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Exciplex fluorescence quenching by lithium perchlorate as a method of investigation of salt dissociation equilibria in solutions

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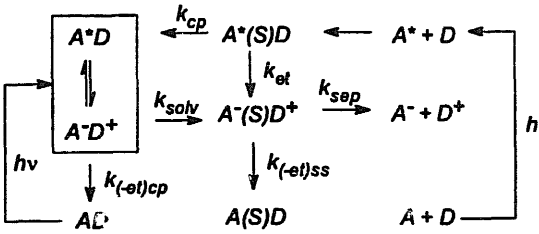
Abstract

Lithium perchlorate has been found as an effective quencher of the fluorescence of dipolar emitting species such as exciplexes. The quenching efficiency is strongly dependent on the contribution of the charge transfer state in the overall exciplex. The Stern–Volmer plots constructed from the exciplex fluorescence lifetimes, exhibit the nonlinear (downward) curvatures, indicating the partial dissociation of the salt even in strongly polar solvents such as acetonitrile. The detailed numerical analysis of the fluorescence quenching data allows for determination of some important parameters characterizing the salt dissociation equilibria in solutions. The discussion of the credibility of the obtained parameters was performed by comparison with the already published results obtained using different methods. © 1997 Elsevier Science S.A.

Keywords: Bimolecular fluorescence quenching; Electron transfer process; Exciplex formation; Special salt effect; Salt association equilibria

1. Introduction

The initially formed species in the photoinduced electron transfer reactions are the contact radical ion pairs (CRIP) and/or solvent separated radical ion pairs (SSRIP) [1–3]. In nonpolar solvents, the former species are usually considered as important but when the solvent polarity increases the later species are dominant. The mechanistic reaction of the formation of charge transfer species in bimolecular photoinduced electron transfer processes is presented in Scheme 1.



Scheme 1. Photophysical processes following the excitation of fluorophore in the presence of the quencher molecules in polar solvents. The following reaction rate constants are introduced into the scheme: k_{cp} formation of the exciplex from the encounter complex. k_{solv} solvation of the contact radical ion pair (CRIP) to form the solvent separated radical ion pair (SSRIP). $k_{(-\mathrm{et})\mathrm{cp}}$ back electron transfer occurring in the CRIP. k_{et} forward electron transfer leading to the SSRIP from the encounter complex. $k_{(-\mathrm{et})\mathrm{ss}}$ back electron transfer occurring in the SSRIP. k_{sep} radical escape leading to the free radicals.

It is difficult to determine when the primary electron transfer step proceeds through the CRIP intermediate since the transient absorption techniques provide similar transient absorption spectra for both charge transfer species (CRIP and SSRIP). However, the existence of the CRIP species may be monitored by the fluorescence techniques [1–5]. The emission from the CRIP state is called the exciplex emission. Generally, the electronic state of the exciplex may be described by a sum of the locally excited state (A^*D) and that of the charge transfer state (A^-D^+) [6]. The term exciplex is more general than the contact radical ion pair (CRIP) because the latter is appropriate for the species in which the extent of the charge transfer state is dominant. The mechanism of deactivation of exciplex by photophysical and photochemical processes should depend on the extent of charge transfer. When the contribution of the charge transfer state in the overall exciplexes is dominant, their fluorescence band shapes may be analyzed in terms of the Marcus theory for the radiative transitions [7]. The detailed analysis of such emission yields the important parameters which characterize the back electron transfer process occurring in the CRIP state leading finally to the donor and acceptor molecules in their ground states [1–6,8].

In general, the rate constants of the back electron transfer processes occurring in the CRIP and SSRIP states differ significantly from each other. The most important reason which

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differentiates the both states with respect to the back electron transfer process is the large difference in the energies of the solvent reorganization that accompanies the electron motions during the electron transfer process.

It has been shown in a previous paper [8] that if the contribution of the charge transfer state is dominant the most important deactivation pathway of the CRIP is the solvation of this state to form the solvent separated radical ion pair (SSRIP). Such type of exciplexes with the largest extent of CT state possess usually very low fluorescence quantum yields and their lifetimes are determined by the solvation rate constant (the fluorescence lifetimes of such exciplexes are of order of 1–2 ns in acetonitrile at room temperature [6,8]). Moreover, the exciplex fluorescence quenching effect by lithium perchlorate was observed [6,9]. This type of the quenching is somewhat strange because neither lithium cation nor perchlorate anion are known as effective in the fluorescence quenching of aromatic molecules. For example, the addition of lithium perchlorate (up to 0.1 M) into acetonitrillic solution of 9,10-dicyanoanthracene does not influence its fluorescence lifetime. The influence of the such type of salts on the photophysics of the dipolar species is known as 'special salt effect' [10]. The quenching mechanism includes the interpenetration of the small lithium cation into the contact radical ion pair, probably to form the nonfluorescing complex as presented below:

$$A^-D^+ + Li^+ \rightarrow A^-Li^+ + D^+$$

This mechanism was confirmed by the transient absorption measurements [11,12]. The addition of lithium cations into the mixture of fluorenone and alkenes after exclusive excitation of fluorenone causes the appearance of new absorption bands assigned to such complex. The concentrations of the free radicals produced in the photoinduced electron transfer step in the presence of lithium salts increase significantly and their lifetimes were longer than those of the unperturbed systems.

We have found in a previous paper [9] that the quenching properties of the lithium perchlorate depend strongly on the contribution of the charge transfer state in the overall exciplex. The more polar exciplex implies the more efficient exciplex fluorescence quenching, for example the quenching rate constant increases in order [9-cyanoanthracene (CNA) + naphthalene] < [9,10-dicyanoanthracene (DCA) + biphenyl] < [DCA + durene]. In the same order the percentage of the charge transfer state in the overall exciplex increases. This quantity may be calculated from the radiative rate constants of the acceptors alone and those relating to the exciplexes, and the energies of 0,0 electronic transitions of the acceptors and the maxima of the exciplex fluorescence [5,6]. In addition, we have observed that the Stern–Volmer dependencies are clearly nonlinear and exhibit the downward curvatures.

On the other hand, it is known that lithium salts dissociate only partially even in strongly polar solvents such as acetonitrile [13,14]. This association process is responsible for the appearance of a minimum in the dependencies of molar conductivity vs. square root of salt concentration in solvents of low polarity [14–18]. The possibility of formation of triple ions was already postulated and the thermodynamic constants of the formation of the triple ions were determined from the conductivity measurements [15–20]. The formation of the ion pairs or triple ions was observed also in other lithium salts and onium perchlorates dissolved in solvents of low and medium dielectric permittivities [16,17,20–26].

Because we assume that only small lithium cations are the exciplex fluorescence quenching species, it seems to be reasonable to apply the simple fluorescence quenching measurements to investigate the salt dissociation equilibria. Such method may be equivalent to the conductivity [14–24] or ultrasonic methods [15,16,22,26]. Therefore, the aim of this work is to analyze such nonlinear Stern–Volmer dependencies with respect to the salt dissociation equilibria in two polar solvents of different polarity.

2. Experimental

9,10-dicyanoanthracene (DCA) and biphenyl (Bi) were purified by crystallization from ethanol. The solvents acetonitrile (Aldrich) and acetone (POCh) of analytical grade as well as anhydrous lithium perchlorate (Fluka) were used without purification. The steady-state and time-resolved fluorescence equipments were described in the previous papers [8,9]. The details of the steady state exciplex fluorescence recovery were also presented in the previous work [9]. The Stern–Volmer dependencies which describe the exciplex fluorescence quenching by lithium perchlorate were constructed from the fluorescence lifetimes estimated from the fluorescence decay functions without and with certain concentrations of $LiClO_4$. The details in numerical calculations will be presented in the next sections.

3. Formation of the ion pairs and triple ions

Fuoss and Kraus [27] rationalized the appearance of the minimum in the molar conductivity vs. concentration of the electrolytes dissolved in media of low polarity by postulating the existence of triple ions, which may be formed by the interactions of the ion (A^+ or B^-) with the ionic pair (AB). The distance between free ions and ion pairs was assumed larger than the distance between ions in the ionic pair. However, it was later postulated that the ions and ion pairs do not need to contact to be treated as the triple ions [21]. Thus, they differ from other chemical species as for instance complexes. The triple ions may be understood as the short and long range interactive species. The interaction of ions with ion pair lowers the activity coefficient of the later species (γ_{pi}). The same effect exist in the interactions between ion pairs themselves (γ_{pp}) and in those of ion pairs with ions (γ_{ip}). Petrucci and Eyring [21] derived the expressions for the above-mentioned activity coefficients. The expressions are presented below:

$$\ln\gamma_{pi}=\frac{\pi N\alpha Cd_T^3}{1000}b^{3/2}\left\{\int_0^b\frac{e^A-e^{-A}}{A^{7/2}}\mathrm{d}A-\int_0^b\frac{e^A+e^{-A}}{A^{5/2}}\mathrm{d}A\right\} \quad (1)$$

$$\ln\gamma_{ip}=\frac{\pi N(1-\alpha)Cd_T^3}{1000}b^{3/2}$$
$$\times\left\{\int_0^b\frac{e^A-e^{-A}}{A^{7/2}}\mathrm{d}A-\int_0^b\frac{e^A+e^{-A}}{A^{5/2}}\mathrm{d}A\right\} \quad (2)$$

$$\ln\gamma_{pp}=\frac{4\pi N(1-\alpha)Cd_p^3}{3000}\sum_{n=1}^{n_{odd}=\infty}\beta^{n+1}$$
$$\times\left(\frac{1}{n(n+2)!}-\frac{1}{n(n+1)!}\right) \quad (3)$$

The activity coefficient γ_{ii} which expresses the interaction between the central ion and the ionic atmosphere is described quite well by the Debye–Hückel theory:

$$\ln\gamma_{ii}=-\frac{S\sqrt{C\alpha}}{1+Bq\sqrt{C\alpha}} \quad (4)$$

The symbols used in the above Eqs. (1)–(4) are explicite explained by the following equations:

$$A=\frac{e\mu}{r^2\epsilon kT},\ b=\frac{e\mu}{d_T^2\epsilon kT},\ \beta=\frac{\mu^2}{\epsilon d_q^3kT} \quad (5)$$

where e is the electron charge, μ the dipole moment of the ion pair, α the fraction of the free ions, d_{T} the minimum approach of the center of the ion pair and ion, d_q the minimum interaction distance between dipoles, q the Bjerrum minimum distance between free ions, ϵ the solvent dielectric constant, N the Avogadro number, k the Boltzmann constant, T-temperature, S and B the Debye–Hückel coefficients. C denotes the analytical concentration of the considered salts.

The total activity coefficient $\Pi\gamma$ is given by the following relationship:

$$\Pi\gamma=\gamma_{pi}\gamma_{pp}/(\gamma_{ii}\gamma_{ip})^2 \quad (6)$$

The total activity coefficient is closely related to the salt association constant K_a:

$$K_a=\frac{1-\alpha}{\alpha^2C}\Pi\gamma \quad (7)$$

Generally, there are two approaches to calculate the association constant, the Bjerrum formalism and the Fuoss formalism. After Bjerrum the association constant is given by the following equation [28]:

$$K_a=\frac{4\pi N}{1000}\left(\frac{z_+z_-e^2}{\epsilon kT}\right)^3\int_2^{b'}e^yy^{-4}\mathrm{d}y \quad (8)$$

where $y=z_+z_-e_0^2/2\epsilon rkT$.

When $b'=z_+z_-e^2/\epsilon akT\gg 2$, Eq. (8) reduces to

$$K_a=\frac{4\pi N^{a^3}}{1000}\frac{e^{b'}}{b'} \quad (9)$$

The Fuoss equation for the association constant has a simpler form [28]:

$$K_a=\frac{4\pi N}{3000^{a^3}}e^{b'} \quad (10)$$

The fraction of the free ions α may be calculated from Eq. (7) and the expression for α has the following form:

$$\alpha=\frac{2}{\sqrt{1+4K_aC(\Pi\gamma)^{-1}}+1} \quad (11)$$

This is a transcendental equation because $\Pi\gamma$ is the function of α (Eqs. (1)–(3)) and must be solved iteratively. Thus, the Stern–Volmer dependence in the systems containing bimolecular charge transfer species such as exciplexes with lithium cations may be expressed as follows:

$$\frac{I_0}{I}=\frac{\tau^0}{\tau}=1+K_{\mathrm{SV}}C\alpha \quad (12)$$

where I_0, $I(\tau_0,\tau)$ are the fluorescence quantum yields (lifetimes) of the exciplex without and with the quencher of concentration C, respectively.

We expect the lowering of the fraction of the free ions with increasing salt concentration and in consequence the downward curvature of the Stern–Volmer dependency.

4. Numerical calculations

Experimentally obtained exciplex fluorescence quenching data, i.e., the relative exciplex fluorescence lifetimes were fitted to the function given by Eq. (12) to recover the Stern–Volmer constant K_{SV} and the fraction of free ions, α, depending on the analytical concentration, C. The following function was minimized:

$$\mathrm{FCN}=\sum_{i=1}^{n}\left(\frac{\tau_0}{\tau_i}-(1+K_{SV}C_i\alpha_i)\right)^2 \quad (13)$$

where τ_0/τ_{i} are the experimentally obtained relative fluorescence lifetimes, C_{i} represents the analytical concentration of $\mathrm{LiClO_4}$, K_{SV} is the Stern–Volmer constant, and α_{i} is the fraction of free ions.

However, this problem calls for the numerical iteration because α depends on the activity coefficients γ, (Eq. (11)) which is dependent on α (Eqs. (1)–(5)). At each analytical concentration C we assume the certain value of α, (for instance 0.5) to calculate the activity coefficient, γ. The resulting value of γ was further used to calculate the corrected value of free ions, α. Such procedure was repeated up to convergence of α. For minimization the MINUITS subroutine from the CERN Library was applied [29]. The parameters recovered from the fitting procedure are: dipole moment of the associate $\mathrm{LiClO_4}$, μ, the association constant, K_{a}, defined by Eq. (7), the dipole–ion distance of closest approach, d_{T}, and the Stern–Volmer constant, K_{SV}.

5. Results

Biphenyl (Bi) is known as an effective quencher of the fluorescence of 9,10-dicyanoanthracene (DCA) in acetonitrile [9,30,31]. The quenching mechanism is the electron transfer from biphenyl to the excited DCA molecule which results in the occurrence of the anion radicals of DCA and cation radicals of Bi. This mechanism was supported by transient absorption measurements [31] and photoconductivity measurements [30]. The exothermicity of the electron transfer step (free energy change, ΔG) which may be calculated from the electrochemical data (reduction potential of DCA and oxidation potential of Bi) and from the energy of the excited singlet state of DCA is equal to -0.09 eV [32]. In such slightly negative ΔG regions, the exciplexes are very often the intermediates in photoinduced electron transfer processes [32]. Indeed, the addition of Bi into a DCA solution in acetonitrile leads to a decrease of the fluorescence intensity and additionally changes the spectral distribution. The weak, red-shifted emission band may be attributed to the exciplex emission. This situation is presented in Fig. 1.

The maximum of this exciplex fluorescence appears at about 524 nm. Similar exciplex fluorescence is observed in the system DCA + Bi in acetone. Again, the addition of Bi alters the fluorescence band shape. In this system, the maximum of the exciplex emission appears at approximately 510 nm. The fluorescence lifetimes of both exciplexes are 6.29 and 9.54 ns for the systems in acetonitrile and acetone, respectively. The detailed analysis of the exciplex fluorescence in acetonitrile which was performed previously shows that the extent of the CT character is rather high (76%) [9]. The exciplex fluorescence is effectively quenched by lithium perchlorate causing the shortening of the exciplex fluorescence lifetime. Fig. 2 represents the fluorescence decay functions of the exciplex in the absence of lithium perchlorate and in the presence of certain quencher concentrations, specified in the figure caption.

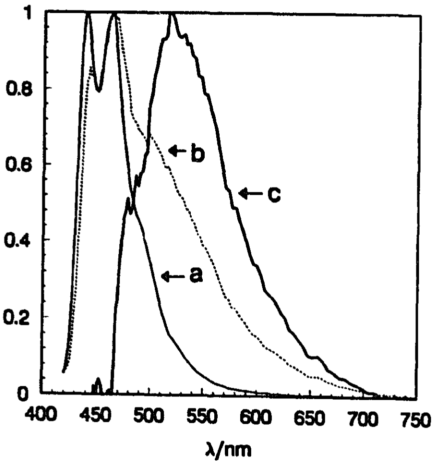

Fig. 1. Fluorescence spectra of acetonitrillic solution of: (a) DCA in the absence of Bi, (b) in the presence of Bi (1.04 M), and (c) their difference spectrum. The spectra were normalized to their maximal intensities.

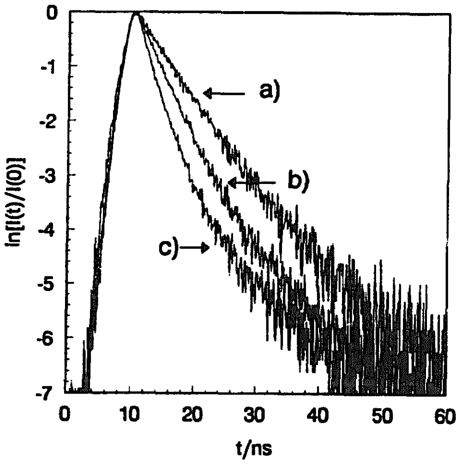

Fig. 2. Exciplex fluorescence decay functions of DCA + Bi (1.04 M) in acetonitrile taken at 550 nm (a) in the absence of $LiClO_4$ and in the presence of (b) 0.06 and (c) 0.4 M $LiClO_4$. Increasing of the salt concentration causes a shortening of the exciplex lifetime.

However, the Stern–Volmer plots are nonlinear for the exciplexes in acetonitrile and acetone. The Stern–Volmer plots are presented in Fig. 3. The correlation lines represent the predictions calculated using Eqs. (1)–(12).

It was not possible to match all experimental points representing the relative exciplex fluorescence lifetimes in the case of acetonitrile as solvent. Therefore, the fitting procedure was limited to the $LiClO_4$ concentration up to 0.2 M. The parameters recovered from the fitting procedure are: dipole moment of the associate $LiClO_4$, μ, the association constant, K_a, defined by the Eq. (7), the dipole–ion distance of closest approach, d_T, and the Stern–Volmer constant, K_{SV}. The fitted parameters are collected in Table 1.

6. Discussion

Petrucci and co-workers [15–22] applied the conductivity measurements to determine the thermodynamic association constants for lithium perchlorate ($LiClO_4$) and lithium hexafluoroarsenate ($LiAsF_6$) in solvents of low dielectric permittivities such as 2-methyl-tetrahydrofuran (2Me-THF $\epsilon_s = 6.24$), 1,2-dimethoxyethane (1,2-DME, $\epsilon_s = 7.0$), dimethyl carbonate (DMC, $\epsilon_s = 3.11$), tetrahydrofuran (THF, $\epsilon_s = 7.36$), 1,3-dioxolane (1,3-DXL, $\epsilon_s = 6.95$) and methyl acetate (MA, $\epsilon_s = 6.66$). Numerical analysis of the conductance data yielded the association constant for solute, dipole moment of ion pair, and the minimum approach distance between ion pairs, d_p. For simplification of the numerical calculations, it was assumed that the distance of closest approach dipole–ion, d_T, was 1.5 times larger that that of dipole–dipole, d_p. The values of dipole moment span the range 10–17.6 D [1] for lithium perchlorate, and 18.8–27.4 D for lithium hexafluoroarsenate. It has been also found that the equilibrium constant of association depends on the solvent

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[1] 1 D = 3.33×10^{-30} C m.

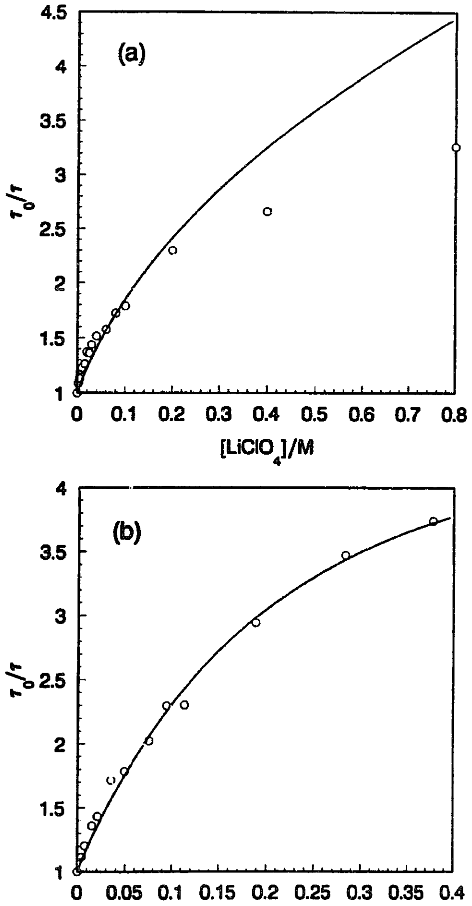

Fig. 3. Stern–Volmer plots of the systems DCA + Bi in acetonitrile (a) and acetone (b) quenched by lithium perchlorate. The correlation lines give the predictions calculated with the parameters collected in Table 1.

polarity. On the other hand, D'Aprano et al. [14] investigated the association equilibria of lithium perchlorate and lithium picrate in strongly polar solvents such as acetonitrile, *N,N*-dimethylformamide, and methanol. They found that although the two substances are in the same dielectric medium the equilibrium association constant of lithium picrate is much higher than that of lithium perchlorate. Their association equilibrium constant for $LiClO_4$ in acetonitrile is equal to 23.0 $dm^3\ mol^{-1}$ which is in good agreement with the value obtained from the exciplex fluorescence quenching analysis (equal to 29.9 $dm^3\ mol^{-1}$). The next plot provides some supports for the credibility of the method described previously.

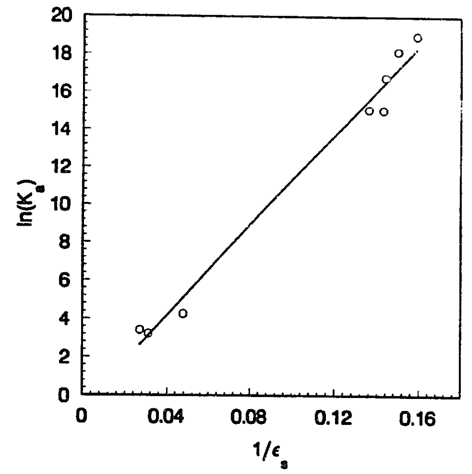

Fig. 4. Fuoss plot for the association constant $\ln(K_a)$ vs. the inverse of the dielectric constant of the solvent, $1/\epsilon_s$.

In Fig. 4 we can see the dependence of the $\ln(K_a)$ vs. the inverse of the dielectric constant, $1/\epsilon_s$. We find a quite good linear relationship between $\ln(K_a)$ and the inverse of ϵ_s that emerges from the Fuoss equation (Eq. (10)).

It remains to explain the discrepancies between the calculated and observed fluorescence quenching data which appear very clearly at higher salt concentration for acetonitrile solutions. This may be explained under the assumption that ternary complex ($Li^+/DCA^-/Bi^+$) which is formed due to dipole–ion interactions undergoes back dissociation to form (DCA^-/Bi^+) fluorescing species. Amounts of perchlorate anions which are the products of the salt dissociation interact with nonfluorescing complex ($Li^+/DCA^-/Bi^+$) and make the back dissociation possible. In acetone, however, the fraction of free perchlorate anions is smaller, therefore the back dissociation of ($Li^+/DCA^-/Bi^+$) is less effective. The concentration dependence of the fraction of free ions in acetonitrile and acetone is presented in Fig. 5.

The calculations of the fractions of free ions as a function of analytical concentration of $LiClO_4$ were done using the parameters obtained from the analysis of the nonlinear Stern–Volmer plots (Table 1). An additional support of this hypothesis lies in a fact that the exciplex fluorescence decay functions in acetonitrile become nonexponential at higher $LiClO_4$ concentration (cf. Fig. 2).

Table 1
Parameters characterizing the $LiClO_4$ association process in acetonitrile and acetone, obtained from the nonlinear least-square fitting method (see text for details)

Parameter	Abbreviation	Acetonitrile	Acetone
Stern–Volmer constant	K_{SV} in M^{-1}	14.2	21.9
Association constant	K_a in M^{-1}	29.9	70.7
Dipole moment	μ in D[a]	19.9	19.7
Minimum approach distance between the center of the dipole and the ion	d_T in Å	8.0	8.05

[a] 1 D = 3.33×10^{-30} C m.

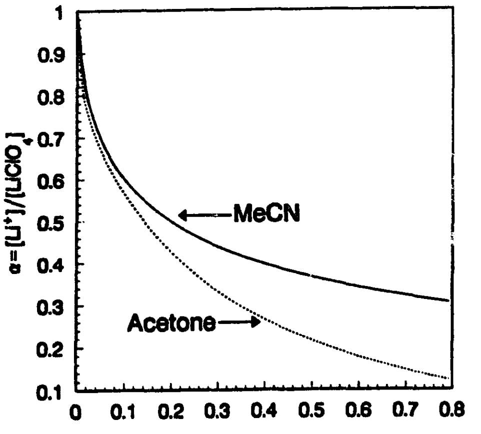

Fig. 5. Calculations of free ion fraction (α) of $LiClO_4$ in acetonitrile and acetone. The calculations were performed with fitted parameters (Table 1).

The next set of plots represents the simple test verifying how good our approach is.

We performed the minimization procedure keeping three parameters constant and varying only one. For example Fig. 6a represents FCN (Eq. (13)) values in logarithmic scale as a function of K_a with other parameters fixed, i.e., K_{SV}, μ, and d_T. Similar plots may be easily obtained for other sets of fixed and varied parameters (Fig. 6b–d). We can see that all these dependencies possess deep minima indicating that the applied procedure is verisimilar.

One important point at this stage of the discussion should be now introduced. In the calculations, it was assumed that the dielectric permittivity is constant upon addition of lithium perchlorate. Such situation does not appear in solvents with low dielectric constants [15–25]. In such systems the static dielectric permittivity increases with the solute concentration. The experimentally observed increasing of ϵ_s is undoubtedly due to the increasing number of ionic pairs. The ion pairs possessing larger dipole moments than those of solvent molecules increase the permittivity of solution. The initial increase of the static permittivity may be expressed by following relationship [23]:

$$\frac{d\epsilon_S}{dc}=\frac{N(\epsilon_\infty+2)^2\epsilon_1^2 10^3}{9\epsilon_0 kT(2\epsilon_1^2+\epsilon_\infty^2)}\mu^2 \qquad (14)$$

The ϵ_s and ϵ_1 indicate the dielectric permittivities of the solution and the pure liquid, respectively, whereas μ indicates the dipole moment of the ionic pair. Indeed, the dielectricity measurements of solutions containing onium perchlorates in solvents of low medium dielectric constants show that the static dielectric constants rise-in at small salt concentrations linearly to reach the saturation at larger concentrations [23–25]. From the initial slopes, the dipole moments of the dissolved salts were calculated giving the results which were comparable with those obtained from other methods.

The opposite situation appears in solvents of large dielectric permittivities such as water. The addition of the salts causes the lowering of dielectric permittivity. For example, the addition of 1 M 1:1 salts lowers ϵ_s of pure water about 10–17% depending on the mean ionic radii. The simplest explanation bases on the saturation effects in the primary hydration shell [33].

In the calculations which were performed in the present work, it was assumed that the addition of lithium perchlorate does not influence significantly the static permittivities of the

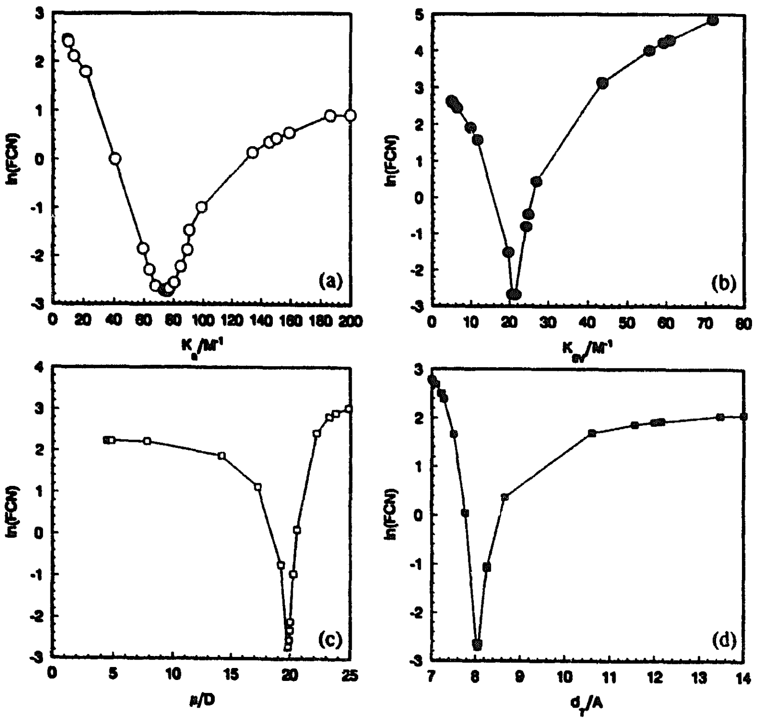

Fig. 6. Dependencies of: ln(FCN) on K_a (K_{SV}, μ, d_T are fixed) (a), ln(FCN) on K_{SV} (K_a, μ, d_T are fixed) (b), ln(FCN) on μ (K_a, K_{SV}, d_T are fixed) (c) and ln(FCN) on d_T (K_a, K_{SV}, μ are fixed) (d).

solutions. Sigvartsen et al. [25] measured the static permittivities of the solutions of tetra-*iso*-pentylammonium nitrate in dioxane–water mixtures. Changing of the dielectric permittivity of the mixture was caused by changing of the water content. From their results, one thing may be concluded: for solutions with the largest initial (without salt) polarity the increasing of ϵ_s due to the added salt is the smallest.

We believe that the changes of polarity of solvents due to addition of lithium perchlorate, if any, will be negligible both in acetone and acetonitrile.

7. Conclusions

The theoretical approach of Petrucci and Eyring [21] was applied to explain the nonlinear Stern–Volmer dependencies which describe the exciplex fluorescence quenching by lithium perchlorate in polar solvents. It has been found that such analysis yields the reasonable parameters which characterize the association process in solutions. This method is nonvalid if the quenching process, i.e., formation of ternary complex ($Li^+/DCA^-/Bi^+$), is reversible. In such case, the downward curvature of the Stern–Volmer plots is the result of the dissociation of ($Li^+/DCA^-/Bi^+$). The existence of the dissociation process of ($Li^+/DCA^-/Bi^+$) might be easily eliminated if we could observe the exponential decay functions in the presence of the quencher. The obtained association constant in acetonitrile agrees quite well with that obtained from the molar conductivity measurements.

We plan further investigations on the same topic in the near future.

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References

[1] I.R. Gould, R.H. Young, R.E. Moody, S. Farid, J. Phys. Chem. 95 (1991) 2068.

[2] I.R. Gould, R.H. Young, S. Farid, in: K. Honda (ed.), Photochemical Processes in Organized Molecular Systems, Elsevier, Amsterdam, 1991, pp. 19–40.

[3] I.R. Gould, S. Farid, J. Phys. Chem. 96 (1992) 7635.

[4] I.R. Gould, S. Farid, R.H. Young, J. Photochem. Photobiol. A: Chem. 65 (1992) 133.

[5] I.R. Gould, R.H. Young, L.J. Mueller, S. Farid, J. Am. Chem. Soc. 116 (1994) 8176.

[6] I.R. Gould, R.H. Young, L.J. Mueller, A.C. Albrecht, S. Farid, J. Am. Chem. Soc. 116 (1994) 8188.

[7] R.A. Marcus, J. Phys. Chem. 93 (1989) 3078.

[8] M. Mac, P. Kwiatkowski, A.M. Turek, J. Luminesc. 65 (1996) 341.

[9] M. Mac, P. Kwiatkowski, A.M. Turek, Chem. Phys. Lett. 250 (1996) 104.

[10] J. Mattay, M. Vandenhof, Topics Curr. Chem. 159, 119.

[11] J. Gersdorf, J. Mattay, J. Photochem. 28 (1985) 405.

[12] J. Gersdorf, J. Mattay, H. Görner, J. Am. Chem. Soc. 109 (1987) 1203.

[13] V. Ittah, D. Huppert, Chem. Phys. Lett. 173 (1990) 496.

[14] A. D'Aprano, B. Sesta, A. Princi, C. Filippi, M. Iammarino, J. Electroanal. Chem. 365 (1994) 119.

[15] P. Jagodzinski, S. Petrucci, J. Phys. Chem. 78 (1974) 917.

[16] H.E. Maaser, M. Delsignore, M. Newstein, S. Petrucci, J. Phys. Chem. 88 (1984) 5100.

[17] M. Delsignore, H. Farber, S. Petrucci, J. Phys. Chem. 89 (1985) 4968.

[18] H. Maaser, M. Xu, P. Hemmes, S. Petrucci, J. Phys. Chem. 91 (1987) 3047.

[19] M. Xu, N. Obeid, E.M. Eyring, S. Petrucci, J. Phys. Chem. 93 (1989) 989.

[20] M. Salomon, M. Uchiyama, M. Xu, S. Petrucci, J. Phys. Chem. 93 (1989) 4374.

[21] S. Petrucci, E.M. Eyring, J. Phys. Chem. 95 (1991) 1731.

[22] H. Farber, D.E. Irish, S. Petrucci, J. Phys. Chem. 87 (1983) 3515.

[23] B. Gestblom, J. Songstad, Acta Chem. Scand. B 41 (1987) 396.

[24] T. Sigvartsen, B. Gestblom, E. Noreland, J. Songstad, Acta Chem. Scand. 43 (1989) 103.

[25] T. Sigvartsen, J. Sonstad, B. Gestblom, E. Noreland, J. Solut. Chem. 20 (1991) 565.

[26] S. Nishikawa, S. Morinaga, M. Yoshio, Bull. Chem. Soc. Jpn. 66 (1993) 3627.

[27] R.M. Fuoss, C.A. Krauss, J. Am. Chem. Soc. 55 (1933) 21, 476.

[28] J. O' M. Bocris, A.K.N. Reddy, in: Modern Electrochemistry, Vol. 1 (Plenum, New York, 1973) Ch. 3.

[29] F. James, M. Ross, Comput. Phys. Chem. 20 (1980) 29.

[30] E. Vauthey, P. Suppan, E. Haselbach, Helv. Chim. Acta 71 (1988) 93.

[31] I.R. Gould, D. Ege, J.E. Moser, S. Farid, J. Am. Chem. Soc. 112 (1990) 4290.

[32] K. Kikuchi, J. Photochem. Photobiol. Chem. A 65 (1992) 149.

[33] B.E. Convay, in: Ionic Hydration in Chemistry and Biophysics, Elsevier, Amsterdam, 1981, Ch. 14.