Electron Hydration Dynamics Using the 2-Anilinonaphthalene Precursor

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Abstract: Picosecond spectroscopy is used to study spontaneous ionization and electron hydration dynamics from the charge-transfer state of 2-anilinonaphthalene in water/alcohol mixtures. Hydration of the electron is the rate-limiting step in the overall kinetics. Results are also presented for 8-(phenylamino)-1-naphthalenesulfonate, and the dynamical differences caused by the sulfonate group are discussed. As in other systems (electrons and protons), a water cluster of 4 ± 1 members is the effective charge acceptor. Comparison with other electron and proton precursors such as 6,2-TNS, indole, and 2-naphthol in mixed water/alcohol solvents is made.

Picosecond and femtosecond spectroscopic techniques[1,2] have provided a means whereby ultrafast dynamics of chemically interesting systems can be directly studied. The rapid hydration dynamics[3,4] of the *elementary ions*, electrons and protons, have thus become accessible to investigation in those cases where the precursor molecule can be produced on time scales comparable to or shorter than the hydration times.

The photophysical properties of the biological probe molecules 8-(phenylamino)-1-naphthalenesulfonate (8,1-ANS) and 6-*p*-toluidino-2-naphthalenesulfonate (6,2-TNS) are sensitive to solvent polarity and solvent structure.[5,6] Compared with the alcohols and other nonaqueous solvents, both of these molecules show highly red-shifted emission spectra and very small fluorescence quantum yields in water.[6,7] These results in water have been interpreted in terms of absorption into the singlet state (S_1) followed by the formation of an intramolecular charge-transfer state (S_{CT})[6,8,9] on

ultrashort (<10 ps) time scales,[10] then spontaneous ionization (i.e., charge transfer to solvent, CTTS) of this CT state,[11] and hydration of the electron.[12] The nonradiative photoionization process, which strongly quenches the fluorescence, does not readily occur in nonaqueous media.[11] Molecules such as the ANS derivatives can therefore act as precursors for the study of electron hydration dynamics as the solvent is systematically changed from a pure nonaqueous solvent to pure water.

Recent experimental work on other electron and proton precursors[3,4] in water/alcohol mixtures has given further support to the idea that the dominant deactivation process for certain classes of molecules in an aqueous solvent involves the formation of this CTTS state. The data analysis points to a water cluster having

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(10) G. W. Robinson, J. M. Morris, R. J. Robbins, and G. R. Fleming, *SPIE Annu. Tech. Symp., Proc., 22nd* **113**, 13 (1977).

(11) G. R. Fleming, G. Porter, R. J. Robbins, and J. A. Synowiec, *Chem. Phys. Lett.*, **52**, 228 (1977); P. J. Sadkowski and G. R. Fleming, *Chem. Phys.*, **54**, 79 (1980). In nonaqueous solvents, where spontaneous ionization is improbable, electrons must usually be produced by a two-photon process in order to acquire sufficient kinetic energy to escape the local cationic environment. The one-photon photoionization interpretation in water has been criticized [H. Nakamura et al., *Bull. Chem. Soc. Jpn.*, **55**, 1795, (1982)]. Certainly, because of the probably brief lifetime of "threshold electrons" (ref 3), one must be wary of conclusions based on solvated electron measurements carried out on too slow a time scale. However, the detection of highly non-linear quantum yields and rates with increasing water concentration in water/alcohol solvents is at variance with suggestions of Nakamura et al. and others (e.g., ref 8) that these effects in water are caused by solvent perturbations on intersystem crossing. A near-linear dependence is expected and observed [G. R. Fleming et al., *J. Am. Chem. Soc.*, **99**, 4306 (1977)] for such an effect. Moreover, using the low water concentrations of Nakamura et al., one would not expect to produce a significant number of hydrated electrons by a one-photon process. The single photon photoelectron–hydration process in 2-AN is unimportant in 1:1 water/alcohol mixtures as indicated in our work.

(12) R. A. Moore, J. Lee, and G. W. Robinson, *J. Phys. Chem.*, **89**, 3648 (1985).
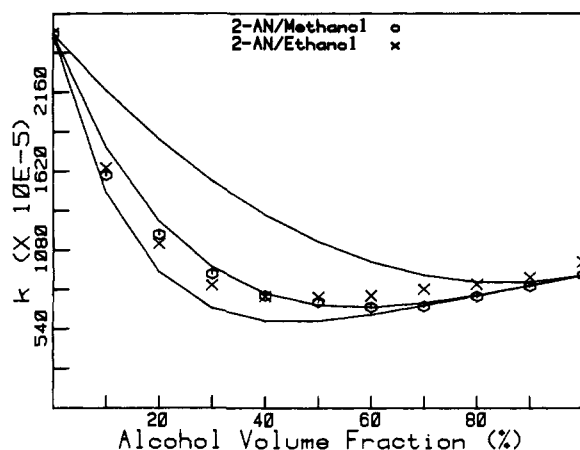
Figure 1. Overall rate constants τ^{-1} for 2-AN as a function of alcohol volume fraction: experimental values for the methanol solvent (O) and the ethanol solvent (X). Calculated values for cluster size of 2 (top), 4 (middle), and 6 (bottom).

4 ± 1 members as the effective charge acceptor, independent of the polarity of the charge or the type of molecular precursor employed.

The precursor 2-anilinonaphthalene (2-AN) lacks the complications that could be caused by the presence of the strongly polar sulfonate group in the ANS derivatives. However, this simpler compound exhibits a qualitatively similar solvent response as 8,1-ANS and 6,2-TNS when the solvent is changed from alcohol to water. Hence, to gain a better understanding of electron hydration dynamics, as well as to learn more about the "threshold photoionization" process[3] in biological probe molecules, it is of interest to investigate the photophysical properties of 2-AN as a function of water/alcohol solvent mixtures.

Experimental Section

2-Anilinonaphthalene (*N*-phenyl-2-naphthylamine) of 99+% purity was purchased from Molecular Probes, Inc.[13] Spectroscopic grade 8,1-ANS was purchased from Eastman. HPLC grade methanol (Fisher), USP absolute ethanol (U.S. Industrial Chemical Co.), and demineralized water were used to prepare water/alcohol solvent mixtures. Except for the crucial removal of atmospheric oxygen contamination, all chemicals were used without further purification. Eleven water/alcohol mixtures having water concentrations between 0 and 100% were prepared in volume fraction. The concentration in each case was maintained at ~0.2 × 10⁻⁵ M for 2-AN and ~1.0 × 10⁻⁵ M for 8,1-ANS.

Absorption and fluorescence spectra were measured on a Perkin-Elmer Lambda 5 UV–VIS spectrophotometer and an MPF-44 fluorescence spectrophotometer, respectively. The absolute quantum yield (Q_f), corrected by a quinine sulfate standard ($Q_f = 0.546$), was obtained by integrating the emission spectrum from 305-nm excitation. A single photon-counting apparatus using a Coherent Inc. argon ion synchronously pumped dye laser was used for the fluorescence lifetime measurements. The nominal output of such a laser system provides ~15 ps UV pulses with <0.1 nJ energy per pulse. The low peak power of this laser and the close connection between these lifetime measurements and quantum yields obtained with weak spectrofluorimeter light sources—thus the overall insensitivity of our results to the intensity of the light source used (i.e., a Nd³⁺/glass laser with ~1 mJ energy per pulse)—remove any possibility that two-photon processes play a role in these experiments. A fuller description of the experimental methods can be found elsewhere.[14,15]

Results

The absorption spectrum of 2-AN shows no observable shift as the solvent is changed from pure alcohol to pure water, while

(13) 2-AN is carcinogenic and must be handled with care. See the following references: R. A. Thuraisingham and S. H. M. Nilar, *J. Theor. Biol.*, **86**, 577 (1980); E. Brill, J. L. Radomski, and W. E. MacDonald, *Res. Commun. Chem. Pathol. Pharmacol.*, **18**, 353 (1977).

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Table I. Experimental Data for 2-AN in Pure Water and Alcohols[a]

solvent	τ (ns)	Q_f	k_r ($\times 10^{-7}$)	k_{nr} ($\times 10^{-7}$)	λ_{ems} (nm)	fwhm (nm)
H_2O	3.9	0.082	2.10	23.5[b]	435	96
alcohol[c]	11.0	0.444[d]	4.04	5.05	410	56

[a] The error is estimated to be 10%. [b] The intramolecular nonradiative decay rate is small in comparison to the intermolecular charge-transfer rate in water. Therefore, as an approximation, this value is attributed fully to the intermolecular charge-transfer rate. [c] Deoxygenated solvents, methanol, or ethanol. [d] This value is in excellent agreement with that obtained in ref 8.
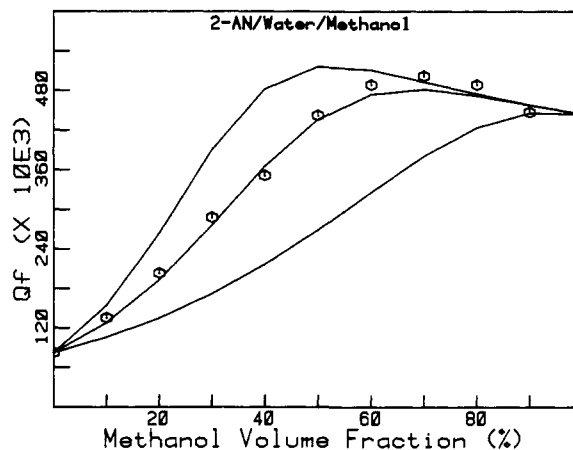

Figure 2. Quantum yields (Q_f) for 2-AN as a function of methanol volume fraction: experimental values (O). Calculated values for cluster size of 6 (top), 4 (middle), and 2 (bottom).
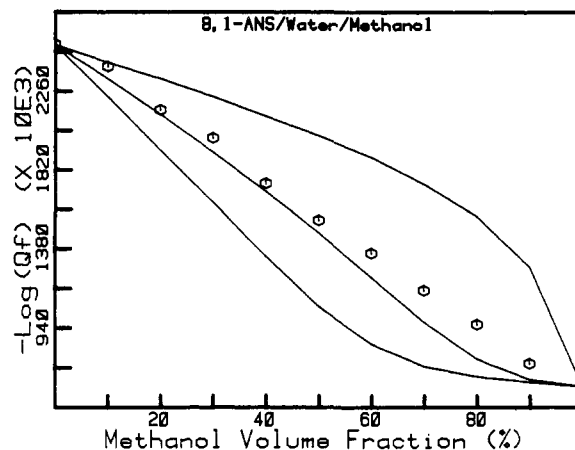

Figure 3. Quantum yields (Q_f) for 8,1-ANS as a function of methanol volume fraction: experimental values (O). Calculated values for cluster size of 1 (top), 3 (middle), and 5 (bottom).

the fluorescence spectrum is continuously red-shifted and broadened as the water concentration increases.[6] Table I lists the experimental parameters for 2-AN in water and methanol solvents. Figures 1 and 2 plot total decay rate constants ($1/\tau$) and quantum yields (Q_f) of 2-AN as a function of methanol volume fraction. Substitution of ethanol for the methanol solvent produces little change in these quantities, providing the concentration unit employed is volume fraction.[16] See Figure 1.

8,1-ANS, containing the sulfonate group, is somewhat more sensitive to solvent composition. The experimental parameters in water, methanol, and ethanol are shown in Table II. The molecule shows a more red-shifted and broadened fluorescence

(16) R. A. Auerbach, J. A. Synowiec, and G. W. Robinson in "Picosecond Phenomena II", R. M. Hochstrasser et al., Eds. Springer-Verlag, Berlin, 1980, pp 215–219. This reference uses *mole fraction* in a crude analysis of the data. Such fits do not provide a consistent picture for different precursors and different solvents. See ref 12.

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Table II. Experimental Data for 8,1-ANS in Pure Water and Alcohols[a]

solvent	τ (ns)	Q_f	k_r ($\times 10^{-7}$)	k_{nr} ($\times 10^{-7}$)	λ_{ems} (nm)	fwhm (nm)
H_2O	0.2^b	0.003^b	1.20	398.8^c	556	132
$MeOH^d$	7.1	0.240	3.40	10.61	484	108
$EtOH^d$	11.0	0.523	4.75	4.34	480	96

[a] The error is estimated to be 10%. [b] Value is taken from ref 7. [c] The intramolecular nonradiative decay rate is small in comparison to the intermolecular charge-transfer rate in water. Therefore, this value is attributed fully to the intermolecular charge-transfer rate. [d] Deoxygenated solvents.

spectrum and a smaller Q_f and τ than does 2-AN as the water concentration increases. Figure 3 presents the log plot of Q_f for 8,1-ANS as a function of methanol volume fraction. (We are forced to use log plots for 8,1-ANS and 6,2-TNS[12] because of the great range of the parameters with changing water concentration.) In contrast to the case of 2-AN, 8,1-ANS shows a modest increase of Q_f and τ as the solvent changes from methanol to ethanol. A similar type of solvent response has been observed for 6,2-TNS. The τ and Q_f for 2-AN and 8,1-ANS decrease sharply as the concentration of water is raised to values exceeding 50%. Furthermore, as in the case of 6,2-TNS, these parameters are rather insensitive to temperature variations from 0 to 80 °C in water, indicating a low or zero activation energy process.

Discussion

The formation of the S_{CT} state following S_1 excitation is well established for 2-AN and its derivatives.[6,8,9,17,18] In polar solvents, such as water and alcohol, S_{CT} is lower and more stable than S_1. Since formation of S_{CT} from S_1 in nonviscous polar solvents has been found[10] to take place in <10 ps, it is this S_{CT} state that determines the kinetics of these excited molecules. Hence, dual photophysics from S_1 and S_{CT}, to a good approximation, can be treated as a single process from S_{CT} in the small polar solvents used here. An additional *intermolecular* relaxation channel, spontaneous ionization (CTTS), is opened in aqueous solvents.[7,11] This additional channel is responsible for the shorter lifetime ($3\times$ for 2-AN and $50\times$ for 8,1-ANS) and smaller quantum yield ($5\times$ for 2-AN and $170\times$ for 8,1-ANS) observed in water (Tables I and II).

In water/alcohol mixtures, the intermolecular deactivation process is retarded, then completely terminated, as the alcohol concentration increases. At high alcohol concentrations, only the intramolecular channels of radiative decay, internal conversion, and intersystem crossing remain (Figures 1, 2, and 3). This remarkable difference in ion-accepting capacity between water and the alcohols is particularly well borne out when the photoionization process is temperature sensitive.[3,4] This behavior is obviously highly nonlinear with respect to dielectric constant or parameters related to dielectric constant[19] and hints at a molecular basis for the dielectric properties of matter.

Interestingly, an increase of the methanol concentration above 50% in the case of 2-AN slightly increases the total decay rate constant (or decreases the quantum yield) and results in a minimum in Figure 1 (a maximum in Figure 2) near 60% methanol concentration. This turnover phenomenon is caused by a larger *intra*molecular rate in pure methanol ($\sim 9.09 \times 10^7$) than in pure water ($\sim 2.1 \times 10^7$). Competition between intermolecular and intramolecular decay processes therefore accounts for these observed extrema. The same phenomenon has been detected in some of our other studies.[3,4]

The nonlinear dependence of total decay rate constants and quantum yields as a function of water/alcohol concentration has been observed for other CTTS systems—electrons[3,12] as well as protons.[4] The data have been analyzed on the basis of a "compound quenching" theory,[12] with a $(H_2O)_{4\pm1}$ cluster found to be the charge acceptor. This theory uses only end-point data (pure water and pure alcohol) with no adjustable parameter other

than the cluster size. A similar kinetics scheme can be applied to the 2-AN and 8,1-ANS data in order to determine the nature and structure of the quencher. The calculated data (2-AN) for water clusters of two, four, and six members are given by solid lines in Figures 1 and 2; and for one, three, and five members in Figure 3 (8,1-ANS). The cluster sizes of 4 for 2-AN and 3 for 8,1-ANS fit both experimental lifetimes and quantum yields well, considering the $\sim 10\%$ experimental error and the conceptual simplicity of the model used in the analysis. The similarity of the fits for all the electron and proton transfer data thus far obtained therefore supports the proposed mechanism, with $(H_2O)_{4\pm1}$ as the effective charge acceptor.

Effect of the Sulfonate Group. The intramolecular decay rate constants of 2-AN are of the same order as those of 8,1-ANS. However, the CTTS rate constant for the S_{CT} state of 2-AN in water is smaller by a factor of ~ 17 than that of 8,1-ANS in water, and the degree of lowering the CT state from alcohol to water solvents is much smaller in 2-AN. Compared with the $\sim 14\%$ red shift in the case of 8,1-ANS, there is a $\sim 6\%$ red shift in the case of 2-AN. These results suggest that the presence of the sulfonate group lowers the CT state and increases the CTTS character of the molecule in water, but does not affect the qualitative aspects of the relaxation process.

A comparison of ethanol with methanol solvents is also of interest for these two classes of compounds. In 8,1-ANS the lifetime and quantum yield show a small decrease when the solvent is changed from ethanol to methanol. However, the lifetime and quantum yield of 2-AN show no decrease (Figure 1), and the emission spectra show neither apparent shift nor broadening when the solvent is changed from ethanol to methanol. Furthermore, a cluster size of 4 fits the data well for 2-AN in both water/methanol mixtures and water/ethanol mixtures. Addition of a sulfonate group to 2-AN must impose to methanol a slight charge-accepting character. For 8,1-ANS, a smaller than "normal" cluster size of 3 occurs in water/methanol, but a cluster size of 4 is again found for water/ethanol solvents. These findings exactly parallel those for 6,2-TNS,[12] which also contains the sulfonate group.

Activation Energy. In contrast to the large activation energies observed for indole[3] (electron precursor) and 2-naphthol[4] (proton precursor) in water, 10.4 and 3.4 kcal mol⁻¹, respectively, the intermolecular charge-transfer rates for 2-AN, 8,1-ANS, and 6,2-TNS are nearly insensitive to temperature variation. In the case of indole and 2-naphthol, energy is required to break up and rearrange the nearby H-bonded structure of normal liquid water prior to reconstructing the charge-accepting entity. In the case of 2-AN, 8,1-ANS, and 6,2-TNS, on the other hand, the near-zero activation energy implies that a considerable weakening of the H-bonded structure has occurred during the ultrashort (<10 ps) $S_1 \rightarrow S_{CT}$ relaxation process. Following Kenney-Wallace and Jonah,[20] we have called such clusters "preformed".[16] More will be said about this terminology later.

Some preliminary pressure experiments[21] (0 to 3 kbar) indicate that the activation energies for indole and 2-naphthol decrease as the pressure increases, while little pressure dependence on the rates is observed for 8,1-ANS. Similar effects of pressure on the viscosity[22] and electrical conductivity[23] of liquid water are known

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(21) D. Steyert, P. M. Rentzepis, J. Lee, D. Statman, and G. W. Robinson, unpublished results.

to occur in this pressure range. With increasing pressure, the H bonds in the liquid water network become distorted and weakened.[24] Consequently, pressure reduces the energy required to break up the neighboring water structure when the energy barrier is intact, as in indole and 2-naphthol, but has no effect on the CTTS process in the AN derivatives, where the appropriate H-structure reorientations can take place without having to break H bonds.

"Preformed Clusters". With regard to the charge hydration dynamics discussed here, a clearer description of the terminology "preformed cluster" is required. The integrity of the quasitetrahedral structure of the oxygen framework in condensed water under many different thermodynamic and chemical perturbations has been well documented by X-ray and neutron diffraction studies.[24,25] Therefore, we believe the charge-accomodating O_4 framework has a high propensity to be "preformed" in pure liquid water, or in mixed solvents having high water content, and furthermore that it essentially retains its integrity throughout the entire hydration process. This aspect is a unifying feature that should conceptually simplify discussions of the hydration dynamics.

Adaptation of the H atoms to the new charged structure is quite another matter. The H-atom/H-bond configurations in pure liquid water can certainly not be very close to those in the hydrated H_3O^+ ion[25] or the hydrated electron. To form the new structures, H-bond-length changes and molecular reorientations must take place on characteristic time scales. Normally, when there is no large amount of polarization of the water by the precursor molecule, an improbable fluctuation[26] is needed to bring the charge-accepting cluster into the required form. Such a fluctuation may last only a small fraction of the characteristic reorientational time. At this subpicosecond point in time, the electronic (or protonic) eigenfunction must collapse onto this short-lived cluster configuration, thus stabilizing it. The rate of hydration is then guided by the average time between these fluctuations, with entropic as well as enthalpic considerations playing a role.[27] Because of possible perturbations by the precursor molecule and the exothermicity of the final state, this time is not necessarily equal to rotational correlation time in pure water.[20] Larger, more slowly moving ions must present a somewhat different picture. In any case, for the solvation of elementary ions in water, there must be a long-time-scale "preformation" concerning the O_4 framework, and a short-time-scale "preformation" concerning the H atoms and H bonds.

For the AN derivatives, where the photophysics occurs from an intramolecular CT state that undoubtedly possesses a large dipole moment,[8] the normal water structure in the microenvironment is expected to be strongly polarized, with the H atoms in awkward orientations for the formation of H bonds. Thus, as in other kinds of perturbations (i.e., pressure), where the H-bond structure is disrupted, the activation energy barrier is lowered, in this case essentially removed, by the local field of the precursor molecule.

Conclusions

In conclusion, three aspects are apparent from the above findings. First, addition of a sulfonate group to 2-AN enhances its intramolecular CT characteristics and increases the intermolecular charge-transfer rate, but does not change the qualitative aspects of the charge-transfer process. Secondly, $(H_2O)_n$ with $n = 4 \pm 1$ is found to be the effective charge acceptor and quencher for 2-AN and related molecules, n being closer to 3 in the case where the solvent is methanol and a sulfonate group is present. Finally, the zero activation energy obtained for 2-AN, 8,1-ANS, and 6,2-TNS is attributed to the presence of preformed[16,20] water clusters that are helped to be created by the large S_{CT} dipole during the $S_1 \rightarrow S_{CT}$ relaxation process.

Our results here, the results on indole[3] and 6,2-TNS,[12] and those for proton transfer in the 2-naphthol experiments,[4] show that single water molecules are not effective as electron or proton acceptors. In addition, good agreement between theory and the experimental data in all these cases can be achieved by assuming that larger clusters are not measurably better than the 4-cluster as a charge acceptor.[12] The study of gas-phase charged water clusters.[28,29] not lead to these same conclusions, pointing to the difference between purely structural and dynamical considerations in chemical rate theory. Just because a certain entity is stable under isolated cluster conditions does not mean that it necessarily plays a role in dynamical processes. The reason that the alcohols are poor charge acceptors is not because a charged alcohol structure is unstable, but rather because the required reorganization times for such sterically bulky molecules are too long compared with other competing rate processes. These competing rates determine the equilibrium properties of ionic solutions and the dielectric character of pure liquids.

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