and independently Brailsford [7], showed that the first correction to the steady-state reaction rate in terms of the concentration has a nonanalytical behaviour

$$k(c) = k_S \left( 1 + \sqrt{3\phi} + \dots \right), \quad (4)$$

where  $\phi = 4\pi R^3 c / 3$  is the material volume fraction of the total volume occupied by sinks (quenchers). Since these pioneering works, several theories of the concentration dependence of the rate coefficient have been proposed [1, 2, 8, 9]. It has been shown that for the fluorescence quenching the concentration dependence leads to positive deviation from the Stern–Volmer law [10–13].

Theoretical studies of the concentration dependence in the case of reactants which are subjected to the influence of a dynamical potential are very few. In a series of papers [14–16] using both the mean field approach and the effective medium theory, Cukier came to the conclusion that for ionic reactions the structure of the concentration dependence remains the same as in the case of neutral reactants, equation (4), but with renormalized value of  $\phi$ , i.e.

$$k(c) = k_D \left( 1 + \sqrt{3\tilde{\phi}} + \dots \right), \quad (5)$$

where  $\tilde{\phi} = 4\pi \tilde{R}^3 c / 3$  is the so-called effective volume fraction and  $\tilde{R}$  is the effective radius defined by the Debye formula for the steady-state rate coefficient in the case of the Coulomb interaction potential [17]

$$k_D = 4\pi D \tilde{R}, \quad \text{i.e. } \tilde{R} = -\frac{\alpha^*}{1 - e^{\alpha^*}} R. \quad (6)$$

Here  $\alpha^* = \alpha / R$ ,  $\alpha = z_A z_B r_c$ , with the Onsager length  $r_c = \beta e^2 / 4\pi \epsilon \epsilon_0$ ;  $z_A e$  and  $z_B e$  are the charges of sink and fluorophore, respectively;  $e$  is the electronic charge;  $\epsilon$  and  $\epsilon_0$  are the dielectric constant of the solution and free space, respectively;  $\beta = 1 / k_B T$ , where  $k_B$  is the Boltzmann's constant and  $T$  is the absolute temperature. One can see that in the case of strong attractive Coulomb potential the magnitude of  $\tilde{R}$  becomes much larger than the reaction radius  $R$  (e.g. in cyclohexane  $\tilde{R} / R \simeq 40$ ) and, therefore, even for small material volume fraction  $\phi$  the effective volume fraction  $\tilde{\phi}$  attains large values. Thus, according to Cukier's theory, the long-range attractive potential causes the dramatic concentration effects and leads to nonlinear Stern–Volmer relation even for low sink concentrations. On the other hand, in the case of a repulsive potential the situation is opposite and we can ignore the concentration effects for the strong repulsion.

One can see that the concentration dependence is due to the diffusive interaction (competition) for diffusing reactants. That is the reason why we investigated analytically [18] and numerically [19] the relatively simple problem on diffusive interaction between two static charged sinks. It was shown there that for unlike charged particles at large enough values of the Onsager length the diffusive interaction is negligibly small. It is worth noting that a similar problem occurs if we treat the electron reactions with the positive ions when the solution of the latter is not dilute [15]. Obviously this case is a special one of  $\tau_0 \rightarrow \infty$  in the above example and so we will treat here only the case of quenching.

The main purpose of the present paper is to treat concentration effects in nondilute systems of charged reactants interacting by Coulomb potential for the model of quenching by immobile sinks. This paper is organized as follows. In section 2 we consider the mean field approach within the framework of the so-called tilde space method [20]. Section 3 contains some application of the time-dependent solution of the Debye–Smoluchowski equation to the problem at issue. In section 4 we present discussion of results obtained and compare them with known experimental data on the luminescence quenching of ions  $\text{W}_6\text{I}_{14}^{2-}$  by bipyridinium ions. The main conclusions of the paper are given in the last section 5.

## 2. Mean field approach

### 2.1. Statement of the problem

It is well-known that the deviation of the fluorophore local concentration  $n_{\text{B}}(\mathbf{r})$  from its bulk value is the largest for totally diffusion-controlled reactions [1, 14, 16]. Thus to assess the maximum effects of concentration on the linear Stern–Volmer law we restrict our calculation to the fully diffusion-controlled limit, i.e. we will use the Smoluchowski boundary condition. It is worth noting here that the result for the Smoluchowski boundary condition may be immediately generalized to the case of the Collins–Kimball one [21, 22], if we take into account the connection between the relevant solutions for the time-dependent boundary-value problems (see section 3).

The mean field approach (MFA) [1, 14, 16, 23] is a well-known and simple method to calculate the first correction to the concentration dependence of the rate coefficient. We assume that the characteristic relaxation time is small, and consider the steady-state problem (see section 4). It is worth noting that the reaction-induced fluctuations in the reactant densities make the reaction rate time-dependent at all reaction times, although it is not known how big this effect is under given conditions (initial defect densities, observation times, etc) (see, e.g. [24] and references therein). The mean field equation is described in terms of the deviation of the fluorophore local concentration  $n_{\text{B}}(\mathbf{r})$  from its bulk value  $n_0$  about a test quencher:  $n(\mathbf{r}) = n_0 - n_{\text{B}}(\mathbf{r})$ . So the function  $n(\mathbf{r})$  describes the local inhomogeneity in the vicinity of the test quencher and obeys the following equation

$$D\nabla(\nabla n + n\nabla\beta U) = k_{ss}cn + \tau_0^{-1}n, \quad (7)$$

where the second term on the right-hand side describes the nonreactive decay due to the intrinsic lifetime of the fluorophore. The value of the rate coefficient  $k_{ss}$  should be found with the aid of some self-consistent procedure given below. We supplement equation (7) with the boundary condition and condition at infinity

$$n|_{r=R} = n_0, \quad n|_{r \rightarrow \infty} \rightarrow 0. \quad (8)$$

One can see that the boundary condition (8) corresponds to the Smoluchowski condition as regards  $n_{\text{B}}(\mathbf{r})$ . Further we set  $\tau_0 \rightarrow \infty$  for the sake of simplicity.

According to the MFA we should equate the appropriate rate coefficient determined by the equations (7), (8) to the rate coefficient  $k_{ss}$  on the right-hand side of equation (7), i.e.

$$-4\pi DR^2 \frac{1}{n_0} \frac{dn}{dr} \Big|_{r=R} = k_{ss}. \tag{9}$$

Equations (7) and (9) indicate that  $k_{ss}$  is a function of  $ck_{ss}$  and  $\alpha$  and so we assume the existence of the fixed point of the dependence  $ck_{ss}(ck_{ss}; \alpha)$ , i.e.

$$ck_{ss}(ck_{ss}; \alpha) = ck_{ss} \tag{10}$$

with the normalization condition  $k_{ss}|_{c=0} = k_D$ .

In order to obtain the first correction to the rate constant Cukier used an approximate tilde space method suggested by Flannery [20] for the time-dependent Debye–Smoluchowski equation (DSE) with a Coulomb potential. Following Flannery he assumed that the tilde space time-dependent solution works well for all times and, therefore, in the case at issue it is valid for all values  $k_{ss}c$ .

### 2.2. Tilde space method

To compare our consideration with that done in other works [14–16] it is useful to rewrite equation (7) in the form

$$D \nabla \cdot e^{-\beta U} \nabla e^{\beta U} n = k_{ss} cn. \tag{11}$$

It was shown in [20] that after the transformation to the so-called ‘tilde’ space

$$r \rightarrow \tilde{r}(r) = \left[ \int_r^\infty \frac{1}{\xi^2} e^{\beta U(\xi)} d\xi \right]^{-1}, \quad n(r) \rightarrow \tilde{n}(r) = n(r) e^{\beta U(r)} \tag{12}$$

we can formally reduce the differential operator in equation (11) to the form of the ‘free’ diffusion equation

$$D e^{\beta U} \nabla \cdot e^{-\beta U} \nabla e^{\beta U} n = \tilde{D}(\tilde{r}) \nabla_{\tilde{r}}^2 \tilde{n}. \tag{13}$$

Here  $\tilde{D}(\tilde{r}) = D(d\tilde{r}/dr)^2$  is a space dependent effective ‘diffusion’ coefficient, where

$$\frac{d\tilde{r}}{dr} = \left( \frac{\tilde{r}}{r} \right)^2 e^{\beta U} \tag{14}$$

and particularly for the Coulomb potential we have

$$\tilde{r} = \frac{\alpha}{\exp(\frac{\alpha^*}{x}) - 1}, \quad \frac{d\tilde{r}}{dr} = \frac{(\alpha^*/x)^2}{[\exp(\frac{\alpha^*}{x}) - 1]^2} \exp\left(\frac{\alpha^*}{x}\right), \tag{15}$$

hereafter  $x = r/R$ .

To solve the equations (7), (8) analytically following [20], it was assumed in works [14–16] that

$$d\tilde{r}/dr = 1. \tag{16}$$

It is important to note that for solution of the posed problem we need to have a uniform approximation of the equation at issue for the whole domain of its determination. One can see from (15) that in the case of Coulomb potential the condition (16) leads to the transcendental equation

$$z = \sinh z, \tag{17}$$

where  $z = r_c^*/2x$ ,  $r_c^* = r_c/R$ . Equation (17) has the only solution  $z = 0$ , i.e. it holds either at  $r_c^* = 0$  or in the limit  $x \rightarrow \infty$  when  $r_c^* \neq 0$  is fixed. Nevertheless, we can assume that

$d\tilde{r}/dr \approx 1$  in the whole domain of determination, when  $0.5r_c^* \ll 1$ , i.e. asymptotically for very small values of the Onsager length. This is a quite severe restriction of the ‘tilde’ method (see [25] for details).

Within the framework of the ‘tilde’ method equation (11) under the boundary conditions (8) may be approximately reduced to the following equation

$$D\nabla_{\tilde{r}}^2 \tilde{n} = k_{ss} c \tilde{n}, \tag{18}$$

and boundary conditions

$$\tilde{n}|_{\tilde{r}=\tilde{R}} = n_0 e^{\beta U(R)}, \quad \tilde{n}|_{\tilde{r} \rightarrow \infty} = 0. \tag{19}$$

It is well-known that the solution of this problem is

$$\tilde{n} = n_0 e^{\beta U(R)} \frac{\tilde{R}}{\tilde{r}} \exp \left[ -\sqrt{\frac{ck_{ss}}{D}} (\tilde{r} - \tilde{R}) \right] \tag{20}$$

and the relevant rate coefficient (9) reads

$$k_{ss} = -4\pi DR^2 \frac{1}{n_0} \frac{d}{dr} \left( e^{-\beta U} \tilde{n} \right) \Big|_{r=R}.$$

Performing simple calculations one gets

$$k_{ss} = 4\pi D \tilde{R}(\alpha) \left[ 1 + \sqrt{\frac{ck_{ss}}{D}} \tilde{R}(\alpha) e^{\alpha^*} \right]. \tag{21}$$

It is interesting to note that the structure of the concentration correction accurate to the sign is the same as in formula (37) of [18] for the diffusive interaction between two charged sinks. It may be shown that this is the exact asymptotic of the rate constant as  $ck_{ss}/D \rightarrow 0$ .

One can see that equations (7), (8) are formally identical with the equations satisfied by the recombination probability of a geminate ion pair interacting through a Coulomb potential with opposite sign in the presence of scavengers [26]. Thus using the result of [26] we can represent the exact solution to the boundary-value problem (7), (8) and when  $ck_{ss}$  is sufficiently small this taking into account (9) leads also to expression (21).

After the first iteration in (21) in terms of the effective volume fraction  $\tilde{\phi}$  we readily obtain

$$k_{ss} = 4\pi D \tilde{R}(\alpha) \left( 1 + \sqrt{3\tilde{\phi}} e^{\alpha^*} \right) \quad \text{as } c \rightarrow 0. \tag{22}$$

This equation is different by a factor of  $e^{\alpha^*}$  from the similar result obtained in [14–16].

Let us show that the recent Gopich–Berezhkovskii–Szabo theory [27] and the earlier works of Richards [28, 29] also leads to the same result. According to this theory,

$$(ck)^{-1} \sim \int_0^\infty dt \exp \left( -c \int_0^t k_1(t') dt' \right), \quad \text{as } c \rightarrow 0, \tag{23}$$

where  $k_1(t)$  is the time-dependent rate coefficient for a single sink. In the case of an attractive Coulomb potential the exact long time asymptotic is given by [30, 31]

$$k_1(t) \sim k_D \left( 1 + \frac{\tilde{R} e^{\alpha^*}}{\sqrt{\pi Dt}} \right). \tag{24}$$

Taking equation (24) into account, one can find the integral in (23) as follows:

$$\int_0^\infty dt \exp \left( -c \int_0^t k_1(t') dt' \right) = (ck_D)^{-1} \left( 1 - \sqrt{\pi} \zeta e^{\zeta^2} \operatorname{erfc} \zeta \right),$$

where

$$\zeta = \sqrt{\frac{3}{\pi}} \tilde{\phi} e^{\alpha^*}.$$

Thus for small concentrations expression (23) again yields formula (22).

### 2.3. Cukier's calculation

Since it has turned out that the use of the same approach leads to different results, now we will re-examine the derivation given by Cukier [14–16]. In these papers the local concentration was transformed as follows:

$$\tilde{n}_B(r) = n_B(r)e^{\beta U(r)} \quad (25)$$

then the following function was introduced

$$\delta\tilde{n} = n_0 - \tilde{n}_B. \quad (26)$$

For this function the following boundary-value problem was considered [14, 16]

$$D\nabla_{\tilde{r}}^2\delta\tilde{n} = k_{ss}c\delta\tilde{n}, \quad \delta\tilde{n}|_{\tilde{r}=\tilde{R}} = n_0, \quad \delta\tilde{n}|_{\tilde{r}\rightarrow\infty} = 0. \quad (27)$$

Thus, by modifying (20) for the given boundary condition one has

$$\delta\tilde{n} = n_0 \frac{\tilde{R}}{\tilde{r}} \exp\left[-\sqrt{\frac{ck_{ss}}{D}}(\tilde{r} - \tilde{R})\right],$$

and the corresponding rate coefficient is given by

$$k_{ss} = -4\pi D\tilde{R}^2 \frac{1}{n_0} \frac{d\delta\tilde{n}}{d\tilde{r}} \Big|_{\tilde{r}=\tilde{R}} = \tilde{R}(\alpha) \left[1 + \sqrt{\frac{ck_{ss}}{D}}\tilde{R}(\alpha)\right] \quad (28)$$

or

$$k_{ss} = 4\pi D\tilde{R}(\alpha) \left(1 + \sqrt{3\tilde{\phi}}\right). \quad (29)$$

However this result is not valid for the problem at issue. It is evident that

$$D\nabla \cdot e^{-\beta U} \nabla e^{\beta U} n_0 = n_0 \beta \nabla^2 U$$

and therefore for the case of Coulomb potential we have

$$\begin{aligned} D\nabla \cdot e^{-\beta U} \nabla e^{\beta U} (n_0 - n_B) &= -D\nabla \cdot e^{-\beta U} \nabla e^{\beta U} n_B \\ &= D\nabla \cdot e^{-\beta U} \nabla (n_0 - e^{\beta U} n_B) = D\nabla \cdot e^{-\beta U} \nabla \delta\tilde{n}. \end{aligned}$$

After the tilde transformation  $r \rightarrow \tilde{r}$  using (14) we get

$$D\nabla \cdot e^{-\beta U} \nabla \delta\tilde{n} = De^{\beta U} \left(\frac{\tilde{r}}{r}\right)^4 \nabla_{\tilde{r}}^2 \delta\tilde{n} = De^{-\beta U} \left(\frac{d\tilde{r}}{dr}\right)^2 \nabla_{\tilde{r}}^2 \delta\tilde{n}.$$

Setting then  $d\tilde{r}/dr = 1$  we arrive at

$$D\nabla_{\tilde{r}}^2 \delta\tilde{n} = k_{ss} c e^{\beta U} (n_0 - n_B) \neq k_{ss} c \delta\tilde{n}.$$

Thus substitution (26) does not lead to the first equation in (27).

Direct calculation shows that equation (29) may be obtained provided one uses the function  $\delta\tilde{n} = n_0 e^{-\beta U} - n_B$ . It means that in equation (7) the deviation from the local Boltzmann's distribution was considered, although it is claimed in [14, 16] that the deviation from the bulk concentration  $n_0$  is considered. To compare with analytical results, the numerical solution was performed in [16]. However, instead of the deviation of the local concentration from its bulk value, i.e.  $n = n_0 - n_B$  the deviation from its equilibrium value  $n_0 e^{-\beta U} - n_B$  was considered in the numerical calculations as well. So good agreement obtained there between numerical results and analytical formula for small concentration  $c$  is not surprising.

### 3. MFA and subsidiary time-dependent problem

#### 3.1. Subsidiary time-dependent problem

As shown in [1], the problem at issue is related to a time-dependent boundary-value problem for the DSE with Coulomb potential. The boundary-value problems for the DSE are well investigated (see [25] and references therein), and therefore it is convenient to reduce the original problem to a corresponding subsidiary one.

Let us consider the following subsidiary initial boundary-value problem for the DSE with a Coulomb potential

$$\frac{\partial \rho}{\partial t} = \left( \frac{2}{x} - \frac{\alpha^*}{x^2} \right) \frac{\partial \rho}{\partial x} + \frac{\partial^2 \rho}{\partial x^2}, \tag{30}$$

$$\rho|_{t=0} = 0, \quad \rho|_{x=1} = 1, \quad \rho|_{x \rightarrow \infty} \rightarrow 0, \tag{31}$$

where  $\rho = 1 - \rho_B/\rho_0$  and  $\rho_B(x, t)$  is the local time-dependent concentration of excited ions  $B^*$  around a test ion quencher  $A$  with the random initial distribution  $\rho_B|_{t=0} = \rho_0$  and the Smoluchowski boundary condition. Hereafter  $t$  is the dimensionless time normalized by the characteristic relaxation time for pure diffusion  $t_d = R^2/D$ . As it was noted in [1] the mean field boundary-value problem (7), (8) is formally identical with the Laplace–Carson transform of the initial boundary-value problem (30) and (31), i.e.

$$\frac{d^2 \bar{\rho}}{dx^2} + \left( \frac{2}{x} - \frac{\alpha^*}{x^2} \right) \frac{d\bar{\rho}}{dx} = \lambda \bar{\rho}, \tag{32}$$

$$\bar{\rho}|_{x=1} = 1, \quad \bar{\rho}|_{x \rightarrow \infty} \rightarrow 0. \tag{33}$$

Here

$$\bar{\rho}(x; \lambda) = \int_0^\infty \lambda \rho(x, t) e^{-\lambda t} dt, \quad \lambda = t_d (k_{ss}c + \tau_0^{-1}). \tag{34}$$

Contrary to the standard Laplace–Carson transform, we assume  $\lambda$  to be a positive real number.

It is evident that

$$\bar{k}(\lambda; \alpha) = \int_0^\infty \lambda k(t; \alpha) e^{-\lambda t} dt = - \left. \frac{d\bar{\rho}}{dx} \right|_{x=1}$$

is the corresponding  $\lambda$ -transformed time-dependent reduced rate coefficient. Thus using the mean field self-consistency condition we have [1]

$$k_{ss}(c) = k_S \bar{k}(\lambda; \alpha)|_{\lambda=t_d(k_{ss}c + \tau_0^{-1})}. \tag{35}$$

Consider now some important properties of the exact solution.

**Property 1.** One can show directly or using results of [31] that

$$\bar{\rho}(x, \lambda; \alpha) = \exp \left[ \alpha^* \left( 1 - \frac{1}{x} \right) \right] \bar{\rho}(x, \lambda; -\alpha), \tag{36}$$

$$\bar{k}(\lambda; \alpha) = -\alpha^* + \bar{k}(\lambda; -\alpha). \tag{37}$$

These relationships are exact, so if we know functions  $\bar{\rho}(x, \lambda; \alpha)$  and  $\bar{k}(\lambda; \alpha)$  for the case of attraction potential  $\alpha < 0$  we can calculate them for the case of repulsion.

Taking this property into account hereafter we restrict ourselves only to the case of attractive potential.



**Property 2.** Let functions  $w_1(x, t)$  and  $w_u(x, t)$  be the uniform lower and upper boundaries for  $\rho(x, t)$  when  $x \geq 1, t \geq 0$ , i.e.  $w_1(x, t) \leq \rho(x, t) \leq w_u(x, t)$  then one can readily show that the following relations hold

$$\overline{w}_1(x; \lambda) \leq \overline{\rho}(x; \lambda) \leq \overline{w}_u(x; \lambda). \quad (38)$$

For the corresponding rate constants one has  $k_1(t) \geq k(t) \geq k_u(t), t > 0$ , and therefore

$$\overline{k}_1(\lambda) \geq \overline{k}(\lambda) \geq \overline{k}_u(\lambda) \quad \text{for all } \lambda > 0. \quad (39)$$

Inequalities (38) and (39) are useful for deriving approximations for the exact solution and corresponding rate coefficients.

### 3.2. Approximations for the rate constant

The exact analytical solution of the boundary-value problem (32) and (33) is known [32, 33]. However, it is represented in a very cumbersome form which, except for the case of very small values of  $\lambda$  or the Onsager length  $r_c^*$ , renders practical calculations difficult. The most interesting physical result was predicted just for the large values of the Onsager length  $r_c^*$  [14–16] and this very case may be studied by the singular perturbation method [31]. It was shown that for the DSE with the attractive Coulomb potential and the random initial condition, the reduced time-dependent rate constant is approximated by the expression

$$k_{as}(t; r_c^*) = \left(1 + \frac{1}{\sqrt{\pi t}}\right) e^{-\frac{1}{4}r_c^{*2}t} + \frac{r_c^*}{2} \left[1 + \operatorname{erf}\left(\frac{r_c^*}{2}\sqrt{t}\right)\right]. \quad (40)$$

This formula gives the correct asymptotics in the cases: (a) as  $r_c^* \rightarrow \infty$ ; (b) as  $t \rightarrow 0$  and moreover it leads to the exact limit as  $r_c^* \rightarrow 0$ . Using the Laplace–Carson like transformation (34) in  $t$  we arrive at

$$\overline{k}_{as}(\lambda; r_c^*) = 1 + \frac{r_c^*}{2} + \sqrt{\lambda + \frac{r_c^{*2}}{4}} - \frac{r_c^{*2}}{4\lambda + r_c^{*2}}. \quad (41)$$

Another approximation for the rate constant is well-known as the Rice *et al* formula [2]

$$k_R(t; \alpha) = k_D^*(\alpha) + \frac{k_D^*(\alpha)k_D^*(-\alpha)}{\sqrt{\pi t}}, \quad k_D^* = k_D/k_S.$$

This formula gives correct asymptotics for the cases: (a) as  $r_c^* \rightarrow 0$ ; (b) as  $t \rightarrow \infty$ . It leads to

$$\overline{k}_R(\lambda; \alpha) = k_D^*(\alpha) + \sqrt{\lambda}k_D^*(\alpha)k_D^*(-\alpha). \quad (42)$$

One can easily verify that both approximations (41) and (42) satisfy the property 1 for the exact solution.

It has been shown in [31] that for all times the following inequalities hold true

$$k_{as}(t; r_c^*) < k(t; r_c^*), \quad k_R(t; r_c^*) < k(t; r_c^*).$$

Moreover, curves  $k_{as}(t; r_c^*)$  and  $k_R(t; r_c^*)$  intersect at a change point  $t_c$  and

$$k_R(t; r_c^*) < k_{as}(t; r_c^*) \quad \text{if } t < t_c, \quad k_{as}(t; r_c^*) < k_R(t; r_c^*) \quad \text{if } t_c < t.$$

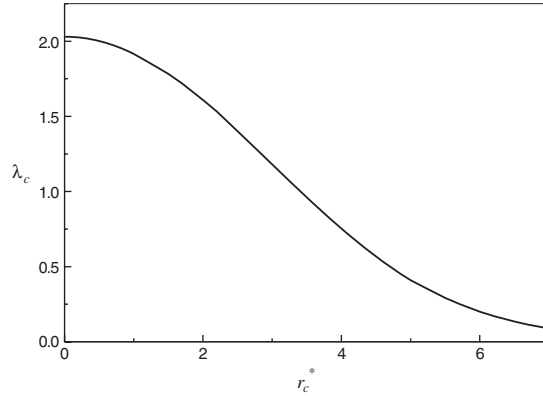
Using property 2, we have the following inequalities

$$\overline{k}_R(\lambda; r_c^*) \leq \overline{k}(\lambda; r_c^*), \quad \overline{k}_{as}(\lambda; r_c^*) \leq \overline{k}(\lambda; r_c^*), \quad (43)$$

and

$$\overline{k}_R(\lambda; r_c^*) > \overline{k}_{as}(\lambda; r_c^*) \quad \text{if } \lambda < \lambda_c, \quad (44)$$

$$\overline{k}_{as}(\lambda; r_c^*) > \overline{k}_R(\lambda; r_c^*) \quad \text{if } \lambda_c < \lambda. \quad (45)$$



**Figure 1.** Dependence of the change point on the dimensionless Onsager length  $r_c^*$ .

Inequalities (43)–(45) show that within the range  $\lambda < \lambda_c$  the function  $\bar{k}_R(\lambda; r_c^*)$  approximates the exact function  $\bar{k}(\lambda; r_c^*)$  better than  $\bar{k}_{as}(\lambda; r_c^*)$ , while for  $\lambda_c < \lambda$  the function  $\bar{k}_{as}(\lambda; r_c^*)$  is a better approximation than  $\bar{k}_R(\lambda; r_c^*)$ . We can obtain the simplest approximation just by gluing functions  $\bar{k}_R(\lambda; r_c^*)$  and  $\bar{k}_{as}(\lambda; r_c^*)$  at the change point  $\lambda_c$  [34]. Thus we get the compound approximation

$$\bar{k}_c(\lambda; r_c^*) = \bar{k}_R(\lambda; r_c^*) [1 - \theta(\lambda - \lambda_c)] + \bar{k}_{as}(\lambda; r_c^*) \theta(\lambda - \lambda_c). \quad (46)$$

One can see that the change point  $\lambda_c$  (which is defined by the transcendental equation  $\bar{k}_{as}(\lambda_c; r_c^*) = \bar{k}_R(\lambda_c; r_c^*)$ ) strongly depends on the Onsager length, being a decreasing function of  $r_c^*$  (see figure 1). It is clear from this figure that to describe  $\bar{k}(\lambda; r_c^*)$  for large  $r_c^*$  we can use  $\bar{k}_{as}(\lambda; r_c^*)$ .

Consider now the absolute error of the compound approximation. For the relevant subsidiary problem and some approximation  $k_a(t)$  it reads  $\delta^{(a)}(t) = |k(t) - k_a(t)|$ . So it is evident that in  $\lambda$ -space the following inequality holds

$$\bar{\delta}^{(a)}(\lambda) = \int_0^\infty \lambda \delta^{(a)}(t) e^{-\lambda t} dt \leq \max_{t>0} \delta^{(a)}(t) = \delta_*^{(a)}.$$

Taking the maximum for both sides of this inequality we get  $\max_{\lambda>0} \bar{\delta}^{(a)}(\lambda) \leq \delta_*^{(a)}$ . The relative percentage error in  $\lambda$ -space is defined by  $\bar{\delta}(\lambda) = \bar{\delta}^{(a)}(\lambda) / \bar{k}(\lambda)$ . One can see that taking into account the inequalities (43)–(45) we have the estimate

$$\bar{\delta}(\lambda) < \frac{\bar{\delta}^{(a)}(\lambda)}{\bar{k}_c(\lambda; r_c^*)} \leq \frac{\delta_*^{(a)}}{\bar{k}_c(\lambda; r_c^*)} \sim \frac{\delta_*^{(a)}}{r_c^*} \quad \text{as } r_c^* \rightarrow \infty. \quad (47)$$

This is a rather rough estimate, however it shows that provided we have a good approximation for  $k(t)$ , its value in  $\lambda$ -space gives a good approximation for  $k_{ss}(\lambda)$  particularly for large enough values of the Onsager length.

Solving equation (35) by iteration, we can derive the value of  $k_{ss}(c)$  for  $r_c^* \ll 1$

$$k_{ss}(c) \sim k_D(\alpha) \left[ 1 + k_D^*(-\alpha) \sqrt{\frac{t_d}{\tau_0}} + \frac{3}{2} \phi k_D^*(\alpha) k_D^*(-\alpha) \times \left( k_D^*(-\alpha) + \sqrt{\frac{\tau_0}{t_d}} \right) \right] \quad \text{as } c \rightarrow 0. \quad (48)$$

In a particular case of uncharged reactants this formula leads to the well-known result which was obtained by the superposition approximation [13, 35]

$$k_{ss} \sim k_S \left[ 1 + \sqrt{\frac{t_d}{\tau_0}} + \frac{3}{2} \phi \left( 1 + \sqrt{\frac{\tau_0}{t_d}} \right) \right] \quad \text{as } c \rightarrow 0. \quad (49)$$

Similarly for  $r_c^* \gg 1$  we get

$$k_{ss}(c) \sim k_{ss}^0(\alpha) \left[ 1 + 3\phi \left( \frac{1}{\sqrt{r_c^{*2} + 4t_d/\tau_0}} + \frac{4r_c^{*2}}{(4t_d/\tau_0 + r_c^{*2})^2} \right) \right] \quad \text{as } c \rightarrow 0, \quad (50)$$

where

$$\frac{k_{ss}^0(\alpha)}{k_S} \sim 1 + \frac{r_c^*}{2} + \sqrt{\frac{t_d}{\tau_0} + \frac{r_c^{*2}}{4}} - \frac{r_c^{*2}}{4t_d/\tau_0 + r_c^{*2}}.$$

One can see from equations (48)–(50) that for large values of the Onsager length the term with  $\phi$  is positive and negligibly small. Therefore in the case of strong attractive Coulomb potential the correction to the concentration dependence may be ignored and we can use the classical linear Stern–Volmer relation.

#### 4. Discussion

According to our calculations, even for nondilute ion quenchers the fluorescence decay constant  $1/\tau$  exhibits a negligibly small positive deviation from the linear Stern–Volmer law. Let us compare the obtained results with available experimental data on the luminescence quenching of ions  $W_6I_{14}^{2-}$  by bipyridinium ions in acetone [36]. Cukier's theory (formula (29)) predicts nonlinear behaviour of the Stern–Volmer law for the lifetime [36]

$$\frac{\tau_0}{\tau} = 1 + \frac{4\pi N_A D_{SV} \tilde{R}_{SV} \tau_0 [Q]}{1000} \left[ 1 + \left( \frac{4\pi N_A \tilde{R}_{SV}^3 [Q]}{1000} \right)^{1/2} \right], \quad (51)$$

where  $\tilde{R}_{SV}$  and  $\tilde{D}_{SV}$  are the effective reaction radius and diffusion coefficient, respectively. To calculate  $\tilde{R}_{SV}$  [36] one should take into account the charge screening. Within the Debye–Hückel framework it is given by [36]

$$\tilde{R}_{DH} = r_c e^{-\kappa r_c}. \quad (52)$$

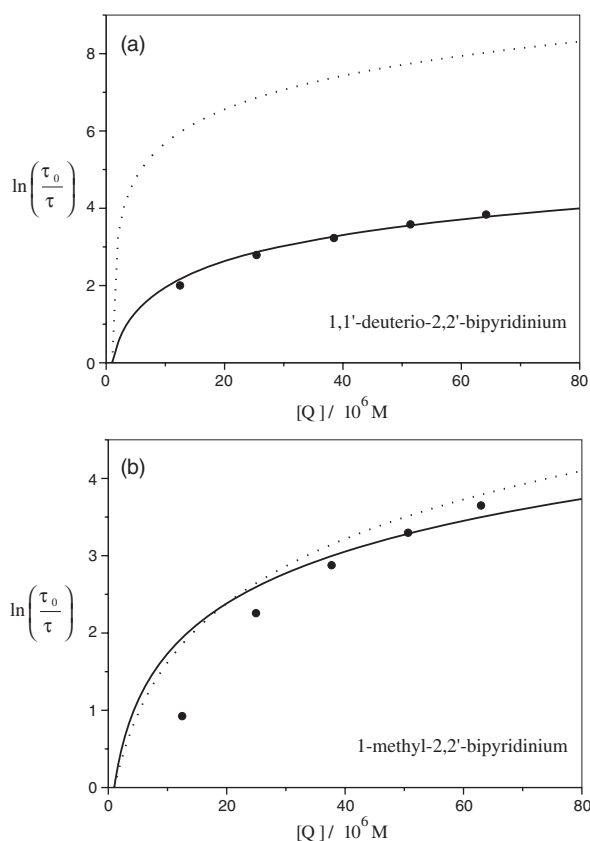
Here  $\kappa^2$  is determined by  $\kappa^2 = 2e^2 N_A \rho_s \beta I / 1000 \epsilon_0 \epsilon_r$ , where  $\rho_s$  is the solution density, and  $I$  is the ionic strength. In the case of acetone at  $T = 296$  K and  $I = 0.001$  M the calculation yields  $\tilde{R}_{DH} = 38$  Å, and at the temperature under consideration we have  $\tau_0(W_6I_{14}^{2-}) = 25$  μs [36].

Performed calculations based on the Marcus formula [37, 38] show that for the present case we can describe the electron-transfer reaction by using the contact approximation. Moreover due to the fact that the intrinsic electron-transfer rates for the bipyridinium ion quenchers are much greater than the diffusion rate, one can assume that the reaction is fully diffusion controlled.

Choosing  $R = 5$  Å, we have  $r_c^* = 7.6$ . In order to calculate  $k_{ss}(c)$  for this value of  $r_c^*$  we can use approximation (50). As  $\tilde{R}_{SV}$  we took the value calculated with the help of equation (52) and the best fit of the theoretical results with experimental data is obtained for the values of diffusion coefficients  $D_{SV}$  presented in table 1 (diffusion coefficients and reaction radii are given in  $\text{cm}^2 \text{s}^{-1}$  and Å; superscripts  $a$  and  $b$  correspond to results of [36] and the present study, respectively).

**Table 1.** Calculated diffusion coefficients and effective quenching distances for the reaction of  $W_6I_{14}^{2-}$  with bipyridinium quenchers.

Lumophore/bipyridinium quencher	$D_{SV}^a$	$\tilde{R}_{SV}^a$	$D_{SV}^b$	$\tilde{R}_{DH}^b$
$W_6I_{14}^{2-}/1,1'$ -deuterio-2,2'-bipyridinium	$90 \times 10^{-6}$	136	$9.4 \times 10^{-6}$	38
$W_6I_{14}^{2-}/1$ -methyl-2,2'-bipyridinium	$1 \times 10^{-6}$	157	$7.2 \times 10^{-6}$	38

<sup>a</sup> Results of [36].<sup>b</sup> Present study.**Figure 2.** Decay rates of  $W_6I_{14}^{2-}$  due to quenching reaction by 1,1'-deuterio-2,2'-bipyridinium (a) 1-methyl-2,2'-bipyridinium (b). The present study (solid line), Cukier's result (51) (dashed line); experimental data (black circles).

One can see from table 1 that the values of  $D_{SV}$  for 1,1'-deuterio-2,2'-bipyridinium and 1-methyl-2,2'-bipyridinium are reasonably close to each other, whereas the corresponding values obtained in [36] differ by a factor of 90. It is worth noting that to fit experimental results we used the value  $\tilde{R}_{SV} = \tilde{R}_{DH} = 38 \text{ \AA}$  calculated from equation (52) and adjusted only the diffusion coefficients. It is clear from figures 2(a) and (b) that our results are in better agreement with experimental data than those obtained in [36]. In figure 2(b) we can see a deviation from the linear dependence for small concentrations. This may be explained by experimental errors. Moreover direct calculations indicate that for the present intrinsic lifetime  $\tau_0$  the finiteness of the lifetime is not important, i.e. we can take the limit  $\tau_0 \rightarrow \infty$ .

Note also that the characteristic relaxation time  $t_r$  (the root of the equation  $k(t_r) = 2k_D^*$ ) for the attractive Coulomb potential satisfies the inequality [31]

$$\frac{4\chi_0}{k_D^{*2}} t_d \leq t_r \leq \frac{1}{\pi k_D^{*2}} t_d, \quad (53)$$

where  $\chi_0 \approx 0.0380$ . Thus

$$t_r \leq \frac{1}{\pi k_D^{*2}} t_d \approx 2 \times 10^{-2} \text{ ns} \quad (54)$$

this value is rather small compared to the characteristic time for the development of the ionic atmosphere  $\tau_{\text{atm}} \approx 1/D\kappa^2 \approx 4.5 \text{ ns}$  [36]. So the time-dependent effects for the development of the ionic atmosphere may lead to an increase in  $\tilde{R}$ , anyway one can consider that the quenching occurs in the steady-state regime. Note also that within the time-dependent MFA framework in the  $s$ -space the rate coefficient is  $\bar{k}_0(s + \lambda)$ , where  $\bar{k}_0(s)$  is the corresponding rate for the DSE ( $\lambda = 0$ ). In the original  $t$ -space we get  $e^{-\lambda t} k_0(t)$ . Hence it is clear that the characteristic relaxation time in this case is smaller than in the case of  $\lambda = 0$ , i.e. (54). This allows us to assume the steady-state MFA.

Now we will give an explanation of our results using simple physical pictures. For clarity we will treat here the case of attraction, considering a test ionic sink. It is well-known that the steady-state solution of the DSE with attractive Coulomb potential is

$$n(r, r_c^*) = \frac{1 - \exp[-r_c^* (1 - \frac{1}{x})]}{1 - \exp(-r_c^*)}. \quad (55)$$

In the case under consideration when  $r_c^* \gg 1$  a diffusion boundary layer (DBL) is formed near the reaction surface. We define here the DBL as a domain where the concentration changes sharply. It is clear from (55) that inside the DBL

$$n \sim n^{\text{in}}(r, r_c^*) = 1 - \exp[-r_c^* (x - 1)] \quad \text{for } 0 \leq x - 1 \leq \mathcal{O}\left(\frac{1}{r_c^*}\right),$$

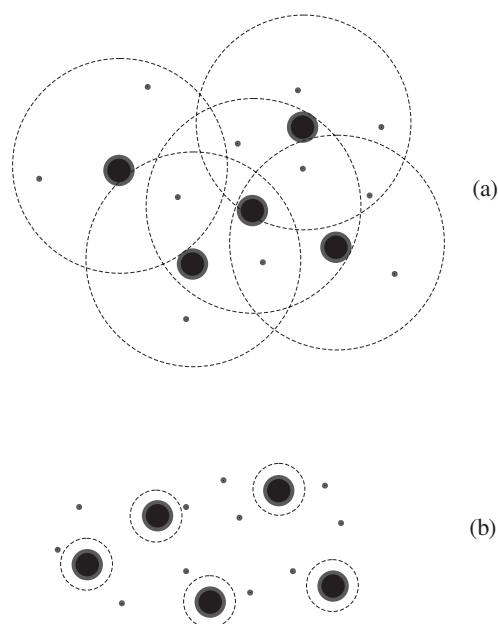
and outside it

$$n \sim n^{\text{out}}(r, r_c^*) = 1 - \frac{1}{x} \frac{r_c^* e^{-r_c^*}}{1 - e^{-r_c^*}} \approx 1 - \frac{R_{\text{ren}}}{r} \quad \text{for } \mathcal{O}\left(\frac{1}{r_c^*}\right) < x - 1,$$

where we introduced  $R_{\text{ren}} = R r_c^* e^{-r_c^*}$ . Hence one can see that the thickness of the DBL may be estimated by  $\delta_d \approx R/r_c^*$  and, therefore, the characteristic relaxation time is just the time for passing over the thickness of the DBL by diffusion, i.e.  $t_r \approx \delta_d^2/D = t_d/r_c^{*2}$ . This result is in agreement with rigorous estimates (53), (54). It is clear that the long-range concentration field for pure diffusion  $1/r$  is screened in the case at issue, i.e. sinks can 'feel' each other only through the screened long-range dependence of the form

$$\delta n = 1 - n^{\text{out}} \approx \frac{R_{\text{ren}}}{r}. \quad (56)$$

The function  $\delta n$  is the normalized deviation of the fluorophore concentration from the bulk value. The deviation occurs around each sink as a result of the reaction of fluorophores with the sink. The deviation  $\delta n$  is largest at the encounter distance around each sink. In the fully diffusion controlled case it is unity at the encounter distance. The region where the deviation  $\delta n$  is sufficiently large (close to unity) around each sink is the region where the presence of the sink has substantial influence on the fluorophore concentration profile. In the case of uncharged reactants, the deviation  $\delta n$  decays slowly with distance according to  $1/r$ . Therefore, the region of influence of each sink is rather large and overlaps with those of other sinks (see figure 3(a)). On the other hand, in the case of charged reactants the deviation  $\delta n$  decays according to



**Figure 3.** Scheme of the influence on the fluorophore concentration profile: in the case of uncharged reactants (a) and unlikely charged reactants (b).

equation (56). The decay is very fast when  $r_c^*$  is large, so the region of influence of each sink is rather small and does not overlap with those of other sinks (see figure 3(b)). Therefore, sinks do not interfere with each other in reaction with fluorophores. This assertion is confirmed by both analytical and numerical calculations in the case of two static sinks [18, 19].

## 5. Conclusions

In this paper we applied the mean field approach to the calculation of the rate coefficient in the Stern–Volmer law for nondilute reactants interacting by Coloumb potential. Our calculations were restricted to the fully diffusion-controlled regime in order to find the maximum effects of concentration. We have shown that for ions of opposite charge the deviation from the classical Stern–Volmer relation is negligibly small when the dimensionless Onsager length  $r_c^*$  is large. However for ions of like charge, the corresponding positive deviation due to the quencher concentration may be essential.

The above results may be understood by noting that the long-range ( $1/r$ ) influence of each sink on fluorophore concentration in the case of uncharged reactants is ‘screened’ in the case of oppositely charged reactants. The concentration screening rapidly increases with increasing Onsager length, according to equation (56). We verified the obtained results by comparison with available experimental data on the bipyridinium electron-transfer reactions.

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