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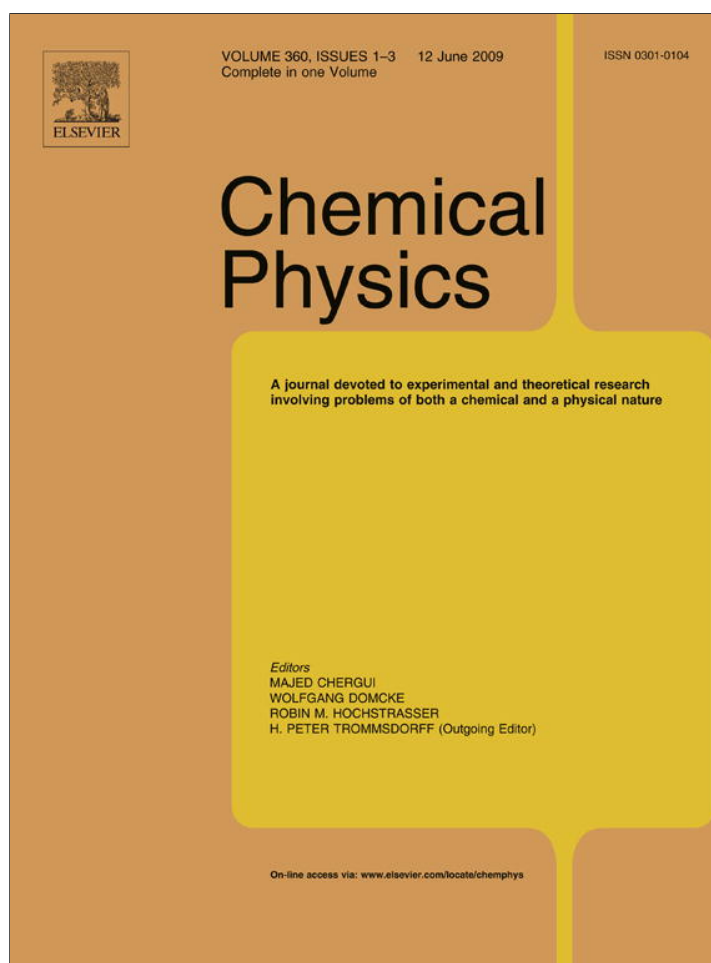


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Investigation of geminate recombination of radical ion pairs generated by dissociation of exciplexes in moderately polar solvents using the photoconductivity technique

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ABSTRACT

A new approach to determination of the recombination rate of radical ion pairs in moderately polar solvents is presented. It is based on an investigation of transient photocurrents caused by dissociation of exciplexes generated in photoinduced electron transfer reactions. It has been shown that the recombination rate of geminate ion pairs can be found from the photocurrent rise time. We have applied such an approach to transient photocurrents observed by Hirata et al. [Y. Hirata, Y. Kanda, N. Mataga, J. Phys. Chem. 87 (1983) 1659] for the pyrene/dicyanobenzene system in solvents of moderate polarity. The increase of the obtained recombination rate of photogenerated ions with increasing polarity of solvent testifies that ions recombine mainly by the backward electron transfer from the dicyanobenzene anions to solvent-separated cations of pyrene.

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1. Introduction

Photoinduced charge transfer reactions taking place between electronically excited states of the electron donor (D) and electron acceptor (A) molecules in polar solvents result in formation of the radical ion pairs $A^- + D^+$, also called the solvent-separated radical ion pairs, and exciplexes ($A^{\cdot-}, D^{\cdot+}$), also called the contact ion pairs [1–12]. The ions produced can recombine or separate under the thermal motion forming free ions. The competition between the charge recombination and charge separation determines the efficiency of the light energy conversion in donor–acceptor systems. For polar solvents, like acetonitrile, the geminate recombination rates of the radical ion pairs $A^- + D^+$ have been determined from measurements of the free ion yield for many donor–acceptor systems using the transient optical absorption or other time-resolved techniques [1–3,7–12]. As to non-polar and moderately polar solvents, it is difficult to measure small yields of free ions by means of laser absorption spectroscopy. In addition, in the case that solvent-separated radical ions can arise from dissociation of exciplexes ($A^{\cdot-}, D^{\cdot+}$), an investigation of the decay of the radical ion pairs by the transient optical absorption technique is hampered by the fact that optical absorption spectra of the contact and solvent-separated ion pairs are closely related to each other.

The photoconductivity technique is of frequent use for determination of quantum yields of free ion formation in the photoinduced electron transfer (ET) reactions [9,13–22] and for measurements of

excited-state dipole moments and exciplex dipole moments [23]. Recently, it has been shown [24] that measurements of transient photocurrents enable one to find the recombination rates of solvent-separated radical ion pairs in the case that the ions arise from dissociation of exciplexes, a primary product of the photoinduced ET reactions. It has been known that for many exciplex systems the exciplex fluorescence decay observed after short light pulses is accompanied by a build-up of the d.c. photocurrent attributed to dissociation of exciplexes into ions [9,13–15,20–22]. The decay curves of the exciplex fluorescence and the photocurrent rise curves following a short photoexcitation pulse at time $t = 0$ were reproduced approximately by simple exponential functions, $I_f(t) \propto \exp(-t/t_{fluor})$ and $J(t) \propto 1 - \exp(-t/t_{rise})$, respectively. However, the photocurrent rise time (t_{rise}) was found to be, as a rule, less than the decay time (t_{fluor}) of the exciplex fluorescence [9,13–15,20–22]. As shown [24], the explanation of the distinction between t_{rise} and t_{fluor} is that the life time of the exciplexes, precursors of ions, is comparable to the diffusion separation time of the geminate ion pair $A^- + D^+$ generated by dissociation of exciplexes. In this case, the photocurrent measured is the displacement current, and its time profile is determined not only by the exciplex life time, but by the time dependent electric polarization of the spatial distribution for the ion pairs $A^- + D^+$ in the electric field as well. In the work [24], a simple diffusion model has been proposed that establishes a link between the photocurrent rise time and the recombination rate of geminate ions. The model has explained the discrepancy between t_{rise} and t_{fluor} observed for solutions of 9,10-dicyanoanthracene and simple aromatic electron donors, like durene or hexamethylbenzene, in solvents of modest polarity.

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The present paper is devoted to analysis of the recombination kinetics of radical ion pairs formed in the solutions of pyrene and *p*-dicyanobenzene (DCNB) in weakly polar solvents. The pyrene/DCNB system is of interest for determination of the recombination rate of the ions because both the photocurrent rise curves and the fluorescence decay curves were studied in the same experimental conditions by Mataga and co-workers [13–15] for this donor–acceptor system. It has been shown that the photoconductivity rise time can be either rather close to the t_{fluor} time or distinctly less than that depending on solvent [15]. The discrepancy between t_{rise} and t_{fluor} was the main argument against a “two-state model” of ion formation in which $(A^{\cdot-}, D^{\cdot+}) \rightarrow A^- + D^+$. To explain the observed results, Mataga and co-workers [9,15] have assumed the existence of multiple exciplex and solvent-separated ion pair states with different life times. However, the consideration [24] of the time dependent spatial polarization of recombining radical ion pairs $A^- + D^+$ in the electric field has shown that even for exciplexes of the same type, the photocurrent rise time is determined by the recombination rate of geminate ions $A^- + D^+$, and therefore the recombination rate can be evaluated from the experimentally determined photoconductivity rise time. So, the goal of the present study is to find the recombination rate constants of the solvent-separated radical ions $A^- + D^+$ from the transient photocurrents observed previously [15]. The second goal is to test the validity of the model [24] for the pyrene/DCNB pair in moderately polar solvents.

In this paper, we show that the measurements of the d.c. transient photoconductivity make it possible to obtain the recombination rate of the geminate ions $A^- + D^+$ generated by dissociation of exciplexes. We demonstrate that the photoconductivity technique in combination with the time resolved fluorescence spectroscopy can be used in the study of the radical ion pair recombination in a polar medium. It is concluded that for the pyrene/DCNB system under investigation, the recombination of geminate ions occurs mainly by the return transfer of the electron from A^- to D^+ at the distances between ions of the order of 0.8–1 nm.

2. Comments on the photoconductivity experiments

Table 1 summarizes the photoconductivity rise times (t_{rise}) and exciplex decay times (t_{fluor}) obtained by Hirata et al. [15] for the solutions of pyrene and *p*-dicyanobenzene (DCNB) at temperature $T = 298$ K. For the pyrene/DCNB pair, pyrene was an electron donor, while DCNB was an electron acceptor. The solvents used were tetrahydrofuran (THF), dichloromethane (DCM), 1,2-dichloroethane (DCE), *o*-dichlorobenzene (DCLB), and pyridine (PRN).

The solutions under study were excited in the optical absorption band of pyrene with picosecond laser pulses at 347 nm. In the photoconductivity experiments, the laser beam illuminated the liquid sample between electrodes of the photoconductivity cell as shown in Fig. 1. The time resolution of the measuring circuit was about 2 ns [15]. In the time resolved fluorescence measurements,

the exciplex fluorescence decay following the 347 nm excitation pulse was observed to be mono-exponential with the life times t_{fluor} listed in Table 1. For the pyrene/DCNB system under investigation, the DCNB concentration used was 0.058, 0.05, 0.03, 0.05 and 0.042 M for the solutions in PRN, DCE, DCLB, DCM and THF, respectively.

As Table 1 illustrates, the photocurrent rise time is less than the exciplex life time. In particular, for the *o*-dichlorobenzene solutions the time t_{rise} is less than t_{fluor} by a factor of two. For other solvents the times t_{rise} and t_{fluor} , as seen from Table 1, differ only by about 10–20%. A discrepancy between t_{rise} and t_{fluor} , as noted above, was observed for different donor–acceptor systems in solvents of low and moderate polarity: for the solutions of 9,10-dicyanoanthracene used as the electron acceptor and simple aromatic donors, like durene [20,21], and for the solutions of pyrene and *N,N*-dimethylaniline [15]. As shown in [24], the relationship between t_{rise} and t_{fluor} can depend on the geminate recombination rate of the radical ions $A^- + D^+$ generated by dissociation of exciplexes. Below we try to find the ion recombination rates from the transient photocurrent and fluorescence kinetics.

Table 1 shows also the quantum yield of free ion formation (Y_{FI}) for the pyrene/DCNB system. For the PRN, DCM and DCE solvents the values of Y_{FI} were obtained by Hino et al. [14]. As to THF and DCLB, the free ion yields have not been measured for these solvents, but they can be found from the values of Y_{FI} measured for the pyrene/DCNB system in other solvents (acetone, acetonitrile, pyridine, DCM and DCE) by using the following empirical equation for the relationship between Y_{FI} and static dielectric constant (ϵ_{st}) of solvent [14]

$$\lg\left(\frac{1}{Y_{\text{FI}}} - 1\right) = \frac{d_1}{\epsilon_{\text{st}}} + d_2 \quad (1)$$

where d_1 and d_2 represent constants.

3. Relation between the photocurrent kinetics and time dependent polarization of the radical ion pairs in the electric field

As noted previously [24], a build-up of photocurrent following a short photoexcitation pulse is a good indicator of the existence of a long-lived immobile precursor of solvent-separated radical ions. We assume that for the pyrene/DCNB and pyrene/dimethylaniline systems [15] such a precursor is an exciplex dissociating into the ions $A^- + D^+$. Thus, we assume the exciplex mechanism of ion formation shown in Scheme 1 in which exciplexes are the primary product of the bimolecular ET reaction between the photoexcited pyrene (D^*) and 1,4-dicyanobenzene (A) molecules.

According to Scheme 1, the dissociation of exciplexes leads first to formation of a transition state or a transition complex $(A^{\cdot-} \cdots D^{\cdot+})_{\text{TS}}$ which eventually separates into the solvent-separated radical ion pairs $A^- + D^+$. For exciplexes, the distance between cen-

Table 1

Experimentally determined parameters for the pyrene/DCNB exciplex system at 298 K, namely, photocurrent rise times (t_{rise}), exciplex fluorescence decay times (t_{fluor}), quantum yields (Y_{FI}) of free ions, exciplex rise times (t_{gen}), and the values of $4\pi DR_c/\sigma$ at which the calculated photoconductivity rise time coincides with t_{rise} . The times t_{rise} and t_{fluor} were measured by Hirata et al. [15], and the yields Y_{FI} were measured by Hino et al. [14]. The solvents were pyridine (PRN), 1,2-dichloroethane (DCE), *o*-dichlorobenzene (DCLB), dichloromethane (DCM) and tetrahydrofuran (THF). Numbers in brackets are a static dielectric constant and viscosity of solvent (in cP) at 298 K taken from Ref. [25].

Solvent	t_{fluor} (ns)	t_{rise} (ns)	Y_{FI}	R_c (nm)	R_c^2/D (ns)	t_{gen} (ns)	$4\pi DR_c/\sigma$
PRN ($\epsilon_{\text{st}} = 12.99$, $\eta = 0.879$ cP)	5.7 ± 0.1	5.5 ± 0.3	0.14	4.318	13.3	2.32	25.0
DCE ($\epsilon_{\text{st}} = 10.19$, $\eta = 0.779$ cP)	19.3 ± 0.2	16.4 ± 0.8	0.11	5.503	19.2	2.4	128.0
DCLB ($\epsilon_{\text{st}} = 10.0$, $\eta = 1.324$ cP)	47 ± 0.4	28.3 ± 1.5	0.099 ^a	5.608	33.92	6.8	< 30
					42.0		$\approx 25 \pm 15$ (from 10 to 40)
DCM ($\epsilon_{\text{st}} = 8.93$, $\eta = 0.413$ cP)	20.9 ± 0.3	18.1 ± 1.7	0.08	6.279	13.26	1.27	340
THF ($\epsilon_{\text{st}} = 7.44$, $\eta = 0.456$ cP)	56.2 ± 0.4	46.0 ± 1.6	0.049 ^a	7.537	21.1	1.67	830 ± 100

^a The yields were found from Eq. (1) by using the values of Y_{FI} measured [14] for other solvents.

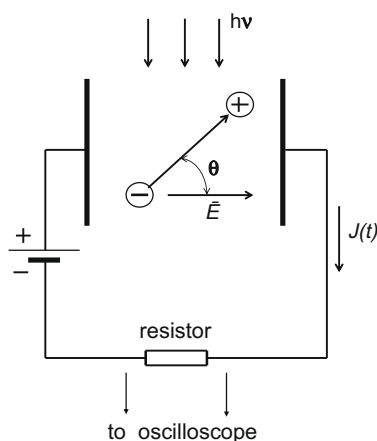
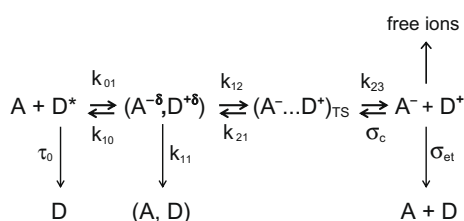


Fig. 1. Schematic of the circuit for measurements of the transient photocurrents induced by a light pulse ($h\nu$). The photoconductivity signal is measured across the load resistor, E is the vector of the external electric field strength.



Scheme 1.

ters of the ions is of the order of $r_{AD} \approx 0.35$ nm [12]. Within the complex $(A^{\cdot-} \dots D^{\cdot+})_{TS}$, both the ion solvation and desolvation take place, and the number of the solvent molecules in the first shell around each ion is changed in the process of solvation and desolvation. As the result, the centre-to-centre distance (r) between $A^{\cdot-}$ and $D^{\cdot+}$ in the complex $(A^{\cdot-} \dots D^{\cdot+})_{TS}$ varies from $r_{AD} \approx 0.35$ nm to the value of the order of $a \approx 1$ nm at which at least one solvent molecule can be placed between $A^{\cdot-}$ and $D^{\cdot+}$ [24]. It is unlikely that motion of the ions in the complex (at $r < a$) can be considered as a diffusion in a structureless medium because in the course of solvation and desolvation the inter-ionic distance is changed by the value of the order of a molecular diameter of solvent, that is of the order of r .

The separated ion pair $A^{\cdot-} + D^{\cdot+}$ can disappear either by the back transfer of the electron from $A^{\cdot-}$ to $D^{\cdot+}$ or by the repeated formation of the complex $(A^{\cdot-} \dots D^{\cdot+})_{TS}$ when distance r reaches the recombination sphere of radius a . In Scheme 1, σ_{et} and σ_c are the intrinsic recombination rate constants (measured in cm^3/s) corresponding to these processes, respectively. For the pyrene/*N,N*-diethylaniline pair, the formation of exciplexes due to ionic recombination has manifested itself in the magnetic field effect on the exciplex fluorescence [26]. It is thought that the interconversion $(A^{\cdot-}, D^{\cdot+}) \rightleftharpoons A^{\cdot-} + D^{\cdot+}$ between exciplexes and solvent-separated ions is responsible for non-exponential decay of the exciplex fluorescence intensity observed for some donor–acceptor systems [27,28]. However, the value of σ_c/σ_{et} is unknown. For the pyrene/DCNB system the repeat formation of exciplexes due to ionic recombination does not disrupt the exponential decay of the exciplex fluorescence following a photoexcitation pulse [15].

We shall consider a case of photoexcitation of the sample solution by an infinitely short light pulse at time $t = 0$. As well as in [24], in the present work the consideration of the photocurrent kinetics is based on the following assumptions.

- (i) For the solvent-separated radical ion pairs the centre-to-centre distance (r) between $A^{\cdot-}$ and $D^{\cdot+}$ is greater than a value of the order of $a \approx 1$ nm, so that at $r > a$ the motion of ions can be described by a diffusion equation with the combined Coulomb and external electric field potentials.
- (ii) The life time of the complex $(A^{\cdot-} \dots D^{\cdot+})_{TS}$ is far less than the time resolution of photocurrent and fluorescence measurements (about 1 ns). Thus, the transition complex turns instantly either into the exciplex or into the radical ion pair $A^{\cdot-} + D^{\cdot+}$ with the distance between the ions $r > a$. We assume, for simplicity, that the initial spatial distribution of the solvent-separated radical ions $A^{\cdot-} + D^{\cdot+}$ generated by dissociation of the transition complex is isotropic and given by a simple trial function $f_0(r)$ defined in the range between $r = a$ and $r = a + b$ where $a \approx 1$ nm and $b = 0.1$ – 0.5 nm are the parameters determined by the sizes of the ions and solvent molecules [24].
- (iii) The time dependent number (N) of exciplexes produced in liquid between electrodes of the photoconductivity cell (Fig. 1) in the course of the ET quenching of the photoexcited pyrene by DCNB can be approximated by the relationship $N = N_{ex}u(t)$ where the function $u(t)$ is given by [5]

$$u = \frac{t_{fluor}}{t_{fluor} - t_{gen}} [\exp(-t/t_{fluor}) - \exp(-t/t_{gen})], \quad (2)$$

and $N_{ex} = N_0 k_{01} C_A t_{gen}$. Here, C_A is the concentration of DCNB, t is time, and N_0 is the initial number of the electronically excited pyrene molecules between the electrodes photogenerated at $t = 0$. Both the exciplex rise time t_{gen} and the exciplex life time t_{fluor} can be expressed [5] in terms of rate constants of the elemental processes shown in Scheme 1. An Eq. (2) can be derived for Scheme 1 for the following two limiting cases. (1) When the probability of exciplex dissociation is relatively low ($k_{12} < k_{11}$), and the exciplex life time is determined mainly by the rate constant k_{11} and by equilibrium between $D^{\cdot+} + A$ and $(A^{\cdot-}, D^{\cdot+})$ according to the reaction scheme (6) of Ref. [5]. (2) Repeated generation of exciplexes due to recombination of the separated ion pairs $A^{\cdot-} + D^{\cdot+}$ does not affect the exponential exciplex decay, i.e. $\sigma_c \ll \sigma_{et}$.

It should be noted that for the pyrene/DCNB system, Eq. (2) agrees well with the exciplex fluorescence decay [15] which has been observed to be exponential during at least several life times after a photoexcitation pulse. So, we shall use the notation $u(t)$ for the experimental time dependence describing well the exciplex fluorescence decay curves for which the exciplex life times t_{fluor} have been measured (Table 1). As to the exciplex rise time, its value can be estimated taking into account that at $C_A \approx 0.05$ M the equilibrium between $D^{\cdot+} + A$ and the exciplex $(A^{\cdot-}, D^{\cdot+})$ is strongly shifted to the right, and $t_{gen} \ll t_{fluor}$ [15]. It can be shown that at $k_{01}C_A + \tau_0^{-1} \gg k_{10} + k_{11} + k_{12}$ the number of exciplexes is $N_{ex} \approx N_0$, and the exciplex rise time can be determined by [24]

$$t_{gen}^{-1} \approx k_{01}C_A \left(1 + \frac{k_{10}}{\tau_0^{-1} + k_{01}C_A} \right) + \tau_0^{-1} \quad (3)$$

The time t_{gen} was evaluated assuming the diffusion controlled rate constant k_{01} . (Although both t_{gen} and t_{fluor} depend on C_A , we shall call t_{gen} and t_{fluor} the exciplex rise time and exciplex life time, respectively.) Effect of t_{gen} on the photocurrent kinetics is discussed in the next section.

In an electric field applied, photogeneration of exciplexes and their dissociation into ions induce in the external circuit a transient photocurrent consisting of two components: the dipole current arising from re-orientation of the exciplex dipoles in the electric field [23] and the ion current caused by motion of the separated ions $A^{\cdot-} + D^{\cdot+}$ in the combined Coulomb and external electric fields.

The dipole current was not observed in [15] probably because of rather large values of Y_{FI} . (The other possible reason is a small dipole moment of the pyrene/DCNB exciplexes or a poor time resolution of the photoconductivity measurements.) So, we consider below only the ion component of transient photocurrents.

If a pair of free ions A^- and D^+ drifts between electrodes of the conductivity cell in the electric field applied, its drift causes in an external circuit the current $J_0 = emE/L$ where e is the electron charge, L is the distance between electrodes, m is the sum of the ion mobilities, and E is the electric field strength. The free ion current lasts until the ions arrive at the electrodes. However, in the case of photochemical ion generation the ion current, measured on the time scale of the order of the ion pair diffusion separation time, is not constant because it is determined by the time-varying electric dipole of the recombining ion pair. Thus, for every exciplex generated in liquid between the electrodes of the photoconductivity cell after an infinitely short light pulse at $t = 0$, the projection of the electric dipole of the geminate ion pair $A^- + D^+$ on the direction of the external electric field is given by [24]

$$P = k_d \int_0^t u(t') P_{gip}(t - t') dt' \quad (4)$$

where $k_d N_{ex} u(t') dt'$ is the number of the radical ion pairs generated during the time interval $(t', t' + dt')$ due to dissociation of exciplexes, k_d is the exciplex dissociation rate constant (measured in s^{-1}), and $P_{gip}(t_1)$ is the electric dipole gained at time t_1 by that ion pair $A^- + D^+$ which was generated at $t_1 = 0$.

In the displacement current mode of the photoconductivity measurements [23], the displacement current (J) across the load resistor of the external circuit, caused by the time variation of P , is given by

$$J = L^{-1} \frac{dP}{dt} = k_d L^{-1} \int_0^t \frac{du(t - t_1)}{dt} P_{gip}(t_1) dt_1 \quad (5)$$

where the condition $u(0) = 0$ was used to obtain Eq. (5).

The theory of reversible charge separation [29,30] describes the time dependent distribution function of separated ion pairs over inter-ionic distances and the time dependent exciplex concentration by the set of interconnected integro-differential equations. However, the use of the experimental time profile $u(t)$ of the exciplex population allows us to simplify the consideration and take into account possible reversibility of the exciplex dissociation. In fact, since the function $u(t)$ in Eqs. (4) and (5) is the experimental one, the value of $k_d N_{ex} u(t') dt'$ is the number of ions arising from dissociation of all exciplexes during the time interval $(t', t' + dt')$ including both the primary exciplexes generated in the course of the ET quenching of the photoexcited pyrene by DCNB and the secondary exciplexes formed prior to time t' due to ionic recombination. As to the calculation of P_{gip} , we shall find the spatial distribution of the ions $A^- + D^+$ in the model of the irreversible contact recombination when the irreversible ion recombination is thought to be possible only on the recombination sphere of radius a . In this approximation, the electric dipole of the solvent-separated ion pair $A^- + D^+$ produced at $t = 0$ is determined by

$$P_{gip} = e \int_{r>a} r \cos \theta \cdot f(r, \theta, t) d^3r \quad (6)$$

where the probability density $f(r, \theta, t)$, defined at $r > a$, satisfies the Smoluchowski equation

$$\frac{\partial f}{\partial t} + (\nabla, \vec{j}) = 0 \quad (7)$$

$$\vec{j} = -D \cdot \nabla f + m(\vec{E}_c + \vec{E})f \quad (8)$$

with the initial condition $f = f_0(r)$ at time $t = 0$. Here, \vec{j} is the vector of the flux density, $D = mk_B T/e$ is the sum of diffusion coefficients of the

ions A^- and D^+ , k_B is the Boltzmann constant, T is temperature, \vec{E}_c and \vec{E} are the vectors of the Coulomb and external electric field, respectively, $f(r, \theta, t) d^3r$ is the probability for the coordinates (r, θ) of the ion pair $A^- + D^+$ to be in the infinitesimal volume $d^3r = r^2 dr 2\pi \sin \theta d\theta$, and θ is the angle between the radius-vector directed from A^- toward D^+ and the external electric field. (The external field is directed along $\theta = 0$ as shown in Fig. 1.) We assume that the initial distribution function f_0 is independent of θ , and $\int f_0 d^3r = 1$. To solve the Smoluchowski equation, the following boundary condition [31] was used at $r = a$

$$\sigma \cdot f(a, \theta, t) = -4\pi a^2 j_r(a, \theta, t) \quad (9)$$

$$j_r(r, \theta, t) = -D \left[\frac{\partial f}{\partial r} + \left(\frac{R_c}{r^2} - \frac{eE \cos \theta}{k_B T} \right) \cdot f \right] \quad (10)$$

where $\sigma = \sigma_c + \sigma_{et}$, j_r is the radial component of the flux density, and $R_c = e^2/\epsilon_s k_B T$ is the Onsager length. The boundary condition (9) is given in terms of an intrinsic recombination rate constant σ (measured in cm^3/s) on a recombination sphere of radius a .

As Eqs. (5) and (6) suggest, the time dependence of the displacement current J carries information about the recombination parameter σ because the value of σ determines the evolution of the distribution function $f(r, \theta, t)$. So, we try to obtain the value of σ from the transient photocurrent observed [15]. The photocurrent J can be presented as $J = \Psi J_2(t)$ where $\Psi = k_d t_{fluor}$ is the probability for an exciplex to dissociate into ions, and J_2 is the time dependent ion photocurrent determined by the following convolution integral

$$J_2 = (L t_{fluor})^{-1} \int_0^t \frac{du(t - t_1)}{dt} P_{gip}(t_1) dt_1 \quad (11)$$

The ion photocurrent can be also expressed in terms of the displacement current of geminate ion pairs. Differentiating Eq. (4) with respect to time t , we obtain that

$$J_2 = t_{fluor}^{-1} \cdot \int_0^t u(t') J_{gip}(t - t') dt' = t_{fluor}^{-1} \cdot \int_0^t u(t - t_1) J_{gip}(t_1) dt_1 \quad (12)$$

where $J_{gip}(t) = L^{-1} dP_{gip}/dt$ is the displacement current of the geminate ion pair $A^- + D^+$ generated at $t = 0$. Deriving an Eq. (12), we assume that the initial spatial distribution of the ion pairs $A^- + D^+$ is isotropic, and hence $P_{gip}(0) = 0$. (The effect of the initial electric polarization of the ion pairs $A^- + D^+$ on the photocurrent kinetics was discussed in [24].) An Eq. (11) has been used for calculations of J_2 while Eq. (12) is more convenient for analysis. In particular, at sufficiently long times the J_{gip} current tends to the free ion current $J_{gip} \rightarrow J_0 q$ at $t \rightarrow \infty$, and hence the time dependence of the electric dipole P_{gip} tends to the linear function of time, i.e. $P_{gip} \rightarrow eqmEt$ at $t \rightarrow \infty$ where q is the probability that the radical ion pair $A^- + D^+$ will escape neutralization in the external electric field E . From Eq. (12) it follows that at $t \rightarrow \infty$, $J_2 \rightarrow J_0 q$, and hence, $J \rightarrow Y_{FI} J_0$ at $t \rightarrow \infty$ where $Y_{FI} = q\Psi$ is the free ion quantum yield.

4. Results

We assume, for definiteness, that the initial function of the spatial distribution of the radical ion pairs has the form of the quasi-equilibrium distribution

$$f_0(r) = \begin{cases} A_1 \cdot \exp\left(\frac{R_c}{r}\right), & \text{at } a < r < a + b; \\ 0, & \text{at } r > a + b; \quad r < a; \end{cases} \quad (13)$$

where the parameters $a = 0.9 \pm 0.2$ nm and $b = 0.1 - 0.5$ nm lie in the range reasonable for aromatic ions under investigation [24]. The coefficient A_1 is determined by the condition that f_0 is normalized to 1.

Fig. 2 shows the dissociation probability (q_0) of the ion pairs at $E = 0$ as a function of the parameter $4\pi DR_c/\sigma$ where $4\pi DR_c$ is the

Langevin rate constant for recombination of free ions. The value of q_0 is determined by

$$q_0 = 4\pi \int_a^\infty r^2 f_0(r) y(r) dr \quad (14)$$

where $y(r)$ is the dissociation probability for a single ion pair with the initial distance r between ions in the absence of an electric field given by [32,33]

$$y(r) = \frac{\exp(-R_c/r) + (4\pi DR_c/\sigma - 1) \exp(-R_c/a)}{1 + (4\pi DR_c/\sigma - 1) \exp(-R_c/a)} \quad (15)$$

Calculations presented in Fig. 2 were carried out for the reasonable value of $a = 0.9$ nm and for the widths of the initial function $b = 0.1$ and $b = 0.5$ nm. As seen from Table 1 and Fig. 2, the values of $q_0 > Y_{FI}$ can be obtained only at $4\pi DR_c/\sigma > 20$ –30. In addition, Fig. 2 demonstrates that at sufficiently large values of $4\pi DR_c/\sigma$ the q_0 probability weakly depends on the parameter b in the interval of b from 0.1 nm to at least 0.5 nm. This is due to a weak dependence of the escape probability on initial distance r as the distance varies between $r = a$ and $r = a + \delta a$ where δa is of the order of 0.5 nm. For example, for $4\pi DR_c/\sigma = 50$, $R_c = 6$ nm and $a = 0.9$ nm, the escape probability determined by Eq. (15) increases moderately from $y \approx 0.06$ at $r = a$ to $y \approx 0.072$ at $r = a + 0.5$ nm.

To find $f(r, \theta, t)$, the Smoluchowski Eq. (7) was solved numerically. A computational method used is described in Appendix A. Calculations were performed for temperature 298 K, at which the measurements [15] were carried out, and for small values of the parameter $c = eER_c/k_B T < 0.2$ that corresponded to the electric field $E < 10$ kV/cm, typical for the photoconductivity measurements of moderately polar liquids. (The effect of the electric field on the conductivity kinetics of geminate charges was studied previously [24,34,35].)

Diffusion coefficients of ions have been estimated by the Stokes formula $D_{ion} = k_B T / (6\pi r_{ion} \eta)^{-1}$ where η is the viscosity of solvent. The Stokes radii $r_{ion} = 0.4$ nm [36] and $r_{ion} = 0.32$ nm [24] have been used for the pyrene ion and the DCNB ion, respectively. The sum (D) of the diffusion coefficients of the pyrene and DCNB ions determined with the Stokes formula at 298 K is 1.4×10^{-5} ,

1.576×10^{-5} , 0.927×10^{-5} , 2.973×10^{-5} , and 2.693×10^{-5} cm²/s for the solvent PRN, DCE, DCLB, DCM and THF, respectively. Table 1 illustrates that the diffusion separation times R_c^2/D of the ion pair $A^- + D^+$ are really comparable to the life times of exciplexes, precursors of ions.

Figs. 3 and 4 show the effect of the recombination parameter σ on the time dependence of the value of J_{gip}/J_0 and the survival probability (W) for the ion pair $A^- + D^+$ generated at $t = 0$ in DCE and THF, respectively. The survival probability is given by

$$W = \int_{r>a} f(r, \theta, t) d^3r \quad (16)$$

The horizontal dotted lines in Figs. 3 and 4 show the dissociation probability (q) of ion pairs in the external electric field determined by

$$q = q_0 \left(1 + \frac{eER_c}{2k_B T} \right) \quad (17)$$

where q_0 was calculated by Eqs. (14) and (15). As seen from Figs. 3 and 4, at sufficiently long times both J_{gip}/J_0 and W really tend to the q probability found from Eq. (17).

Fig. 5 demonstrates examples of the time dependence of the J_2 current for the case of dissociation of exciplexes in DCE and THF. To obtain J_2 , first we found the function $f(r, \theta, t)$ by performing the numerical solution of the Smoluchowski equation and then the dipole P_{gip} from Eq. (6). Thereafter the function $J_2(t)$ was found from Eq. (11). As seen from Fig. 5, the J_2 current reaches its maximum magnitude J_2^{max} at time t^{max} that depends on the value of $4\pi DR_c/\sigma$. In particular, for the DCE solvent the t^{max} time is about 100 ns for $4\pi DR_c/\sigma = 300$ and about 49 ns for $4\pi DR_c/\sigma = 2$. The maximum of the function $J_2(t)$ is very wide and smooth. At $t > t^{max}$, the J_2 current slowly decreases with increasing time, so that the value of $J_2/J_0 q$ approaches unity from above at sufficiently long times. An insignificant decrease of photocurrent at $t > t^{max}$ is difficult to identify experimentally because it is superimposed on the usually observed decay of photocurrent on the microsecond scale [17–19]

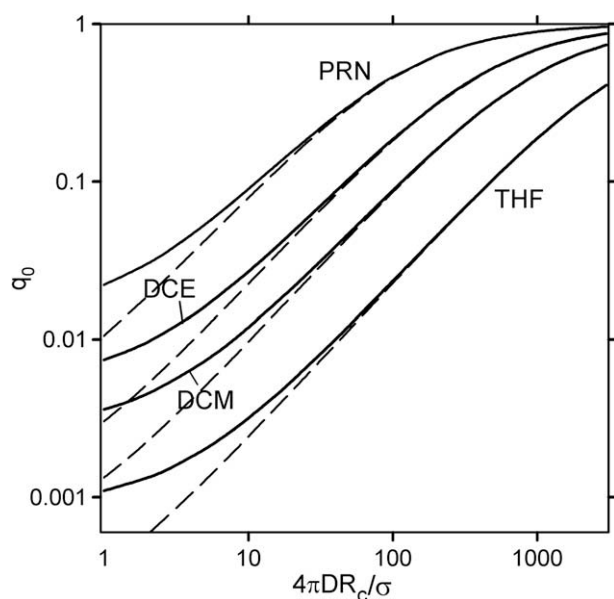


Fig. 2. The dissociation probability of a solvent-separated radical ion pair versus parameter $4\pi DR_c/\sigma$ calculated by Eqs. (14) and (15) for the following solvents: pyridine (PRN), 1,2-dichloroethane (DCE), dichloromethane (DCM) and tetrahydrofuran (THF). The parameters of the initial distribution function were $a = 0.9$ nm, $b = 0.5$ nm (solid curves) and $b = 0.1$ nm (dashed curves).

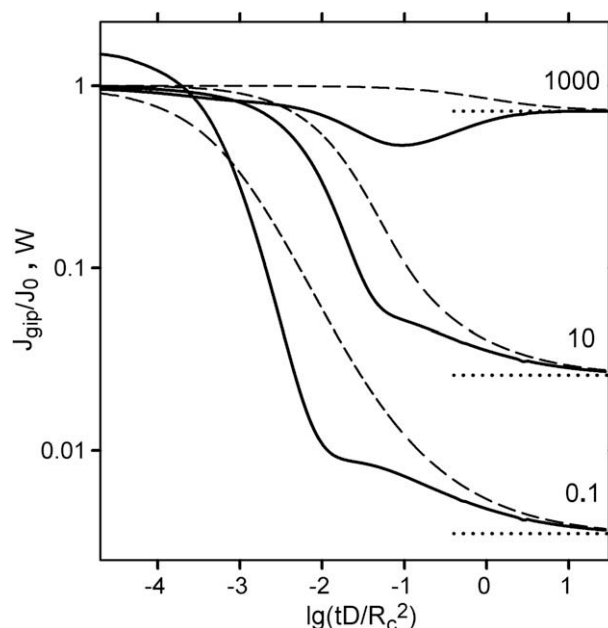


Fig. 3. Time dependence of the reduced current J_{gip}/J_0 (solid curves) and survival probability (dashed curves) calculated for the geminate ion pair generated at $t = 0$ in 1,2-dichloroethane. The numbers near curves are the values of $4\pi DR_c/\sigma$. The parameters used were $a = 0.9$ nm, $b = 0.3$ nm and $c = 0.1$. The horizontal dotted lines show the level of the dissociation probability $q = q_0(1 + c/2)$.

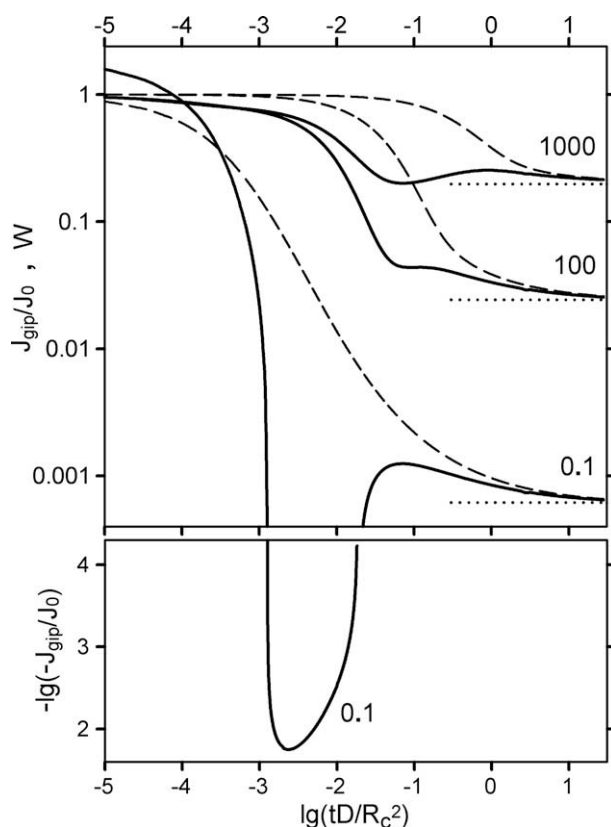


Fig. 4. Time dependence of the reduced current J_{gip}/J_0 (solid curves) and survival probability (dashed curves) calculated for the geminate ion pair generated at $t = 0$ in tetrahydrofuran. The numbers near curves are the values of $4\pi DR_c/\sigma$. The parameters used were $a = 0.9$ nm, $b = 0.3$ nm and $c = 0.1$. The horizontal dotted lines show the level of the dissociation probability $q = q_0(1 + c/2)$.

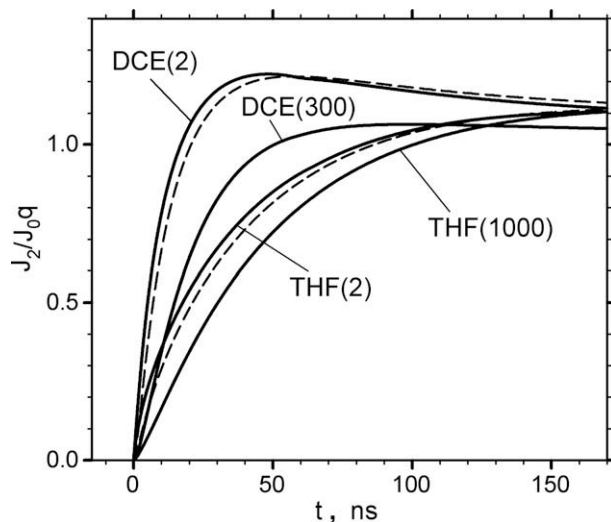


Fig. 5. Time dependence of the J_2 current calculated for two solvents: 1,2-dichloroethane (DCE) and tetrahydrofuran (THF). The exciplex rise time (t_{gen}) used in calculations was 2.4 ns and 1.67 ns for DCE and THF, respectively. The solid curves were obtained by using the Smoluchowski equation. The parameters used were $a = 0.9$ nm, $b = 0.3$ nm, $c = 0.1$. Numbers in brackets are the values of $4\pi DR_c/\sigma$. Other parameters used were taken from Table 1. The dashed curves were calculated by Eqs. (21)–(24). The parameters used were $q = 0.01$, $\alpha = 0.5$, $\beta = 2.728$ for DCE and $\beta = 2.767$ for THF.

which is caused by the bulk ion recombination with ions of other photogenerated ion pairs and with “intrinsic” ions responsible for

conductivity of the sample in the dark. So, as well as in [24], we consider only a rise of the J_2 current at $t < t^{max}$ and define the exponential rise time t_{632} by the condition

$$J_2(t_{632}) = [1 - \exp(-1)] \times J^{max} = 0.6321 \times J^{max} \quad (18)$$

Comparison of the curves $J_2(t)$ in Fig. 5 with the exponential function $[1 - \exp(-t/t_{fluor})] \times J^{max}$ demonstrates that $t_{632} < t_{fluor}$ at $4\pi DR_c/\sigma < 10$.

The purpose of the present work is to clarify a possibility to choose the intrinsic recombination constant σ so that the calculated rise time t_{632} is equal to the experimental rise time of photocurrent. To clear up the question, the t_{632} time has been plotted against the parameter $4\pi DR_c/\sigma$ over a wide range of $4\pi DR_c/\sigma$. The results obtained are shown in Fig. 6. For every solvent, we have used the exciplex life-time and diffusion separation time of ion pairs given in Table 1. The exciplex rise times have not been measured. They were estimated with the formula $t_{gen} = (k_{01}C_A)^{-1}$ assuming that the rate constant k_{01} of exciplex formation is limited by diffusion, that is $k_{01} = 4\pi D_{mol}a_{ex}$ where a_{ex} is the reaction radius, and D_{mol} is the sum of the diffusion coefficients of acceptor and do-

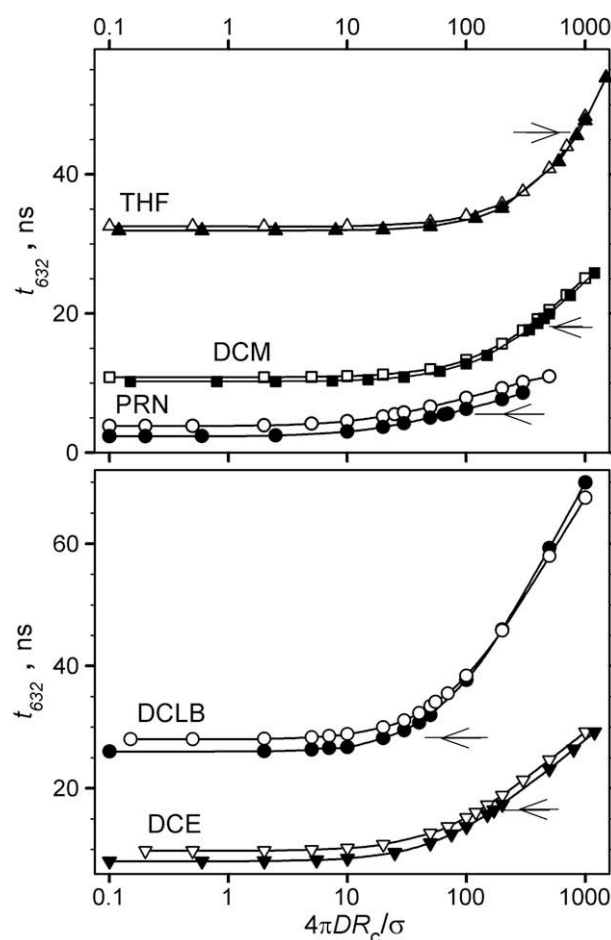


Fig. 6. The rise time of the J_2 current as a function of the parameter $4\pi DR_c/\sigma$ obtained for the following solvents: tetrahydrofuran (THF), dichloromethane (DCM), pyridine (PRN), o-dichlorobenzene (DCLB) and 1,2-dichloroethane (DCE). The parameters used for calculations were $a = 0.9$ nm, $b = 0.3$ nm and $c = 0.1$. The following exciplex rise times were used. Case of THF: $t_{gen} = 1.67$ ns (open triangles) and $t_{gen} = 1$ ns (black triangles). Case of DCM: $t_{gen} = 1.27$ ns (open squares) and $t_{gen} = 0.7$ ns (black squares). Case of PRN: 2.32 ns (open circles) and 1 ns (black circles). Case of DCLB: $t_{gen} = 6.8$ ns. Case of DCE: 2.4 ns (open triangles) and 1 ns (black triangles). Other parameters used were taken from Table 1. In the case of DCLB, the time R_c^2/D was 33.92 ns (open circles) and 42 ns (black circles). The horizontal arrows indicate the levels of the experimentally determined photocurrent rise times t_{rise} .

nor molecules (we assume that $D_{\text{mol}} = D$). The exciplex rise times estimated at $a_{\text{ex}} = 0.7$ nm are presented in Table 1.

It should be noted that the photocurrent rise times plotted in Fig. 6 are practically independent of the parameter b of the initial distribution function. Calculations have shown that the time t_{632} remains unchanged with an accuracy of 0.05 ns as the width of the initial distribution function $f_0(r)$ increases from $b = 0.1$ nm to $b = 0.5$ nm.

As can be seen from Fig. 6, at $\sigma \rightarrow \infty$ the t_{632} time tends to a limiting value t_{632}^{min} which is distinctly less than t_{fluor} . The minimum rise time t_{632}^{min} depends mainly on t_{fluor} and R_c^2/D , but it is practically independent of the initial distribution function. As discussed in the next section, existence of the minimum photocurrent rise time is caused by the fact that for sufficiently fast rates of geminate recombination the decay kinetics of the displacement current at $t > (0.01 - 0.1) \times R_c^2/D$ becomes independent of σ and other parameters of the model. Fig. 6 demonstrates that at $4\pi DR_c/\sigma < 10$, when the charge recombination is fast, the photoconductivity rise time is rather close to t_{632}^{min} and weakly depends on σ . The t_{632} time increases with decreasing parameter σ .

Fig. 6 shows that for the solvents DCE, DCM and THF the experimental photocurrent rise time is longer than t_{632}^{min} . This implies that geminate recombination is rather slow. In this case, as Fig. 6 demonstrates, the value of $4\pi DR_c/\sigma$ at which t_{632} is equal to t_{rise} can be determined well. The obtained values of $4\pi DR_c/\sigma$ at which t_{632} coincides with t_{rise} are presented in Table 1. As to the *o*-dichlorobenzene solutions, the time t_{632}^{min} obtained at $R_c^2/D = 33.92$ ns coincides practically with the photocurrent rise time $t_{\text{rise}} = 28.3 \pm 1.5$ ns observed for that solvent. This implies that recombination is fast, and $4\pi DR_c/\sigma < 30$. In this case, more exact measurements of the photocurrent rise time, the exciplex rise time and diffusion coefficients of the ions are required to obtain the recombination rate constant. In order to illustrate the influence of R_c^2/D on the obtained value of σ , the time t_{632} found for the DCLB solvent is plotted in Fig. 6 for two values of the diffusion separation time: $R_c^2/D = 33.92$ ns and $R_c^2/D = 42$ ns. The former value was calculated for the sum of the ion diffusion coefficients 0.927×10^{-5} cm²/s obtained as described above. The use of the latter value of 42 ns, as Fig. 6 demonstrates, makes it possible to determine $4\pi DR_c/\sigma$, although the difference between 33.9 ns and 42 ns corresponds to a decrease in the value of D only by 25%. The recombination constants σ obtained are presented in Table 2. As Table 2 demonstrates, the value of σ increases with increasing polarity of solvent.

To estimate the effect of the exciplex rise time on the value of $4\pi DR_c/\sigma$ found, the times t_{632} were plotted in Fig. 6, for comparison, for two values of t_{gen} . For tetrahydrofuran solutions where

$t_{\text{fluor}} = 56.2$ ns $\gg t_{\text{gen}}$, a formal change in t_{gen} of about 1 ns leads to insignificant change of t_{632} , so that the obtained value of $4\pi DR_c/\sigma$ increases from 130 to about 180 as t_{gen} decreases from 1.67 ns to 1 ns. Similar results were obtained for the solutions in DCM, DCLB and DCE. As to pyridine solutions, the time $t_{\text{gen}} = 2.32$ ns estimated at $a_{\text{ex}} = 0.7$ nm is rather close to the exciplex fluorescence decay time $t_{\text{fluor}} = 5.7$ ns. In this case, as seen from Fig. 6, the formal decrease of t_{gen} from 2.32 ns to 1 ns leads to an increase of the obtained value of $4\pi DR_c/\sigma$ from about 25 to 65. Thus, for the pyridine solutions, the measurements of t_{gen} are required to obtain an accurate value of σ .

The results presented in Figs. 2–6 were obtained at the recombination radius $a = 0.9$ nm. Table 3 shows the effect of the value of a on the calculated rise time of photocurrent. As seen from Table 3, in the case of fast recombination, when $4\pi DR_c/\sigma < 10$, the influence of the recombination radius on t_{632} is insignificant while at $4\pi DR_c/\sigma \gg 100$ uncertainty in the recombination radius of 0.1–0.2 nm can introduce an error into the rise time of the order of few nanoseconds.

The results obtained demonstrate that knowledge of the ion mobilities and the exciplex concentration time profile is required to derive the parameter σ from the experimental photocurrent rise time, especially in the case of fast ionic recombination when t_{rise} is markedly less than the exciplex life time. The exciplex time profile $u(t)$ can be found from the time resolved fluorescence measurements by using the single photon counting technique. As to an ionic mobility, for non-polar solvents the mobility of aromatic ions has been measured by using the time-of-flight conductivity method [36,37] and the method of the time-resolved electric field effect in recombination fluorescence [38–41]. For polar solvents, diffusion coefficients can be determined by the electrochemical methods [42,43]. However, direct measurements of the mobility of the pyrene and DCNB ions in moderately polar solvents have not been carried out yet.

5. Discussion

5.1. Conductivity kinetics of geminate radical ion pairs

As indicated above, kinetics of the transient photocurrents caused by dissociation of exciplexes is determined by the time dependence of the geminate ion current at times $t > 0.1$ –1 ns corresponding to the dimensionless time interval $tD/R_c^2 > 0.01$ –0.1 for $R_c^2/D \approx 10$ ns. However, the theory of geminate recombination in the external electric field [31] cannot predict the time dependence of $f(r, \theta, t)$ and J_{gip} for the most interesting intermediate time interval between $(0.01 - 0.1) \times R_c^2/D$ and $10 \times R_c^2/D$. In addition, since $J_{\text{gip}}/J_0 \rightarrow q$ at sufficiently long times, knowledge of the escape probability (q) of radical ion pairs in the electric field is of importance for analysis of the photocurrent kinetics. The electric field dependent escape probability of geminate charges in non-polar media is customarily found in the Onsager model [44] which may be inapplicable to polar liquids where finite reactivity of the recombining geminate ions on the recombination sphere can limit the Onsager approach.

Onsager [44] has found an analytical expression for the probability $y(r, \theta, E)$ for a single ion pair with the initial distance r and angle θ to escape geminate recombination in the electric field E . Basing on the Onsager result, many authors [45–47] have shown that at $c = eER_c/k_B T \ll 1$ and $r \ll R_c$ the electric field dependence of escape probability $y(r, E)$ averaged over θ takes the form $y \approx (1 + c/2)\exp(-R_c/r)$ and therefore, at low electric fields the average dissociation probability of geminate ion pairs with an isotropic initial distribution $f_0(r)$ is approximated by the relationship $q \approx q_0(1 + c/2)$ where q_0 is the Onsager dissociation probability in the absence of an electric field given by

Table 2

The recombination rate constants (σ) derived from the photocurrent traces, the rate constants (k_{et}) of the return electron transfer estimated as $k_{\text{et}} = \sigma/\Delta v$, the solvent component of the reorganization energy (λ_s), and free energy (ΔG_{et}) of the return transfer of the electron from A^- to D^+ . The values of ΔG_{et} and λ_s were calculated by Eq. (26) and Eq. (29), respectively, at $r = 0.9$ nm, and $r_D = r_A = 0.3$ nm. The solvents are pyridine (PRN), 1,2-dichloroethane (DCE), *o*-dichlorobenzene (DCLB), dichloromethane (DCM), and tetrahydrofuran (THF). Numbers in brackets are static dielectric constants at 298 K [25].

Solvent	σ (10^{-12} cm ³ /s)	k_{et} (10^8 1/s)	λ_s (eV)	$-\Delta G_{\text{et}}$ (eV)
PRN ($\epsilon_{\text{st}} = 12.99$)	3.05	12.1	1.354	2.955
DCE ($\epsilon_{\text{st}} = 10.19$)	0.85	3.37	1.286	3.023
DCLB ($\epsilon_{\text{st}} = 10.0$)	$>2.2^a$ 2.6 ± 1.5^b	$>8.6^a$ 10.3 ± 6^b	1.28	3.029
DCM ($\epsilon_{\text{st}} = 8.93$)	0.7	2.78	1.242	3.067
THF ($\epsilon_{\text{st}} = 7.44$)	0.31	1.23	1.17	3.139

^a the diffusion separation time $R_c^2/D = 33.92$ ns was used to find σ .

^b the time $R_c^2/D = 42$ ns was used.

Table 3

The rise times (t_{632}) of the displacement current calculated at different recombination radii. The solvents are 1,2-dichloroethane (DCE) and tetrahydrofuran (THF). The parameters used for calculations were $b = 0.3$ nm and $c = 0.1$. The exciplex rise time used was $t_{gen} = 2.4$ ns and $t_{gen} = 1.67$ ns for DCE and THF, respectively. Other parameters used are given in Table 1.

Solvent	$4\pi DR_c/\sigma$	t_{632} (ns)		
		At $a = 0.8$ nm	At $a = 0.9$ nm	At $a = 1.1$ nm
DCE	0.5	9.74 ns	9.79 ns	9.91 ns
	10	9.9	10.24	11.25
	100	13.0	15.24	19.35
	500	21.64	24.6	27.5
THF	0.5	32.47	32.53	32.65
	10	32.47	32.57	33.0
	100	33.04	34.0	37.95
	500	36.5	40.9	52.8

$$q_0 = 4\pi \int_0^\infty r^2 f_0(r) \exp(-R_c/r) dr \quad (19)$$

Thus, for low electric fields, Eq. (17) can be obtained in the Onsager model. It should be noted that the Eqs. (17) and (19) describe well experimental data on free ion yields in non-polar liquids and solids, including organic crystals and polymeric photoconductors [48]. However, in the approach of Onsager [44], it is assumed that the recombination radius is infinitesimally small, i.e. $a = 0$. By analogy with the Onsager model, we assume that for weakly polar solvents and finite recombination radius, the electric field dependence of q at $c \ll 1$ may be also approximated by Eq. (17) for all recombination parameters σ where q_0 is determined by Eq. (14). Such an assumption agrees with the electric field dependence of the dissociation constant K of weak electrolytes [49] which takes the similar form $K(E)/K(0) \approx 1 + c/2$ at low electric fields. As seen from Figs. 3 and 4, at long times the calculated values of W and J_{gip}/J_0 do approach the q probability found from Eqs. (14) and (17). Nevertheless, analytical expressions for the electric field dependence of q and $y(r, \theta, E)$ for the case of finite recombination rate constants σ on the recombination sphere of a finite radius still remain to be found.

Numerical methods for solving the Smoluchowski equation with the joint Coulomb and external fields by a differential-difference approximation have been developed [50–53]. Some peculiarities of kinetics of the J_{gip} current are discussed in Appendix B. Below we discuss the obtained dependence of t_{632} on σ . At $4\pi DR_c/\sigma < 10$ the photocurrent rise time, as seen from Fig. 6, weakly depends on the value of σ . The existence of the minimum photocurrent rise time corresponding to the limiting case of the infinitely fast geminate recombination can be explained as follows.

As seen from Figs. 3 and 4, the decay of the geminate ion current is not described by a simple function. At $t > 0.001 \times R_c^2/D$, the value of J_{gip}/J_0 is less than W . This is caused, as noted previously [24,50,51], by electric polarization of the spatial distribution of geminate ions in the electric field resulting in a non-monotonic time dependence of the average electric field acting on geminate ions (see Appendix B). Figs. 3 and 4 demonstrate that under certain conditions (at small values of a/R_c and $4\pi DR_c/\sigma$) it may be that the time dependence of J_{gip} has a depression in a certain time interval which looks like a local minimum. Moreover, as seen from Fig. 4, under certain conditions the current can be even negative at certain times. (Negative currents have been obtained by many authors [50–52].) However, at $4\pi DR_c/\sigma < 20$, the value of J_{gip}/J_0 decreases monotonically with increasing time at $t > 0.1 \times R_c^2/D$ approaching from above the q probability. At long times, the value of $\lg(J_{gip}/J_0q - 1)$ was plotted versus $\lg(tD/R_c^2)$ where q was calculated by Eqs. (17) and (14). The straight line obtained indicates that in the case of fast geminate recombination ($4\pi DR_c/\sigma < 20$), the time dependence of J_{gip} at $t > 0.1 \times R_c^2/D$ may be approximated by the power function $J_{gip}/J_0q = 1 + \beta^{-1}(R_c^2/Dt)^\alpha$ where the obtained parameters are $\alpha \approx 0.5$, $\beta \approx 2.77$ for THF and $\beta \approx 2.73$ for DCE. It

should be emphasized that both α and β are independent practically of σ at $4\pi DR_c/\sigma < 20$. This enables us to understand why the rise time of the J_2 ion current tends to a limiting value at $\sigma \rightarrow \infty$. To estimate the photocurrent rise time at large σ , let us neglect a possible non-monotonic decay of J_{gip} at short times and approximate J_{gip} by the following model function

$$J_{gip}/J_0 = \begin{cases} 1, & \text{at } t < t_0 \\ q \cdot \left[1 + \beta^{-1} \left(\frac{R_c^2}{Dt} \right)^\alpha \right], & \text{at } t > t_0 \end{cases} \quad (20)$$

where the time $t_0 = (R_c^2/D)[q/\beta(1-q)]^{1/\alpha}$ is determined by the condition of continuity of J_{gip} at $t = t_0$. Eq. (20) expresses the current J_{gip} in terms of the q probability which depends on $4\pi DR_c/\sigma$. Substitution of Eq. (20) into Eq. (12) gives

$$J_2/J_0q = C_1(t) + C_2(t) \quad (21)$$

$$C_1 = t_{fluor}^{-1} \int_0^t u(t-t_1) dt_1 \\ = 1 - \frac{t_{fluor}}{t_{fluor} - t_{gen}} \exp\left(\frac{-t}{t_{fluor}}\right) + \frac{t_{gen}}{t_{fluor} - t_{gen}} \exp\left(\frac{-t}{t_{gen}}\right) \quad (22)$$

$$C_2 = t_{fluor}^{-1} \cdot \int_0^t u(t-t_1)G(t_1) dt_1 \quad (23)$$

$$G(t_1) = \begin{cases} (1-q)/q, & \text{at } t_1 < t_0 \\ \beta^{-1} \left(\frac{R_c^2}{D \cdot t_1} \right)^\alpha, & t_1 > t_0 \end{cases} \quad (24)$$

The C_1 function describes the rise of the ion current in the case that exciplexes instantly dissociate into free ions ($R_c^2/D \ll t_{fluor}$, $q = 1$). At $t_{gen} \ll t_{fluor}$, the exponential rise time of C_1 is about $t_{fluor} + t_{gen}$. Since R_c^2/D is comparable to t_{fluor} , the value of C_2 reaches its maximum at a time of the order of R_c^2/D and then tends to zero at $t \rightarrow \infty$. As the result, the rise time of the sum $C_1 + C_2$ is less than t_{fluor} . Fig. 5 demonstrates the time dependence of J_2 calculated by using Eqs. (21)–(24). A numerical analysis shows that at fixed times t_{fluor} , t_{gen} and R_c^2/D , both the shape and the rise time of the J_2 current found from Eqs. (21)–(24) are practically independent of q at $q < 0.2$, and hence independent of σ . Thus, for the case of fast recombination ($4\pi DR_c/\sigma < 10$) the t_{632} time is determined mainly by the power law of the decay of the value of $J_{gip}/J_0q - 1 = \beta^{-1}(R_c^2/Dt)^\alpha$ at sufficiently long times where the degree $\alpha \approx 0.5$ is practically independent of other parameters of the model.

From Eqs. (21)–(24) it follows that the rise time of the J_2 current decreases with increasing the diffusion separation time of ion pairs. (The conclusion is supported by the numerical solution of the Smoluchowski equation.) Thus, the photocurrent rise time cannot be interpreted as the characteristic time of the ion escape from

the Coulomb well which is expected to increase with increasing the R_c^2/D time.

In the other limiting case of the absence of geminate recombination ($\sigma \rightarrow 0$), the rise time of photocurrent would be expected to be longer than the exciplex life time. Such a conclusion is based on the following consideration.

At large values of $4\pi DR_c/\sigma$ the time dependence of J_{gip} differs from that obtained for the case of the fast geminate recombination. Figs. 3 and 4 demonstrate that a rather wide minimum of the function $J_{gip}(t)$ appears at time of the order of $0.1 \times R_c^2/D$ as the recombination rate constant decreases. In particular, for the DCE and PRN solvents the ion pair dissociation probability becomes close to unity at $4\pi DR_c/\sigma > 1000$. In this case, as seen from Fig. 3, the reduced current J_{gip}/J_0 increases with increasing time at $t > 0.1 \times R_c^2/D$ and approaches from below the q value at sufficiently long times. At $\sigma = 0$, the time dependence of J_{gip} is unknown. However, basing on the estimates made in Appendix B, one can concede that at $\sigma = 0$ the geminate ion current is $J_{gip} = J_0$ at $t \rightarrow 0$ and $t \rightarrow \infty$. At times of the order of $0.1 \times R_c^2/D$, the function $J_{gip}(t)$ is thought to have a minimum caused by polarization of the spatial distribution of the ion pairs in the electric field. Thus, we assume that at $\sigma \rightarrow 0$ the function $J_{gip}(t)$ can be written in the limiting form $J_{gip}^{lim}(t) = J_0(1 - H)$ where $H(t)$ is a positive function so that $0 < H < 1$, and $H \rightarrow 0$ at $t \rightarrow 0$ and $t \rightarrow \infty$. Insertion of J_{gip}^{lim} into Eq. (12) gives that $J_2/J_0 = C_1(t) - C_3(t)$ where C_3 is given by

$$C_3 = t_{fluor}^{-1} \cdot \int_0^t u(t - t_1)H(t_1)dt_1 \quad (25)$$

Since the width of the function $H(t)$ is comparable to R_c^2/D and the t_{fluor} time is also comparable to R_c^2/D , the maximum of C_3 lies at time of the order of R_c^2/D . In addition, $C_3 \rightarrow 0$ at $t \rightarrow 0$ and $t \rightarrow \infty$. Thus, the exponential rise time of the difference $C_1 - C_3$ can be even longer than the rise time of C_1 which is approximately equal to $t_{fluor} + t_{gen}$.

As noted above, the rise time of the J_2 photocurrent is independent practically of the parameter b of the initial distribution function in the range between $b = 0.1$ nm and at least $b = 0.5$ nm. This implies that the decay kinetics of J_{gip} at sufficiently long times depends weakly on the initial function $f_0(r)$ if it is narrow. This arises from the fact that at long times a broad part of the function $r^2 f(r, t)/q$ takes an universal form that depends only slightly on $f_0(r)$ [24]. Similar results were obtained previously for non-polar liquids [54,55].

Weak dependence of the charge separation kinetics at long times on the initial distances between ions is explained by the fast diffusion relaxation of initially created ion pairs near the recombination sphere. As noted [56,57], both the time dependence of the survival probability of the inverse power type and its weak dependence on the initial distances between reactants are typical for separation processes. Shushin [56–58] has considered kinetics of the diffusion dissociation of interacting molecules for the general shape of the interaction potential possessing a well and a barrier at small distances. It has been shown that the kinetics of the diffusion escape from a well is exponential at short times and follows a power law at long times [56–58].

5.2. Comparison with other investigations

The increase of the ionic recombination rate constant σ with increasing polarity of solvent testifies that recombination of radical ion pairs occurs mainly by the return transfer of the electron from A^- to its geminate solvent-separated cation D^+ , i.e. $\sigma_{et} > \sigma_c$. It is interesting to compare the obtained values of σ with the rates of the distant electron transfer (ET) reactions for other donor–acceptor systems found from the measurements of quantum yields of free radical ion formation. However, in the present work the values

of σ were obtained in the model of the contact recombination in which recombination of the ions occurs only as the center-to-center distance (r) between ions reaches the recombination radius a . To estimate the ET rate from the value of σ , let us assume that the electron transfer occurs as the inter-ionic distance between ions lies in a narrow layer $a < r < a + \Delta a$ of the width $\Delta a \ll a$. In this case, the ET rate (measured in 1/s) can be evaluated as $k_{et} = \sigma/\Delta v$ where $\Delta v = (4\pi/3) \times [(a + \Delta a)^3 - a^3]$ is the reaction volume. The rate constants $k_{et} = \sigma/\Delta v$ obtained at $\Delta a = 0.2$ nm and $a = 9$ nm are presented in Table 2. (Rather arbitrary width of the reaction layer $\Delta a = 0.2$ nm was used, for simplicity, to estimate k_{et} .) Table 2 shows also the free energy (ΔG_{et}) of the return electron transfer in solvents under investigation calculated by using the Weller equation [4]

$$-\Delta G_{et} = G_{SSRIP} = E_D - E_A - \frac{e^2}{\epsilon_{st}r} + \Delta_\epsilon \quad (26)$$

where G_{SSRIP} is the free energy of formation of the solvent-separated radical ion pair $A^- + D^+$ from the neutral molecules A and D in the ground state, $E_D = 1.2$ eV [2] is the oxidation potential of pyrene as an electron donor, $E_A = -1.64$ eV [2] is the reduction potential of 1,4-dicyanobenzene as an electron acceptor in acetonitrile, and Δ_ϵ is the change of the energy of the radical ions in solvent under study with respect to acetonitrile where E_D and E_A have been measured. The value of Δ_ϵ has been calculated by using a formula [4]

$$\Delta_\epsilon = \frac{e^2}{2} \cdot \left(\frac{1}{r_D} + \frac{1}{r_A} \right) \cdot \left(\frac{1}{\epsilon_{st}} - \frac{1}{\epsilon_{acn}} \right) \quad (27)$$

where $\epsilon_{acn} = 36.6$ is dielectric constant of acetonitrile, r_D and r_A are the Born radii of the ions D^+ and A^- , respectively.

The values of $k_{et} = \sigma/\Delta v = 10^8$ – 10^9 1/s presented in Table 2 are rather close to recombination rates obtained by many investigators [17,18,59–65] for those solvent-separated radical ion pairs for which the return ET energy is also about -3 eV. Fig. 7 demonstrates a plot of k_{et} versus ΔG_{et} for the ion pairs of pyrene cations with DCNB anions obtained in the present work. For comparison, the data on k_{et} for ion pairs of 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA) anions with simple aromatic donor cations in acetonitrile, obtained by Gould, Farid and co-workers [62,63], are also plotted in Fig. 7. In these works, quantum yields of free ion formation were measured by transient optical absorption spectroscopy. Then, the recombination rate constants (k_{et}) were obtained assuming a constant rate of ion separation. Similar results were obtained by several groups [8,9,11,12]. For all the sets of data, the constant k_{et} decreases as the reaction exothermicity ($-\Delta G_{et}$) increases. This is consistent with a Marcus inverted region effect [66]. The theory treats the electron transfer as a radiationless transition and gives the ET rate constant as the product of an electronic matrix element squared (V^2) and a Franck–Condon factor [67–71]

$$k_{et} = \frac{V^2}{h} \left(\frac{\pi}{\lambda_s k_B T} \right)^{1/2} \sum_{n=0}^{\infty} \frac{s^n \exp(-s)}{n!} \exp \left[-\frac{(n \cdot h\nu_v + \Delta G_{et} + \lambda_s)^2}{4\lambda_s k_B T} \right] \quad (28)$$

Here, $s = \lambda_v/h\nu$, h is the Planck constant, λ_s and λ_v are the solvent reorganization energy and the skeletal vibration component of reorganization energy, respectively. It is assumed that the important skeletal vibrations can be approximated by a single average mode with the energy $h\nu = 1500$ cm⁻¹ which is a typical value for carbon–carbon skeletal vibrations. Fig. 7 demonstrates examples of how parameters V and λ_s have been obtained [62,63] by fitting Eq. (28) to a plot of k_{et} versus ΔG_{et} at fixed values of λ_v and $h\nu$ estimated from absorption and emission spectra.

As seen from Fig. 7, for the pyrene/DCNB system under study the curve $k_{et}(\Delta G_{et})$ shows a steeper decline than that of the curves

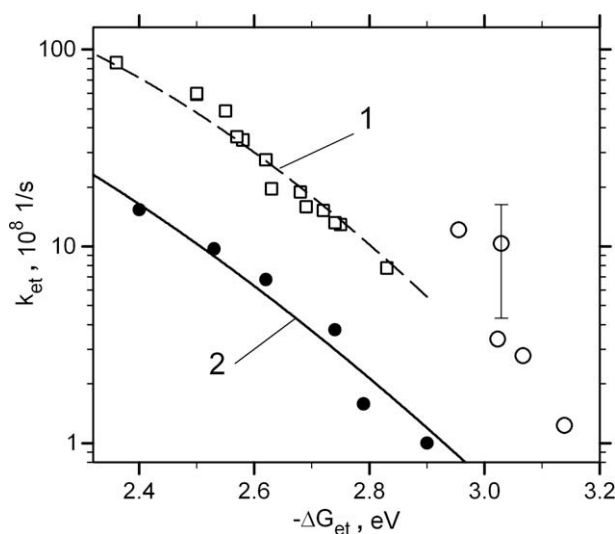


Fig. 7. The return electron transfer rate constant (k_{et}) versus the reaction free energy (ΔG_{et}) for recombining radical ion pairs. Open circles show the values obtained as $k_{et} = \sigma/\Delta\nu$ in the present work for the pair of pyrene cations with DCNB anions in weakly polar solvents (from Table 2). Squares – for ion pairs of DCA and TCA radical anions with “one-ring” donor radical cations in acetonitrile (from Fig. 3 of Ref. [63]). Black circles – for ion pairs of DCA anions with different aromatic donor cations in acetonitrile (from Ref. [62]). The lines 1 and 2 were obtained by Gould et al. [62,63] from Eq. (28). The following parameters were used in calculations. For dashed curve 1: $V = 11.5 \text{ cm}^{-1}$, $h\nu = 1500 \text{ cm}^{-1}$, $\lambda_v = 0.25 \text{ eV}$, $\lambda_s = 1.63 \text{ eV}$ [63]. For solid curve 2: $V = 11 \text{ cm}^{-1}$, $h\nu = 1500 \text{ cm}^{-1}$, $\lambda_v = 0.6 \text{ eV}$, $\lambda_s = 0.9 \text{ eV}$ [62].

obtained for other donor/acceptor pairs. This can be explained by the decrease of the solvent reorganization energy (λ_s) with a decrease in polarity of solvent (Table 2). The values of λ_s were calculated by the following equation [72]

$$\lambda_s = e^2 \left[\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r} \right] \cdot \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{st}} \right) \quad (29)$$

where r is a center-to-center separation between the ions, and ϵ_{opt} is the optical dielectric constant.

For ion pairs of DCNB anions with pyrene cations, the parameters of Eq. (28) are unknown. (It can be shown that the curve $k_{et}(\Delta G_{et})$ is described by Eq. (28) at reasonable parameters when the dependence of λ_s on ϵ_{st} is also considered.) However, Fig. 7 demonstrates that for the pyrene/DCNB system the values of $k_{et} = \sigma/\Delta\nu$ agree with experimentally determined rate constants for other donor/acceptor systems which have been described by the ET theory. This supports the assumption that the geminate pyrene cations and DCNB anions recombine mainly through the return electron transfer.

5.3. Photoconductivity kinetics for different mechanisms of free ion formation

It is now well established that free ion formation in bimolecular photoinduced ET reactions between excited reactants $D^* + A$ (or $D + A^*$) may proceed either by an exciplex mechanism shown in Scheme 1 or by a mechanism shown in Scheme 2. The former mechanism was proposed by Weller [3,4,73] and widely used for interpretation of data on fluorescence quenching and free ion formation in exciplex systems.

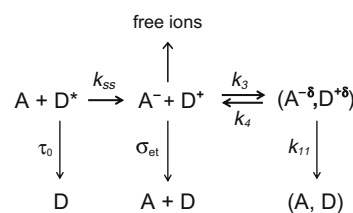
In the reaction scheme shown in Scheme 2, the initially created solvent-separated ion pairs $A^- + D^+$ can turn into exciplexes with rate constant k_3 or disappear due to the return electron transfer. (For the sake of simplicity, the transition complex $(A^{\dots}D^+)_{TS}$, an intermediate in the reactions of exciplex formation and dissocia-

tion, is not shown in Scheme 2.) For $k_3 = 0$, the reaction scheme, like that presented in Scheme 2, has been used by Rehm and Weller [2] to analyze fluorescence quenching rate constants in the acetonitrile solutions. It should be noted that the general reaction scheme of free ion formation, suggested by Weller [3,4] and used by many authors [8,64,74], comprises two parallel ET quenching pathways described by Schemes 1 and 2.

Charge recombination in solvent-separated ion pairs and in contact ion pairs (exciplexes) differs by degree of the electronic coupling between reactants. Gould, Farid and co-workers [8,64,74] have found that the electronic matrix element V for the return ET within exciplexes, formed from the DCA and TCA anions with cations of simple aromatic hydrocarbon donors, is almost two orders of magnitude higher than that for the solvent-separated ion pairs, and the solvent reorganization energy for the return ET in exciplexes is about 1 eV lower than that of separated ion pairs. Mataga and co-workers [9,75,76] have found the non-Marcus (exponential) energy gap dependence of the recombination rate for contact ion pairs produced by excitation of charge transfer (CT) complexes. For solvent-separated radical ion pairs generated by encounters in bimolecular fluorescence quenching reactions, a bell-shaped free energy gap law was observed which was discussed in terms of the Marcus theory of ET [9,75]. To account for the lack of the normal region of recombination in contact ion pairs, Tachiya and Murata [77] have considered non-equilibrium dynamics and proposed a mechanism based on an interplay between ET and solvent relaxation.

Although most data on the recombination rates of ion pair states are obtained, as mentioned above, from the time-resolved extinction and emission measurements and from other time-resolved techniques [9,11,12], the photoconductivity method can furnish additional information on significant details and parameters that control charge separation. From the view-point of conductivity measurements, the main distinction between two pathways of the bimolecular ET quenching reactions discussed above is that for Scheme 2 the primary product of the ET quenching is a pair of mobile ions $A^- + D^+$ while in Scheme 1, there is a long-lived precursor of the mobile ions, an exciplex. Therefore, the transient photocurrent measurements can distinguish between these mechanisms of photo-ionization. In particular, for Scheme 2 the rise time of photocurrent is expected to be very short ($<1 \text{ ns}$) at sufficiently large quencher concentrations because the solvent-separated ions $A^- + D^+$ contribute to the photoconductivity signal immediately after their generation, without a delay, as if they were free. As to Scheme 1, the rise time of the ion component of photocurrent is much longer because it is determined, as shown in the present work and in the work [24], by the exciplex life-time and by the diffusion separation time R_c^2/D of ion pairs. Such a conclusion about a photocurrent rise time for Scheme 2 is confirmed by the following arguments.

Let us consider the case of the fast quenching of photoexcited electron donor molecules D^* by acceptor A in a bimolecular fluorescence quenching reaction with the diffusion-controlled Stern–Volmer quenching rate constant $k_{qu} \approx 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in solvent with



Scheme 2.

viscosity $\eta \approx 1$ cP. We assume first that free ion formation occurs in accordance with Scheme 2, i.e. the transfer of the electron from D^+ to A leads directly to the solvent-separated ion pair $A^- + D^+$. The time dependence of photocurrent (J) induced by a short light pulse at $t = 0$ is given by [24]

$$J = \int_0^t g(t') J_{gip}^{ss}(t - t') dt' = \int_0^t g(t - t_1) J_{gip}^{ss}(t_1) dt_1 \quad (30)$$

where $g(t')dt'$ is the number of geminate ion pairs $A^- + D^+$ generated in the time interval $(t', t' + dt')$, and $J_{gip}^{ss}(t_1)$ is the current of the geminate ion pair generated at $t_1 = 0$. Neglecting the transient effect in the fluorescence quenching, $g(t')$ may be approximated by the simple exponential function $g(t') = N_0 k_{ss} C_A \exp(-k_{qu} C_A t')$ where k_{ss} is the rate constant of the solvent-separated ion pair formation in Scheme 2. If an infinitely high energy barrier of exciplex formation from the solvent-separated ions exists (i.e. $k_3 = 0$ in Scheme 2), the time dependence of J_{gip}^{ss} is similar to that of J_{gip} shown in Figs. 3 and 4. The current J_{gip}^{ss} depends on the initial distribution function $f_{qu}(r)$ over the electron transfer distances which is different from the trial function given by Eq. (13). However, at $t > (0.01 - 0.1) \times R_c^2/D$, as noted [24], the current J_{gip}^{ss} depends only slightly on $f_{qu}(r)$ and drops on the nanosecond scale down to the free ion current with the characteristic decay time of the order of R_c^2/D as shown in Figs. 3 and 4. One would expect that the convolution of J_{gip}^{ss} with a smooth function $g(t')$ in Eq. (30) will average a possible non-monotonic decay of J_{gip}^{ss} at short times. Thus, for $k_3 = 0$, $C_A = 0.1$ M and $q \ll 1$, the time profile of the J photocurrent, as seen from Eq. (30) and Figs. 3 and 4, is the peak with a duration of the order of the quenching time $(k_{qu} C_A)^{-1} \approx 1$ ns followed by smooth decay down to the free ion current $J_0 q$ with the characteristic decay time of the order of R_c^2/D . (Such a time profile of photocurrent induced by photogeneration of geminate electron–cation pairs with nanosecond laser pulses was observed in non-polar solvents [50].) It should be noted that the photocurrent rise time is thought to be also of the order of $(k_{qu} C_A)^{-1} \approx 1$ ns at $C_A = 0.1$ M even if the escape probability q is close to unity because $J_{gip} \approx J_0$ at short times as Figs. 3 and 4 show.

If the ion pairs $A^- + D^+$, initially produced in Scheme 2, collapse in the course of their desolvation and form exciplexes, the calculation of J_{gip}^{ss} is a challenging task. In this case, exciplexes play a role of a “trap” for mobile charge carriers A^- and D^+ . The time dependence of J_{gip}^{ss} will be determined by the rate constants of all elemental processes shown in Scheme 2. The dissociation probability (q) of the ion pair $A^- + D^+$ and, hence, free ion current will depend not only on the initial distribution $f_{qu}(r)$, but also on the rate constants k_3 , k_4 and on the exciplex life time. Little experimental data on the rate constants k_3 and k_4 have been reported. For 1,2,4,5-tetracyanobenzene as the electron acceptor and *p*-xylene as the donor, rate constants k_3 and k_4 were found to be of the order of 10^9 s $^{-1}$ in different solvents with dielectric constants in the range between 7 and 25 [28]. It should be noted that even if the reaction $A^- + D^+ \rightarrow (A^{\cdot-}, D^{\cdot+})$ has no an energy barrier, exciplex formation from the solvent-separated ions in Scheme 2 takes a finite time because the solvent-separated ions must approach each other and change their orientation to form the sandwich configuration. Thus, the lower boundary of k_3^{-1} can be estimated crudely as a rotational reorientation time (t_{rot}) of ions, i.e. $k_3^{-1} > t_{rot}$. (For plane aromatic molecules and radical ions that have three or four aromatic rings, the time t_{rot} is about 0.2–0.3 ns in solvents of viscosity of 1 cP [23,78,79]). Let us assume, for the sake of definiteness, that the parameters of Scheme 2 are $k_3^{-1} = 1$ ns, $R_c^2/D = 10$ ns, and exciplex life time is of the order of 10 ns. The time $k_3^{-1} = 1$ ns corresponds to the dimensionless time $k_3^{-1} D/R_c^2 = 0.1$ in the diffusion model (Figs. 3 and 4). At $t \ll k_3^{-1}$, the main channel of decay of the ions $A^- + D^+$ is recombination due to the return transfer of the electron from A^- to D^+ . Because of this, the time dependence of J_{gip}^{ss} at short times $t < 0.001 \times R_c^2/D$ is close

to that of J_{gip} shown in Figs. 3 and 4. Therefore, at $t < 1$ ns, the current $J_{gip}^{ss}(t)$ is thought to decrease with increasing time from the initial value $J_{gip}^{ss} \approx J_0$ at $t = 0$ down to a lower value at $t \approx 1/k_3$. Then, J_{gip}^{ss} tends to a free ion current at sufficiently long times. From Eq. (30) it follows that the rise time of the J photocurrent will be of the order of the quenching time $(k_{qu} C_A)^{-1}$ or even less than $(k_{qu} C_A)^{-1}$ if the free ion current is far less than J_0 . This implies that Scheme 2 predicts rather short photocurrent rise time of the order of $(k_{qu} C_A)^{-1} \approx 1$ ns at $C_A \approx 0.1$ M and $k_{qu} \approx 10^{10}$ M $^{-1}$ s $^{-1}$.

Thus, Scheme 2 cannot explain a rise of photocurrent with the characteristic rise time 10–40 ns [15,20,21] observed after the completion of the quenching of excited states because in Scheme 2 there is no a long-lived immobile precursor of the ions. In addition, for Scheme 2 the photocurrent rise time t_{rise} is expected to decrease with increasing the quencher concentration. This is inconsistent with the increase of the t_{rise} time with increasing concentration of the fluorescence quencher observed for the pyrene/*N,N*-dimethylaniline system in the pyridine solutions [15] where *N,N*-dimethylaniline was the pyrene fluorescence quencher.

On the other hand, for Scheme 1 the ion component of photocurrent caused by dissociation of exciplexes rises after the completion of the ET quenching with the characteristic rise time comparable to the exciplex life time. The increase of the photocurrent rise time with increasing concentration of the fluorescence quencher [15] is naturally explained in the framework of Scheme 1 by the increase of the exciplex life time due to the shift of the equilibrium between excited reactants $A^* + D$ (or $A + D^*$) and exciplexes to the right.

Such a semi-quantitative consideration of the photoconductivity kinetics shows that the time dependence of photocurrent for Scheme 1 is different from that presumed for Scheme 2. In this connection it is worth while mentioning the results of the study of exciplex formation in photoinduced reactions of TCA * and DCA * used as the excited electron acceptors with the alkyl-substituted benzene donors in different solvents [8,63,64,74]. Gould et al. [64,74] have concluded that the efficiency with which exciplexes are formed in the bimolecular ET reactions of TCA * and DCA * with electron donors is unity for most of the acceptor/donor/solvent systems studied. However, the high efficiency of exciplex formation can be attained, as mentioned [74], not only in Scheme 1, but also in Scheme 2, if the rate k_3 of exciplex formation from the solvent-separated ions $A^- + D^+$ is much larger than the rates of the solvent-separated ion pair dissociation and recombination. In this case, the photoconductivity technique, together with optical absorption and fluorescence measurements, could distinguish between two possible mechanisms of exciplex formation.

The results obtained demonstrate that the kinetics of transient photocurrents observed for the pyrene/DCNB system in moderately polar solvents, as well as for the DCA/durene system [24], is in good agreement with the exciplex mechanism of photoionization shown in Scheme 1. The build-up of photocurrent observed after the completion of the fluorescence quenching is a good indicator of the existence of a long-lived precursor of ions, an exciplex, even if the photocurrent rise time is markedly shorter than the exciplex life time.

The approximation of the contact recombination used in the present work is convenient for investigation of the photoconductivity kinetics because the recombination rate is determined by only one parameter σ . The present-day theory of photochemical charge separation takes into account both the diffusion motion of ions and their distant recombination due to a remote transfer of the electron from A^- to D^+ at large distances between the ions [10,29,80]. It is based on the assumption that the distance r_{max} at which k_{et} is a maximum can be larger than the distance of the closest approach of the ions. If $r_{max} > a$, the photocurrent kinetics will depend on several parameters which determine the function $k_{et}(r)$ as Eq. (28) suggests. However, in this case, the main peculiarities of

the geminate ion pair current kinetics remain as described above for the case of the contact recombination. In particular, at short times the current J_{gip} is expected to be equal to J_0 , and at sufficiently long times the value of J_{gip} will tend to the free ion current J_{0q} . The point is that at times $t > 0.1 \times R_c^2/D$, the spatial distribution of geminate charges becomes broad with the characteristic width of the order of (or larger than) the Onsager length which is much more than r_{max} . On the other hand, a consideration of the distant recombination of the ion pair $A^- + D^+$ will attenuate the dependence of the photocurrent rise time on the recombination radius (Table 3). However, for the case of a distant geminate recombination, even a determination of the escape probability in the external electric field is a challenging task which includes rather complex calculations [80].

6. Conclusions

- (1) A new experimental approach to determination of the recombination rate of geminate radical ion pairs in moderately polar liquids is suggested in the case that the ion pairs are generated due to photoinduced ET reactions. The method is based on the fact that the time dependence of the geminate charge displacement current is sensitive to the rate of geminate recombination. Kinetics of transient photocurrents caused by ion generation following a short light pulse has been analyzed in the framework of the exciplex mechanism of photo ionization. Effect of the ionic recombination rate on the photocurrent kinetics has been studied over a wide range of the intrinsic recombination rate constant (σ) of geminate ions. It has been shown that parameter σ can be derived from the photocurrent rise time. For the pyrene/*p*-dicynobenzene exciplex system the found value of σ is $3.05 \times 10^{-12} \text{ cm}^3/\text{s}$, 0.85×10^{-12} , $(2.6 \pm 1.5) \times 10^{-12}$, 0.7×10^{-12} , and $0.31 \times 10^{-12} \text{ cm}^3/\text{s}$ for the solutions in pyridine, 1,2-dichloroethane, *o*-dichlorobenzene, dichloromethane, and tetrahydrofuran, respectively. The results obtained demonstrate that the transient photoconductivity technique in combination with the time resolved fluorescence measurements allows one to determine the recombination constant σ for weakly polar solvents.
- (2) The rise of photocurrent observed for the solutions of pyrene and DCNB after a short light pulse agrees well with the reaction scheme in which exciplexes are assumed to be an immobile precursor of the ions (Scheme 1). As to the photocurrent rise time, it may be close to the exciplex life time or markedly shorter than it depending on the geminate recombination rate. Thus, the photoconductivity technique allows one to distinguish between two possible mechanisms of ion generation in exciplex systems: (j) initial formation of exciplexes, as the primary product of ET reactions, followed by dissociation of exciplexes into ions (Scheme 1), and (jj) the direct transfer of the electron in the encounter complex $A + D^*$ (or $A^* + D$) and formation of solvent-separated radical ion pairs $A^- + D^+$ as the primary product of ET reactions (Scheme 2). In particular, observation of the photocurrent rise after a photoexcitation pulse is a good indicator of ion generation through mechanism (j), and a measurement of the photocurrent rise time enables one to determine the recombination rate of radical ion pairs.

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Appendix A

We consider below parameters of a finite difference scheme used in the present study for the numerical solution of the Smoluchowski equation.

The probability density $f(r, \theta, t)$ was found at $a < r < R$ where radius R of the external sphere was chosen so large that the value of f obtained was independent practically of the further increase of R . The dimensionless variables $x = r/R_c$ and $\tau = tD/R_c^2$ have been used which are natural for the Smoluchowski equation.

The main difficulty of the numerical solution is that at small values of r within a narrow layer near the recombination radius the probability density is a rapidly changing function of inter-ionic distance r . The distribution function $f(r, \theta, t)$ rises sharply with increasing r in the vicinity of the recombination sphere $r = a$, if geminate recombination is fast ($\sigma \gg 4\pi DR_c$), but the function f decays sharply with increasing r , if recombination is slow ($\sigma \ll 4\pi DR_c$). The point is that for weakly polar solvents the width of the layer in which the gradient of $f(r, \theta, t)$ is large is of the order of $\Delta r = a^2/R_c$ that is far less than recombination radius a . On the other hand, in the course of the evolution of $f(r, \theta, t)$ a broad part of the spatial distribution with a width of the order of $(4Dt)^{1/2}$ appears due to a diffusion escape of ions from the Coulomb well. So, to create algebraic equations corresponding to the original differential equation, we have chosen a discrete set of points x_n ($n = 1, 2, \dots, k$) forming a space grid in the range between $x_1 = a/R_c$ (at $n = 1$) and $x_k = R/R_c$ ($n = k$). To take into account both a sharp change of $f(x, \theta, \tau)$ at small values of x near x_1 and a broad part of $f(x, \theta, \tau)$ which appears at $\tau > 0.001$, the entire region $x_1 < x < x_k$ was divided into two intervals: Interval 1 in which $x_1 < x < x_{mod}$, and Interval 2 in which $x_{mod} < x < x_k$ where $x_{mod} \approx 0.5$ – 0.6 and $x_k > 0.8$ – 0.9 . For Interval 1, the space step between adjacent grid points $\Delta x_n = x_{n+1} - x_n$ was independent of time, but was dependent on x_n . The value of Δx_n increased with increasing x_n from $\Delta x_1 \approx 0.01 \times a^2/R_c^2$ at $n = 1$ up to the value of $\Delta x_n = 0.2 \times a^2/R_c^2$ as x_n approached the right boundary $x = x_{mod}$ of Interval 1. For Interval 2, the space step $\Delta x_n = \Delta x$ was independent of x_n , but dependent on time. For Interval 2, both radius R of the external sphere and step Δx increased with increasing time from the values of $R \approx (0.8$ – $0.9) \times R_c$ and $\Delta x \approx 0.0005$ at time $\tau = 0$ up to the values of $R \approx 40 \times R_c$ and $\Delta x \approx 0.025$ at $\tau = 30$. A set of algebraic equations obtained by using finite differences in place of the derivatives $\partial f/\partial x$ and $\partial f/\partial \theta$ in the original equation was solved by a numerical method, similar to that described in [81]. In addition to Eq. (9), the other boundary condition used in calculations was $\partial f/\partial \theta = 0$ at $\theta = 0$ and $\theta = \pi$.

The criterion for the correctness of the function $f(r, \theta, t)$ obtained was that in the course of evolution of $f(r, \theta, t)$ the relationship $dW/dt = -(S_a + S_R)$ was good to 0.01% at $\tau = tD/R_c^2 = 1$ and to about 1% at $\tau = 10$. Here, S_a and S_R are the fluxes of the probability through the spheres of radius $r = a$ and $r = R$, respectively ($S_R \ll S_a$). The other criterion for the computer program used was that at $E = 0$ the condition

$$4\pi \int_a^\infty r^2 f(r) dr = q_0 \quad (\text{A-1})$$

was met for all times where q_0 was given by Eq. (14). The third criterion was that the geminate ion current, obtained as $J_{gip} = L^{-1} dP_{gip}/dt$, was equal to the right hand side of Eq. (B.9) in Appendix B. In addition, the correctness of calculations has been supported by the fact that at sufficiently long times both W and J_{gip}/J_0 approach the escape probability q calculated by Eq. (17) (see Figs. 3 and 4).

Appendix B

We consider below the effect of the recombination parameter σ on the behavior of the displacement current of geminate ion pairs at sufficiently short and sufficiently long times.

By using the Smoluchowski equation, the displacement current, caused by generation of a single ion pair between electrodes at $t = 0$, can be presented as follows

$$J_{gip} = L^{-1} \frac{dP_{gip}}{dt} = \frac{e}{L} \int_{r>a} z \frac{\partial f}{\partial t} d^3r = -\frac{e}{L} \int_{r>a} z(\nabla, \vec{j}) d^3r \quad (B.1)$$

where $z = r \cos \theta$, and the direction of the z axis is assumed to coincide with that of the external electric field vector \vec{E} . Taking into account that $(\nabla, \vec{j}) = z(\nabla, \vec{j}) + j_E$, we can write the displacement current in the form of the sum $J_{gip} = B_1 + B_2$ where

$$B_1 = \frac{e}{L} \int_{r>a} j_E d^3r; \quad B_2 = -\frac{e}{L} \int_{r>a} (\nabla, \vec{j}) d^3r \quad (B.2)$$

Here, j_E is the projection of the vector \vec{j} on the direction of the external field. Insertion of Eq. (8) into Eqs. (B.2) gives

$$B_1 = \frac{e}{L} \left[mE_{av}W + 2\pi Da^2 \int_{-1}^1 \mu \cdot f(a, \theta, t) d\mu \right] \quad (B.3)$$

$$B_2 = \frac{e}{L} \int_{r=a} (\vec{j})_r ds = \frac{ea}{L} \int_{r=a} \mu \cdot j_r(a, \theta, t) ds \quad (B.4)$$

where $\mu = \cos \theta$, and E_{av} is the average electric field acting on the geminate ions given by [82]

$$E_{av} = E - W^{-1} \int_{r>a} E_c \cos \theta f(r, \theta, t) d^3r \quad (B.5)$$

where $E_c = e/\epsilon_{st}r^2$ is the Coulomb field strength. Here, $(\vec{j})_r$ and j_r are the radial components of the vector \vec{j} and \vec{j} , respectively, and $ds = a^2 2\pi \sin \theta d\theta$. Deriving Eq. (B.3), we have used the following relationship

$$\int_{r>a} \nabla f d^3r = -2\pi a^2 \int_{-1}^1 f(a, \mu, t) \mu \cdot d\mu \quad (B.6)$$

where $\nabla f = \partial f / \partial z$ is the projection of the gradient of the distribution function on the external electric field \vec{E} given by

$$\nabla f = \mu \frac{\partial f}{\partial r} + \frac{(1 - \mu^2)}{r} \cdot \frac{\partial f}{\partial \mu} \quad (B.7)$$

Insertion of the boundary condition (9) into Eq. (B.4) gives the following relationships

$$B_2 = -\frac{ea\sigma}{2L} \int_{-1}^1 \mu f(a, \mu, t) d\mu \quad (B.8)$$

$$J_{gip} = \frac{emE_{av}W}{L} + J_{surf} \quad (B.9)$$

where the first and second members in the right hand side of Eq. (B.9) can be called a bulk component and a surface component of the displacement current, respectively. The surface current in Eq. (B.9) is determined by

$$J_{surf} = \frac{ea^2D}{L} \left(1 - \frac{\sigma}{4\pi Da} \right) \int_{-1}^1 2\pi f(a, \theta, t) \mu d\mu \quad (B.10)$$

Using the dimensionless parameters J_{gip}/J_0 , $F = R_c^3 f$ and $c = eER_c/k_B T$, Eq. (B.9) takes the form

$$\frac{J_{gip}}{J_0} = W \frac{E_{av}}{E} + \frac{J_{surf}}{J_0} \quad (B.11)$$

$$\frac{J_{surf}}{J_0} = \frac{a^2}{R_c^2} \cdot \left(1 - \frac{\sigma}{4\pi Da} \right) \int_{-1}^1 2\pi c^{-1} F(a, \theta, t) \mu d\mu \quad (B.12)$$

At short times, the ratio E_{av}/E tends to unity at $t \rightarrow 0$ because of the spherical symmetry of the initial distribution of geminate charges, and hence $WE_{av}/E \rightarrow 1$ at $t \rightarrow 0$. At sufficiently long times, $E_{av} \approx E$ because the separation distance between ions becomes large, and hence $WE_{av}/E \rightarrow q$ at $t \rightarrow \infty$. As to the surface current, its time dependence is determined by the value of σ .

For an isotropic initial distribution function $f_0(r)$ used in the present work, the angle dependence of $f(r, \theta, t)$ in the vicinity of the recombination sphere appearing at short times is determined mainly by the angle dependence of the radial drift component, $m(E_c - E \cos \theta)f$, of the flux density because the radial diffusion component, $-D\partial f/\partial r$, weakly depends on θ at short times. Since the function $f(r, \theta, t)$ in its turn depends very weakly on θ at short times, its change is determined mainly by the electric field $E_c - E \cos \theta$ acting on the charges. In particular, at $\theta = \pi$ the ions drift in the electric field $E_c + E$ towards the recombination sphere $r = a$. They increase the value of $f(a, \pi, t)$ on the recombination sphere to a greater extent than the ions, drifting in the field $E_c - E$ at $\theta = 0$, increase the value of $f(a, 0, t)$. As the result, at $t < (0.0001 - 0.001) \times R_c^2/D$ the distribution function near the recombination sphere, as calculations show, becomes polarized in the external electric field, so that $f(a, \pi, t)$ becomes more than $f(a, 0, t)$, and hence the integral over μ in the right hand side of Eq. (B.10) is negative at short times. Thus, in the case of slow reaction on the recombination sphere ($\sigma < 4\pi Da$), the polarization of $f(a, \theta, t)$ leads to a small negative surface current at short times while for the opposite case of fast recombination ($\sigma > 4\pi Da$), the value of J_{surf} is positive at short times. Calculations have shown that at $t > 0.001 \times R_c^2/D$ a broad part of the distribution function $f(r, \theta, t)$ with the width of the order of $(4Dt)^{1/2}$ appears due to a diffusion escape of geminate charges from the recombination sphere. Now, the ions arrive at the recombination sphere from the region of large distances $r > 0.1R_c$ where the function $f(r, \theta, t)$ is polarized in the external field at long times. The polarization of $f(r, \theta, t)$ at large distances results in a change of the angle dependence of the distribution function at small distances near the recombination sphere, so that $f(a, \pi, t)$ becomes less than $f(a, 0, t)$ at sufficiently long times. As the result, at times longer than about $0.001 \times R_c^2/D$ the surface current becomes positive for $\sigma < 4\pi Da$ and negative for $\sigma > 4\pi Da$. Fig. 8 shows the values of E_{av}/E and J_{surf}/J_0 as a function of time calculated by Eqs. (B.5) and (B.12), respectively. The distribution function $f(r, \theta, t)$ was obtained from the numerical solution of the Smoluchowski equation. As seen, at $4\pi DR_c/\sigma = 1000$ the time profile of E_{av} and J_{surf} has a minimum and maximum, respectively, caused by polarization of a broad part of $f(r, \theta, t)$. What is interesting is that E_{av} can become even negative near its minimum. As can be seen from Fig. 8, the drop in the average electric field is compensated by the peak of J_{surf} .

Although in the limiting case of $\sigma = 0$ the time dependence of J_{gip} is unknown, a time t^* at which J_{gip} is a minimum can be estimated as follows. Since $q = 1$ at $\sigma = 0$, $J_{gip} \rightarrow J_0$ at $t \rightarrow \infty$ and $t \rightarrow 0$. Taking into account that $W = 1$, one can find the order of value of t^* from the condition that in Eq. (B.5)

$$\int_{r>a} E_c \cos \theta f(r, \theta, t^*) d^3r \approx E \quad (B.13)$$

at $t = t^*$. The time dependence of P_{gip} is approximately given by $P_{gip} = e \int r \cos \theta f d^3r \approx emEt$ because $q = 1$ at $\sigma = 0$. On the other hand, at low electric fields the average distance is $r_{av} \approx (4Dt)^{1/2}$. Thus, from Eq. (B.13) one obtains the estimation that $emEt^*/\epsilon_{st}(r^*)^3 \approx E$ where $r^* = (4Dt^*)^{1/2}$. This gives $\tau^* = t^*D/R_c^2 = 1/64$ that is close in order of value to the parameter $tD/R_c^2 \approx 0.04 - 0.08$ at which E_{av} is a minimum (Fig. 8).

Figs. 3 and 4 demonstrate that for $4\pi DR_c/\sigma = 0.1$ the value of J_{gip}/J_0 is even more than unity at short times. This means that the current of geminate charges at short times is more than that of the same number of free charges. To explain this, let us consider the surface current at short times for the case of fast geminate recombination when $\sigma \gg 4\pi DR_c$. It should be noted that in the limiting case of a perfectly absorbing sphere ($\sigma \rightarrow \infty$) we must have $f(a, \theta, t) \rightarrow 0$ as $\sigma \rightarrow \infty$, so that the flux density is finite at $r = a$. We shall take into account this case and estimate J_{gip} at short times

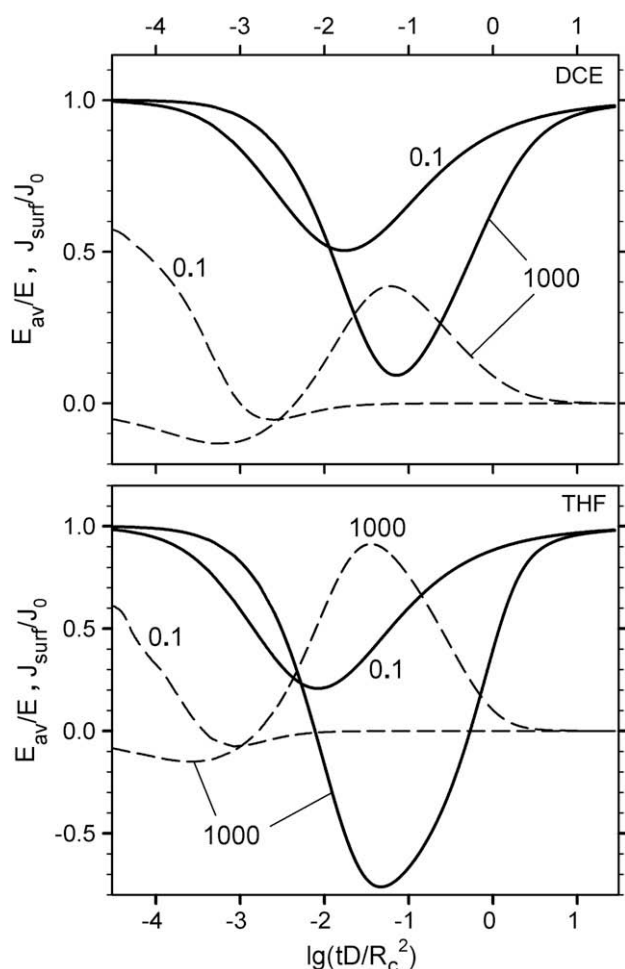


Fig. 8. Time dependence of the average electric field acting on geminate charges (solid lines) and the surface current (dashed lines) obtained for two solvents – 1,2-dichloroethane (top) and tetrahydrofuran (bottom). The parameters used in calculations were $a = 0.9$ nm, $b = 0.3$ nm and $c = 0.1$. Numbers near curves are the values of $4\pi DR_c/\sigma$.

as follows. Because of the large gradient of $f(r, \theta, t)$ in a narrow layer near the recombination sphere, the function f rises sharply with increasing distance r , so that the derivative $\partial f/\partial r$ becomes negligibly small at $r = a + \Delta r$ where the distance Δr is of the order of $a^2/R_c \ll a$. This implies that in weakly polar and non-polar solvents the initial rate of geminate recombination is determined, as mentioned above, mainly by the drift of ions in the strong electric field near the recombination sphere. In this case, the radial component of the flux density may be approximated by the following formula

$$-j_r(a, \theta, t) \approx -j_r(a + \Delta r, \theta, t) = m[E_c(a + \Delta r) - E \cos \theta]f(a + \Delta r, \theta, t) \quad (\text{B.14})$$

At short times we can put $f(a + \Delta r, \theta, t) \approx f_0(a + \Delta r)$ in the right hand side of Eq. (B.14). Insertion of Eq. (B.14) into Eq. (B.4) gives

$$B_2 \approx -\frac{2\pi e m a^3}{L} f_0(a + \Delta r) \int_{-1}^1 [E_c(a) - E \cdot \mu] \mu d\mu = \frac{4\pi a^3 e m E \cdot f_0(a + \Delta r)}{3L} \quad (\text{B.15})$$

Taking into account that $WE_{av}/E \rightarrow 1$ at $t \rightarrow 0$, we obtain that

$$J_{gip}/J_0 \approx 1 + (4\pi a^3/3) \cdot f_0(a + \Delta r) \quad (\text{B.16})$$

at short times. Such an estimation of the initial current is valid for distribution functions $f_0(r)$ with width $b > \Delta r \approx a^2/R_c$. As seen from Fig. 8, at short times the value of J_{surf}/J_0 obtained at $4\pi DR_c/\sigma = 0.1$ is positive and rather large, but at $t > 0.001 \times R_c^2/D$ the surface current becomes negative because of the change in polarization of $f(a, \theta, t)$.

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