J. Phys. Chem. A **1997,** *101,* 3461−3466

Enhanced Nonradiative Decay in Aqueous Solutions of Aminonaphthalimide Derivatives via Water-Cluster Formation

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Received: December 13, 1996; In Final Form: March 10, 1997⊗

The photophysics of two derivatives of 4-aminonaphthalimide have been studied in aqueous, ethanolic, and mixed aqueous/ethanolic solvents, including both normal and deuterated solvents. It is found that the fluorescence quantum yield and lifetime both decrease with increased water content of the solvent and that this is entirely due to increased nonradiative decay, the radiative rate constant being virtually independent of the solvent composition. It is proposed that a mechanism involving the formation of a hydrogen-bonded water cluster is responsible for the observed behavior with the excitation energy of the naphthalimide being distributed amongst the stretching vibrations of the water cluster. The increase in the rate of nonradiative decay is greatly reduced in deuterated solvent mixtures in accord with Siebrand's theory of radiationless processes.

Introduction

The absorption and photophysical properties of molecules are often very sensitive to the nature of the solvent in which they are dissolved. The observed solvent effects can provide information not only about the properties of the excited state(s) of the molecule but also about the nature of the solvent itself.[1] There are now many compounds that are used to probe solvent properties such as polarity (e.g. dansyl compounds[2]) and viscosity (1,6-diphenylhexatriene[3] and TICT compounds such as 4′-(*N*,*N*-dimethylamino)benzonitrile[4]). Of particular current interest is the process of solvent reorganization following photon absorption, the study of which has greatly benefited from the development of femtosecond flash photolysis techniques.[5]

In any solvent system, the properties of a solute will be affected by both the bulk polarity of the solvent and by specific solute−solvent interactions. In binary solvent mixtures there is the additional possibility of a specific interaction between the solute and one of the components of the binary solvent. This may result in preferential solvation; that is, the local concentration of the preferred component of the solvent in the region of the solute is much greater that its bulk concentration. Marcus has reviewed the use of various chemical probes for the characterization of the properties of solvent mixtures[6] and has discussed whether the observed probe properties are distorted by preferential solvation. Banerjee et al. have recently extended existing theories of preferential solvation.[7] Acree and co-workers have used the distribution of vibrational intensity in the fluorescence spectra of several polycyclic aromatic hydrocarbons in various binary solvents to model the preferential solvation of these probe molecules,[8] and Zana and Eljebari have also used changes in the relative vibrational intensity in the pyrene fluorescence spectrum to study self-association of simple alcohols in water.[9]

Other fluorescent systems have been found to exhibit drastic changes in fluorescence intensity/quantum yield and lifetime as the composition of a binary solvent is varied. The best known examples of this are the heavily studied aminonaphthalenes and aminonaphthalene sulfonates.[10−12] For many of these, the addition of a polar solvent (especially water) to a nonpolar solution of the compound causes a large increase in the nonradiative rate constant, which has been variously ascribed to enhanced intersystem crossing, photoionization, the presence of two excited states of similar energy, and specific solute−solvent interactions. It is also possible to observe enhancement of the fluorescence as the proportion of polar solvent is increased.[10] Another excellent example of this effect is acridine, whose photophysics are polarity dependent in pure solvents and whose fluorescence intensity and lifetime decrease dramatically in mixed aqueous/organic solvents as the proportion of the organic component is increased.[13−16] Kokubun has suggested that the cause of this phenomenon was an increase in the nonradiative decay rate, which was linearly related to the concentration of the organic component of the solvent; that is, the organic solvent is acting as a quencher in Stern−Volmer fashion by increasing the nonradiative decay rate. This was found to explain the observed properties of acridine in aqueous glycerol at all solvent compositions[13] and in aqueous alcohols (methanol, ethanol, and 1-propanol) at low alcohol concentrations. However, there was significant deviation from this behavior in the latter at higher alcohol concentrations.[13−16] This has recently been attributed to preferential solvation by the alcohol.[16]

Significant solvent effects are also found in studies of the deprotonation of excited photoacids in both aqueous and mixed aqueous/organic solvents. Robinson et al.[17] and Lee[18] have thereby concluded that the proton acceptor in solvents containing water is a four-molecule water cluster. Other workers suggest that the initial proton transfer may be to a single water molecule which is then solvated,[19] or that it is a water dimer that accepts the proton.[20,21] Whichever of these possibilities proves to be ultimately correct, it is clear that studies such as these can provide information about the microscopic structure of the solvent.

We have been studying the photophysical properties of 4-aminonaphthalimides in various solvents[22,23] and find that there are marked differences between the properties that are observed in organic solvents compared to water.[23] A more in-depth study of the properties of two systems in a binary aqueous/organic solvent mixture has therefore been undertaken to try to

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⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1997.

S1089-5639(96)04061-3 CCC: $14.00

determine the mechanism(s) that operate. The results of that study are presented here.

Materials and Methods

4-Amino-9-(2-*N*-piperidinoethyl)-1,8-naphthalimide (**1**) was prepared by standard methods.[22,23] In brief, 4-nitronaphthalic anhydride was first reduced (stannous chloride/hydrochloric acid) to 4-aminonaphthalic anhydride, and this was then refluxed with 2-*N*-piperidinoethylamine in ethanol for 1 h. The resulting product was recrystallized from ethanol/dimethylformamide (5:1), mp 219−221 °C. Found: C, 70.0; H, 6.7; N, 12.8. $C_{19}H_{21}N_3O_2$ requires C, 70.5; H, 6.6; N, 13.0. *N*-(methoxycarbonylamino)-4-amino-3,6-disulfo-1,8-naphthalimide, dipotassium salt (**2**) was obtained from Molecular Probes (Oregon) and was used as supplied.

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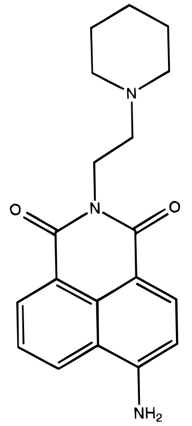

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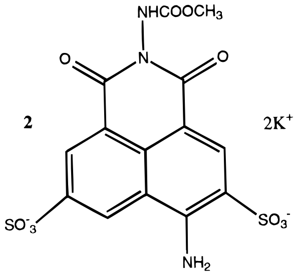


Ethanol, ethanol-*d*, and deuterated water were obtained from Aldrich Ltd. and were either spectrophotometric grade or the highest quality available. Water was doubly distilled and deionized.

Absorption spectra were measured on a Hewlett-Packard 8452A diode array spectrometer on solutions of approximately 10 μM concentration in matched 1 cm quartz cuvettes. Fluorescence spectra were measured on a SPEX Fluoromax spectrofluorimeter and were corrected for instrumental response. Fluorescence quantum yields were determined for optically dilute (absorbance < 0.05) solutions by comparison with fluorescein in 0.1 mol·dm^{-3} sodium hydroxide solution ($\phi_f = 0.90$).[24] Fluorescence decay profiles were measured by the time-correlated, single-photon counting technique[25] using the Synchrotron Radiation Source at the CLRC Daresbury Laboratory as the excitation source. The instrumental setup has been described previously.[26] The profiles were analyzed by computer convolution using a Marquardt least-squares algorithm, and the goodness of fit was judged on the basis of the χ^2 value and the distribution of the residuals.

Results and Discussion

The absorption and emission properties of the two aminonaphthalimide molecules **1** and **2** were studied in aqueous, ethanolic, and aqueous ethanolic solvents. Parallel measurements were also undertaken in deuterated water (D_2O), deuterated ethanol (C_2H_5OD or EtOD), and mixtures of the two deuterated solvents. These two naphthalimides were chosen for study because (i) they both exhibit reasonable solubility (>10 μM) in ethanol and water; (ii) one (**1**) is significantly more soluble in ethanol than in water, while the reverse is true for **2**, thus allowing us to test for possible preferential solvation; (iii) one system is charged (**2**), while the other is neutral (**1**). However, it appears that the behavior exhibited by these two systems is common across this class of molecules.

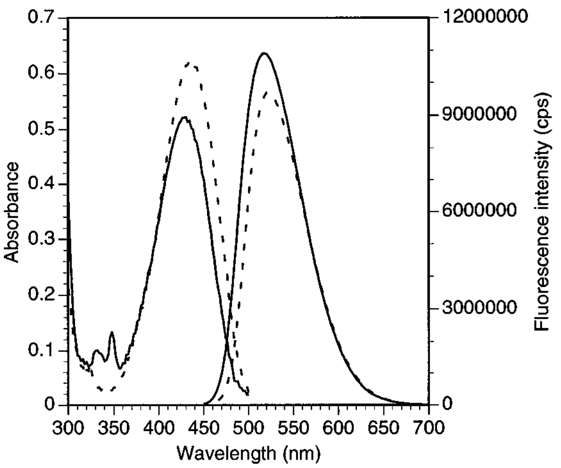


Figure 1. Absorption and fluorescence spectra for **1** (dashed lines) and **2** (full lines) in ethanol (4.0 × 10^{-5} mol·dm^{-3}).

TABLE 1

solvent	property	compound **1**	compound **2**
ethanol	λ_{max} (abs)/nm	435	430
	log ϵ	4.10	4.02
	λ_{max} (em)/nm	525	523
	ϕ_f	0.39	0.46
	τ_f/ns	7.6	11.3
deuterated ethanol	λ_{max} (abs)/nm	434	428
	log ϵ	4.10	4.03
	λ_{max} (em)/nm	520	518
	ϕ_f	0.45	0.54
	τ_f/ns	9.8	14.0
water	λ_{max} (abs)/nm	433	428
	log ϵ	4.08	4.02
	λ_{max} (em)/nm	549	536
	ϕ_f	0.11	0.20
	τ_f/ns	2.5	4.9
deuterated water	λ_{max} (abs)/nm	432	426
	log ϵ	4.08	4.02
	λ_{max} (em)/nm	548	535
	ϕ_f	0.28	0.38
	τ_f/ns	7.3	11.4

The absorption and emission spectra of the two systems in ethanol are compared in Figure 1, and their properties in all four pure solvents are summarized in Table 1. It is noticeable that the absorption properties of both compounds are essentially the same in all four solvents, with just a very slight blue shift of a few nanometers in aqueous as opposed to ethanolic solution. It is therefore somewhat surprising to find that the emission properties are very solvent dependent, with a significant red shift in emission being observed in aqueous solution together with a clear decrease in both the emission quantum yield and lifetime compared to the alcoholic solutions. There are also very clear differences between the properties of the two systems in water and deuterated water and (less noticeably) in ethanol compared to deuterated ethanol.

Calculation of the radiative and nonradiative rate constants from the quantum yield and lifetime data reveals that the former is approximately the same for each compound in all four solvent systems. The changes in the fluorescence quantum yield and lifetime are solely due to differences in the nonradiative decay rates for the different solvents. There appears to be a specific solvent−solute interaction in operation in the excited state, which accounts for the red shift in emission and the increase in the nonradiative decay rate in aqueous solvents. There is also a very pronounced deuterium isotope effect in operation.

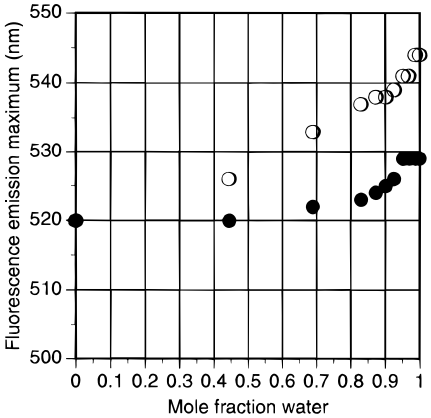
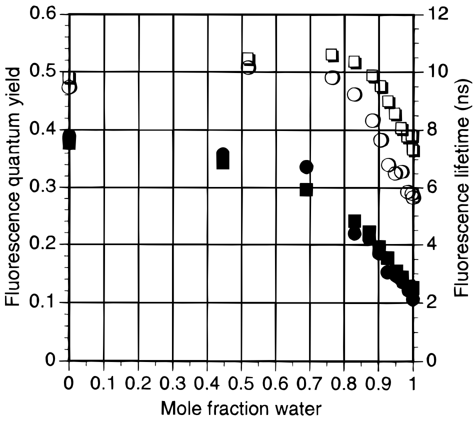


Figure 2. Variation of the maximum emission wavelength for **1** (open circles) and **2** (filled circles) in aqueous ethanol solution.

The same measurements as reported in Table 1 for the four pure solvents have also been carried out for compounds **1** and **2** in water/ethanol and deuterated water/deuterated ethanol mixtures. There is little change in the absorption spectrum as the solvent composition varies, but the emission maximum shifts (as expected on the basis of the results reported in Table 1) to the red as the proportion of water increases (Figure 2). At the same time, the fluorescence quantum yield also decreases (Figure 3a,b). The fluorescence decay profile that is observed for the solvent mixtures remains a clear single exponential at all solvent compositions (as shown in Figure 4), and the fluorescence lifetime of both naphthalimides also decreases as the mole fraction of water increases. However, as Figure 3a,b shows, the variation of the quantum yield and lifetime are by no means a linear function of the solvent composition, with the greatest changes occurring in solutions with the higher water contents. The consistently monoexponential behavior of the fluorescence decays and the variation of the decay lifetime with solvent composition suggest that preferential solvation is probably not the cause of these observations. In addition, the relatively small changes in the absorption and emission spectra suggest to us that a model involving two emitting states (as for the aminonaphthalenes) is also inappropriate.

As mentioned above, the quantum yield and lifetime data may be used to calculate radiative and nonradiative rate constants as a function of solvent composition, and the radiative rate constant is found to be approximately constant for each of the two compounds with changes in the nonradiative rate (see Figure 5 for data on **1**) accounting for the observed variations in quantum yield and lifetime. It is not surprising in view of the comments above about the variation of these two parameters with solvent composition to find that the nonradiative rate constant changes most markedly in solutions with a high water content. However, the variation of the nonradiative rate constant is not linearly dependent on the water content of the solvent mixture. A model such as that developed by Kokubun[13−16] to explain the properties of acridine does not therefore seem to be appropriate in the case of these naphthalimides, although the steep decrease in fluorescence quantum yield and lifetime seen here appears similar to that observed for acridine in aqueous alcohols referred to earlier.

The positive deviation from linearity of the calculated nonradiative rate constants as a function of water concentration in the binary solvents suggests that a compound quenching model of the type developed by Moore et al.[27] may be applicable here. This model deals with a situation where multiple quenching molecules are required to deactivate an excited state by treating it as a one-dimensional random walk with a trap. The kinetic scheme given in Scheme 1 has been applied to the data. In this scheme a number of different solute (N = naphthalimide)/water (S) species are postulated to exist in the ground and excited state (* denotes an excited state). Species that contain less than n water molecules are assumed to have the difference made up with ethanol molecules so that all species contain equal numbers of solvent molecules. Each excited species can either decay back to the ground state (rate constants $k_0...k_n$) or undergo solvent exchange to increase or decrease (where possible) the number of water molecules (rate constants k_{01}, k_{10}, etc.). The rate constants for solvent exchange are much greater than those for decay to the ground state with the exception of k_n for the N*...S$_n$ species, which represents the trap. In this case k_n is much larger than $k_0...k_{n-1}$ and is able to compete more effectively with the solvent exchange processes.



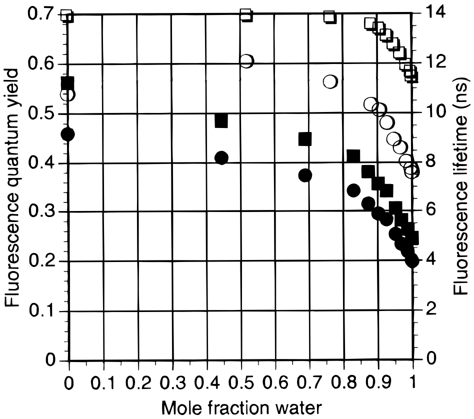


Figure 3. Variation of the quantum yield (circles) and lifetime (squares) of (a) **1** and (b) **2** in aqueous ethanol (filled symbols) and deuterated water/deuterated ethanol mixtures (open symbols).

The distribution of solvent molecules around each naphthalimide ground state molecule is assumed to be random. This results in a binomial distribution of solute/solvent species in the ground state. Given the similarity of the spectral properties of both naphthalimides in all the solvents used here, all the ground state species appear to have identical extinction coefficients, and we can therefore assume that the initial distribution of excited state species will be identical to the ground state distribution. The initial excited state concentration for a species containing m water molecules and $n - m$ ethanol molecules ($C_m(0)$) will be proportional to the weight of this configuration and will be given by[27]

$$C_m(0)\ \alpha \frac{(n-1)!}{m!(n-m)!}[\mathrm{H_2O}]^m[\mathrm{EtOH}]^{n-m}$$

The time evolution of this initial concentration distribution is

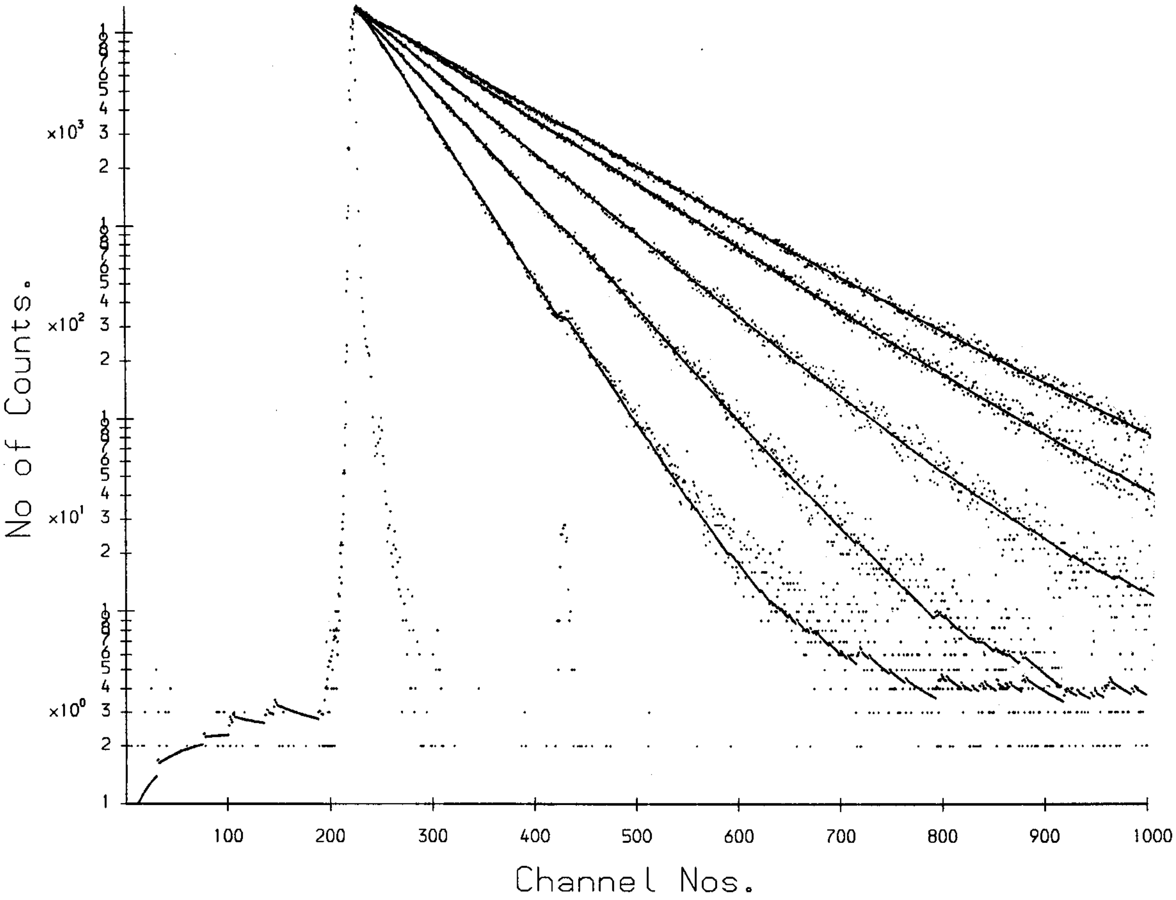


Figure 4. Fluorescence decay profiles and excitation pulse profile for **1** in aqueous ethanol at water mole fractions of 0.0, 0.69, 0.83, 0.93, and 1.0. The decay profiles are all fitted with a single-exponential decay (full line). Time scale 0.0488 ns per channel.

calculated by multiplying these concentrations (in the form of a row matrix **C**) by a reaction rate matrix **R** where

$$\mathbf{R} = \begin{pmatrix} A_{00} & J_{01} & 0 & 0 & \cdots & 0 & k_0\Delta t \\ J_{10} & A_{11} & J_{12} & 0 & \cdots & 0 & k_1\Delta t \\ 0 & J_{21} & A_{22} & J_{23} & \cdots & 0 & k_2\Delta t \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdots & A_{\mathrm{nn}} & k_n\Delta t \\ 0 & 0 & 0 & 0 & \cdots & 0 & 1 \end{pmatrix}$$

The J terms represent the probability that the excited species undergoes an exchange of a solvent molecule in the time interval Δt and are given by

$$J_{m,m+1} = [\mathrm{H_2O}]\frac{n-m-1}{n-2}k_{\mathrm{diff}}$$

$$J_{m,m-1} = [\mathrm{EtOH}]\frac{m-1}{n-2}k_{\mathrm{diff}}$$

where k_{diff} is the diffusional rate constant (estimated as $T/\eta \times 10^8\ \mathrm{s^{-1}}$).[27] The A terms give the probabilities that the excited species remain unchanged during the time interval Δt and are thus given by

$$A_{mm} = 1 - J_{m,m-1} - J_{m,\,m+1} - k_m\Delta t$$

The concentrations of the various excited species at some time t after the initial excitation are then given by $\mathbf{CR}^{\alpha}$, where $\alpha = t/\Delta t$. A profile of excited concentration with time can thus be built up by repeating the matrix multiplication procedure for various values of t.

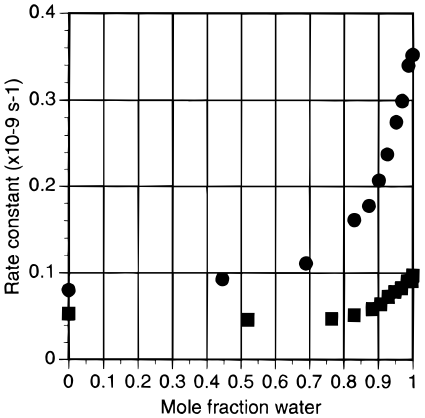
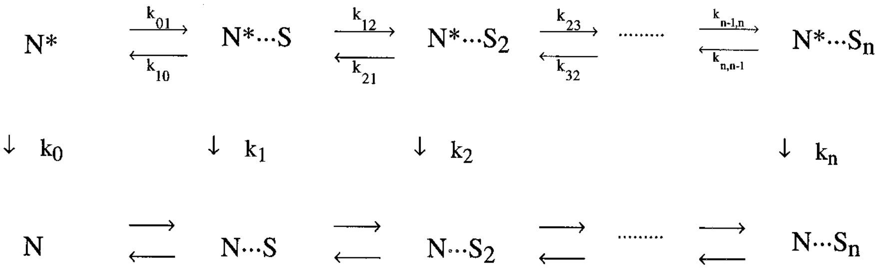


Figure 5. Variation of the nonradiative rate constant for **1** in aqueous ethanol (circles) and deuterated water/deuterated ethanol mixtures (squares).

All the matrix multiplication was undertaken using MathCad. The values of the rate constants $k_0 ... k_{n-1}$ were assumed to be equal to the sum of the radiative and nonradiative rate constants of each naphthalimide in ethanol or ethanol-*d*, while k_n was assumed to be equal to the sum of these two rate constants for the naphthalimide in water or deuterated water. Various values of Δt were used in the initial calculations, but it was found that a Δt value of 1 ps was sufficiently small such that further reduction of its value gave no change in the excited state concentration versus time profile. A series of calculations were then carried out for each naphthalimide at each solvent composition in each of the two binary solvent systems to

SCHEME 1



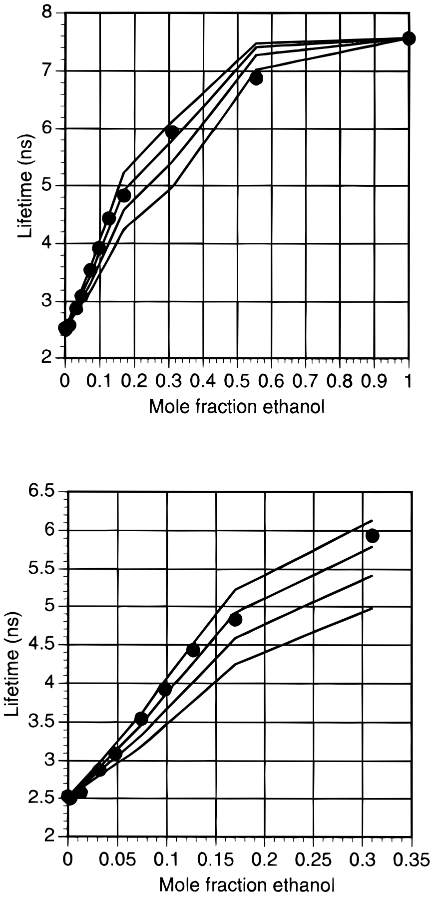


Figure 6. Comparison of experimental and calculated lifetimes for **1** for $n = 6$, 7, 8, and 9 (a) over the whole range of solvent composition and (b) at higher water contents.

determine the concentration versus time profile as a function of the number of solvent molecules that could be associated with each naphthalimide molecule (see Scheme 1).

The first result to note is that this model predicts exponential decays for all the calculations undertaken, an outcome that is in accord with the experimental observation of single-exponential fluorescence decay profiles in all the solvent mixtures used. In ethanol/water mixtures, the best agreement between the experimental and calculated lifetimes for **1** was found for an n value of 7 (Figure 6). For compound **2**, n values of 7 or 8 gave very similar levels of agreement between calculation and experiment. In the deuterated solvent mixtures, much higher values of n were required for the calculated lifetimes to match the experimental ones; $n = 20$ in the case of compound **1** and $n = 18$ in the case of **2**.

On the basis of this model, these calculations indicate that in ethanol/water mixtures, a naphthalimide molecule associated with seven or eight water molecules acts as the "trap" in which nonradiative decay is enhanced. If we assume that the naphthalimide is deactivated back to the ground state by this enhanced nonradiative decay, the amount of excited state energy that has to be dissipated is on the order of 20 650 cm^{-1} for **1** and 21 000 cm^{-1} for **2** (calculated by taking the average of the energies for the absorption and emission maxima). If this energy were dispersed equally among the cluster of water molecules, each one would receive on the order of 3000 cm^{-1}. This value is similar to the fundamental vibrational frequencies of the symmetric (3651.7 cm^{-1}) and asymmetric (3755.8 cm^{-1}) stretching vibrations of water[28] and suggests that the excitation energy of the naphthalimide may be dissipated into the stretching modes of a cluster of water molecules, each one receiving one quantum of vibrational energy. A similar concept has been previously advanced by Förster and Rokos[29] to help explain the photophysics of 1-(*N*,*N*-dimethylamino)naphthalene-5-sulfonate: "...a coupling between the electronic motion within the dissolved molecule and the nuclear motion of one or more solvent molecules. If ...this coupling is very strong, it might provide a mechanism for the transformation of electronic excitation energy into vibrational energy of the solvent and, thus, lead to radiationless interconversion". However, as far as we are aware, no one has previously attempted to calculate the number of solvent molecules that might be involved in the interaction.

If the same concept applies in the mixture of deuterated solvents, at least eight molecules of deuterated water would be required to dissipate the excited state energy from the two naphthalimides. This compares with the values of 20 and 18 for **1**, and **2**, respectively, calculated on the basis of the model. There is obviously considerable discrepancy between these values, which may indicate that the model is inappropriate. However, it is noticeable that the enhancement of the nonradiative decay is much less in the deuterated solvents than in normal water and ethanol. This has the dual effect of making it more difficult to distinguish between the quality of agreement between the experimental and calculated data as the number of associated solvent molecules is changed, and it also means that the effect of errors in the measured data is enhanced. Both these effects indicate that less confidence can be placed in the results obtained from the model for the number of associated solvent molecules required for the enhancement of nonradiative decay in the deuterated solvent mixtures.

It is noteworthy that the deuterated solvents are much less efficacious at enhancing the nonradiative decay than the normal aqueous ethanol mixtures. Comparison of the nonradiative rate constants for **1** and **2** in water and deuterated water reveals that k_{nr} is a factor of 3.6 greater in water than deuterated water for **1** and a factor of 3.34 greater for **2**. The corresponding ratios in ethanol and deuterated ethanol are 1.43 and 1.45 for **1** and **2**, respectively. These values are very similar to those noted by Sadkowski and Fleming for the k_{nr} ratio in 1,8-anilinonaphthalene sulfonate (3.1 for H_2O/D_2O and 1.4 for EtOH/EtOD)[30] and for the fluorescence quantum yield ratios[31] in H_2O/D_2O for 5-aminonaphthalene 1-sulfonate (ratio 3.04) and 8-aminonaphthalene 1,3,6-trisulfonate (3.70), suggesting that a similar mechanism may operate for these compounds.

If the idea that the excitation energy is dissipated among the stretching vibrational modes of the cluster of associated water molecules is correct, then we can look upon these stretching vibrations as the "promoting modes" for the nonradiative transition in a manner similar to that adopted by Siebrand[32] in his treatment of nonradiative transitions in aromatic hydrocarbons. In these compounds,[33] a distinct deuterium isotope effect is observed. The Franck−Condon factors associated with the transition are greatly reduced upon deuteration, which affects the rate constants for the nonradiative transitions. The same effect appears to operate here.

We are continuing our studies of these systems to expand the range of structures under consideration, for instance to determine whether the addition of substituents onto the 4-amino group has an effect on the photophysics in these aqueous alcohols.

Conclusion

The observed decrease in the fluorescence quantum yields and lifetimes of two 4-aminonaphthalimides in aqueous ethanol can be attributed to increased nonradiative deactivation as the proportion of water in the solvent increases. The increase in the nonradiative rate constant is not a linear function of the water concentration, and the experimental data have therefore been analyzed in terms of a model involving multiple quenching species developed by Moore et al.[27] In ethanol/water mixtures, a cluster of some seven or eight water molecules is required to effect the quenching, possibly corresponding to the excitation of one quantum of a stretching mode in each water molecule. Similar results are observed in deuterated solvents, although the observed increase in the nonradiative decay is smaller and the number of deuterated water molecules required to effect the enhancement on the basis of the model is rather larger than would be expected if one quantum of a stretching mode was excited in each molecule. The behavior noted here is similar to that observed for other systems such as the aminonaphthalenes, aminonaphthalene sulfonates, and acridine, and it is possible that the data in these systems could be treated in a manner similar to that adopted here.

Acknowledgment. We thank the University of Central Lancashire for consumable support and for a research studentship (D.Y.) and the EPSRC for granting access to the Daresbury Laboratory.

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