Transient photokinetics of Rhodamine 3B$^+\text{ClO}_4^-$ in water:toluene mixtures

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Abstract

The kinetic behavior of the first excited singlet state of an ionic dye, Rhodamine 3B perchlorate, was studied in the region of total miscibility of water:toluene mixtures. The solute exists in two forms: the associated ion pair and cationic, both preferentially solvated by the more polar component (Chem. Phys. Lett. 307 (1999) 139). The transient photokinetics of the excited state hydrated ion pair’s conversion into the cationic species is studied. An anisotropic distribution of the nearest neighbor accounts satisfactorily for the transient effects induced in the dihedral behavior of water molecules in a dielectric cluster solvation sphere around the solute. A kinetic model is proposed to evaluate the dependence of the reactional rate constant $k_a$ and the mutual diffusion coefficient $D$ on the water concentration, temperature, and the effect of friction. It is found that both $k_a$ and $D$ decrease with the water concentration but, while the overall friction ($k_BT/D$) decreases with the temperature, the rate constant $k_a$ is not affected. Overall, the kinetic data is in good agreement with the interpretation derived on the basis of steady-state results, and the recovered lifetimes of each individual species are similar to those observed in pure solvents. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The dynamics of polar solvation of charged or dipolar species is a subject of great importance to the understanding of chemical reaction kinetics [1]. Several studies on this topic have been reported and are of special relevance for intramolecular and intermolecular electron transfer processes [2–4]. Namely, the stabilization of a given species by the solvent determines the rate of the process, which in turn affects the reaction pathways underlying the global mechanism.

The charge alterations created upon electronic excitation induce the relaxation of solvent molecules which is related with the longitudinal dielectric relaxation time $\tau_L$, through the decay rate of the temporal autocorrelation function of the dielectric polarization. Thus, the Stokes shift’s temporal evolution monitors the fluorophore solvation dynamics, which in a homogeneous solution follows the magnitude of $\tau_L$ in the long time regime [6,7]. Besides the orientational solvent response to the torque induced by the new charge...
distribution, there are also inertial contributions to the energy release [8–13].

Solvation dynamics in mixtures has not been often studied in particular when there is a large difference in polarity between the components of the binary mixture. From experimental [14–16] and theoretical data [17,18], it was shown that the solvation process occurs also with translational diffusion of the mixture components. The dielectric enrichment of the solute solvation sphere due to a molar fraction increase of the more polar component is observed when an increase in dipole moment or charge separation in the solute occurs. According to the theory, this enrichment is diffusion controlled and provides a microscopic view on the effect of specific solvent–solute interactions [19].

In laser xanthene dyes, such as rhodamines, ion pairs have been observed in weakly polar media, presenting significant photophysical differences from those reported for the cation [20–22]. Semi-empirical calculations established that rhodamine ion pairs have large interionic distances when this is the only species present [23,24]. Therefore, it is likely that the distance at which the counter-ion locates away from the cationic part may be responsible for some differences in the photophysical behavior of each species.

In a previous paper, we showed that in mixtures of water:toluene Rhodamine 3B perchlorate coexists solubilized in the ground state as a distribution of ion pair and cation with similar spectral characteristics. An abrupt variation of the radial distribution of the polar solvent was also predicted. In the excited state, the driving force for the conversion of the ion pair into the cation was attributed to the unbalance of electrostatic forces and changes in inter-ionic distances in the water cluster solvation sphere created around the ion pair by dielectric enrichment [25]. Very recently, single molecule spectroscopic studies of rhodamines on glass surfaces detected two emitting species, which the authors attributed to the contact ion pair (CIP) and cation supporting our observations [26].

The purpose of this paper is to describe the kinetics of the excited hydrated ion pair’s conversion into the first electronic excited state of Rhodamine 3B cation and perchlorate in water:toluene mixtures. Using time-resolved fluorescence studies in the picosecond range, we present evidence that the water’s dielectric clusters have a special role in the dynamic aspects which originate an overall diffusion controlled process, within the ion pair solvation sphere, which then triggers the separation of the counter-ion. The photophysics of each species, CIP and solvated cation in the mixture, is recovered and compared to that already observed for the individual species in pure solvents, supporting the adequacy of the kinetic model used. The results confirm that the production of the excited cationic species from the associated ion pair has a diffusional behavior, which depends on the distribution of polar molecules around the ions in the solution.

2. Experimental

2.1. Materials and samples

Rhodamine 3B perchlorate (Rhodamine 3B) provided by Radiant Dyes Chemie (laser grade) was used to prepare the solutions. Rhodamine 3B solubilization requires about 5 mM water, depending on the amount of dye. The water needed is provided, in part, by the undried toluene from the bottle. These mixtures were prepared in the following fashion: 3.5 ml aliquots of water (distilled twice under quartz) were diluted in several volumes (25–200 ml) of raw toluene (spectroscopic grade, % H₂O (w/w) < 0.01, Labscan, Spectroscan). The exact water contents were determined through Karl–Fischer titration (10 ml aliquots). The final water concentration ranged from 9 to 16 mM. Rhodamine 3B/H₂O/toluene solutions with C_Rhodamine 3B = 0.4 μM, C_Rhodamine 3B = 0.7 μM and C_Rhodamine 3B = 1.4 μM at water:dye molar ratios (⟨N⟩) ranging from 6600:1 to 26 700:1 were prepared.

2.2. Apparatus

Absorption spectra were taken in a JASCO-V560 UV–Vis spectrophotometer. The excitation and emission spectra were recorded in a Perkin-Elmer LS-50B spectrofluorimeter. Both apparatus and procedures were described elsewhere [25].
Fluorescence decays were acquired in a single photon timing equipment [27] with excitation at 295 nm. The excitation light delivered by a cavity-dumped Rhodamine 6G dye laser (Coherent 701-2) (5–6 ps pulses, ≈40 nJ per pulse) was synchronously pumped by a mode locked Ar$^+$ laser (Coherent Innova 400-10). The instrumental response function was tuned to ≈30 ps FWHM. The emission was collected through a properly positioned polarizer (magic angle) and thermostated using a temperature gauge (±0.2 K) which in turn was connected to the cell holder. The decays were stored in a multichannel analyzer operating with 1024 channels and a time base of 10.80–11.12 ps per channel.

2.3. Fluorescence decays

The fluorescence decays of Rhodamine 3B in water:toluene mixtures were collected in the blue ($\lambda_{em} = 550$ nm) and red ($\lambda_{em} = 588$ nm) regions of the emission spectra (see Fig. 1). Firstly, they were analyzed by a sum of exponential functions [28]. While in pure water the decays are well described by a single exponential function irrespectively of the emission wavelength, in water:toluene mixtures even a global two exponential fit is not adequate as shown in Fig. 2. Weakly temperature dependent short time (<500 ps) constants with positive contributions in the fluorescence decays collected in the blue at 550 nm and negative ones in the decays collected in the red at 588 nm are detected in a three exponential fit (globally analyzed). The transient data imply a more complex behavior rather than just the excitation and decay of each species, suggesting a conversion process in the excited state. A kinetic model is presented in Section 3 to account for the ensemble of the experimental results. The details of data analysis formulated within this framework are given in Appendix A.

3. Model

3.1. Background phenomenology

The coexistence of two species of Rhodamine 3B in water:toluene solutions was monitored by following changes in absorbance with the water content and temperature. The thermodynamic analysis of the spectral data yielded values of enthalpy (−8.4 kJ mol$^{-1}$) and entropy (−35.9 J K$^{-1}$ mol$^{-1}$) [25] which are consistent with the ion-pair cation equilibrium [20,29,30]. Changes in the excitation spectra obtained at various emission wavelengths were interpreted as originating from two species (ion pair and cation), rather than a continuous distribution of differently solvated/ion paired species, once the two main Gaussian peaks evolve as a sigmoid function of the emission energy [25].

The steady-state dynamics reported earlier in water:toluene mixtures could be treated as a bimolecular fluorescence quenching of the rhodamine ion pair by water. In order to evaluate the dependence of the fluorescence quantum yield on the water concentration, Stern–Volmer type kinetics were applied. The additional fluorescence quenching process of the ion pair was its
dissociation with the generation of excited cation and counter-ion [25].

3.2. Transient kinetics

Upon electronic excitation there is a dipole moment change in the chromophoric part of the ion pair which triggers alterations in the dielectric enrichment. The vector dipole moment arising from the two opposite charges, in module, is larger than that of the chromophore and since it has an inverse direction, the total dipole moment decreases. The reduced dipole–dipole interaction in the water cluster around the ion pair allows the creation of a water shell equivalent to the volume of a molecule located at the encounter reactional distance. This situation is described in Fig. 3 in terms of the dipole induced variations of the solvation profiles [25]. Cases 1–3 depict, respectively, the shell radii of the ground state ion pair, excited ion pair and excited cation at the miscibility limit.

The water migration which will occur can then initiate the ion-pair solvation before another water molecule arrives from the bulk solution. The overall process promotes the growth of the ions’ individual shells enabling the increase of the interionic distance.

In the present paper, Scheme 1 is the same as that used to study the excited steady-state kinetics, but now \( k(t) \) is a time-dependent rate coefficient which describes the conversion of the excited ion pair \( (X^+) \) in its excited cation \( (Y^+) \) and anion \( (A^-) \) and \( K \) is the ground state equilibrium constant. In the frame of this kinetic description, the water molecule is the perturbation, which induces the growing of rhodamine solvation shell (redistribution) enabling a larger separation of the counter-ion. The overall process can be rationalized as a water reaction with the excited ion pair. The new inter-ionic distance is such that the photophysics, revealed by the created cationic species, presents the characteristics [21,22] of the cationic form (this one also present in the ground state). If the polar dielectric cluster can be envisaged as a drop constituted by highly polar molecules where both cation and anion are located, it can be assumed that the electrostatic interaction between ions occurs in a medium with a dielectric constant close to that of a polar layer. For highly polar molecules such as water, the inter-ionic potential is screened by the high dielectric constant. This will diminish the recombination probability within the cluster of the newly born cationic species with the anion. The presence of the Coulomb potential is, thus, not explicitly taken into account in our kinetic model.

The process of excited cation production, starting from the associated species is determined by the water diffusion since the dissociation step and the following resolvation of the excited cation is affected by the distribution of water molecules.

The time dependence on the rate coefficient \( k(t) \) comes then from the contribution of transient effects arising from the local and bulk distribution of water molecules implicit in the diffusional nature of the dielectric enrichment. Infrared studies [31,32] have shown that only water monomers are present in water:toluene solutions.

The concept of nearest neighbor distribution [33,34] was applied to the reversibility of monomer-eximer kinetics to study the geminate recombination [35]. The long time translational
contribution to exciplex solvation in binary mixtures was treated in terms of the Smoluchowski’s model [16]. The phenomenology described above can be treated using an approximation which considers only one water molecule within capturing reactional distance \( R_e \) and all the other neighbors randomly distributed. In these conditions, the rate coefficient (for \( d \) pulse production) is given by [35]

\[
k_d(t) = k_0^d \frac{d \ln k_0^d(t)}{dr} + \frac{d \ln k_0^d(t)}{dr}
\]

(1)

where the first term gives the contribution from the water molecules present in the bulk solution and the second one from those at encounter distance in water–ion-pair clusters.

The radiative boundary condition introduced by Collins and Kimball [36] within the framework of the Smoluchowski equation was considered to be the more adequate to describe the diffusional process. Thus,

\[
k_d'(t) = [\text{H}_2\text{O}] [a + bE(x)]
\]

(2)
$E(x) = e^{-\frac{x^2}{2}} \text{erfc}(x); \quad x = ct^{1/2}$

$$a = \left( \frac{1}{x_T} + \frac{1}{x_R} \right)^{-1}; \quad b = \frac{a x_R}{x_T};$$

$$c = \left( 1 + \frac{b}{a} \right) \frac{D^{1/2}}{R_e}$$

$x_R = k_a; \quad x_T = 4\pi DN_A R_e$

In this case erfc is the complementary error function, $D$ is the mutual diffusion coefficient, $R_e = R_x + R(H_2O)$ is the capture radius, $N_A$ is the Avogadro constant and $k_a$ is the rate constant at the encounter distance $R_e$. The rate accounts for ions’ generation if all the water needed to produce the complete solvation shells was already present. When the reactional rate constant is greater than the diffusion controlled rate constant at long times, $(x_R \gg x_T)$, the diffusional control is observed.

The encounter radius previously obtained [25] using $R_T$ and the radius of a water molecule, $R(H_2O)$, is employed for the value of the capture radius ($R_e = 6.9$ Å). This and the experimental water concentrations [25,32] were fixed in all the calculations.

### 3.3. Analytical solution

The species temporal evolution can be written in terms of convolution kinetics [37]. The concentrations of the excited hydrated ion pair ($X^*$) and cation ($Y^+$) (Scheme 1), are then respectively given by

$$[X^*](t) = [X^*](0) \exp \left( \frac{-t}{\tau_x} \right) \times \exp \left( - \int_0^t k_\delta(u) du \right)$$

$$[Y^+](t) = [Y^+](0) e^{-t/\tau_Y} + k_\delta(t) [X^*](t) \otimes e^{-t/\tau_Y}$$

The second term in Eq. (4) reflects the conversion of $X^*$ in $Y^+$. The rate coefficient and its integral time dependence are respectively expressed by

$$k_\delta(t) = [H_2O][a + bE(x)] - b \frac{c^2 E(x) - \frac{c^2}{2\pi}}{a + bE(x)}$$

$$\int_0^t k_\delta(u) du = [H_2O] \left( at + b \frac{c^2}{2\pi} \left\{ [E(x) - 1] + \frac{2x}{\sqrt{\pi}} \right\} \right)$$

The fraction of light absorbed by the species $X$ in the ground state may be given by

$$\xi = \frac{\varepsilon_X [X]}{\varepsilon_X [X] + \varepsilon_Y [Y]} = \frac{[X^*](0)}{[X^*](0) + [Y^+](0)}$$

This quantity can be rearranged to relate with the equilibrium constant ($K$) in the ground state to give

$$K = \frac{[Y]}{[X]} = \frac{1 - \xi \varepsilon_X}{\xi \varepsilon_Y}$$

where $\varepsilon_{X,Y}$ are the molar absorption coefficients at the excitation wavelength.

### 4. Results

In the fluorescence decays the corresponding two time constants, associated with both forms, are invariant to the excitation and emission wavelengths. In a multiexponential analysis (see Section 2) the remaining components were linked to water distribution around the chromophores, thereby creating a time dependence in the rate coefficients, which is associated to the mutual diffusion. Changes in water concentration do not seem to affect the lifetimes.

The association (reverse) mechanism was tested in preliminary calculations by exchanging the production term between $X^*$ and $Y^+$ in Eqs. (3) and (4). This would imply that the two decay process corresponded to $Y^+$ and not to $X^*$ species. The production of excited ion pair from geminate recombination of ions was excluded since the convolution of the kinetic scheme solution, modified for reversibility, could not be fitted to the experimental data. However, it is expected that at longer times, the non-geminate recombination step should occur since the cationic form and
counter-ion can survive in individual shells at distances comparable to those of a separated ion pair in a single shell.

The decays obtained at the two wavelengths, $\lambda_{em} = 550$ and $588$ nm, (see spectra in Fig. 1) and the respective fittings to the kinetic model proposed are presented in Fig. 4 together with residuals and their autocorrelation functions. The parameters are listed in Table 1.

The fitting parameter $a$ (Eq. (8)) gave an average value around 0.4 for the ground state equilibrium constant ($K$). It can be concluded that it is nearly invariant with the amount of water present or with the temperature, in good agreement with the steady-state results [25]. This finding means that both species, the associated ion pair and the cationic forms, are preferentially solvated by water in solution.

The value [20–22] of the radiative rate, $k_f = 2 \times 10^8$ s$^{-1}$ was used to calculate the $k_{nr}$ from the fluorescence lifetimes $(\tau_{X,Y})$ obtained from the numerical procedure. The photophysical behavior of each species was discriminated and both fluorescence lifetimes, extracted at several temperatures, are very similar to the ones observed for isolated species. Indeed, at $T = 296$ K, the cation in aqueous solution has the experimental lifetime $\tau_f = 1.49$ ns and, that of the ion pair [20] in 1-chloronaphthalene is $\tau_f = 3.733$ ns, in close agreement with the values obtained in similar conditions.

The Arrhenius dependencies of the corresponding non-radiative rate constants, $k_{nr}$ are given in Fig. 5. Likewise in the homogeneous solvents, the non-radiative decay from the singlet state of the cationic species has an activation energy ($E_a$)

![Fig. 4. Dependence of fluorescence decays and model functions globally convoluted at two emission wavelengths of Rhodamine 3B perchlorate in water:toluene mixtures at different temperatures, $T$, (a and b); and average occupation numbers, $\langle N \rangle$, (c and d). a and c: $\lambda_{em} = 550$ nm, b and d: $\lambda_{em} = 588$ nm. The time windows correspond to 11.059 ns in a and b and to 11.387 ns in c and d.](image-url)
nearly fivefold higher than that of the associated ion pair species. The value of \( E_a = 23.4 \text{ kJ mol}^{-1} \) compares well with \( E_a = 25.1 \text{ kJ mol}^{-1} \) obtained for the Rhodamine 3B cation in pure water and \( E_a = 4.2 \text{ kJ mol}^{-1} \) is also similar with the value of \( E_a = 5.9 \text{ kJ mol}^{-1} \) obtained for the ion pair in 1-chloronaphthalene [20]. The fluorescence changes with temperature show that one non-radiative rate constant has a high activation energy, as it happens with the molecular cationic form in homogeneous polar media. The photophysics of the cationic species, either produced from its ground state or from the increased ionic separation at the excited ion pair, corresponds to that of a rhodamine cation in water. This fact indicates that the water properties obtained in the dielectric clusters [16] are close to the bulk, since the activated non-radiative process of the cationic form is dependent on the medium properties [21,22]. The other non-radiative rate constant has the characteristic low activation energy of the rhodamine ion pair [20]. The presence of the counter-ion at a given distance from the chromophore moiety determines its non-radiative activated processes just as it happened in 1-chloronaphthalene [20].

These findings confirm that the ion pair non-radiative decay is essentially affected by the presence of the counter-ion. The effect of the solvation sphere in the cationic species has a good confirmation in its photophysics.

Different water/dye ratios at several water and dye concentrations were used as shown in Table 1. These experiments were devised to test both the influence of the water content in the mixture as well as that of the dye concentration. No correlation can be established between the data obtained and the dye concentration ruling out the contribution of dimers in solution. Using our highest dye bulk concentration (1.36 \( \mu \text{M} \)) and assuming dimerization constants of the order of \( 10^3–10^4 \text{ M}^{-1} \), the calculated percentage of the dimer would not

Similar studies carried out with Rhodamine 3B in reversed AOT micelles, where the perchlorate counter-ion exchanges with bis-ethylhexyl-sulfosuccinate anion, exhibit the same phenomena but the equilibrium constant between ion pair and the cation is significantly higher.
exceed 1.4% of the total amount of species in solution. J-dimers found in toluene for Rhodamine 6G (chloride and perchlorate) are not reported for Rhodamine 3B (perchlorate), perhaps due to the fact that this molecule is not soluble in dry toluene. Their existence, however, is assumed in the kinetic data in 1-chloronaphthalene but the authors outline the invisibility of the Rhodamine 3B J-dimer in the absorption spectrum [20].

In Table 1 it is also shown that either \( k_a \) or \( D \) decrease with the amount of water present which reflects the variation with the spatial occupation \( \langle N \rangle = [\text{H}_2\text{O}]/[\text{Rhodamine 3B}] \).

The friction \( (k_B T/D) \), evaluated by the Stokes–Einstein equation, decreases with the temperature whereas \( k_a \) is temperature independent. The dependencies of the reactional rate constant \( k_a \) and the mutual diffusion constant, \( D \) on both \( T \) and \( \langle N \rangle \), are shown in Fig. 6 and discussed in Section 5.

5. Discussion

The “water-dragging effect” [38] has often been reported in several examples in the literature and it is a special feature of the preferential solvation. Indeed, a great variety of solutes partitioned between organic and water phases drag the first sphere of aqueous solvation to the organic phase.

The approach undertaken led to the observation of intrinsic photophysical aspects of each individual species with the additional generation of the cation through the diffusion of a preferential water molecule [39].

Indeed, the kinetic model used is based on a physical phenomenon: the alterations in the solute are due to a combination of non-equilibrated forces that initiate the diffusion process thereby originating separation and resolvation of the ions in the excited state. The total dipole moment decrease, induced by changes in charge density, affects the spatial reach of the dipole–dipole interactions and enables that the polar shell diffuses immediately after excitation to reequilibrate the resulting dipole.

The photodissociation mechanism used to evaluate the transient kinetics of the hydrated ion pair and cationic species is completely consistent with the interpretation of the steady-state data recently reported [25]. The value of the equilibrium constant \( (K = 0.4) \) is independently reproduced in the present work.

The reaction rate at encounter distance depends on the efficiency of the capturing event. This is modeled in terms of Collins–Kimball radiative boundary condition taking into account the experimental results at all the water:dye ratios, \( \langle N \rangle \). However, for ratios higher than the lowest, the Smoluchowski absorbing boundary condition was also able to describe the experimental data.

The variations observed with the amount of water show that besides the decrease of \( k_a \) there is also a decrease of the mutual diffusion coefficient. Those may anticipate frictional differences dependent on the distribution profile of water molecules around the associated ionic solute. A second aspect lies on the fact that \( k_a \) is temperature independent which is likely to be associated with a very small barrier to the photodissociation process in the hydrated excited solute. The dissociation induced upon photoexcitation may proceed if the encounter complex starts with a non-reactive encounter \( (nr) \) and evolves to a reactive encounter \( (r) \) as described in Scheme 2.
The global rate $k_a$, at the reaction encounter distance, can be expressed by Eq. (9)

$$k_a = \frac{k_1 k_{\text{diss}}}{k_{\text{diss}} + k_{-1}}$$

which contains two limits: (1) $k_{\text{diss}}/k_{-1} \gg 1$ leading to $k_a = k_1$ and (2) $k_{\text{diss}}/k_{-1} \ll 1$ leading to $k_a = k_1 k_{\text{diss}}/k_{-1}$.

The rate constants $k_1$ and $k_{-1}$ may be seen as motion frequencies of orientational diffusive nature between the water molecules and ions, whereas the $k_{\text{diss}}$ would correspond to the rate constant of ionic separation after the reaction of $X^+$ with $H_2O$ at the reactional distance, $R_e$. We can then estimate these rate constants through the equations [40,41]

$$k_{-1} = \frac{3D}{R_e^2} \exp\left(-\Delta H/k_BT\right)$$

$$k_{\text{diss}} = \frac{3Dr_C}{R_e^3 \left(\exp\left(r_C/R_e\right) - 1\right)}$$

where $r_C$, the Coulomb radius, is given by

$$r_C = \frac{Z_Y Z_A e^2}{4\pi\varepsilon_0 \varepsilon_r k_BT}$$

### Scheme 2.
General representation of the processes occurring at encounter reactional distance, leading to counter-ion separation.

### Fig. 6.
Dependence of the reaction rate at encounter distance, $k_a$, and mutual diffusion coefficient, $D$ (or overall friction, $k_BT/D$) on temperature, $T$, (a and b); and on average occupation number, $\langle N \rangle$: c and d.
$\Delta H$ is the interaction enthalpy between the associated ionic species and water in the encounter complex and $D$, is the mutual diffusion coefficient of the ionic species, which are the reaction products. The substitution of Eqs. (10)–(12) in Eq. (9) shows that, in fact, $k_a$ is not temperature dependent. Therefore, it is possible to understand the dependencies of $k_a$ and $D$ on the effective dielectric constant of the water cluster. In each step, there will be frictional contributions to the transmission coefficient, which are within this framework, felt through $k_a$ and $D$.

Using molecular dynamics, Rey and Guàrdia [42], have studied the association between a CIP, Na$^+$Cl$^-$ with water molecules to form the solvent separated ion pair (SSIP). These authors found out that the energy barriers for the interconversion between the CIP and the SSIP are $2.8k_B T$ and $3.7k_B T$ respectively, for the forward (CIP $\rightarrow$ SSIP) and the reverse process (SSIP $\rightarrow$ CIP). The energy barrier observed for the dissociation process in ions (SSIP $\rightarrow$ I) is of the order of $k_B T$ and corresponds to larger inter-ionic distances. They have found a rate constant of $8 \times 10^{10}$ s$^{-1}$ for CIP $\rightarrow$ SSIP. The $k_a$ values obtained in the present study correlated with the conversion of SSIP into ions are in the range of $(0.5-2.0) \times 10^{10}$ M$^{-1}$s$^{-1}$. Both rates are similar considering the water concentration in the solvation shell. Following the formalism proposed by Rey and Guàrdia [42], the dependence of the mean force potential on the reaction coordinate for dissociation shows lower energy barrier and frequency than the CIP $\rightarrow$ SSIP conversion. Then, it may be expected that the transmission coefficient will be smaller for the dissociation step than for the barrier crossing in CIP $\rightarrow$ SSIP reaction. Indeed, Grote–Hynes theory [43,44] predicts small transmission coefficients since low frequencies are associated with the barrier top, in the vicinity of the transition state configuration.

The results reported in this paper may also be related with relevant aspects of the ionic conductivity of solvent mixtures. Since there is a dipolar medium, its relation with the friction felt by the reaction coordinate may provide a clue to the decrease of both $D$ and $k_a$ with the amount of water present in the mixture. Particularly, the diffusion coefficient should vary with the reciprocal of the ionic solute radius, thus explaining its decrease with the water present.

Balabai and Waldeck [45] showed that it is not possible to describe the orientational correlation time in electrolytes without friction contributions due to the ionic atmosphere and dielectric friction. Nevertheless, the Stokes friction remains the dominant term in the overall friction and in fact, the interplay of structural differences, make these systems suitable to the study of dynamical effects [45–48].

Furthermore, Biswas and Bagchi have shown [49,50] that by using a microscopic theory it is possible to recover the concept, developed by Franck and Wen [51], of a virtually immobile solvent layer around the solute. This model predicts that molecules close to it diffuse slower than the ones further away. Specifically, at large water concentrations, diffusion occurs from polar solvent layers close to the virtually immobile one, whereas at lower concentrations, diffusion of polar molecules from the bulk could contribute to the mutual diffusion coefficient. In this way, both the experimental and calculated values of the diffusion coefficient of water in toluene [25] obtained using the Stokes–Einstein equation would be closer at lower than at higher concentrations. The frictional contribution will increase if a solvent layer of small mobility covers the solute. In this perspective, the decrease of $D$ with $T$ (less than two times from 293 to 361 K) may explain variations in the occupation density of the solvation sphere. This would be compatible with the contribution from changes in the mutual diffusion regime between stick and slip conditions, promoted by the existence of intermolecular potentials. Particularly, a superstick limit was found by simulating a situation of a strong interaction between solute and solvent [19].

Biswas et al. [52] emphasize the importance of the binary friction as regards the global friction. Should the nearest neighbor determine the reaction profile this contribution to the friction may be dominant. Local polarity changes induced in the cluster solvation shell and caging effects [53–55] may play an important role in the solvation dynamics of the excited ion pair dissociation process.
6. Conclusions

Following our previous report on Rhodamine 3B in water:toluene mixtures [25], this study provides kinetic evidence for the contribution of transient solute–solvent interactions in the ion pair dissociation into the solvated cation. Changes in the dielectric enrichment in mixtures of polar and non-polar components introduce water clusters reorganization, which leads to local phase separation and to the individualization of ionic solutes when viewed microscopically.

Distribution effects give rise to concentration gradients that are reflected in transient effects in the mutual diffusion of water and associated rhodamine ion pair.

The transient photokinetics in the excited state of the hydrated ion pair of Rhodamine 3B perchlorate was studied using a nearest neighbor distribution in the solution of the diffusion equation. The presence of an aqueous solvation sphere determines the photophysical behavior of the cationic species and dielectric clusters have a special role in dynamic aspects of the dissociation of the excited ion pair.

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Appendix A. Data analysis

The fluorescence decays were globally analyzed (Eq. (A.1)) at two emission wavelengths by convoluting the instrument response functions \( R(t; \lambda) \) with a linear combination of Eqs. (3) and (4). In these were introduced Eqs. (2), (5) and (6) after taking into account Eqs. (7) and (8).

\[
I(t; \lambda) = R(t; \lambda) \otimes (S_{X}^{m}(\lambda)X^{*}(t) + S_{Y}^{m}(\lambda)Y^{*}(t))
\]

(A.1)

where \( I(t; \lambda) \) is the fluorescence intensity at time \( t \) and wavelength \( \lambda \), \( S_{i}^{m}(\lambda) \) is the normalized spectral distribution of each species, representing the emission intensity of species \( i \) at the wavelength \( \lambda \). Decay pairs, collected at \( \lambda_{em} = 550 \text{ nm} \) and \( \lambda_{em} = 580 \text{ nm} \), were globally analyzed at a given water concentration and/or temperature. The global \( \chi^2 \) was optimized by the Levenberg–Marquardt algorithm, using a global analysis program [56] adequately adapted to the calculation of convolutions and other necessary functions. External routines were used [57].

The fitting coefficients \( S_{i}^{m}(\lambda) \) of the linear combination were treated as local parameters [56]. The reactional rate constant \( k_{a} \), the mutual diffusion coefficient \( D \), the fraction of light absorbed by species \( X \), \( z \), and the excited state lifetimes \( \tau_{X} \) and \( \tau_{Y} \) of both species are global fitting parameters [56].

An important aspect which must be stressed is that Eq. (7) cannot be calculated for \( t = 0 \), since it is not defined at that time. Therefore, the discrete time values were shifted according to \( t_{i} = t_{i} + \gamma t_{s} \) with \( \gamma = 10^{-2} \) where \( t_{s} \) is the time per channel \( (i) \) relation at which any given decay was measured.

The calculations were carried out in two independent ways: (1) using an algorithm which is based on the fast Fourier transform (FFT) through routine DRCONV [57] to calculate the convolutions and \( E(x) \) calculated through the function DERFCE [57]. (2) both convolutions were calculated using the trapezoid rule and \( E(x) \) through the approximation proposed by Press et al. [58]. The results were then compared and no meaningful differences were detected.

References

[57] IMSL, Microsoft®.