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Charge separation in liquids

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Abstract. The common theory of reversible charge transfer (RCT) at low donor system excitation power in liquids is examined. The space averaging procedures describing the kinetics of RCT in the liquid space are discussed. The reaction space is presented as a totality of independent subgroups with one excited donor and some group of acceptors effectively interacting only with the donor in the given "subgroup". We have shown that the theory [3–5] gives questionable results for cation state probability for the usual parameters of this problem. If the acceptor concentration or the charge transfer rate constants are low, then the cation state probability behaves the same in the two theories [3–5] and [7,8]. The correct account of the donor's ground state change and charge back transfer in the RCT theory gives the new, not contradictory results, different from the behavior of the results in references [3–5], but near to results of [7,8]. The molecules motion accelerates the ionization of donors and neutralization of ions. The influence of the motion of neutral and ionized molecules on charge transfer kinetics is different. The Coulomb interaction of ions is taken into account; the effect depends on the space averaging method used. The new approximation in this article in comparison with references [3–6,9] consists in the space averaging procedure of the donor cation state probability, which takes into account the donor's ground state.

PACS. 78.20.Bh Theory, models, and numerical simulation – 71.90.+q Other topics in electronic structure

1 Introduction

Reversible charge transfer (RCT) in solutions is responsible for quantitative and qualitative alterations in such important relaxation processes as solar energy conversion [1,2], is among the most important elementary chemical reactions. Recently numerous studies have been devoted to photo-induced electron transfer and geminate recombination (back electron transfer) in solutions [3–9] for low and high excitation power [10]. Different theories for describing RCT in solutions, giving different results [3–9], are based on different methods of space averaging for the donor-cation state probability $P(t)$. A proper account of back charge transfer, which prevents the charge separation in the RCT processes, is of crucial importance [3–6,9].

In the new theory of RCT (the NAP model [3–6]), a 'new' averaging procedure is used to calculate forward and back charge transfer. The ions created with a distant-dependent ionization rate, either recombine or separate by diffusion, according to the kinetic scheme:

$$[\mathrm{D}\ldots\mathrm{A}] \leftarrow \left[\mathrm{D}^{+}\ldots\mathrm{A}^{-}\right] \rightarrow \mathrm{D}^{+} + \mathrm{A}^{-}. \tag{1}$$

In the NAP model, instead of solving the differential equation for the radicalion population and then averaging over all of the acceptor configurations, the equation is first averaged over N-1 acceptors, and then solved. To get the total probability $P(t)$ of a donor's cation state, the pair distribution function is averaged over the final coordinate and the thermodynamic limit is taken [3,4]. The space averaging procedure is done only for the forward charge transfer stage, resulting in questionable behavior of the probability $P(t)$ [15].

The assertion by authors in reference [6], that the theory [3–6] is "exact" but the theory [7] is "erroneous" is not convincing and requires a more detailed discussion of the donor cation state probability. In this work we present the common theory of RCT kinetics for liquids and discuss different averaging procedures.

Charge separation in solutions is determined by charge transfer rate constants, depending on intermolecular distances, which are a random function of time in liquids as an accidental Brownian value. The random Hamiltonian influences rate constants, which are modulated by molecular motion [11]. In slow reactions many collisions between molecules have to take place prior to reaction. Moreover, a relatively long time of reaction permits the restoration by diffusion of the initial distribution of acceptors around the un-reacted donor molecules [14]. It is well known [9,12–14] that the diffusion of excitations markedly affects the yield of energy transfer. In previous theories [3–6] charge back

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transfer has not been taken into account correctly, creating incorrect results for the influence of random Hamiltonian in the increase of donor's cation state probability [15]. This point should be discussed. We discuss here the space averaging procedure for the probability $P(t)$ and comparison of results is presented from computer simulations.

2 Reversible charge transfer theory

Here we give a more detailed description of charge separation kinetics, which has been discussed recently [3–10]. The model that is studied theoretically is a three-level system. The lowest level (ground state) is a neutral ground state donor and neutral acceptor. The highest level is an electronically excited donor (at the time $t = 0$) and neutral acceptor. The third level is an unexcited donor – cation and one acceptor – anion with the rest of the acceptors remaining neutral. Forward electron transfer can take place from the excited donor to any acceptor. However, back electron transfer is taken to be geminate. Back transfer can occur only from the anion that initially receives the electron. Transfer of the electron to another donor – cation is not possible at low concentration of excited donors. Electron transfer from the acceptor anion to another neutral acceptor is not included in the treatment, although this is physically possible. The excited donor, with surrounding acceptors effectively interacting with this donor, presents the independent subgroup [12–14]. There is no back transfer between acceptor – anion from any subgroup and donor – cation from another subgroup due to the low concentration of reactants.

The probability $P(t)$ of the cation state of donor S may be obtained [7–9] using a certain generalization of the method, which was first proposed by Antonov-Romanovskii and Galanin [12,13] for the description of an electronic energy transfer in a solid solution and subsequently used [14] for liquids. At a sufficiently low concentration of acceptors the latter may be considered as point particles [9]. In this case the differential encounter theory properly describes the quenching kinetics and quantum yield of luminescence [5,7,14], using the binary approximation. The reaction space with randomly distributed donors S and acceptors A with a concentrations $C_S \ll C_A$ can be presented as a totality of the independent subgroups – "vessels" [14] with one excited donor and some group of acceptors effectively interacting only with the donor in the given subgroup. In such case the average probability over all subgroup donor cation states is an increasing function of the acceptor's concentration [7,15].

Let $P^+(r,t)$ represent the probability that acceptor anion A^- is located at a distance r, $r + dr$ from the donor molecule S^+ which is in the cation state [7–9], calculated for one molecule S^*. It is assumed that the two molecules are separated by a distance r at zero time and that molecular collisions occur only as a result of Brownian motion. We accept that molecules undergo a motion by a diffusion coefficient $D = D_S + D_A$ [14,16]. It should thus be expected that the charge transfer kinetics will be determined by the combined diffusion coefficient D. The variation of $P^+(r,t)$ with time occurs due to the forward electron transfer between S^* and A molecules and the back charge transfer from A^- to S^+ and also due to their motion according to the Fick's diffusion equation [16]. The initial condition is:

$$P^+(r,0) = 0. \tag{2}$$

The changing of $P^+(r,t)$ occurs due to the charge transfer and the molecular motion. For one pair of molecules $P^+(r,t)$ satisfies the equation [7–10,14]:

$$\partial P^+(r,t)/\partial t = k_f(r)n(r,t) - k_b(r)P^+(r,t) + \left(D_1/r^2\right)(\partial/\partial r)r^2e^{-V}(\partial/\partial r)e^{V}P^+(r,t) \tag{3}$$

where D_1 is the encounter diffusion coefficient of ions. The attractive Coulomb potential $V = -r_c/r$ is expressed through Onsager radius $r_c = e^2/\varepsilon kT$ [16]. The partially reflecting or only reflecting boundary conditions are [16]:

$$4\pi r^2 D_2 \partial\left[e^V P^+(r,t)\right]/\partial r|r_{12} = k_{act}P^+(r,t), \tag{4}$$

$$\partial \mathrm{P}^+(r,t)/\partial r|r_{12} = 0. \tag{5}$$

k_{act} is the rate of the additional reaction, which differs from k_b. Above r_{12} – is an encounter distance – approximated by a sum of radii of two interacting molecules. $n(r,t)$ is a pair distribution function of reactants and is determined by the equation:

$$\partial n(r,t)/\partial t = D_2 \Delta n(r,t) - k_f(r)n(r,t). \tag{6}$$

D_1 is the encounter diffusion coefficient of neutral molecules. In equations (3) and (6) $4\pi r^2 n(r,t)$ is the probability that the acceptor molecule is located at a distance between r and $r + dr$ from the excited donor molecules S^*, calculated for one of excited molecule [12–14]. The initial and boundary conditions for $n(r,t)$ are [16]:

$$n(r,0) = 1 \tag{7}$$

$$\partial n(r,t)/\partial r|r_{12} = 0. \tag{8}$$

Equation (8) implies no reaction on the encounter. At time $t = 0$ the ensemble of donors is optically excited by an external source. Deactivation of donors occurs due to the donor's natural decay and the intermolecular charge transfer in liquids with rate constants [12–17]:

$$k_o = 1/\tau \quad \text{rate of excitation's natural decay} \tag{9}$$

$$k_f = (1/\tau)\exp[(R_f - r)/a_f], \quad \text{forward transfer} \tag{10}$$

$$k_b = (1/\tau)\exp[(R_b - r)/a_b], \quad \text{back transfer.} \tag{11}$$

Here τ is the time of donor excitations natural decay, R_f and R_b are characteristic distances of the Ferster-Dexter excitation resonance transfer theory. For deriving of the probability of the donor – cation states, reference [7] uses the obvious equality of derivatives for donor-cation and non-cation states probabilities:

$$P'(t) = -N'_{nc}(t) \tag{12}$$

and derived the formula of donor cation-state probability for low excitation power

$$P(t) = 1 - \exp\left[-4\pi C_A \int_{r_{12}}^{\infty} P^{+}(r,t) r^2 dr\right]. \tag{13}$$

At a low concentration C_A of molecules A or at small $k_f(r)$ the integral term in equation (13) has a small value. The decomposition of equation (13) with a such low parameter gives the result [3–5] – equation (14).

This averaging method is an approximation, which does not differentiate between donor's excited and ground states $N^*(t)$ and $N_{gr}(t)$ in the averaging process, and thus does not give full account of the back reaction, particularly the role of diffusion (see discussion).

3 RCT according to the theory [3,6], the NAP method

In the theory [3–6] the donor cation state probability $P(t)$ is associated with the distribution of ions $m(r,t)$ by the relation:

$$P(t) = 4\pi C_A \int_{r_{12}}^{\infty} m(r,t) r^2 dr. \tag{14}$$

One should take into account simultaneously the back and forward electron transfer, as in equation (9) of [5]:

$$\begin{aligned}\partial m(r,t)/\partial t &= k_f(r) n(r,t) N(t) - k_b(r) m(r,t)\\ &\quad + \left(D_1/r^2\right)(\partial/\partial r) r^2 e^V (\partial/\partial r) e^{-V} m(r,t).\end{aligned} \tag{15}$$

Equations (3) and (15) are different by the function $N(t)$ in the right side of equation (15). Moreover, here the back transfer recombination term proposes and assumes that the donor in the reaction subgroup is in the cation state with probability $P(t) = 1$. This leads to serious differences in qualitative and quantitative results. For the study of the photo-induced charge separation kinetics this method restricts us to the conventional encounter theory [5], which is binary when applied to liquid solutions. We will see that equation (15) for $m(r,t)$ contradicts the condition of the binary approximation.

After pulse excitation of the sample, the total number of excited donors $N(t)$ obeys the conventional kinetic equation of the differential non-Markovian encounter theory (see Refs. in [5,9]):

$$dN(t)/dt = -k_I(t) C_A N(t) - N(t)/\tau \tag{16}$$

$$k_I(t) = \int k_f(r) n(r,t) d^3 r. \tag{17}$$

The diffusion of neutral or ionized molecules exerts different influences on the cation state probability of a donor in liquids according to the theory [3–5]. If in lacking of back transfer the motion of molecules only promotes ionization [5], increasing $P(t)$, then when back transfer is available, the greater mobility of ions promotes recombination, decreasing $P(t)$.

The effect of intra-molecular radiation and radiationless decay of the donor may be incorporated [9] into the final results by multiplication with an $\exp(-t/\tau)$. An additional discussion of the role of τ is given in reference [21]. In the binary approximation $P(t)$ must be linear in the acceptor concentration C_A [5]. At time zero, $t = 0$, the acceptor molecules are uniformly distributed, the function $m(r,t)$ satisfies the initial condition:

$$m(r,0) = 0 \tag{18}$$

at $r > r_{12}$ – the sum of the radii of two molecules.

The NAP model uses the reflecting boundary condition [9]:

$$\partial e^V m(r,t)/\partial r | r_{12} = 0. \tag{19}$$

It is useful in the general case of partially reflecting boundary conditions [15], particularly when R_f is small and D has a moderate value.

For a pair distribution function of reactants $n(r,t)$ the NAP method uses the equation (6) with initial condition and reflecting boundary condition, equations (7) and (8). The donor excited state probability is [12–14]:

$$\begin{aligned}N(t) &= \exp(-t/\tau)\exp\left[-4\pi C_A \int_{r_{12}}^{\infty} n(r,t) r^2 dr\right]\\ &= \exp(-t/\tau)\cdot S(t).\end{aligned} \tag{20}$$

Shown below is the crucial role of the function $S(t)$ in the NAP model [15]. It is also shown that physically correct results in the theory [3–6] occur only on condition $S(t) \approx 1$. For a high concentration of acceptors the multiplier $S(t) \ll 1$ and then a back charge transfer role in equation (15) is not properly justified [15]. For point particles, R_m – the minimum distance between reactants – is set equal to zero. The NAP method results in plausible behavior of probability $P(t)$ only for low concentration of acceptors, or low rate constants of charge transfer [15].

The third averaging procedure; the new account of back transfer reaction

We discuss the reaction:

$$\mathrm{D}^* + \mathrm{A} \rightarrow \left[\mathrm{D}^{+} \ldots \mathrm{A}^{-}\right], \tag{21}$$

according to the kinetic scheme, equation (1). The basic equations are:

$$N(t) + N_{gr}(t) + P(t) = 1 \tag{22}$$

$$N_{nct}(t) + P(t) = 1. \tag{23}$$

The forward and back reaction occur with rate constants (10) and (11).

For donor excited state averaged probability we have the known equation [12–14]:

$$dN(t)/dt \;=\; -N(t)\left[1/\tau - 4\pi C_A \int_{r_{12}}^{\infty} \partial n_f(r,t)/\partial t r^2 dr\right]. \tag{24}$$

$$P_{ct}(0) = 0,$$
$$n_f(r,0) = 1. \tag{24*}$$

For liquids:

$$\partial n_f(r,t)/\partial t = -k_f(r)n_f(r,t) + \left(D_2/r^2\right)(\partial/\partial r)r^2(\partial/\partial r)n_f(r,t). \tag{25}$$

Using equation (23), it follows:

$$dP(t)/dt = -dN(t)/dt - dN_{gr}(t)/dt. \tag{26}$$

In equation (24) the integral term is determined according to the model of independent "vessels" [7,18]. We need to examine equation (26). In every "vessel" at time $t = 0$ there exists only one excited donor [14] due to the low excitation power. In any following time $t > 0$ in the "vessels" there can be an excited donor $N(t)$ a donor in the ground state N_{gr}, or a donor in the cation state, $P(t)$. In this last case we have in the "vessel" also an acceptor in anion state. In this case, considering a donor in a cation – state, we are interested in its transfer into the donor ground state due to the charge back transfer from acceptor-anion to donor in its cation state. In the given "vessel" any acceptor can be in the anion state – but only one acceptor. It is evident that this case has the same mathematical properties as the case of a "vessel" containing an excited donor. Here the decrease of the probability $P(t)$ (due to the back charge transfer) means an increase of the donor's ground state probability.

$$dN_{gr}(t)/dt = -dP(t)/dt|_{(\text{due to back transfer})} \tag{27}$$

$$dN_{gr}(t)/dt = -4\pi C_A P(t) \int \partial n_b(r.t)/\partial t r^2 dr. \tag{28}$$

Finally, we have:

$$dP(t)/dt = 4\pi C_A \int [N^*(t)\partial n_f(r.t)/\partial t - P(t)\partial n_b(r.t)/\partial t]r^2 dr. \tag{29}$$

And for liquids:

$$\partial n_b(r,t)/\partial t = -k_b(r)n_b(r,t) + \left(D_1/r^2\right)(\partial/\partial r)r^2 e^{-V}(\partial/\partial r)e^{V} n_b(r,t). \tag{30}$$

This equation must be solved with initial condition:

$$n_b(r,0) = 1. \tag{30*}$$

Equation (30) uses the Coulomb effect unlike equation (25). Since the position dependent rates in equations (29) and (30) account for the reaction wherever it happens, the reflecting boundary condition must be used:

$$\partial n_{f,b}(r,t)/\partial r|r_{12} = 0$$

and this determines the influence of the diffusion.

In place of the expression (29), previous theory [3–5] states here erroneously $P(t) = 1$. In equations (25), (30) the diffusion coefficients D_1, D_2 have different influence on $P(t)$: the first results in its increase, the second in its decrease. This is a reason for considering different D_1 and D_2 in equations (25) and (30).

4 Discussion

It follows from a simple physical consideration that the donor cation state probability $P(t)$, as a result of the reversible charge transfer in a liquid solution independent of the space character (the Euclidean infinite or restricted space, or fractal media [17–22] of various dimensions), must satisfy the following simple conditions as an effect of the causality principle:

A. The probability $P(t)$ must be an increasing function of the acceptor concentration for any relation between the rate constants of the forward and back charge transfer or between the characteristic parameters of these rates for any viscosity of the solution. The NAP theory [3–5] does not satisfies this condition [15]. As shown in reference [21]a (Eq. (1)) this probability is an increasing function of C_A in the case of $k_b(r) = 0$ and $D = 0$. Such a behavior must be expected in the common case $k_b(r) > 0$.

B. $P(t)$ must be an increasing function of the characteristic distance $R_f = R_b$ in any case. These conditions formulated in reference [15] for solids are not fulfilled in the theory of [3–6] for RCT. Obviously however, these conditions are also just for liquids. It follows from our analysis that the NAP results do not satisfy these conditions and demands for liquids or for solids [15]. Moreover, in the case of low rate constants of the charge transfer, when the remote transfer is not effective, the boundary conditions for equation (30) are essential and the partially reflecting boundary condition [16] must be used.

C. The probability $P(t)$ must be an increasing function of the lifetime τ. In fact, if time $\tau \to 0$, then there is no reaction: the donor 's transition to the ground state occurs prior to the charge transfer.

RCT in infinite space

In infinite space, obviously, $N(t) < N_q(t)$ where q means restricted or fractal space. The first term in the right side of the equation (15) decreases with the increase of C_A and R_f, and it is strongly sensitive to the space character. In particular, it is minimum in infinite space, and that in its turn increases the role of the second term in the right side of equation (15). The role of the charge back transfer increases with the increase of the reaction space and its dimension. Such a growth is physically not properly founded and inexplicable. Let us discuss condition A of Section 5.

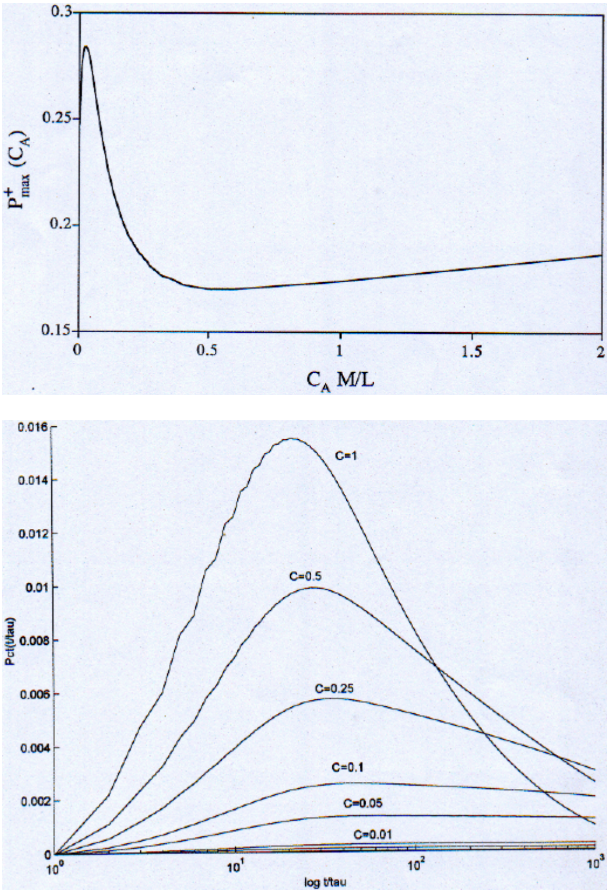

Fig. 1. (a) The dependence $P(t)$, the role of C_A for the NAP model, equation (14). $D = 10^{-5}$ cm^2/s, $R_f = 7$, $R_b = 8$, $a_f = a_b = 1$, $r_{12} = 5$, $r_c = 10$, all in Å. (b) The dependence $P(t)$, the role of C_A for new theory, equation (30). Rest of parameters as in Figure 1a.

The cation state probability cannot be (as a result of the causality principle) a decreasing function of the acceptor concentration, of the reaction volume and of the rate constant of the forward charge transfer (for any back transfer rate constant and at every moment of time t). The functions (14) and (15) do not satisfy these demands (Fig. 1). Here, it is assumed that the concentration of acceptors is much larger than that of the donor, and acceptor-acceptor excluded volume effects are neglected. Figures 1a and b shows the dependences of $P_{max}(t, C_A)$ – the maximum value of the probability $P(t)$ as a function of the acceptor concentration according to the NAP model [3,4,9] and new theory [Eqs. (29) and (30)], respectively. We see a decreasing branch and then an increase of this probability in Figure 1a, which contradicts the evident condition A and its increase as seen here for the new theory, equation (30). In the restricted space the integral in equation (24) is small and, as a result, $N(t) \approx \exp(-t/\tau)$. When $S(t) \approx 1$, the donor – cation state probability becomes a normal increasing function of the acceptor concentration.

The probability $P(t)$ is a decreasing function of D (Fig. 2a) for $R_f = R_{b,} = 1$ Å in the NAP model [3–5]

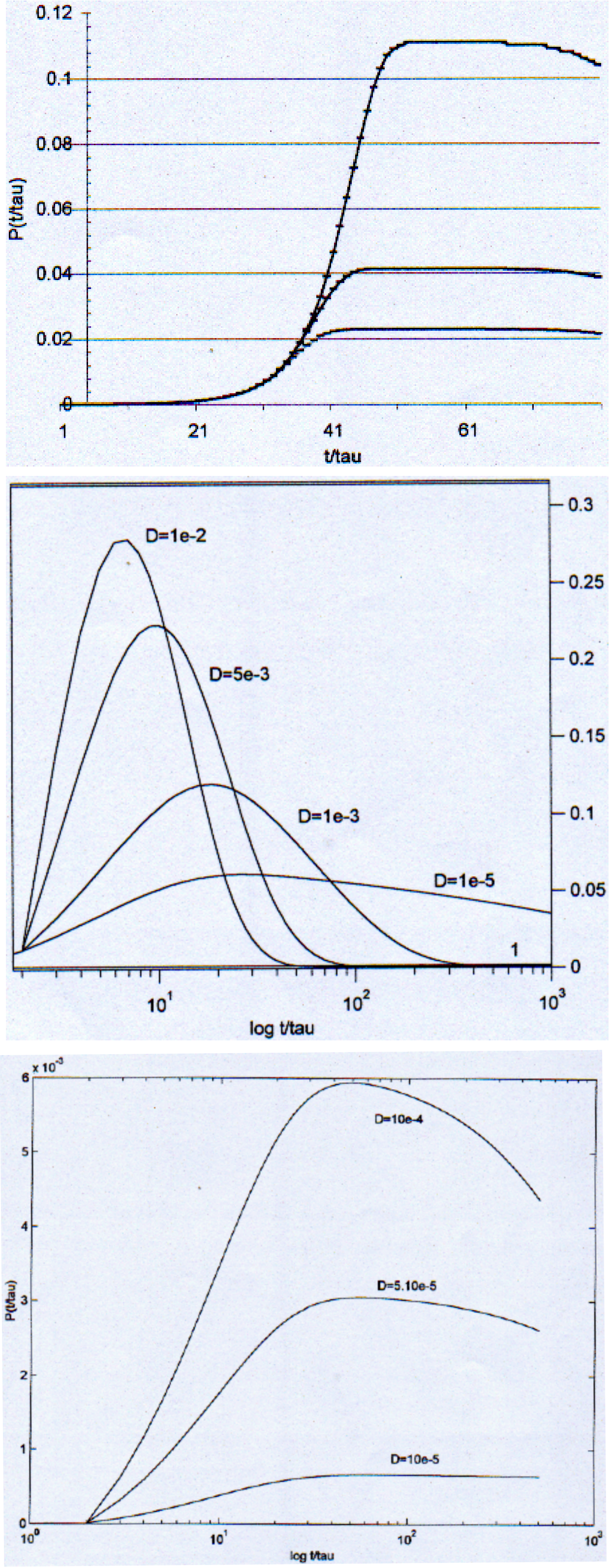

Fig. 2. (a) The role of D, the NAP model, equation (14). $R_f = R_b = 1$ Å, $a_f = a_b = 1$ Å, $r_{12} = 5$ Å; $D = 10^{-4}$, 5×10^{-5}, and 10^{-5} (bottom up) is given by cm^2/s, $r_c = 10$ Å. $C_A = 0.1$ M/L. (b) The role of D, results of new theory, equation (30). $R_f = R_b = 8$ Å, $a_f = a_b = 1$ Å, $r_{12} = 5$ Å, D is given by cm^2/s, $r_c = 10$ Å. $C_A = 0.1$ M/L.

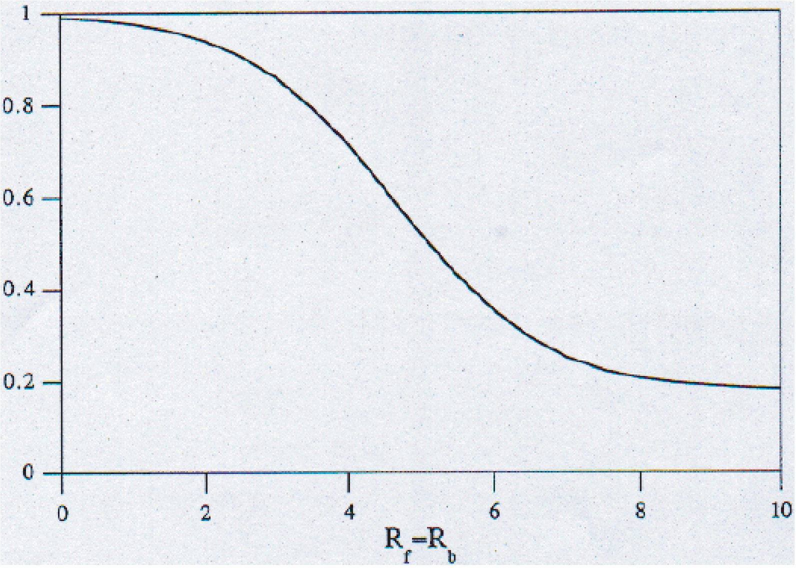

Fig. 3. The dependence $P(R_f = R_b)$. $a_f = 1.5$; $a_b = 1$ Å. $C_A = 0.2$ M/L. Euclidean space. $D = 10^{-5}$ cm^2/s. $r_c = 10$ Å. NAP model.

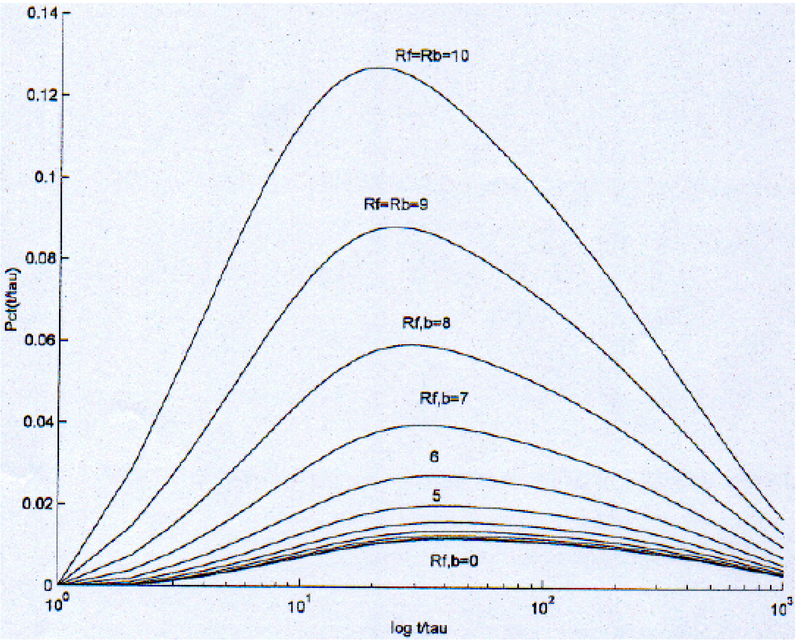

Fig. 4. The dependence $P(R_f = R_b)$ for new theory, equations (29) and (30). The rest of parameters as in Figure 3.

and is an increasing function of D in our theory (Fig. 2b). As shown in reference [11], the charge transfer rate constant is proportional to $1/D$ for low R_f and is $\sim D$ for high R_f. However, our numerical analysis shows that this fact is not relevant when considering the kinetics of our new model (Eq. (30)).

Figures 3 and 4 show the dependences $P_{max}(R_f = R_b)$. Here a breach of the logical condition B also takes place in the NAP model, Figure 3, namely there should be an increase of P_{max} according to the new theory, equation (30). Hence, the behavior of functions (14) and (15) do not correspond to the physical sense of the donor-cation state probability $P(t)$.

It should be noted that the mobility of excited neutral molecules and ions have different influences on charge separation kinetics. The first results in an increase of the probability $P_{max}(t)$, but the second should result in a decrease of this probability. However, in Figures 5 and 6 we see the different results for the two theories under consideration: the NAP model not gives a decrease of $P_{max}(t)$ with increase of D_2, the ion mobility, in contrast with the new theory.

Figures 5 and 6 demonstrate the role of ion mobility. Obviously, ion diffusion should increase the role of the back reaction and therefore decrease the probability $P(t)$. Figure 5 shows that the NAP model does not give such

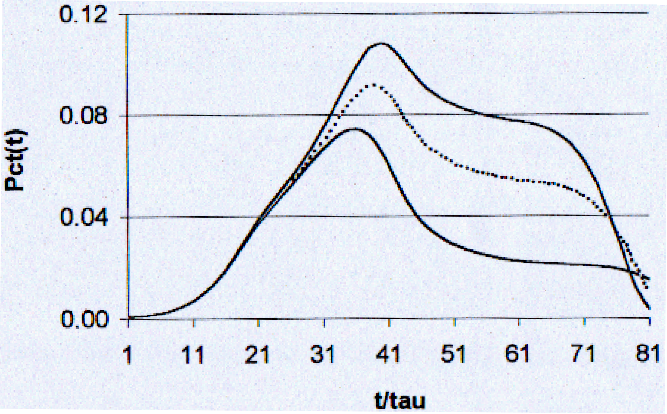

Fig. 5. The role of ion motion for NAP model, [Eq. (14)]. $R_f = R_b = 10$ Å; $a_f = a_b = 1$ Å, $r_c = 10$ Å; $r_{12} = 5$ Å; $D =$ 1e-5; 5e-6 and 1e-6], cm^2/s [bottom up], $C_A = 0.1$ M/L.

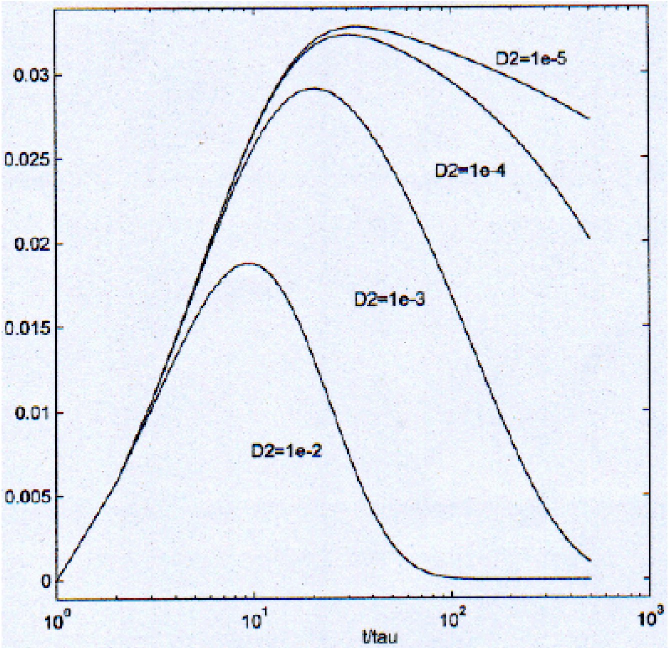

Fig. 6. The role of ion motion for new theory, [Eqs. (29, 30)]. $R_f = R_b = 8$ Å; $a_f = a_b = 1$ Å, $r_c = 10$ Å; $r_{12} = 5$ Å; $D =$ 1e-2; 1e-3, 1e-4 and 1e-5], cm^2/s [bottom up], $C_A = 0.1$ M/L.

behavior. The new theory [Eq. (30)] however, in Figure 6 verifies this statement.

Thus the theory of references [3–6] is correct only for low C_A. This is because according to this theory, the effect of back transfer increases if C_A increases, while the increase in forward transfer effect is restricted by the non – exponential law $N(t)$.

In all cases the logical behavior of the donor cation state probability is broken when the condition $S(t) \approx 1$ in equation (20) is broken [15]. In the restricted, fractal space of a low dimension, for $C_A \ll 1$, for $R_f \approx 0$, the behavior of $P(t)$ is correct, as has been shown in reference [15]. In conclusion, we note that at a high diffusion constant D, when the charge back transfer is only weakly effective, the NAP method gives the correct results. As shown in references [15,21] the NAP method is strong when $k_b = 0$. Thus, the conclusion of reference [6] (that the theory [7] is correct only for $C_A \ll 1$ M/L) is not grounded; there are many cases when these theories give coincident results, even for $C_A \sim 1$ M/L. The NAP model is correct, if there is no back charge transfer [5]b and it may approximately describe this phenomena for a low C_A in infinite Euclidean space. So, the theory of references [3–6] is preferable only for low C_A because, according to this theory, the effect of back transfer increases without limit, if C_A increases, while the increase of forward transfer effect is restricted by the non – exponential law $N(t)$.

5 Conclusions

1. We discuss the remote electron transfer theory for liquids, which has no alternative for the case of moderate or slow diffusion, in the frame of an unified theory [Eqs. (16–17)] but not the more general integral encounter theory reviewed in [9].

2. The 'novel' averaging procedure, suggested in references [3–6] for describing the kinetics of the reversible charge transfer in the liquid infinite Euclidean space, is correct for very low C_A and low rate constants of charge transfer. The probability of the donor cation state $P(t)$ for RCT [Eqs. (14, 15) with supplementary Eqs. (16, 17)], given by the theory [3–6], results in the dependencies of this function on high C_A and on the many parameters of the charge transfer rate constant, which contradict their physical sense. Such results determine incorrectly RCT kinetics.

3. The correct averaging procedure, incorporating the first stage (forward transfer) and the second stage (back transfer) independently, accounting for the donor's ground state, gives the new interesting and not contradictory results [Eq. (30)] which differ from the results of the theory in [3–6]. In particular, an increase of ion mobility gives a decrease of cation state probability, in contrast to the theory presented in [3–5].

4. The different effects of Coulombic ion interaction are determined by the space averaging procedure, used in different theories [3–6] and [24].

5. The geometry of emission and absorption spectra of reacting molecules results in a qualitative and quantitative (the value of R_f and R_b [11]) influence on RCT kinetics, but it depends on the space averaging procedure. This influence in our new theory is not essential.

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