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Probing preferential solvation and ion aggregation with charge transfer triplet states of aromatic amino–nitro compounds

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Abstract

The charge transfer triplet states of *p*-aminonitroterphenyl (PANT), *p*-aminonitrobiphenyl (PANB) and aminonitrofluorene (ANF) were used as probes of preferential solvation and ion clustering in a variety of binary media. The excited states of the above molecules are characterized by very large static dipole moments (''giant dipoles''). As a result, the corresponding transient absorption spectra are highly sensitive to the local polarity of the environment and are very well suited to the study of solvation and association in mixed solvents and solutions of electrolytes.

The spectroscopic study of the dynamics and energetics of association of charge-separated species with chemically inert electrolytes has been extended to non-polar solvents. Whereas in tetrahydrofuran (THF) the association process is dominated by ion pairs of the electrolyte, in non-polar solvents the salt is present in the form of larger clusters consisting of several ions. The degree of aggregation strongly depends on the identity of the ions. These results find support in early cryoscopic and conductometric studies.

Solvent mixtures consisting of a non-polar component and a strongly polar cosolvent were investigated over a range of concentrations and temperatures. A non-linear dependence of the free energy of solvation on the concentration of the polar component was observed in all instances, indicating that polar enrichment in the vicinity of the probe had occurred. The non-linearity cannot be fully accounted for by the simple dipole–dipole interaction model, marking the importance of more specific interactions between the probe and molecules of the polar component. The transient spectra of the probes exhibit thermochromic behavior in all the solvent mixtures studied, whereas analogous spectra in neat solvents are virtually independent of temperature. Thermochromic shifts approaching 50 $\text{cm}^{-1}\ \text{K}^{-1}$ were measured in toluene–dimethylsulfoxide mixtures. © 1997 Elsevier Science S.A.

Keywords: Binary solvent mixtures; Non-polar solutions of electrolytes; Photoinduced charge transfer triplet states

1. Introduction

While the influence of the solvent medium on the reaction energetics and dynamics in polar solvents has been extensively explored, much less is known about non-polar solvents [1]. Accordingly, specific interactions between dipole–dipole (mixed solvent systems) or ion–dipole (electrolyte solutions) solvates in a non-polar environment are not yet fully understood.

From the outset, it should be pointed out that the processes of ion aggregation and specific solvation, which are the topics of this paper, differ considerably from the more frequently studied solvation by a dielectric continuum or by an ''ionic atmosphere''. The last two concepts correspond to the far field approximation of the relaxation of the polarization of a homogeneous polar liquid (or a homogeneous electrolyte solution) following the creation of a non-equilibrium charge distribution. As a result, during the relaxation of the medium, the entire spectrum of the probe solute undergoes a shift.

Ionic aggregation and specific solvation are, by nature, primarily diffusive processes which cannot be described by the evolution of a bulk polarization vector. Indeed, the solvation (aggregation) process can be viewed as a diffusion-controlled ''reaction'' which leads to the formation of a new species, a complex involving the probe molecule and the ions of the electrolyte (or the molecules of the polar cosolvent). Consequently, it is possible to resolve clearly the spectral peak of the ''reactant'' (free probe molecule) and the ''product'' (fully solvated or associated probe molecule).

In general, time-resolved fluorescence Stokes' shift experiments have provided the majority of contributions towards

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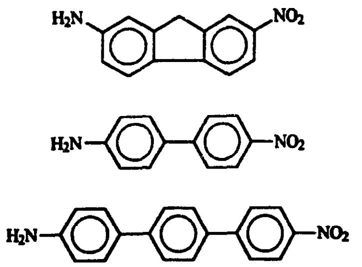

Fig. 1. Probe molecules aminonitrofluorene (ANF), *p*-aminonitrobiphenyl (PANB) and *p*-aminonitroterphenyl (PANT).

the understanding of specific interactions between a charge-separated probe species and its cosolutes [2]. Recently, time-resolved triplet absorption shift measurements have been developed as an approach for the determination of similar phenomena [3], but applicable to a much wider variety of systems. Although slightly different in implementation, the two spectroscopies are analogous. The main difference is reflected in the choice of the probe state. Both techniques require compounds which, on excitation, form charge transfer (CT) states with large dipole moments. Another prerequisite is that the rates of forward electron transfer and intersystem crossing (triplet studies) are much faster than the deactivation rates.

We report a series of time-resolved absorption measurements of ionic association and preferential solvation in non-polar solution. The three aromatic amino–nitro probe solutes employed in these studies, *p*-aminonitroterphenyl (PANT), *p*-aminonitrobiphenyl (PANB) and aminonitrofluorene (ANF), are shown in Fig. 1. PANT, PANB and ANF exploit the well-known tendencies of nitro–amino aromatics to form CT states [4]. The long-wavelength triplet CT absorption bands and singlet CT emission bands of these compounds are displayed in Fig. 2 and Fig. 3.

A combination of calculated and experimental data indicate the change in the molecular dipole of these compounds from the ground to CT excited states. Dipole moments in the range of 7–8 D were determined for the ground states; excited singlet CT states and excited triplet CT states have dipole moments of approximately 20 D and 50 D respectively [5–7]. The "giant dipole" quality of the CT triplet states of PANT, PANB and ANF makes them highly sensitive to short-range intermolecular forces. Their long lifetime makes them suitable for the study of dilute solutions of electrolytes in non-polar solvents.

In the first part of this paper, the spectroscopic investigation of the dynamics and energetics of association of charge-separated species with tetrabutylammonium nitrate (TBANO$_3$), tetrabutylammonium thiocyanate (TBASCN) and tetrabutylammonium tetrafluoroborate (TBABF$_4$) in toluene is reported.

Early work on the properties of electrolyte solutions in non-polar media was based on the analysis of either cryoscopic or conductometric measurements [8,9]. Both types of investigation led to the same conclusion: as the concentration of the salt is increased, the simple salt ion pairs (dipoles) combine to form aggregates (multipoles) of varying size. Results indicated that the electrolytes became highly associated even at low concentrations (less than 10^{-3} M). The or aggregation of ions was found to be governed by two factors: the dipole moment of the salt ion pair and the size and symmetry of the ions. An analysis of the dynamics and energetics of the ionic association between the highly polar CT triplet probe states and salts in toluene should provide a description of the nature of the complex equilibria present in non-polar solutions of electrolytes.

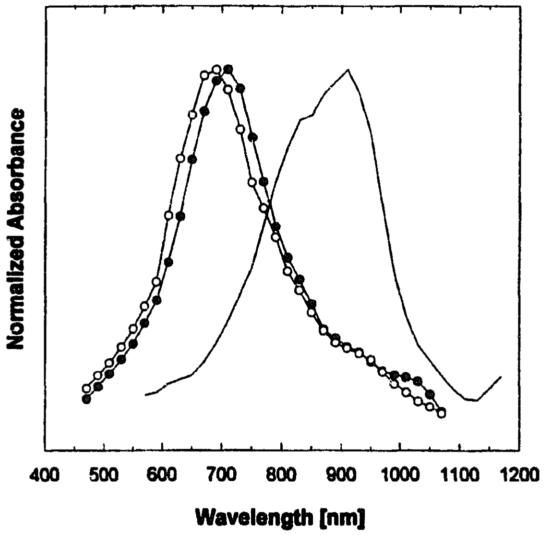

Fig. 2. Room temperature time-resolved triplet absorption spectra (λ_{ex} = 355 nm) of PANT (———), PANB (●) and ANF (○) in toluene. The delay time after the excitation pulse is 100–200 ns.

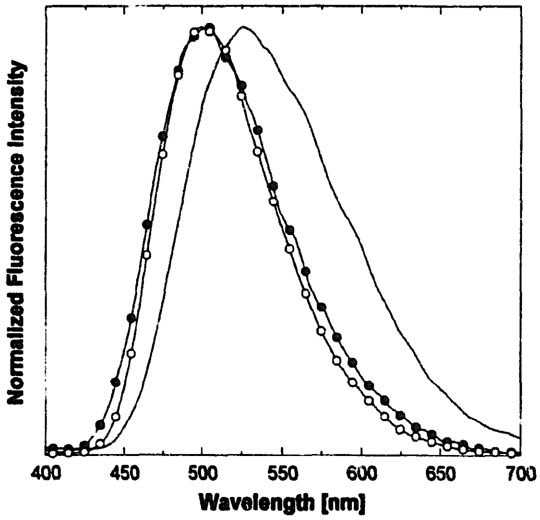

Fig. 3. Room temperature steady state emission spectra (λ_{ex} = 355 nm) of PANT (———), PANB (●) and ANF (○) in toluene.

In the second part of this paper, preferential solvation of charge-separated species by strongly polar cosolvents is reported. Time-resolved triplet absorption spectroscopy was employed to study these effects. Probing with triplet states provides a new addition to a body of work previously concerned only with the solvatochromic shifts of singlet states.

Preferential solvation is often described in terms of polar enrichments i.e., the diffusion of polar molecules from the bulk of the solution into the solvent shell around dipolar solutes [10]. The disparity between the effective dielectric constant of the enriched shell and that of the bulk medium is well known from steady state fluorescence data [11]. Time-resolved studies of the spectral shifts of fluorescence in binary solvent mixtures have provided evidence that the dynamics of polar enrichment obey diffusion models [12,13].

2. Experimental

PANT, PANB and ANF were prepared by partial reduction of 4,4′-dinitro-*p*-terphenyl (Lancaster), 4,4′-dinitro-*p*-biphenyl (ICN) and 2,7-dinitrofluorene (Lancaster) respectively. $TBASCN$ (Aldrich) and $TBABF_4$ (Aldrich) were recrystallized from anhydrous ethyl acetate and dried in vacuum at 50 °C for 24 h. $TBANO_3$ (Aldrich) was recrystallized from benzene–ether and dried in vacuum over P_2O_5 at 60 °C for 48 h. The solvents were of spectroscopic grade (Aldrich) and were used as received.

The transient absorption experiments were performed using a nanosecond time-resolved spectrometer built around a Continuum NY61-10 Nd:YAG laser and a Tektronix SCD1000 ultrafast digitizer. The third harmonic output of the Nd:YAG laser (355 nm), with a typical pulse energy of approximately 30 mJ and a pulse length of 5 ns, was used as the excitation source. A Hamamatsu Super-Quiet flash lamp served as the analyzing light. The transients were isolated with an Oriel 77250 monochromator resolving between 5 and 13 nm and were detected using a silicon photodiode (Thorlabs FDS100) in the visible range and a germanium photodiode (EG&G Judson J-16-R01M-HS) in the near-IR. The samples were degassed by five freeze–pump–thaw cycles prior to photoexcitation.

Variable temperature control was achieved by flowing cooled nitrogen gas through a heater with a feedback loop into a dewar with optical windows containing the sample cell. The temperature near the sample cell was measured with a thermocouple.

Fluorescence spectra were recorded using a Perkin–Elmer LS-5B fluorometer. The excitation wavelength was 355 nm.

3. Results and discussion

3.1. Solutions of electrolytes in non-polar solvents

On addition of small amounts of electrolytes, dynamic blue shifts of the triplet CT absorption for each probe compound in toluene were observed. Fig. 4 displays a typical spectral response for the amino–nitro probe compounds in non-polar solutions of electrolytes, which in this case is the PANB CT triplet spectrum in toluene containing 5 mM $TBABF_4$. As the delay after the laser pulse increases, a salt-induced blue shift of the probe triplet CT absorption spectrum is observed. The spectral shift corresponds to the disappearance of the free probe peak and the appearance of the probe–salt complex. A well-behaved isosbestic point can be observed.

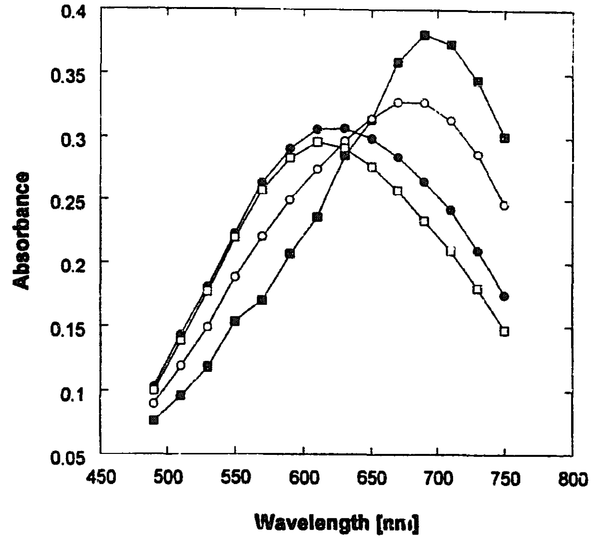

Fig. 4. Time evolution of the PANB transient CT triplet spectrum in toluene containing 5 mM $TBABF_4$. The delay times after the excitation pulse are 0–10 ns (■), 25–50 ns (○), 100–200 ns (●) and 250–500 ns (□).

A similar behavior was recorded for all three probe molecules. The salt-induced electrochromic shifts, relative to the λ_{max} value of uncomplexed probe absorption, are large and vary from 2000 to 4000 cm^{-1}. $TBASCN$ and $TBANO_3$ produce nearly identical shifts, and these values are always larger than the corresponding shifts found in the presence of $TBABF_4$. The largest spectral shifts were measured for the PANT triplet CT state, which has the largest static dipole moment.

The energetics of ionic association observed in toluene differs from the results obtained in more polar media. For identical salt species in solution with PANT, the spectral shifts are always larger in toluene than in tetrahydrofuran (THF) [14]. Although this observation can be rationalized on the basis of the stronger electrostatic intermolecular forces in non-polar solvents than in more polar solvent, where all Coulombic effects are substantially attenuated, the actual shift differences are not nearly as large as the $\epsilon_{toluene}/\epsilon_{THF}$ ratio would predict.

It is important to note the dependence of the spectral shift on the salt concentration. In THF, the upper limit of the blue shift is reached for all tested salts at relatively high concentrations of the salt. In toluene, the blue shift is largely concentration independent at lower salt concentrations. However, when the salt concentration is increased to its highest levels, a slight shift back to the red can be detected, suggesting the presence of different electrolyte species associating with the probe.

While the CT triplet absorption decay profiles for all three probes are monoexponential in neat solvents, biexponentiality is observed in solutions of electrolytes. The fast component of the decay corresponds to the rate of ionic association and the slow component to the lifetime of the probe state. Biexponential curve fitting models the observed decay pro-

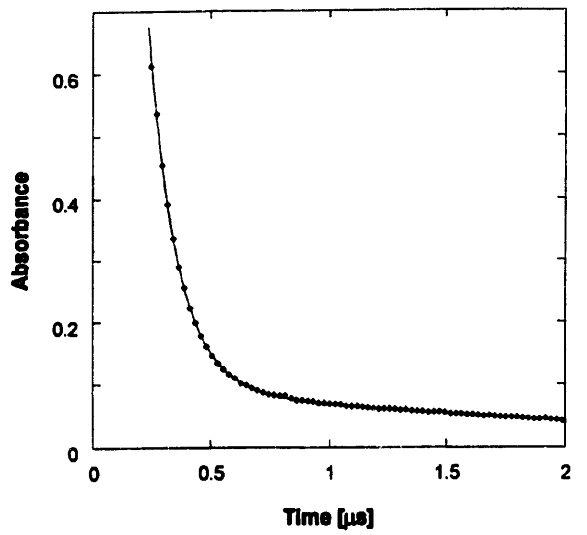

Fig. 5. Example of a typical biexponential fit (◆) ($k_1 = 8.19 \times 10^6$, $k_2 = 4.31 \times 10^5$, $\chi^2 = 0.0025$) to a triplet CT state absorption decay profile (———) (PANT in toluene containing 3 mM $TBABF_4$ at 910 nm; $\lambda_{ex} =$ 355 nm).

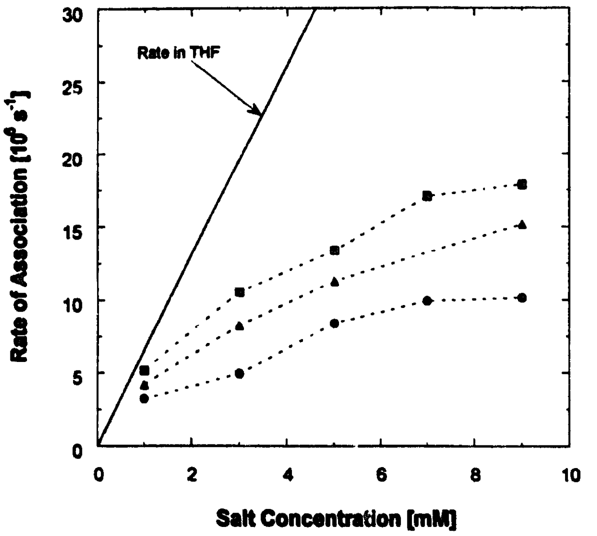

Fig. 6. Rate of association between the CT triplet state of PANT and TBASCN (''), $TBABF_4$ (▲) and $TBANO_3$ (●) in toluene plotted as a function of salt concentration.

files closely (Fig. 5), thereby allowing extraction of the electrolyte association rates. Rates were obtained from fits to transients measured at wavelengths corresponding to the λ_{max} value of the CT triplet absorption in neat solvents. No significant wavelength dependence of the association kinetics was found.

Rate vs. concentration data for a series of salts in toluene solution of PANT are presented in Fig. 6. Also included is the pseudo-unimolecular rate for electrolyte association in THF. The association process in THF was found to be nearly diffusion controlled and linearly dependent on the overall concentration of the salt [3].

Fig. 6 demonstrates that the electrolyte association rates in toluene are much slower than the diffusion-controlled rate, and the rates increase with the overall salt concentration but less than linearly. In addition, the identity of the salt appears to influence the rate of association, which is not the case in THF [14]. The fastest rates are found for solutions of TBASCN, while the slowest are detected with $TBANO_3$. Measurements with ANF and PANB probes yield similar effects.

The results in toluene suggest the presence of a complex electrolyte equilibrium, as opposed to more polar media where all the observed effects can be adequately accounted for by considering only simple ion pairs of the electrolytes. As the electrolyte concentration is increased in non-polar solutions, salt ion pairs self-associate to a high degree resulting in a change in the type and number of electrolyte species available for association with the probe molecule.

3.2. *Preferential solvation in binary solvent mixtures*

Since the triplet CT states of ANF, PANB and PANT are highly dipolar and their transient lifetimes are long, it is expected that strong dielectric enrichment effects should exist in solvent mixtures. A solvatochromic shift was observed in toluene solutions of all three probe molecules with the addition of a polar cosolvent. Shifts were induced using polar components ranging from acetonitrile to ethylene carbonate. Generally, the measured spectral shifts were hypsochromic (triplet absorption spectra) or bathochromic (fluorescence spectra) and increased with increasing polar component concentration. Both transitions originate from CT states with very large dipole moments and lead to final states with small dipole moments: the S_0 ground state and T_n higher triplet state, respectively.

Fig. 7 and Fig. 8 show the solvatochromic shifts of the triplet absorption spectra and emission spectra of the probe compounds in toluene–dimethylsulfoxide (DMSO) mixtures. Considerable non-linearities exist with respect to the DMSO concentration for all investigated CT states. A

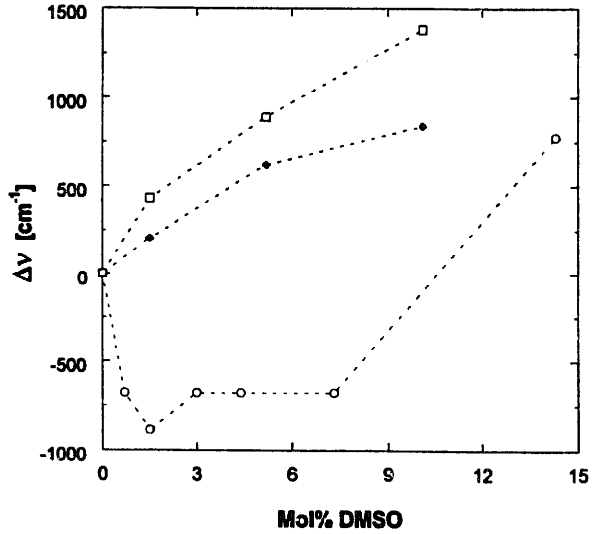

Fig. 7. Shifts of the triplet CT absorption band maxima of PANT (○), PANB (◆) and ANF (□) vs. DMSO (mol.%) in a toluene–DMSO mixture.

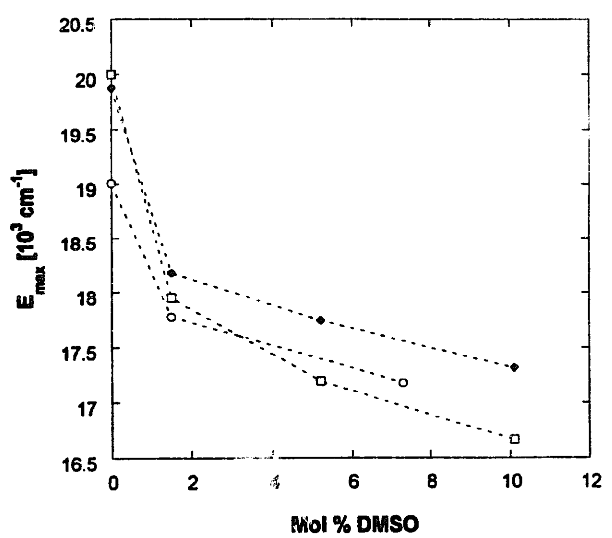

Fig. 8. Positions of the CT emission band maxima of PANT (○), PANB (◆) and ANF (□) vs. DMSO (mol.%) in a toluene–DMSO mixture.

progressive red shift is seen until the fluorescence is quenched on reaching relatively polar conditions. The fluorescence yields of these compounds decrease as the medium polarity is increased, indicating that the non-radiative decay becomes faster, which in turn suggests that the CT singlet-to-ground state recombination is in the "inverted region". No fluorescence can be detected in neat solvents more polar than acetone ($\epsilon > 20.7$); however, the blue shift of the CT triplet absorption spectra can be followed from neat toluene to neat DMSO ($\epsilon = 2.38$ to $\epsilon = 46.45$) [15].

Usually, correlations are made between the observed transition energies and the Onsager or Debye polarity functions when discussing solvatochromic behavior [10]. Linear combinations of these functions, according to the solvent mole fractions, do not adequately describe the changes in solvation free energy (ΔG_{sol}) of our CT probe states. In addition, for toluene–DMSO mixtures, the bulk dielectric constant, as measured by the capacitor method, is known to vary linearly with the DMSO concentration [13], and therefore a linear dependence of the spectral shift on the medium composition would be expected for this mixture in the absence of specific solvation effects. The lack of linear dependence for the recorded probe responses indicates differences between the bulk dielectric constant and the effective dielectric constant sampled by the probes, i.e. preferential solvation.

Investigating the dynamics of dielectric enrichment was not possible using the current experimental set-up. Under diffusion-controlled conditions, the concentrations of DMSO required to produce observable solvatochromic effects are too high to permit the observation of dynamic effects within our nanosecond time resolution. For example, a toluene–DMSO mixture which contains 5 mol.% DMSO would require only approximately 2×10^{-10} s for the first molecule of DMSO to collide with a probe molecule, assuming random diffusion.

Temperature-dependent transient absorption measurements of the photoinduced triplet CT states were performed

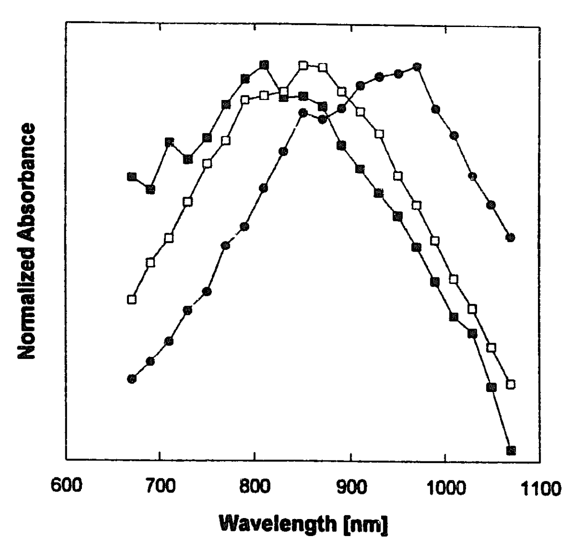

Fig. 9. Temperature-dependent CT triplet spectra of PANT in a toluene–DMSO mixture (5 vol.% DMSO). The solution temperatures of the spectra are 22 °C (●), 0 °C (□) and −20 °C (■).

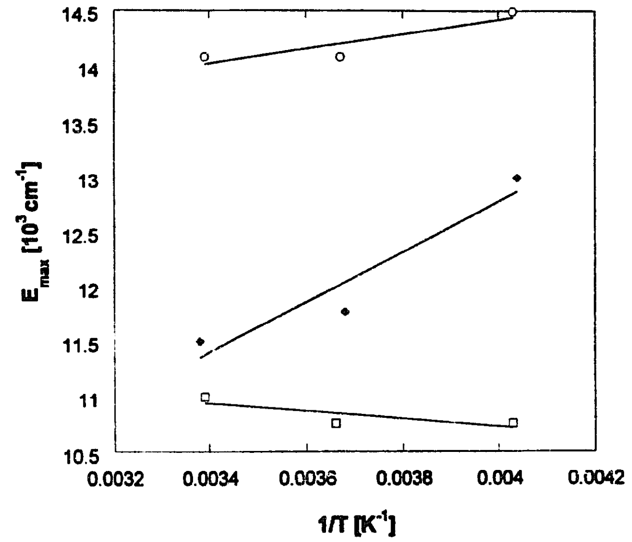

Fig. 10. Thermochromic shifts of the PANT triplet CT absorption band in toluene (□), acetonitrile (○) and in a 34 mol.% acetonitrile mixture with toluene (◆). The lines are only suggestive.

in various solvent mixtures. Generally, lowering the solution temperature induces blue shifts of the triplet absorption spectra (Fig. 9). Such thermochromic shifts have been measured for the triplet absorption spectra of ANF, PANB and PANT.

Fig. 10 demonstrates that the thermochromic effects are much larger for a mixture than for either of its components. The specific thermochromic shift ($\Delta\nu_T$) for the toluene–CH$_3$CN solvent mixture is -31 cm^{-1} K^{-1}, whereas $\Delta\nu_T = 5$ cm^{-1} K^{-1} in neat toluene and $\Delta\nu_T = -9$ cm^{-1} K^{-1} in neat CH$_3$CN. Thermochromic shifts as large as -50 cm^{-1} K^{-1} were measured for the triplet absorption spectrum of PANT in toluene–DMSO.

Questions regarding the nature of the triplet CT states of aromatic nitro–amino compounds and their non-radiative decay mechanisms are an interesting side product of this work. In the case of the PANT triplet CT state, on addition of small amounts of DMSO to toluene, an initial red shift is seen, which is then followed by the expected progression towards shorter wavelengths at higher DMSO concentrations (Fig. 7). Measurements in neat solvents have also shown reverse solvatochromism over a dielectric constant range from $\epsilon=2$ to $\epsilon=7$ [14]. Only the PANT triplet CT state produces such behavior. ANF and PANB exhibit the expected monotonic hypsochromic shifts. The singlet CT states of all three probes display monotonic spectral shift patterns. An explanation of this behavior may lie in the possibility of the population of more than one excited state of PANT, or perhaps an involvement of several conformers.

4. Conclusions

An explanation for the electrolyte and specific solvation effects on the triplet CT absorption bands of ANF, PANB and PANT in toluene is based on the specific interactions between the salt or polar cosolvent and the chromophore, not on changes in the bulk dielectric properties. Once the triplet CT probe states are formed, encounters with salt or polar cosolvent molecules result in the formation of discrete complexes or solvation aggregates.

This work has shown that the behavior of electrolytes in non-polar media is considerably different from that observed in more polar solvents. The salt-induced spectral shifts in toluene are not as large as expected when compared with the results in THF. The electrolyte association rates in toluene are much slower than the diffusion-controlled rates, and increase non-linearly with the overall salt concentration. In addition, the identity of the salt species appears to influence the association process in toluene. These factors are consistent with the aggregation of salt ion pairs into higher order multipolar clusters in non-polar media.

Preferential solvation of both the singlet and triplet CT states of ANF, PANB and PANT in various mixed solvent systems was observed. The dielectric enrichment of the probe molecules was found to exhibit a noteworthy temperature dependence.

Acknowledgements

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