

Intramolecular Charge Transfer Reaction in Solutions of Low to High Electrolyte Concentrations: Interplay between Friction and Solvation

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Abstract Fluorescence emission spectroscopy have been used to investigate the effects of electrolytes on the excited state intramolecular charge transfer (ICT) reaction in 4-(1-azetidiny)benzotrile (P4C) in very dilute to concentrated electrolyte solutions of ethyl acetate (EA), acetonitrile (AN) and ethanol (EtOH). In the limit of very low electrolyte concentrations, the reaction rate ($= 1/\tau_{\text{rxn}}$, τ_{rxn} being the reaction time) is found to *decrease* with increasing electrolyte concentration, the extent of decrease being the maximum in EA and the minimum in AN. At moderate to higher electrolyte concentrations, however, the rate increases upon further addition of electrolyte. The observed non-monotonic electrolyte concentration dependence of rate is believed to occur due to a novel interplay between friction and solvation experienced by the photo-excited reactant in solution. Moreover, the long time decay constant and amplitude of the bi-exponential decay of the time resolved fluorescence emission intensity also show a significant electrolyte concentration dependence which corroborates the relevant steady-state results.

Keywords Intramolecular charge-transfer reaction · Non-monotonic electrolyte concentration dependence · Time resolved spectroscopy

1 Introduction

Understanding the effects of electrolytes on simple chemical events in the solution phase is an interesting area of research as many biologically relevant and industrially important reactions occur in electrolyte solutions [1–5]. In addition to ions, complex species such as

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ion-pairs, triple ions and neutral ion-solvent aggregates [6–11] are also present in electrolyte solutions which make the structure and dynamics of the environment more complex and different from host solvents. For example, the average solvation time of a polarity probe in electrolyte solutions is in the nanosecond regime [6–8, 12] which is at least 1000 times larger than that in pure dipolar solvents at room temperature. Also, the average solvation time has been found to decrease considerably as the electrolyte solution is changed from low to moderately concentrated ones [12]. In addition, the square root of the medium polarity (dielectric constant, ϵ_0) dependence of the Debye screening length [13] opens up the possibility of stronger ion-probe direct interactions in electrolyte solutions of low polarity solvents.

The modification of solution structure and dynamics in the presence of electrolytes can affect a simple chemical event, such as an intramolecular charge-transfer reaction, in the following manner. As the charge-transfer (CT) state is more polar in nature [14–16], the presence of ions in solution can increase the formation of the CT state via the relatively stronger ion-dipole interaction. This is an equilibrium effect and is a manifestation of the increased stabilization of the product through solvation. However, if the formation of the CT state involves simultaneous intramolecular rotation [14–20], the rate of the reaction (that is, formation of CT state) would be slowed down as the rotating moiety will experience higher friction due to the same ion-dipole interaction [21–23]. Since the ion-atmosphere relaxation time scale ($\sim\langle\tau_{\text{solv}}\rangle$, the average solvation time) is much slower than the reaction time scale ($\sim\omega_b^{-1}$, inverse of the barrier frequency), the ion-atmosphere remains out of equilibrium during barrier crossing [21, 22]. This non-equilibrium effect, in turn, exerts more electrodynamic friction [21, 22] on the reactive (rotating) mode. Therefore, a competition between these two opposing effects (extra stabilization versus electrodynamic friction) may give rise to non-monotonic electrolyte concentration dependence of the intramolecular reaction rate. The reaction rate at higher electrolyte concentrations is further affected by, at least, two other factors: (i) the barrier height ($\sim 6k_B T$ [16]) changes [24, 25] due to the modification of the average solution dielectric constant upon addition of electrolyte and (ii) the faster solution dynamics at higher concentrations reduces the dynamic friction arising from non-equilibrium effects. These two factors can act simultaneously to enhance the rate of the intramolecular reaction significantly in solutions containing electrolyte in the moderate to high concentration range.

In this article we present results of our spectroscopic studies on the photo-excited intramolecular charge-transfer reaction in 4-(1-azetidiny)benzonitrile (P4C) in LiClO_4 solutions of ethyl acetate, ethanol and acetonitrile with the electrolyte (LiClO_4) concentrations ranging from very dilute to the highest concentrations accessible (limited by the solubility) in these media. While the three solvents considered here represent solvents from three different categories (non-associating weakly polar, associating and non-associating strongly polar), the reaction rate being the slowest [16–19] in P4C among the molecules in the PnC series is best suited within the broad time resolution available to us. As before, the formation of the locally excited (LE) state upon photo-excitation of P4C and its subsequent conversion to the charge-transfer (CT) state is explained in terms of the well-known twisted intramolecular charge-transfer (TICT) mechanism [14–20]. In this mechanism, charge transfer in the photo-excited molecule is believed to take place *simultaneously* with the rotation of the donor (D) moiety around the central bond joining the acceptor (A) group (see, for example, Scheme 1 of Ref. [20]). As described earlier [14–20], the LE state can either lead to the formation of the CT state with a forward reaction rate, k_f , or, decay to the ground state with an average (radiative + non-radiative) rate, k_{LE} . Similarly, the CT state can populate back the LE state with a reverse reaction rate, k_r and also can come back to the ground state with

an average rate, k_{CT} . The activation barrier [16] associated with the LE \rightarrow CT conversion reaction in the photo-excited P4C molecule is $\sim 6k_B T$. We use the Eq. 3.5 derived (assuming rapid solvent reorganization) in Ref. [16] in order to analyze the time dependence of the LE or CT intensity as well as to determine the rate of the LE \rightarrow CT conversion reaction in P4C. We would like to mention here that data (both from steady state and time-resolved studies) obtained for solutions with very low electrolyte concentrations ($< 0.10 \text{ mol}\cdot\text{L}^{-1}$) in ethyl acetate and data in ethanol for the entire electrolyte concentration range as well as the time-resolved data for electrolyte solutions in acetonitrile are presented here for the first time. In order to show the continuous variation of the reaction yield and rate in the full range of electrolyte concentrations (from very low to very high) in these solvents, earlier results [18, 19] at high LiClO_4 concentrations in ethyl acetate and acetonitrile (steady state only) are also presented.

The main results of the article are as follows. The total red-shift in the absorption spectrum of P4C for increasing the concentrations of LiClO_4 up to $1.0 \text{ mol}\cdot\text{L}^{-1}$ in ethyl acetate, ethanol and acetonitrile is in the range of $300\text{--}400 \text{ cm}^{-1}$, which increases to $\sim 1000 \text{ cm}^{-1}$ and 700 cm^{-1} , respectively, in ethyl acetate and ethanol upon increasing the concentration to $3.0 \text{ mol}\cdot\text{L}^{-1}$. A further increase of LiClO_4 concentration up to $5.0 \text{ mol}\cdot\text{L}^{-1}$ in ethanol produces an additional red shift of about 50 cm^{-1} only. Even though the electrolyte-induced red-shift in the LE band is very small ($\sim 100 \text{ cm}^{-1}$) in all these solvents, the total shift in the CT band is quite large, approximately 3000 cm^{-1} in ethyl acetate and $\sim 1100 \text{ cm}^{-1}$ in ethanol and acetonitrile for the full concentration range studied. As observed earlier in electrolyte solutions of ethyl acetate and acetonitrile [18, 19], the total emission quantum yield of P4C in ethanol also decreases exponentially with electrolyte concentration.¹ In all these solvents, the formation of the CT population increases with the increase in electrolyte concentration, the rate of increase being the steepest for ethyl acetate. A bi-exponential function of time has been found to fit adequately the time-resolved LE or CT fluorescence-emission intensity at all concentrations in these solvents. Most interestingly, the reaction time for the LE \rightarrow CT conversion in P4C has been found to increase with electrolyte concentration in the low electrolyte concentration range ($\leq 0.10 \text{ mol}\cdot\text{L}^{-1}$) which, upon further increase of concentration, decreases, giving rise to a non-monotonic electrolyte concentration dependence of the reaction rate. The non-monotonic nature is found to be the strongest for ethyl acetate and weakest for ethanol, even though the electrolyte-induced increase in reaction rate at higher concentrations is the highest in ethanol.

The organization of the rest of the paper is as follows. Experimental details are given in the next section. Section 3 contains experimental results from our steady-state and time-resolved studies. Supporting information is given wherever necessary. The article then ends with concluding remarks in Sect. 4.

2 Experimental Details

2.1 Sample Preparation

4-(1-azetidiny)benzotrile (P4C) was synthesized by following a protocol given in the literature [26, 27] and re-crystallized twice from cyclohexane (Merck, Germany). Purity of

¹The electrolyte concentration (M , $\text{mol}\cdot\text{L}^{-1}$) dependence of net quantum yield (Φ) of P4C in ethanol can be fitted to the following bi-exponential function of concentration: $\Phi(M) = a \exp[-bM] + c[dM]$, where $a = 0.007$, $b (\text{L}\cdot\text{mol}^{-1}) = 5.619$, $c = 0.014$, $d (\text{L}\cdot\text{mol}^{-1}) = 0.229$ with $R = 0.99$.

the compound was checked by thin-layer chromatography and monitoring the excitation wavelength dependence of fluorescence emission in several bulk polar and non-polar solvents. Ethyl acetate, ethanol, acetonitrile and LiClO_4 were used as received (highest grade, Aldrich). Electrolyte solutions at the desired concentrations in a given solvent were made by diluting a stock solution which was prepared by dissolving a calculated amount of electrolyte in a given solvent.

2.2 Steady-State Measurements and Estimation of Spectral Properties

Steady-state absorption spectra were recorded using a Shimadzu, UV-2450 spectrophotometer. Steady-state emission spectra were recorded by using a fluorimeter (SPEX fluoromax-3, Jobin-Yvon, Horiba) after adjusting the absorbance of the sample to ~ 0.1 (concentration of P4C in solution $< 10^{-5}$ mol·L $^{-1}$). Measurements were made in a quartz cuvette with 1 cm optical path length. For a given sample, the peak wavelength (λ) of the absorption spectrum was used as excitation wavelength for the corresponding emission scan. The fluorescence spectra were corrected for the wavelength dependence of the sensitivity of the apparatus; the solvent background was subtracted and converted properly to the frequency plane before calculating several steady state properties. A few samples were bubbled with dry argon gas and the absorption and emission spectra were collected. As observed earlier [16–20], these runs showed very little or no effects on the spectra of P4C in solutions and also on the decay kinetics.

The equilibrium constants (K_{eq}) and the change in reaction Gibbs energy ($-\Delta G_r$) for the LE \rightarrow CT conversion reaction in P4C were then determined from the area under the LE and CT bands obtained after deconvolution of the full emission spectrum of P4C into two fragments by using the reference emission spectrum of P4C in perfluorohexane [16–20]. The following formula [16] has been used to obtain K_{eq} and ΔG_r : $\Delta G_r = -RT \ln K_{\text{eq}} = -RT \ln(\alpha_{\text{CT}} \nu_{\text{LE}}^3 / \alpha_{\text{LE}} \nu_{\text{CT}}^3)$, where α_x ($x = \text{LE}$ or CT) and ν_x represent respectively the area under a band and the peak frequency of that band. Algebraic addition of the shifts of the emission spectra from the peak of the reference emission spectrum to the *average* peak frequency of the reference emission spectrum then provided the emission peak frequencies of the LE and CT bands. The *average* of the reference emission peak frequency was calculated by averaging the numbers obtained by fitting the upper half of the reference emission spectrum with an inverted parabola, first moment and the arithmetic mean of the frequencies at half intensities on both blue and red ends of the emission spectrum [16–20]. Absorption peak frequencies were obtained by calculating the first moments of the absorption spectra. The error associated with the peak frequency determination is typically ± 250 cm $^{-1}$ and that with the band area is $\sim 10\%$ (of the reported value), unless otherwise mentioned.

2.3 Time-Resolved Measurements

Time-resolved fluorescence emission intensity decays were collected using time-correlated single-photon-counting (TCSPC) technique based on a laser system (Lifespec-ps, Edinburgh, UK) with a light emitting diode (LED) that provided 299 nm light as excitation. The full width at half maximum of the instrument response function (IRF) with the above excitation was approximately 475 ps. The emission decay was collected at the magic angle at both LE and CT peak positions (of the steady-state spectrum) with an emission band pass of 8 nm. Subsequently, the collected emission decays were deconvoluted from the IRF and fitted to bi-exponential function of time using an iterative reconvolution algorithm [16]. For all concentrations of LiClO_4 in all these solvents, each of the LE emission decays was

found to fit with one short-time constant and one long-time constant, whereas each of the CT emission decays (collected wherever possible) could be fit with one rise time (similar to short-time constant of LE decay) and one long-time constant. Therefore, the short-time constant associated with the LE decay was considered as the reaction time. In non-polar pure solvents, such as in heptane or hexane, the LE decay of P4C was found to decay single-exponentially with one time constant in the range of a couple of nanoseconds [16, 20]. For a few cases, emission decays were collected at two or three different emission wavelengths around the LE and CT peaks and the analyzed data were found to vary within a small uncertainty. All the experiments were performed at room temperature, 295 ± 0.5 K.

3 Results & Discussion

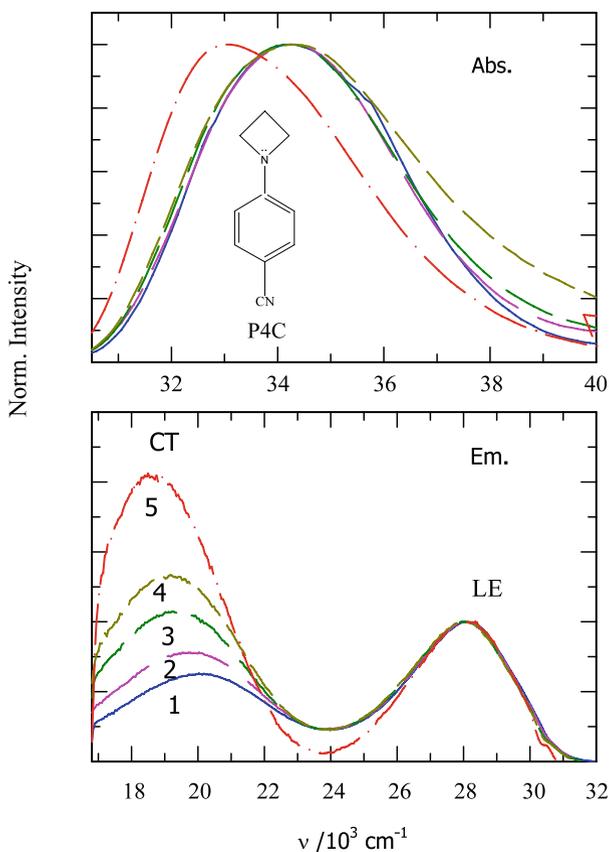
3.1 Steady-State Spectroscopic Studies

Representative absorption and emission spectra of P4C in LiClO_4 solutions of ethanol at five different concentrations are presented in Fig. 1 in order to show the effects of electrolyte on absorption and emission spectra of this intramolecular charge-transfer molecule. Figure 1 shows that relative to the absorption spectrum (upper panel) in pure ethanol, electrolyte concentrations as high as $1.0 \text{ mol}\cdot\text{L}^{-1}$ does not induce much shift in the spectrum ($\sim 350 \text{ cm}^{-1}$), except broadening the envelop by another $\sim 250 \text{ cm}^{-1}$. Upon increasing the concentration to $5.0 \text{ mol}\cdot\text{L}^{-1}$, the absorption spectrum broadens further by $\sim 500 \text{ cm}^{-1}$ with a concomitant red-shift by $\sim 750 \text{ cm}^{-1}$. Relative to the observed moderate effects on the absorption spectrum, the electrolyte-induced change in the emission spectrum is more pronounced. The emission spectra of P4C in pure ethanol and ethanolic solutions of LiClO_4 shown in the lower panel clearly suggest that the CT population increases as the electrolyte concentration is increased in the solution. In fact, the CT population increases by almost a factor of four at $5.0 \text{ mol}\cdot\text{L}^{-1}$ from that in pure ethanol along with a red-shift in the CT band by about 1150 cm^{-1} . These changes are discussed in more detail below.

The electrolyte concentration dependence of spectral peaks (absorption and CT emission) and band-widths of P4C in solutions of ethyl acetate, ethanol and acetonitrile are shown respectively in Figs. 2 and 3. As already discussed, the absorption spectra in all these solvents at $1.0 \text{ mol}\cdot\text{L}^{-1}$ LiClO_4 solutions show a red-shift by $\sim 400 \text{ cm}^{-1}$ from those in pure solvents, which is further shifted by $\sim 300\text{--}500 \text{ cm}^{-1}$ upon increasing the concentration to $3.0 \text{ mol}\cdot\text{L}^{-1}$ in ethyl acetate and ethanol. The electrolyte concentration dependence of the LE band is negligible and is summarized in Table S1 of the Supporting Information. The shift in the CT band is, however, much larger and in presence of $3.0 \text{ mol}\cdot\text{L}^{-1}$ LiClO_4 the red-shift is approximately 3.5 times more in ethyl acetate than that in ethanol even-though the dielectric constant (ϵ_0) of the former is approximately four times lower than the latter. Note that the increase of electrolyte concentration to $0.5 \text{ mol}\cdot\text{L}^{-1}$ produces $\sim 70\text{--}80\%$ of the total observed shift in all these solvents which indicates the presence of direct ion-solute interaction in dilute electrolyte solutions. Further increase in concentration does contribute to the stabilization energy (red-shift) but by relatively a small amount and originates mostly from the increase in average dielectric constant of the solution because of the presence of ion pairs at high electrolyte concentrations. The large concentrations of ion pairs (solvent-separated and solvent-shared) are also probably responsible for making the solution dynamics faster at the high concentration regime because the fast rotational motion of these ion pairs enhances the rate of the orientational polarization relaxation [23] of the medium.

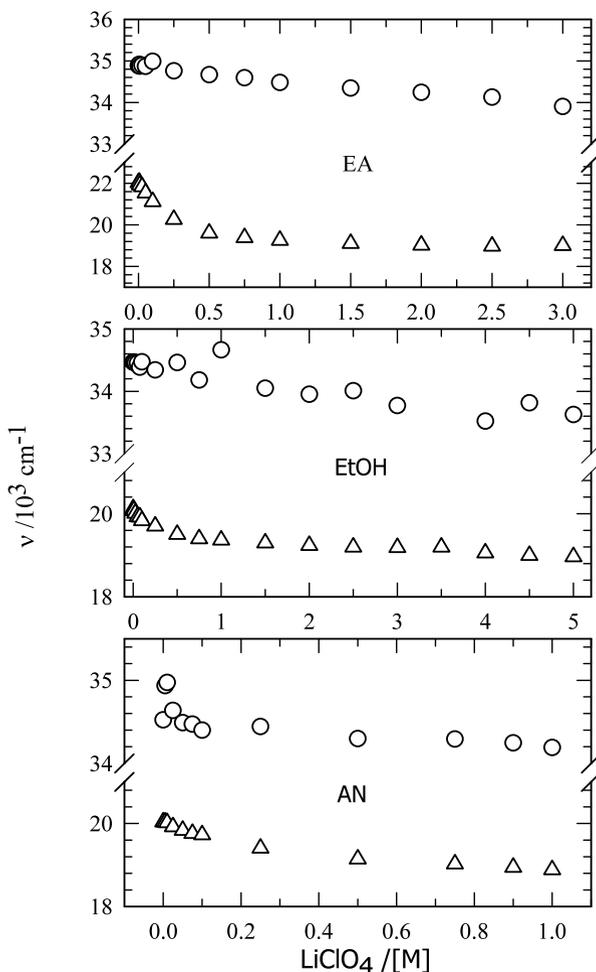
The electrolyte (LiClO_4) concentration dependence of the width of the absorption spectrum and that of the inhomogeneous width of the CT emission band, shown in Fig. 3,

Fig. 1 Representative absorption (*upper panel*) and emission (*lower panel*) spectra of 4-(1-azetidiny)benzonitrile (P4C) in several concentrations of LiClO₄ in ethanol. Spectra shown in color here are for the following LiClO₄ concentrations (M): 0.0 (1), 0.1 (2), 0.5 (3), 1.0 (4) and 5.0 (5). The color code remains the same for both the absorption and emission spectra. The molecule (P4C) is shown in the *inset of the upper panel*



warrants the following comments. As it is seen here and also was observed earlier [17] that in both ethyl acetate and acetonitrile, the CT width shows a non-monotonic electrolyte concentration dependence. Relative to the inhomogeneous CT width in neat ethyl acetate and acetonitrile, the CT band broadens by more than 1500 cm^{-1} and 500 cm^{-1} in 0.25 $\text{mol}\cdot\text{L}^{-1}$ LiClO₄ solutions in ethyl acetate and acetonitrile, respectively. Recently, this dependence for the CT width has also been found for another closely related ICT molecule in AOT/heptane/water reverse micelles where the static dielectric constant of the confined water pool has been estimated to be similar to those of moderately polar organic solvents [20]. As the spectral width depends both on solute-environment interactions and solution heterogeneity, the presence of ion-solute direct interaction contributes to the width. Secondly, formation of various ion-solvent complexes in electrolyte solutions gives rise to microscopic heterogeneity in the medium that can also modify the spectral width. Upon further addition of electrolyte, concentrations of ion pairs increase which make the environment less heterogeneous. This, in turn, reduces the spectral width at moderate and high electrolyte concentrations. However, the non-monotonic electrolyte concentration dependence of the CT band-width is not found for LiClO₄ solutions in ethanol, even though the CT width at higher electrolyte concentrations ($>0.50 \text{ mol}\cdot\text{L}^{-1}$) remain very similar for P4C in all these solvents. Whether the different concentration dependence of the CT width in ethanol is because of its associative nature or not, cannot be ascertained from this study as that would require further investigation with several other alcohols. While the LE width does

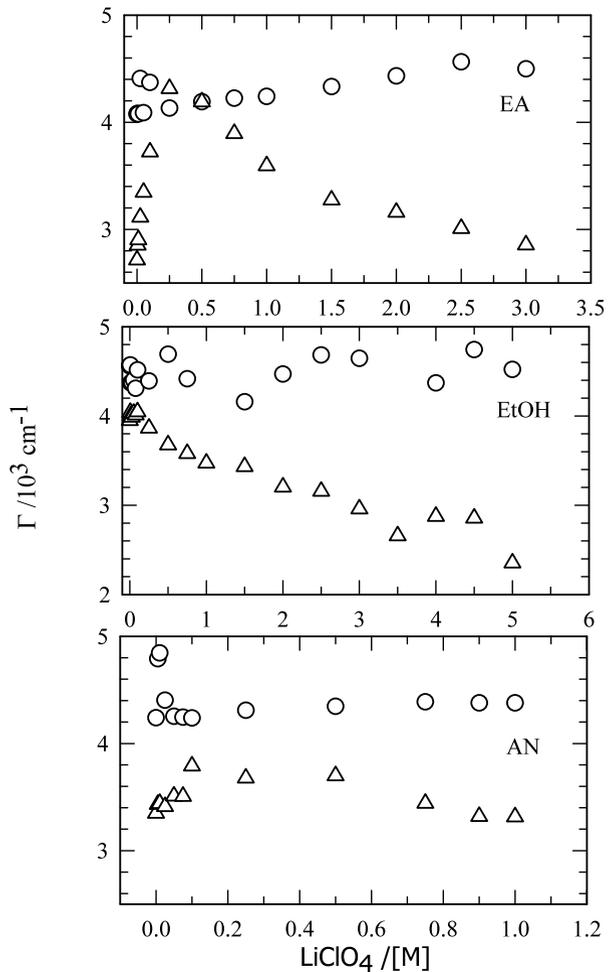
Fig. 2 Electrolyte (LiClO_4) concentration dependencies of absorption (circles) and emission (triangles) peak frequencies 4-(1-azetidiny)benzonitrile (P4C) in solutions of ethyl acetate (upper panel, 'EA'), ethanol (middle panel, 'EtOH') and acetonitrile (lower panel, 'AN'). For discussions, see text



not change with electrolyte concentration (Table S1), the absorption band-width varies by a small amount ($<500 \text{ cm}^{-1}$) in electrolyte solutions of these solvents.

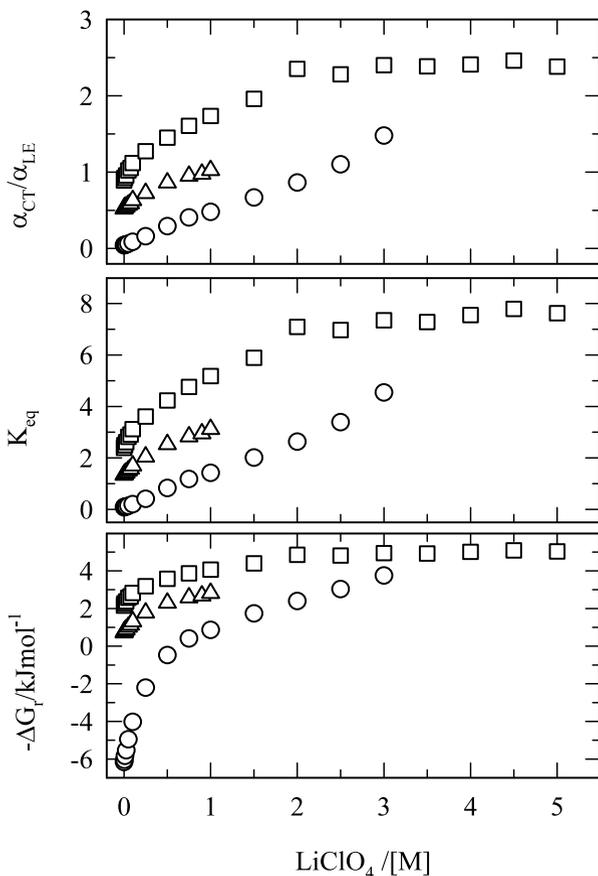
Figure 4 shows the variations of CT/LE area ratio ($\alpha_{\text{CT}}/\alpha_{\text{LE}}$), equilibrium constant (K_{eq}) for the $\text{LE} \rightarrow \text{CT}$ conversion reaction in P4C and change in reaction Gibbs energy ($-\Delta G_r$) associated with the conversion in ethyl acetate, acetonitrile and ethanol as a function of LiClO_4 concentration. Note that the CT/LE area ratio (upper panel) increases with electrolyte concentration and the rate of increase is the steepest for ethyl acetate. For example, the area ratio increases by a factor of 36 in ethyl acetate upon increasing the electrolyte concentration from 0.0 to 3.0 $\text{mol}\cdot\text{L}^{-1}$. On the other hand, the area ratio increases by a factor of 2.5 and 2 for increasing the electrolyte concentration from 0.0 to 5.0 $\text{mol}\cdot\text{L}^{-1}$ in ethanol and to 1.0 $\text{mol}\cdot\text{L}^{-1}$ in acetonitrile. These changes in area ratio then lead to the increase in equilibrium constant by a factor of ~ 57 in ethyl acetate, ~ 3 in ethanol and ~ 2 in acetonitrile. This means that the formation of the CT state is most strongly favored upon addition of electrolyte in the lowest polarity solvent (ethyl acetate) among these three solvents considered here. This is further reflected in the electrolyte concentration dependence of the reaction

Fig. 3 Electrolyte (LiClO_4) concentration dependence of line widths (full width at half maxima, Γ) of the absorption spectra and CT bands of 4-(1-azetidynyl)benzotrile (P4C) in solutions of ethyl acetate (*upper panel*, 'EA'), ethanol (*middle panel*, 'EtOH') and acetonitrile (*lower panel*, 'AN'). Absorption and CT width are denoted by *circles* and *triangles*, respectively. The error bar associated with the fwhm is $\pm 250 \text{ cm}^{-1}$ (of the reported value) which is based on a maximum of 4 different measurements). Note that the CT band-width shown here is the 'inhomogeneous' width required to fit the CT emission band while dissecting the entire emission spectrum into two fragments. For further discussion, see text



Gibbs energy (lower panel) where $-\Delta G_r$ increases by a factor of ~ 2.5 and ~ 4.0 for acetonitrile and ethanol when compared with the data in neat solvents and those at the highest LiClO_4 concentrations considered in these solvents. For ethyl acetate, however, $-\Delta G_r$ increases sharply up to $0.5 \text{ mol}\cdot\text{L}^{-1}$ and finally changes its sign (from negative to positive) around this concentration, indicating an unfavorable reaction is becoming highly favorable upon addition of electrolyte. Note $-\Delta G_r$ for the conversion reaction in ethyl acetate at $1.0 \text{ mol}\cdot\text{L}^{-1}$ LiClO_4 becomes comparable to that in neat acetonitrile even though the solution dielectric constant is estimated to be half of that of neat acetonitrile [6]. This further stresses the role of direct interaction between the reactant and various species present in solutions of low polarity solvents that control the intramolecular charge-transfer reaction in such media. Interestingly, $-\Delta G_r$ in ethanol remains larger than in acetonitrile at all LiClO_4 concentrations which is somewhat counter-intuitive since ethanol is less polar ($\epsilon_0 \approx 24.5$) than acetonitrile ($\epsilon_0 \approx 36$) [28].

Fig. 4 Electrolyte concentration dependencies of ratio the population under the CT and LE emission bands (α_{CT}/α_{LE} , *upper panel*), equilibrium constant (K_{eq} , *middle panel*) and change in reaction Gibbs energy ($-\Delta G_r$, *lower panel*) associated with the LE \rightarrow CT conversion reaction in solutions of ethyl acetate, ethanol and acetonitrile. While the data in ethyl acetate are shown by circles, those in ethanol and acetonitrile are represented respectively by squares and triangles. The error bar associated with the area calculation is typically $\pm 10\%$ (of the reported value) which is based on a maximum of 4 different measurements)

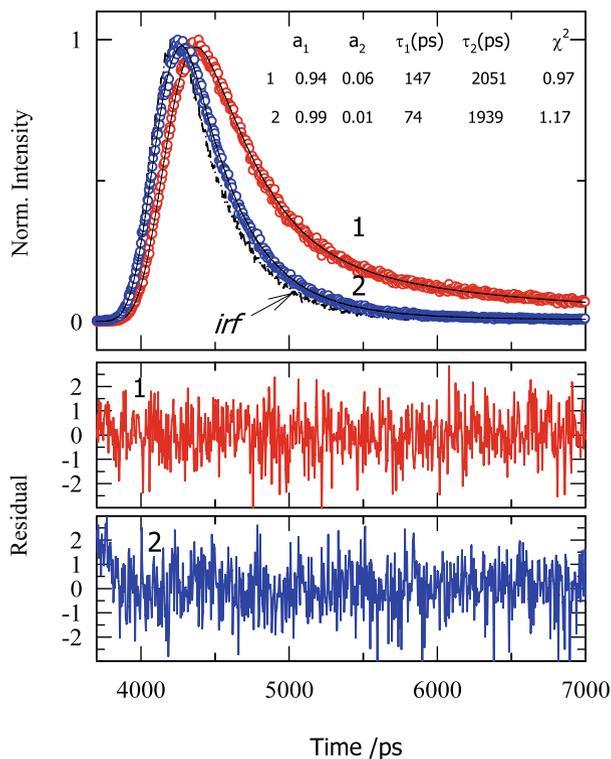


3.2 Time-Resolved Fluorescence Studies

Here we present the electrolyte concentration dependence of reaction rate (inverse of reaction time) for the LE \rightarrow CT conversion reaction of P4C as well as that of the average LE decay time and decay amplitudes in three solvents—ethyl acetate, ethanol and acetonitrile. As already mentioned, the reaction rates in ethyl acetate at higher electrolyte concentrations have already been presented elsewhere and the results at low concentrations in this solvent are new and never presented before. In addition, results obtained from time dependent studies in electrolyte solutions of ethanol and acetonitrile are discussed here for the first time.

Figure 5 shows the time-resolved decay of LE intensity for P4C in neat ethanol ('1') and in ethanolic solution of $2.5 \text{ mol}\cdot\text{L}^{-1}$ LiClO_4 ('2') along with the bi-exponential fits where the fit parameters are also tabulated. Note here that even though the amplitude of the long-time component is very small, a mono-exponential function of time has been found to be insufficient to describe the intensity decay. The values for the 'goodness of fit' parameter (χ^2) and the time dependence of the residuals (shown in the two lower panels) suggest that the bi-exponential function can indeed adequately fit these decays. Similar fits have also been obtained for other concentrations in ethanol as well as in ethyl acetate and acetonitrile at all electrolyte concentrations. It is evident from this figure that electrolyte affects the reaction rate significantly and in fact the reaction rate becomes *double* in ethanolic solution

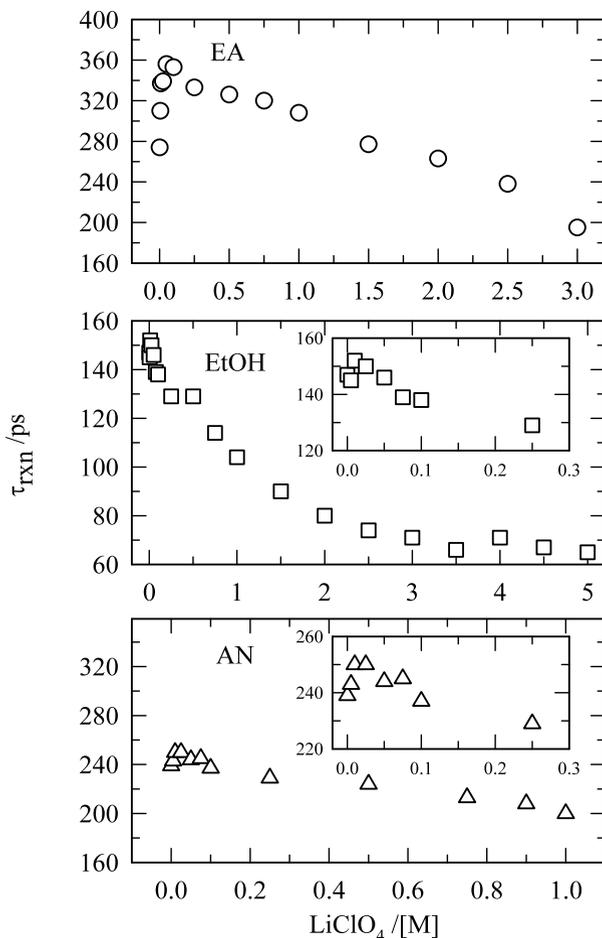
Fig. 5 Representative LE emission decays of P4C in pure ethanol ('1') and in presence of 2.5 (mol·L⁻¹) LiClO₄ ('2'). While the data are represented by the circles, bi-exponential fits through the data are represented by the *solid lines*. The instrument response function (IRF) is also shown (*dashed line*). Results obtained from fits are also provided in the upper panel. Residuals are shown in the *lower panel*. Note that the LE peak count is ~3000



of 2.5 mol·L⁻¹ LiClO₄ than that in neat ethanol. We would like to mention that the collected emission decays at wavelengths near the CT emission peaks could also be fitted to bi-exponential functions with same or similar time constants as found for the corresponding LE decays. For example, in the presence of 0.10 mol·L⁻¹ LiClO₄ in ethanol, fitting of the CT emission decay with no constraints produces time constants 128 ps (rise time) and 2024 ps with $\chi^2 = 1.04$. This time constant (rise time) is very similar to the fast time constants (decay time, 138 ps) of the LE decay, indicating that these time constants are essentially associated with the reaction rate [16–20]. Addition of a third exponential did not produce a better fit which has also been observed in several of our earlier studies [18–20]. However, missing the faster component due to the limited time resolution employed in our experiments may also lead to the observed bi-exponential decay of the time dependent emission intensity. The short time constants obtained from the bi-exponential fits to the LE emission decays are therefore considered as reaction times for P4C in solutions of these solvents at various electrolyte concentrations.

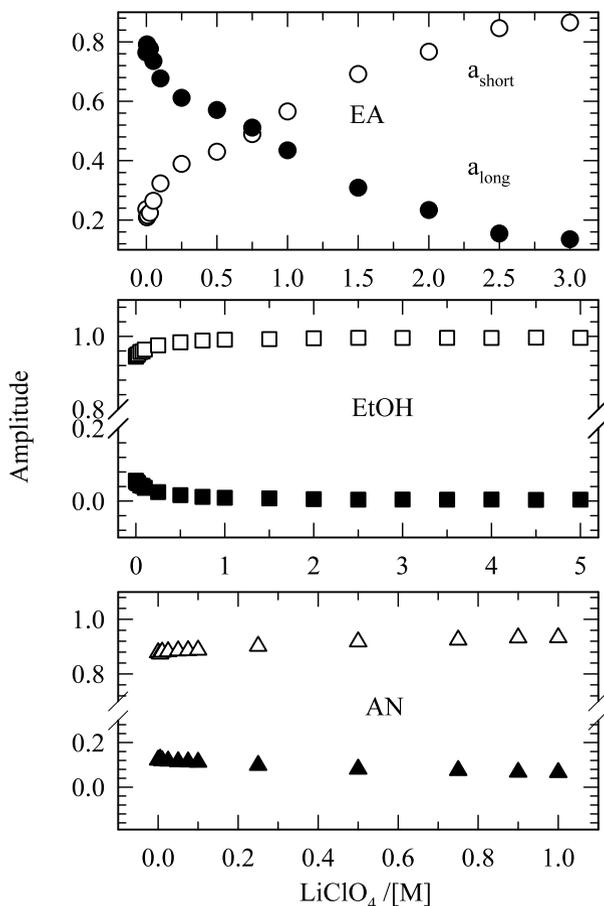
Figure 6 shows the electrolyte (LiClO₄) concentration dependence of reaction time (τ_{rxn}) for P4C in ethyl acetate, ethanol and acetonitrile. The low concentration data for ethanol and acetonitrile are shown separately in the *insets*. Interestingly, in all these solvents, τ_{rxn} increases upon addition of electrolyte in the low concentration regime (<0.05 mol·L⁻¹) and then decreases systematically upon further addition of electrolyte. Relative to the reaction time in neat solvents, τ_{rxn} in the low concentration regime increases by a maximum of ~30% in ethyl acetate and only by ~5% in ethanol and acetonitrile (see Fig. S1, Supporting Information). This electrolyte-induced increase of τ_{rxn} can be explained as follows: (i) electrolyte solution dynamics being very slow at low concentration, the reactive mode (rotating moi-

Fig. 6 Electrolyte (LiClO_4) concentration dependence of reaction time (τ_{rxn}) for the $\text{LE} \rightarrow \text{CT}$ conversion reaction of P4C in solutions of ethyl acetate (*upper panel*), ethanol (*middle panel*) and acetonitrile (*lower panel*). Note that the low concentration data in electrolyte solutions of ethanol and acetonitrile are presented separately in the *insets* in order to show the non-monotonic electrolyte concentration dependence of the reaction rate



ety) experiences excess dynamic friction [21, 22] and (ii) slow stabilization of the charge-transfer state due to slow solution dynamics. In this concentration range the increase in solution dielectric constant is not significant and hence the barrier height remains largely unchanged [24, 25]. However, at higher electrolyte concentrations, the average solution dielectric constant increases considerably which reduces the barrier height. This leads to an increase in reaction rate (static solvent effects). Moreover, the electrolyte solution dynamics being faster at higher concentrations, the dynamic friction experienced by the reactive mode is relatively less in this limit, leading to an enhancement of the reaction rate (dynamic solvent effects) [21, 22]. The combined effects of lowering the barrier height due to an increase in the solution dielectric constant and faster environmental reorganization lead to the $\text{LE} \rightarrow \text{CT}$ conversion reaction of P4C proceeding at a rate $\sim 30\%$ higher at $3.0 \text{ mol}\cdot\text{L}^{-1}$ in ethyl acetate, $\sim 60\%$ higher at $5.0 \text{ mol}\cdot\text{L}^{-1}$ in ethanol and $\sim 15\%$ higher at $1.0 \text{ mol}\cdot\text{L}^{-1}$ in acetonitrile solutions than those in neat solvents (Fig. S1, Supporting Information). Therefore, the different modification of the reaction rate by electrolytes at low and high concentration limits is probably arising out of a novel interplay between environmental friction and reorganization (solvation) effects.

Fig. 7 Electrolyte (LiClO_4) concentration dependence of amplitudes (a_{short} and a_{long}) associated with the $\text{LE} \rightarrow \text{CT}$ conversion reaction of P4C in electrolyte solutions in ethyl acetate ('EA'), ethanol ('EtOH') and acetonitrile ('AN'). Note that a_{short} is denoted by open symbols, whereas a_{long} is represented by the solid ones



Just as the short time constant (considered as τ_{rxn}) is affected by the electrolyte concentration, the long time constant (τ_{long}) associated with the LE decay also shows significant LiClO_4 concentration dependence. In fact, τ_{long} decreases by a factor of ~ 5 at $3.0 \text{ mol}\cdot\text{L}^{-1}$ in ethyl acetate and by a factor of ~ 2.5 at $1.0 \text{ mol}\cdot\text{L}^{-1}$ in acetonitrile from the neat solvent values (Fig. S2, Supporting Information). However, the electrolyte effects on τ_{long} in ethanol are very small, being only $\sim 15\%$ less at $5.0 \text{ mol}\cdot\text{L}^{-1}$ LiClO_4 than that in pure ethanol. The concentration dependence of the respective amplitudes (a_{short} and a_{long}) of the LE decay in ethyl acetate, ethanol and acetonitrile are shown in Fig. 7. As expected, the amplitude that associates with the reaction time (a_{short}) increases with LiClO_4 concentration with simultaneous decrease of a_{long} in all the three solvents. Note that the electrolyte-induced variations of a_{short} and a_{long} are weak in the two relatively more polar solvents (ethanol and acetonitrile) as the driving force (changes in the reaction Gibbs energy) is predominantly supplied by the solvent polarities themselves. For ethyl acetate, the variations of these amplitudes are more dramatic, with a cross-over at $0.75 \text{ mol}\cdot\text{L}^{-1}$ LiClO_4 , a concentration at which $-\Delta G_r$ also shows a change in sign (lower panel, Fig. 4). Also, both the components change by a factor of ~ 4 at $3.0 \text{ mol}\cdot\text{L}^{-1}$ from that in the neat ethyl acetate. As the changes in reaction Gibbs energy are related to the ratio of these amplitudes ($-\Delta G_r \propto \ln[a_{\text{short}}/a_{\text{long}}]$), the variation of these components is also consistent with the steady-state results presented in Fig. 4.

4 Conclusion

The study of the electrolyte concentration dependence of the ICT reaction in P4C in solvents of different polarity and nature (hydroxylic and non-hydroxylic) has revealed several interesting aspects. For example, electrolyte effects seem to be the strongest in ethyl acetate which is the least polar among the three solvents considered here. The reason behind such a strong effect could be the direct ion-reactant interactions in low polar solvents due to ineffective screening of the ions in low polar solvents. Since the driving force for the LE \rightarrow CT conversion reaction of P4C in ethanol and acetonitrile derives much of the contribution from the solvent polarity itself, the equilibrium constant and other related properties grow at a rate with electrolyte concentration in these solvents much slower than in ethyl acetate. Note that even though ethanol is less polar ($\epsilon_0 \sim 24.5$) than acetonitrile ($\epsilon_0 \sim 36$), the area ratio along with reaction equilibrium constant and the change in reaction Gibbs energy are larger in the former than the latter. A similar difference has also been observed while comparing the results obtained from time-resolved studies in these two solvents. Whether this is due to the associative nature of ethanol or due to specific reactant-solvent interactions is not known to us at present and therefore needs further investigation with several other associative and hydroxylic solvents.

The concentration dependence of the time-resolved data are even more dramatic where reaction rate is found to be slowed down in all the three solvents upon addition of electrolyte in the limit of very low LiClO_4 concentration. The slowing down has been found to be as large as $\sim 30\%$ in ethyl acetate solution and $\sim 5\%$ in the other two solvents. However, at the highest electrolyte concentrations investigated in these solvents, the increase in reaction rate (relative to that in the neat solvent) is the maximum in ethanol ($\sim 60\%$) compared to those in ethyl acetate ($\sim 30\%$) and acetonitrile ($\sim 15\%$) solutions. The average solvation times in ethanol, ethyl acetate and acetonitrile are 16 ps, 0.85 ps and 0.26 ps, respectively [28]. The electrolyte concentration induced decrease and increase of reaction rates in these media can therefore be interpreted as arising out of a novel interplay between friction and solvation (environment reorganization) experienced by the reactant while undergoing the conversion reaction.

The friction versus solvation model could be further studied by investigating the reaction rate in confined environments in presence of electrolyte. Since it is known that confinement reduces drastically the bulk polarity of a polar medium, [20] addition of electrolyte in such an environment can lead to a strong non-monotonic electrolyte concentration dependence of reaction rate as observed in ethyl acetate. One can of course correlate the reaction rate with the time-dependent fluorescence Stokes shift observed in such environments—both in time scale and concentration dependence. Studies of the ICT reaction in solvents with even higher electrolyte concentrations would be particularly interesting as a large increase in viscosity would tend to slow down the reaction in this extreme limit.

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Supporting Information

The variations of LE emission frequency, LE band-width, the ratio between the reaction time in electrolyte solutions and that in neat solvents and, long time decay component as a function of electrolyte concentration in ethyl acetate, ethanol and acetonitrile are provided as Supporting Information.

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