Solvation of TICT* states in solvent mixtures

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<u>Abstract</u> - The formation of the twisted intramolecular charge
transfer (TICT) state of 4,4'-dimethylaminobenzonitrile (DMABN)
depends on solvent relaxation around the giant dipole. In solvent
mixtures, dielectric enrichment of the polar solvent in the solvation
shell can become the rate limiting kinetic step.
The translational and rotational solvent relaxations around DMABN
in the course of TICT state formation raise interesting questions
concerning the time scale of the actual electron transfer step in other
types of electron transfer reactions, in particular intermolecular
processes which involve exciplex intermediates.

INTRODUCTION

One of the important characteristics of the TICT states of molecules such as
DMABN is its very large dipole moment which corresponds to nearly complete
charge separation between the amino group which acts as the electron donor and
the cyanophenyl moiety which is the electron acceptor. The magnitude of this
dipole moment of the TICT state has been established by solvatochromic [1] and
thermochromic shifts [2] and other techniques [3] and must be close to 20 Debye.
The process of solvation in polar solvents is necessary for the formation of the
TICT state of DMABN, since it provides the stabilization necessary to bring the
TICT state below the ^1L_a state which emits the "normal" N-fluorescence of the
planar molecule.

In mixtures of solvents of different dielectric polarities a process of preferential
solvation known as dielectric enrichment takes place. In the case of excited
molecules this must be seen as a kinetic process since it can be limited by the
lifetime of the excited state [4]. We report here the preferential solvation effects on
the TICT (A) fluorescence of DMABN in several solvent mixtures, with reference
to the emission quantum yields and lifetimes.

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* TICT = Twisted Intramolecular Charge Transfer

RESULTS

1. Non hydrogen bonding solvents

Figure 1 shows the solvatochromic shifts (a) and the fluorescence quantum yields (b) of the A emission of DMABN in mixtures of 1-fluoropentane and acetonitrile (MeCN). The very large non-linearity ratio of 0.55 is in agreement with the large value of the dipole moment in the TICT state. Although there is a quenching effect of the more polar solvent the emission lifetimes remain sufficiently long to reach dielectric enrichment equilibrium in all the mixtures investigated here. This equilibration time is given as

$$t = (y_p - x_p) \pi M a^2 / k_D x_p 10^3 \delta b^2$$

for solvent molecules of radius b and mean molecular weight M, a being the solute's molecular (onsager cavity) radius. δ is the mean density of the solvents, and k_D is the second-order rate constant for diffusion controlled encounters. The mole fractions of the polar solvent (MeCN in this case) is x_p in the bulk of the mixture, and reaches the equilibrium value y_p in the solvation shell of the solute molecule. When the polar solvent mole fraction is very low, this equilibration time is of several nanoseconds in solvents of low viscosity - and can of course be much longer in viscous liquids. From the reported lifetimes of the TICT state [5] and the measured emission quantum yields in these mixtures it can be concluded that dielectric enrichment must be nearly complete in mixtures of 1-fluoropentane/MeCN.

2. Mixtures of non-protic/protic solvents

An earlier report [6] has given details of the solvatochromic plot of the A fluorescence of DMABN in mixtures of MeCN/H_2O. Water behaves in a very special way towards the TICT state, showing a very large red shift of the emission maximum and an important quenching effect. Similar results are found in mixtures of N,N-dimethylformamide (DMF) and water, as shown in figures 2 and 3. The quenching action is clearly related to proton transfer; addition of a minimal concentration of an acid to an aqueous solution of DMABN results in very efficient quenching of its A fluorescence, but the emission quantum yield is then so low that no quantitative measurements could be made. By comparison with the quenching of the fluorescence of 4-aminophtalimide by acids [7] it can be surmised that it follows diffusion controlled kinetics.

Luminescence quenching by proton transfer has been observed for excited states which have a strong charge transfer (CT) character [8]. In the case of DMABN the protonation site has not been established, but in naphthylamines it has been proved that the proton attacks electron rich centres of the aromatic ring.
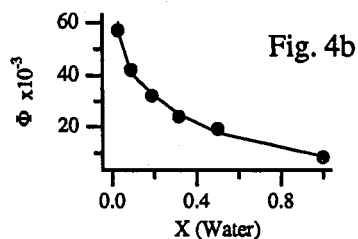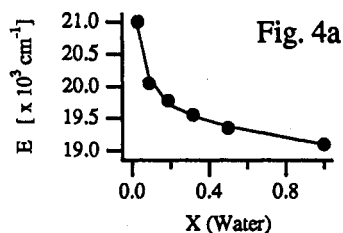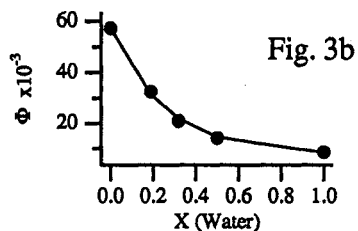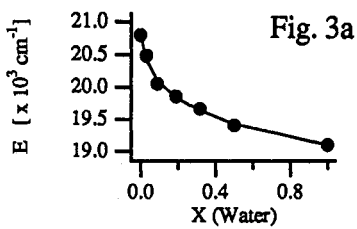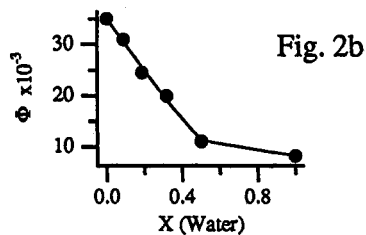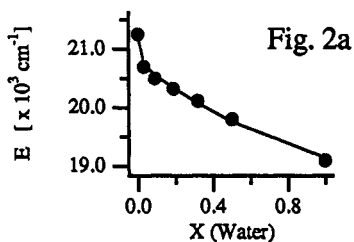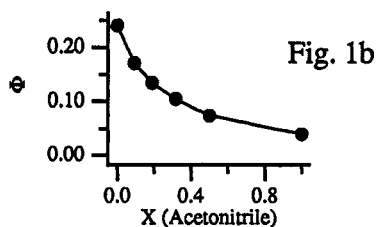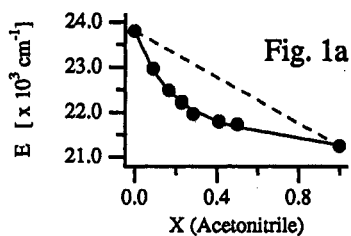
Figures1 to 4: Solvatochromic shifts (a) and emission quantum yields (b) of the
TICT fluorescence of DMABN in solvent mixtures,
1) 1-fluoropentane/acetonitrile
2) acetonitrile/water
3) N,N-dimethylformamide/water
4) 2-propanol/water

Abcissa in mole fraction of the more polar solvent - acetonitrile in figure 1 and
water in figures 2, 3 and 4.
Energy ordinates in 10^3 cm^{-1} measured at the emission maximum; quantum yield
ordinates as indicated

The assesment of the non-linearity ratios of the plots of figures 2 and 3 must take
into account the quenching effect of water on the A emission of DMABN. In neat
water the fluorescence quantum yield drops to about $8 \cdot 10^{-3}$, the actual lifetime of
the TICT state being then estimated to be below 100 ps - a time too short to reach
dielectric enrichment equilibrium in any but the most concentrated water mixtures.

3. Mixtures of protic solvents

Figure 4 shows the solvatochromic plot and the emission quantum yields of the A fluorescence of DMABN in mixtures of 2-propanol/water. In all mixtures which contain water as the more polar solvent there is a sharp drop of the emission quantum yield at low water concentrations, and at the same time there is a marked red shift of the emission maximum, followed by a gradual displacement which is nearly linear with water mole fraction. It is probable that the first very steep red shift results from the formation of hydrogen bonded complexes, possibly to the cyano group. This behaviour is rather exceptional; as a rule dielectric enrichment precedes hydrogen bond formation, because the overall energetics of hydrogen bonding is generally unfavourable owing to the energy spent in breaking the solvent structure. This unusual behaviour of the TICT state of DMABN must result from the exceptionally large association energy with water, in agreement with its large dipole moment of the order of 20 Debye. As the water concentration increases higher order complexes may be formed through association of water molecules with the aromatic ring as in naphthylamines and aminophtalimides. The structures of these complexes cannot be described experimentally at the present time and will provide a challenge for future research.

DISCUSSION

DMABN has proved to be a most important example of intramolecular charge transfer controlled by solvent reorganization. The relationship between solvatochromic plots and luminescence quantum yields shows that both rotational (in single solvents) and translational (in solvent mixtures) motions of the medium are involved in the electron transfer process. This must be seen in contrast to the usual notion of very fast, so to speak "instantaneous" electron jumps which certainly are the rule for conjugated molecules. Now a rather general question does arise: how fast is the actual electron transfer step - the electron jump itself - in intermolecular CT reactions? This is not a trivial question, because it holds the answer to the problem of solvent reorganization in the course of these elementary photoinduced processes.

In the Marcus-Hush model of electron transfer [9] it is held that the solvent must reorganize of its own accord prior to the electron jump, so as to come half-way to resemble the situation it will reach around the final products. Computer simulations have shown that such solvent fluctuations are so unlikely as to be utterly negligible [10], and it was necessary to assume that solvent reorganization occured simultaneously with electron transfer, in a way similar to TICT state formation where solvent relaxation gradually stabilizes the dipole.

The data shown here concerning the wavelength shift of the TICT emission of DMABN and the related quenching effect of polar and protic solvents finds its counterpart in exciplex emissions. Here also the dipole is stabilized in polar

solvents, and at the same time the lifetimes become shorter [11]. Electron transfer within the exciplex is likely to be a gradual process, as the solvent reorganization follows and induces the overlap of the interacting molecular orbitals. In that case there would be no electron "jump" and therefore no requirement of prior reorganization of the solvent; as the electron donor and acceptor molecules come closer together and find the best geometry for the overlap of their frontier orbitals, so the dipole moment increases gradually until full - or nearly full - charge separation is reached. In neat solvents this is expected to occur on a time scale of some tens of picoseconds; in solvent mixtures it could extend to the nanosecond time scale.

CONCLUSIONS

The formation of the TICT state of DMABN may provide a model for other, intermolecular electron transfer reactions which involve exciplex intermediates. The cooperative action of geometrical change (twist angle in the TICT state, molecular overlap in exciplexes) and solvent stabilization implies a slow, gradual electron transfer. The solvent motion then follows the charge transfer, and there is no need to invoke highly improbable prior reorganizations of the solvent.

Acknowledgement

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