so that any evaporation of the solvent was accounted for.

Each photoacoustic experiment was recorded at least twice. The transducer signals and energy meter readings were the average of eight shots.

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Electrolyte Effects on the Photophysical Properties of Intramolecularly Hydrogen-Bonded Molecules

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Abstract: Salt effects on the photophysics of the intramolecular hydrogen-bonded solute molecule 1-aminofluoren-9-one (1-AF) are examined in acetonitrile solution. Unlike previous studies on the related molecule 3-aminofluoren-9-one (3-AF), combined steady-state and time-resolved studies show that 1-AF forms ground-state complexes with dissolved cations. The association between 1-AF and the dissolved electrolytes is dependent on the size of the cation. No complexes are observed between 1-AF and the molecular cations Bu_4N^+ and Me_4N^+. The differences between the photophysics of 1-AF and 3-AF in acetonitrile–salt solutions are discussed in terms of the molecular properties arising from the intramolecular hydrogen bond between the amino nitrogen and the carbonyl group present in 1-AF.

Introduction

Medium effects on the energetics of charge-transfer transitions have played a central role in developing solvation scales for solute molecules in both neat solvents[1] and binary solvent mixtures.[2] In binary mixtures, observed changes in absorption spectra are used to evaluate the importance of specific solvation. In some cases, molecular solutes are solvated by solvent molecules in the same proportion as the bulk concentrations of the mixture components. In other cases, specific solvation by one of the components occurs. In this later limit, it is the degree of specific solvation that plays an important role in determining chemical reactivity of the solute, not the composition of the mixed solvent system. Similar to solvent mixtures, electrolyte solutions have the potential of affecting molecular reactivity through bulk and specific interactions.[3-5] Added salts affect bulk solution properties such as polarity, polarizability, viscosity, and dielectric constant. The solvation of ions also impacts the intermolecular solvent structure and dynamical motion of individual solvent molecules.[6,7] Similar to the cases of specific solvation in mixed liquids, electrolytes also have the potential to form specific interactions with solute molecules, thereby altering both the photophysics and the photochemistry. Isolating the effects of these different types of interactions between electrolyte and solute molecules is a challenging and important problem.

In this paper, electrolyte effects on the solution photophysics of 1-aminofluoren-9-one (1-AF) and 3-aminofluoren-9-one (3-AF) are compared. We recently reported a study of salt effects on the photophysics of 3-AF in acetonitrile solution.[8] That study reported three significant observations that arise from bulk interactions between dissolved salts and molecular solutes. First, the maxima of both the absorption and emission spectra red-shifted with increasing salt concentration. This was interpreted in terms of the salt effects on solution polarity. Second, changes in the radiative rate of 3-AF upon addition of salt were quantitatively accounted for by the Strickler–Berg equation. Third, electrolyte effects on the nonradiative decay rate of 3-AF were quantitatively accounted for in terms of the energy gap law. In this previous report we focused on the inability of current theoretical models to describe these general observations. Comparison between the experimental data and theory was justified as there was no evidence of any specific interactions between the salts and the solute molecule. This enabled us to study the ability of current models to describe bulk effects (both static and dynamic) of electrolyte solutions on solute photophysics. While no current theoretical model could account for the observed dynamics, the experimental results for 3-AF in salt solutions serve as a model case for anticipated effects that electrolyte solutions have on nonreactive "spectator" probe molecules.

Unlike 3-AF, 1-AF can form an intramolecular hydrogen bond between the amino and carbonyl moieties of the molecule. This intramolecular interaction influences the nonradiative dynamics of the electronically excited molecule in protic and aprotic solvents. In particular, a systematic study of the photophysics of 1-AF in neat solvents suggested that the intramolecular hydrogen bond provides a more efficient deactivation pathway than intermolecular hydrogen bonds to protic solvents.[9] This effect was quantified by examining the photodynamics of 1-AF in a mixed solvent system. Addition of small amounts of a strong hydrogen-bond-donating solvent, e.g., 2,2,2-trifluoroethanol (TFE), to a dilute solution of 1-AF in heptane revealed an isosbestic point in the

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(1) (a) Bjerrum, J.; Adamson, A. W.; Bostrup, O. *Acta Chem. Scand.* **1956**, *10*, 329. (b) Burgess, J.; Radulovic, S.; Sanchez, F. *Transition Met. Chem.* **1987**, *12*, 529. (c) Ford, P. C.; Rudd, D. P.; Gaude, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187. (d) Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2098.

(2) (a) Chang, T.-L.; Cheung, H. C. *Chem. Phys. Lett.* **1990**, *173*, 343. (b) Moya, M. L.; Rodriguez, A. *Transition Met. Chem.* **1991**, *16*, 230. (c) Blackbourn, R. L.; Hupp, J. T. *Inorg. Chem.* **1989**, *28*, 3786. (d) Curtis, J. C.; Blackbourn, R. L.; Ennix, K. S.; Hu, S.; Roberts, J. A.; Hupp, J. T. *Inorg. Chem.* **1989**, *28*, 3791.

(3) MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 6108.

(4) (a) Pines, E.; Huppert, D.; Agmon, N. *J. Phys. Chem.* **1991**, *95*, 666. (b) Ittah, V.; Huppert, D. *Chem. Phys. Lett.* **1990**, *173*, 496. (c) Huppert, D.; Ittah, V. In *Perspectives in Photosynthesis*; Jortner, J., Pullman, B., Eds.; Kluwer: Dordrecht, 1990.

(5) Chapman, C. F.; Maroncelli, M. *J. Phys. Chem.* **1991**, *95*, 9095.

(6) Moya, M. L.; Rodriguez, A.; Sanchez, F. *Inorg. Chim. Acta* **1991**, *188*, 185.

(7) Rezende, M. C. *Tetrahedron* **1988**, *44*, 3513.

(8) Thompson, P. A.; Simon, J. D. *J. Chem. Phys.* **1992**, *97*, 4792.

(9) Moog, R. S.; Burozski, N. A.; Desai, M. M.; Good, W. R.; Silvers, C. D.; Thompson, P. A.; Simon, J. D. *J. Phys. Chem.* **1991**, *95*, 8466.

0002-7863/93/1515-1925$04.00/0

absorption spectra and a dramatic increase in the emission intensity with increasing alcohol concentration. These new spectral features were assigned to the formation of a specific complex between the alcohol and 1-AF. Time-resolved measurements revealed that the nonradiative rate for the 1-AF/TFE complex was a factor of 4 lower than that for 1-AF in pure hexane. Thus, the nature of the specific hydrogen-bonding interactions, both intermolecular and intramolecular, in 1-AF provided a means of studying the influence of bulk vs specific interactions in protic solvents.

Closer examination of the ground-state charge distribution of 1-AF shows that the formation of an intramolecular hydrogen bond creates a localized region of high electron density, vide infra. Thus, it is not surprising that this part of the molecule interacts with hydrogen-bonding molecules. Such a structure is missing in 3-AF and provides an explanation for the profound differences reported for the photophysics for these geometric isomers in solution. For the same reasons that 1-AF effectively interacts with hydrogen-bonding solvents, we expect electrolytes to form stable ground-state complexes. This study explores such specific interactions with salts. We show that comparison of the photophysics of 1-AF and 3-AF in salt solutions provides a means by which bulk vs specific interactions with salts can be studied.

Experimental Section

Materials. 1-AF (Aldrich) was purified by sequential recrystallization from methanol and heptane. Acetonitrile (Fisher Scientific) was refluxed for several hours with CaH to remove trace amounts of water. All salts were purchased from Aldrich Chemical Company and were dried in a vacuum oven. Samples were prepared in a drybox under an inert nitrogen atmosphere.

Steady-State and Time-Resolved Spectroscopy. Steady-state absorption spectra were taken with a Varian DMS 300. All samples had a maximum absorbance of less than 0.10 for the lowest-energy transition. Steady-state fluorescence spectra were recorded with a SLM Aminco SPS 500 at an excitation wavelength of 420 nm. The emission quantum yield was determined by comparison to a deoxygenated solution of Coumarin 153 in ethanol ($\phi_f = 0.38$).[10] Infrared spectra were recorded using a Nicolet FTIR spectrometer.

Time-resolved emission data were collected using picosecond upconversion spectroscopy. A detailed description of the apparatus was recently reported.[8,11]

Results and Discussion

The lowest-energy electronic transition in the aminofluorenones involves a charge transfer from the amino group to the carbonyl portion of the molecule. This type of electronic excitation increases the permanent dipole moment of the molecule. Using AM1 calculations and steady-state emission spectroscopy, Moog and co-workers[9] determined the dipole moments of the ground and first electronic excited states of 1-AF to be 2.2 and ~6 D. This change in electronic structure necessitates changes in the surrounding solvent. Equilibrium solvation energies of the two states are expected to be dependent on dielectric properties of the liquid. Thus, changes in the solvent alter the energy gap between the gound and the excited states, influencing both the radiative and the nonradiative rates. Before discussing the spectroscopy and dynamics of 1-AF in salt solutions, it is instructive to consider what effect added salt should have on the $S_0 \leftarrow S_1$ energy gap and the associated radiative and nonradiative rates.

The lowest electronic transition in 1-AF (and 3-AF) involves separation of charge within the molecular framework. This type of transition is similar to that used to define various polarity scales. For example, the $E_T(30)$ scale is quantified in terms of medium effects on the absorption energy between a charge-separated ground state and a neutral excited state.[12] Thus, it is reasonable to assume that the polarity of electrolyte solutions, as quantified using the $E_T(30)$ scale, would provide insight into expected changes in the photophysics of 1-AF. Such an assumption proved useful in understanding salt effects on the photophysics of 3-AF.

Table I. Carbonyl Stretching Frequencies, ν_{CO}, for 1-Aminofluorenone (1-AF) and 3-Aminofluorenone (3-AF) in Different Solvent Environments

molecule	solvent	ν_{CO}, cm^{-1}
1-AF	CH_3CN	1681
	1.0 M $LiClO_4/CH_3CN$	1649[a]
	CH_3CH_2OH	1683, 1670[b]
	CF_3CH_2OH	1710. 1672[b]
3-AF	CH_3CN	1695
	1.0 M $LiClO_4/CH_3CN$	1689
	CH_3CH_2OH	1676[c]

[a] The ν_{CO}, ν_{NH} bend, and $\nu_{C=C}$ all collapse to a single broad band at 1649 cm^{-1}, indicating a strong interaction with the cation. [b] The two peaks correspond to hydrogen-bonded and non-hydrogen-bonded populations. [c] Broad. Width is about 30 cm^{-1} as compared to 10 cm^{-1} in CH_3CN.

For the series of acetonitrile/perchlorate salt solutions studied, the polarity increases in the order pure acetonitrile $\sim Bu_4N^+ \sim Me_4N^+ < K^+ < Na^+ < Li^+ < Mg^{2+}$. Addition of the alkylammonium salts does not change the polarity of the solution. This is observed for concentrations of Bu_4NClO_4 up to 1.0 M. Addition of the smaller alkali and alkaline cations results in an increase of solvent polarity. As well, the solution polarity increases with increasing salt concentration. The increase in solution polarity associated with added salt involves changes in structural and dynamic properties of the solvent. Comparison of acetonitrile–salt solutions of varying anions (e.g., ClO_4^-, and I^-) but the same cation indicates that the solution polarity is determined by the solvation of the cations.[7,8]

With increasing solution polarity, the $S_0 \leftarrow S_1$ energy gap should decrease, reflecting the fact that the excited state, with its larger dipole moment, will be solvated to a greater extent than the ground state. This should lead to a red shift in the emission spectrum and an associated increase in the nonradiative rate. In the case of alkylammonium salts, no changes in the photophysics are expected as the solution polarity is unaffected. This is exactly what was observed for 3-AF in these solutions. As discussed below, 1-AF does not exhibit this predicted behavior. To understand the difference between the photophysics of 1-AF and 3-AF in salt solutions, a variety of spectroscopic and dynamic measurements were made. The remainder of this paper examines these results and is organized as follows. First, the steady-state infrared and electronic spectroscopy of 1-AF in salt solution is examined. This is followed by a discussion of the influence of added electrolytes on the radiative and nonradiative $S_0 \leftarrow S_1$ rates. Finally, a molecular model is proposed to account for the different photophysical behaviors exemplified by these two molecules.

Steady-State Spectroscopy. 1. Infrared Absorption. FTIR absorption spectroscopy was used to determine the effect of added salts on the C=O and C—N stretching and N—H bending frequencies. Table I summarizes the carbonyl stretching frequency, $\nu_{C=O}$, of 1-AF in various solvent environments. Selected values of $\nu_{C=O}$ for 3-AF are listed for comparison. For 1-AF in acetonitrile, a single carbonyl stretching band is observed. However, in protic solvents, e.g., ethanol and trifluoroethanol, two bands are present. These two bands are attributed to two solvated species of 1-AF that exist in equilibrium. The lower-energy band is attributed to 1-AF molecules that form a specific hydrogen-bonded complex between the solvent and the C=O group; the high-energy band reflects 1-AF molecules which are not specifically hydrogen-bonded. Protic solvents do not strongly influence the absorption peaks corresponding to the C—N stretching and N—H bending modes.

Upon addition of 1.0 M $LiClO_4$ to an acetonitrile solution of 1-AF, the IR absorption bands corresponding to the C=O stretch (1681 cm^{-1}), N—H bend (1582 cm^{-1}), and C=C aromatic stretch (1611, 1625 cm^{-1}) all collapse into a single broad band at 1649 cm^{-1}. This collapse of the C=O stretch, N—H bend, and C=C aromatic stretching bands into a single, lower-energy transition strongly supports the conclusion that the lithium cation specifically interacts with the 1-AF molecule in the vicinity of these atoms.

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(10) Jones. G.: Jackson, W. R.: Choi. C.-Y.: Bergmark. W. R. *J. Phys. Chem.* **1985**, *89*, 294.

(11) Kahlow. M. A.; Jarzeba. W.; DuBruil. T. P.; Barbara. P. F. *Rev. Sci. Instrum.* **1988**, *59*, 1098.

(12) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: New York, NY, 1988.

Table II. Electronic Absorption and Emission Data for 1-AF in Acetonitrile with Concentrations of $LiClO_4$, $NaClO_4$, and Bu_4NClO_4 from 0.0 to 1.0 M at Room Temperature

salt	concn, mol/L	λ_{abs}, nm	λ_{emis}, nm	Φ_f
$LiClO_4$	0.0	418.9	496.0	0.064
	0.01	418.9	499.5	0.066
	0.05	419.2	505.0	0.071
	0.10	420.2	506.0	0.075
	0.20	421.2	509.5	0.080
	0.50	423.8	513.5	0.089
	1.0	428.8	514.0	0.092
$NaClO_4$	0.0	418.5	499.0	0.064
	0.01	418.0	498.0	0.065
	0.05	418.9	499.0	0.067
	0.10	418.9	501.5	0.070
	0.20	419.2	505.0	0.074
	0.50	421.2	506.0	0.083
	1.0	426.1	509.0	0.085
Bu_4NClO_4	0.0	418.5	498.0	0.064
	1.0	421.5	499.5	0.064

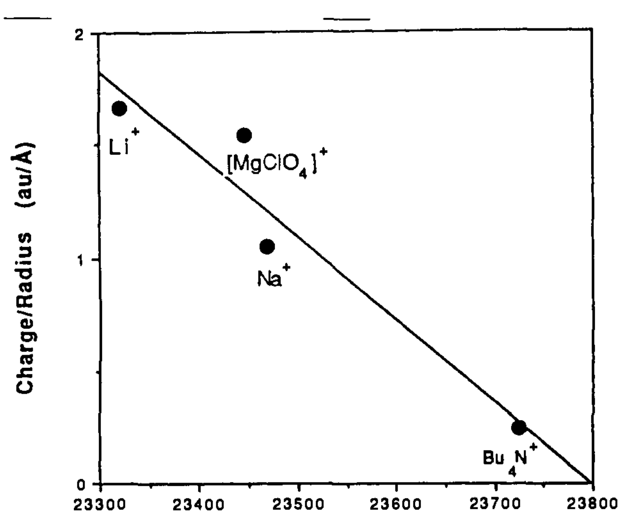

Figure 1. Absorption maxima of 1-AF in a 1.0 M electrolyte solution plotted as a function of the charge/size ratio for the cations Bu_4N^+, Na^+, Li^+, and Mg^+ (all perchlorate salts). The spectrum red-shifts with increasing charge/size ratio.

Comparison of the IR absorption spectra of 1-AF with that of 3-AF in a 1.0 M $LiClO_4$ acetonitrile solution also supports this conclusion. In the case of 3-AF, all stretching and bending frequencies of the respective functional groups are still observed. Only small spectral shifts are observed upon salt addition. These shifts can be accounted for by dielectric effects on vibrational frequencies.[12] The differences between the salt effects on the infrared spectra of 1-AF and 3-AF must result from specific molecular interactions between the metal ions and 1-AF, not bulk solution properties.

In contrast to the addition of metal perchlorates, addition of Bu_4NClO_4 does not perturb the infrared spectrum of 1-AF. This suggests that the Bu_4N^+ cation, unlike Li^+, does not interact with 1-AF. No effects are observed in the infrared spectrum of 3-AF with addition of Bu_4NClO_4, as well.

2. Electronic Absorption. Electronic absorption and emission data for 1-AF in several acetonitrile–salt solutions are summarized in Table II. As determined previously in neat solvents,[9] the $S_0 \rightarrow S_1$ absorption of 1-AF has substantial intramolecular charge-transfer character. Figure 1 plots the dependence of the absorption maximum of 1-AF on the charge-to-size ratio of various cations studied. A red shift in the absorption maximum is observed as the charge-to-size ratio of the cation increases. Increased cation charge-to-size ratio also results in increased solution polarity. Thus, the data in Figure 1 are easily understood in terms of the ion's ability to stabilize the molecular dipole moment in the excited state to a greater extent than that in the ground state. No red shift in absorption is observed upon addition of the alkylammonium salts, consistent with the observations that these salts do not affect the solution polarity. These results show the same trend as that found for 3-AF.[8] This may appear surprising, given the significant differences observed in the infrared spectrum of these two molecules. The infrared absorption data clearly reveal specific interactions between 1-AF and the electrolytes. The similarity between the salt effects on λ_{max} for the absorption of 1-AF and 3-AF suggests that electronic absorption spectroscopy is not a sensitive probe of the specific salt–solute molecular interactions.

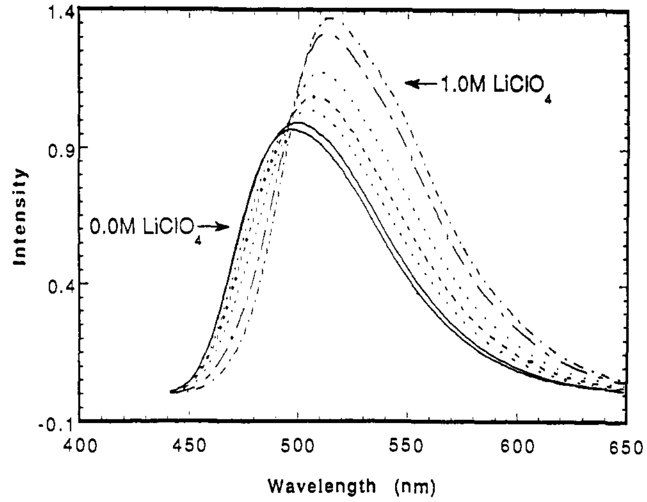

Figure 2. Fluorescence spectra of 1-AF in acetonitrile at room temperature as a function of added $LiClO_4$. With an increase in the amount of $LiClO_4$ there is a red shift and an increase in the fluorescence intensity. The ϕ_{fl} for 0.0 M $LiClO_4$ is 0.064 and increases to 0.092 for 1.0 M $LiClO_4$. The concentrations plotted are 0.0, 0.01, 0.05, 0.10, 0.20, 0.50, and 1.0 M.

3. Electronic Emission. The room-temperature emission spectra for 1-AF in acetonitrile as a function of added $LiClO_4$ are shown in Figure 2. Added salt results in a red shift in the emission maximum and an increase in the fluorescence quantum yield. At 1.0 M $LiClO_4$, the spectrum red-shifts ~700 cm^{-1} and the fluorescence quantum yield increases by a factor of 1.4 compared to pure acetonitrile. The red shift in the emission spectrum is consistent with the expectation that increased solvent polarity stabilizes the excited state to a greater extent than it does the ground state. Similar results are observed with $NaClO_4$; however, the effects are reduced compared to those found with $LiClO_4$. For 1.0 M $NaClO_4$, the emission maximum red-shifts by ~350 cm^{-1} (half that observed with the lithium salt) and the emission quantum yield increases by a factor of 1.3 (similar to the lithium salt). The decreased red shift is consistent with the fact that added $NaClO_4$ increases the solution polarity to a smaller extent than equimolar $LiClO_4$. In sharp contrast to the two alkali salts, addition of Bu_4NClO_4 has no effect on the photophysics of 1-AF. Added salt does not result in any change in the emission maxima or quantum yield. This result is, however, consistent with the fact that Bu_4NClO_4 does not alter the polarity of the solution.

At this point, it is instructive to recall the effects that added salt had on the emission properties of 3-AF. Similar to 1-AF, no changes in the emission spectrum or quantum yield were observed for 3-AF in Bu_4NClO_4 solutions. For the alkali perchlorates, both probe molecules exhibit a red shift with added electrolyte. For example, compared to the spectrum in neat acetonitrile, the emission spectra of 1-AF and 3-AF red-shift 706 and 776 cm^{-1}, respectively, in 1.0 M $LiClO_4$ solution. However, the quantum yield of 3-AF dramatically decreases with increased salt concentration, opposite that observed for 1-AF. Any molecular model proposed needs to account for the similarities and differences in the photophysical behavior of these two molecules.

To address the potential effect of specific interactions between the salts and the emission properties of 1-AF, fluorescence spectra of 1-AF were examined in acetonitrile–$LiClO_4$ solutions as a

Table III. Emission Quantum Yields, Φ_f, for 1-AF in Acetonitrile as a Function of $LiClO_4$ and 12-crown-4 Concentrations

[$LiClO_4$], M	[12-crown-4], M	Φ_f 1-AF in CH_3CN
0.0	0.0	0.0640
0.0	0.50	0.0640
0.50	0.0	0.0890
0.50	0.50	0.0688
1.0	0.0	0.0923
1.0	1.0	0.0744

Table IV. Emission Lifetimes, τ, and Calculated Radiative, k_r, and Nonradiative, k_{nr}, Rate Constants for 1-AF in Electrolyte Solutions

salt	concn, mol/L	τ, 10^{-12} s	$k_r{}^a$ 10^7 s^{-1}	$k_{nr}{}^a$ 10^8 s^{-1}
$LiClO_4$	0.0	1863	3.44	5.02
	0.01	1902	3.49	4.91
	0.05	2107	3.36	4.41
	0.10	2523	2.96	3.67
	0.20	3073	2.61	2.99
	0.50	3689	2.41	2.47
	1.0	4070	2.27	2.23
$NaClO_4$	0.0	1721	3.72	5.44
	0.01	1721	3.80	5.43
	0.05	1873	3.58	4.98
	0.10	2017	3.47	4.61
	0.20	2017	3.69	4.59
	0.50	2620	3.17	3.50
	1.0	2620	3.25	3.49
Bu_4NClO_4	0.0 → 1.0	1750	3.66	5.35

[a] Uncertainty in rate measurements is ±10%.

function of added 12-crown-4 (12-C-4). Crown ethers are effective molecules for binding cations in nonaqueous environments. The ability of the crown ether molecule to bind cations depends on the relative dimensions of the core ring of oxygens and the size of the cation. The cavity of 12-C-4 is 0.7 Å, well matched to the size of the lithium cation, 0.6 Å.[13,14] This is reflected by an equilibrium constant for lithium binding by 12-crown-4 of greater than 10^2 M^{-1}. The fluorescence quantum yield of 1-AF in $LiClO_4$ solutions decreases upon addition of 12-C-4. For equimolar salt/crown solutions, the emission quantum yield is similar to that of neat acetonitrile, see Table III. These results show that the increased quantum efficiency of 1-AF observed upon addition of salt can be eliminated by binding the cations in the crown complex. If we postulate that metal cations form a ground-state complex with 1-AF, eq 1, addition of crown results in competitive formation of the crown salt complex, eq 2. Given the large difference in

$$M^+ + \text{1-AF} \rightleftharpoons M^+\|\text{1-AF} \qquad (1)$$

$$\text{12-C-4} + M^+ \rightleftharpoons \text{12-C-4}\|M^+ \qquad (2)$$

binding energies expected for 12-C-4 vs 1-AF, addition of equimolar crown to salt should completely dissociate any complexes formed between cations and 1-AF. The observed effects of added crown ether on the emission spectrum provides further support that specific complexes form between the dissolved cation and 1-AF.

Time-Resolved Emission. In order to address in greater detail the effects of added electrolytes on the photophysics of 1-AF, the decay dynamics of the electronically excited-state molecule were examined. Combining the experimentally measured lifetimes (τ) and the emission quantum yields (ϕ_f), the radiative (k_r) and nonradiative (k_{nr}) rate constants were determined.

Emission decays for 1-AF with concentrations of $LiClO_4$ from 0.0 to 1.0 M are shown in Figure 3. All decays are well described by a single exponential convolved with an instrument response function. The observed lifetimes and calculated radiative and nonradiative rate constants are given in Table IV. With increasing $LiClO_4$ concentration, the fluorescence lifetime increases. Both the radiative and nonradiative rate constants decrease. The decrease in the radiative rate constant at different salt concentrations can be accounted for in terms of the differences in absorption intensity and the emission frequency. Similar to our previous finding with 3-AF, the data are consistent with the Strickler–Berg equation.[15]

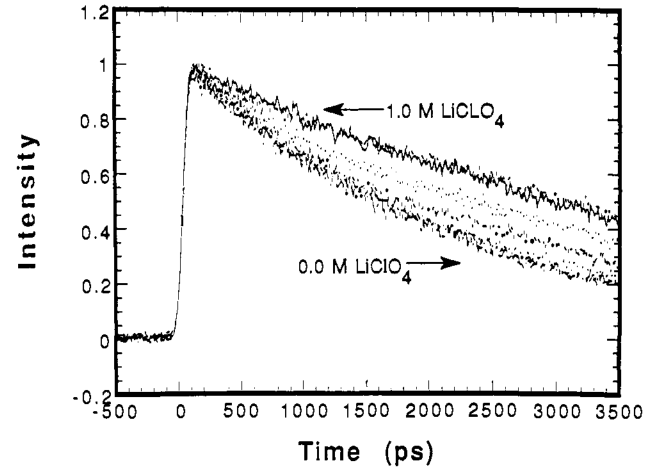

Figure 3. Time-dependent emission of 1-AF in acetonitrile at room temperature as a function of added $LiClO_4$. Decays are collected at magic angle and are plotted as a function of time following excitation at 405 nm. As the concentration of salt is increased from 0.0 to 1.0 M, the emission lifetime is observed to increase from 1.8 to 4.1 ns. The concentrations plotted are the same as in Figure 2.

Evaluation of the data in Table IV reveals similar trends for $NaClO_4$ and $LiClO_4$ solutions. However, on a quantitative level it is important to note that $NaClO_4$ perturbs the photophysics of 1-AF to a lesser extent than $LiClO_4$. Addition of up to 1.0 M Bu_4NClO_4 does not alter the photophysics of 1-AF. Comparison of these results with those for 3-AF under similar conditions reveals that added electrolytes decrease the radiative rate constant of both molecules similarly. In sharp contrast, the nonradiative rate constant of 3-AF increases with increasing salt concentration, opposite to that found for 1-AF. These results reaffirm that the simple structural difference between these two molecules, the presence of an intramolecular hydrogen bond in 1-AF, affects the types of molecular interactions the solute has with the components of the surrounding solution. In the case of these two molecule, the resulting molecular interactions dramatically affect the nonradiative deactivation pathways available.

One of the most useful relationships used to study nonradiative rates is the energy gap law, which predicts an exponential dependence of k_{nr} on the energy gap between the two relevant electronic states.[16] With increasing energy gap, k_{nr} is predicted to decrease. For 3-AF in acetonitrile–salt solutions, the effect of added salt on k_{nr} was consistent with the energy gap law. In Figure 4, $\ln(k_{nr})$ is plotted as a function of the energy gap,[17] ΔE, for 1-AF in the various electrolyte solutions studied. In contrast to expectation based on the energy gap law, 1-AF exhibits an increase in nonradiative rate constant with increasing energy gap. One could conclude that these results represent a failure of the energy gap law; however, as suggested below, the nonradiative dynamics observed for 1-AF are influenced by a distribution of solvated structures in solution. In such as case where multiple species are present in solution, it is difficult to quantitatively apply the energy gap expression.

Molecular Model for Electrolyte Interactions with 1-AF. In a previous study of 1-AF in neat solvents,[9] Moog et al. reported that the $S_0 \leftarrow S_1$ nonradiative rate constant was smaller in protic

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(13) Zhelyaskow, V.; Georgiev, G.; Nickolov, Z.; Miteva, M. *Spectrochim. Acta* **1989**, *45A*, 625.

(14) Vogtle, F.; Weber, E. In *Crown ethers—complexes and selectivity in Crown ethers and analogs*; Patai, S., Ed.; Wiley and Sons: Chichester, 1989; Chapter 4, 207.

(15) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814.

(16) (a) Robinson, G. W. *Excited States*; Academic: London, 1974; Vol. 1. (b) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Marcel Dekker, Inc.: New York, 1970. (c) Avouris, P.; El-Sayed, M. A.; Gelbart, W. M. *Chem. Rev.* **1977**, *77*, 793.

(17) ΔE was determined by averaging the energies of the absorption and emission spectra at the midpoints of the fwhm.

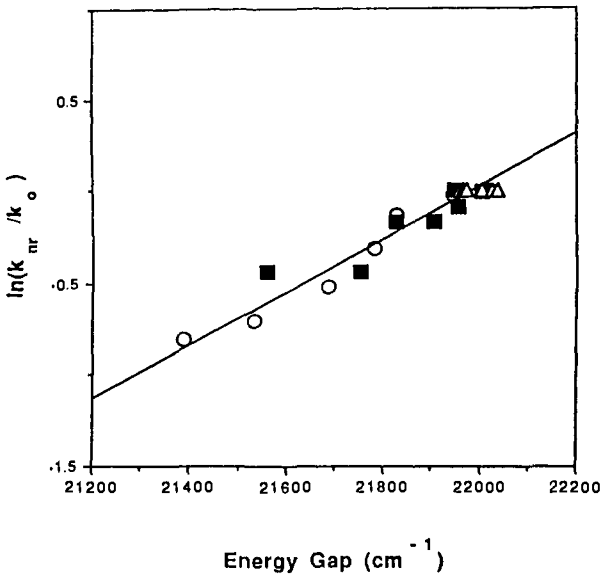
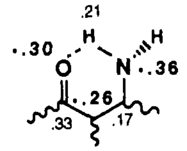


Figure 4. log of the ratio of the nonradiative rate constant in the presence of salt, k_{nr}, to that obtained in pure acetonitrile, k_0, as a function of the experimentally determined energy gap, ΔE, for salt solutions. The nonradiative rate increases with increasing energy gap for both $LiClO_4$ (○) and $NaClO_4$ (■); however, no change is observed for Bu_4NClO_4 (△).

solvents than in aprotics. This was true even when solvents of similar polarity were compared. This general observation was interpreted by proposing that the intramolecular hydrogen bond provides the molecule with efficient nonradiative deactivation channels. Disruption of this hydrogen-bonded structure through the formation of an intermolecular hydrogen bond with alcohol solvent molecules affects these relaxation channels, resulting in a decrease in the nonradiative rate. Based on this argument, it was proposed that in protic solutions 1-AF established an equilibrium between two structures, one which involves intramolecular hydrogen bonding and another where this interaction is broken upon formation of intermolecular hydrogen bonds with the solvent.

Ab initio calculations[18] and NMR spectroscopy[19] show that intramolecular hydrogen bonding is favored over intermolecular hydrogen bonding to aprotic solvents. Even though our original proposal was that the intramolecular hydrogen bond is broken upon formation of a complex between 1-AF and the alcohol, it is just as likely that the solvent only disrupts (not necessarily breaks) the intramolecular hydrogen bond. Mixed solvent studies in which fluorinated alcohols were added to heptane solutions of 1-AF clearly showed the formation of alcohol/1-AF complexes.[9] For these complexes, the nonradiative rate decreased compared to that of 1-AF in pure heptane. On the basis of these studies, it is reasonable to conclude that if alcohols of different hydrogen-bonding ability can affect this equilibrium, cations might be able to as well. In comparing 1-AF in neat solvents and electrolyte solutions, it is seen that both protic solvents and electrolytes decrease the nonradiative rate constant. In both cases, it appears that the protic solvent and the cation disrupt the intramolecular hydrogen bond.

The above discussion reports that the electrolytes $LiClO_4$, $NaClO_4$, Me_4NClO_4, and Bu_4NClO_4 affect the nonradiative rate of 1-AF differently. In developing a model for the general photophysical behavior of 1-AF in salt solutions, it is important to address why the different cations affect the photodynamics to varying degrees. Taken in total, the infrared absorption and electronic emission spectra suggest that the alkali cations interact with the carbonyl, amino, and C=C regions of the molecule. Given that similar spectral changes are observed for all salt concentrations studied, it is likely that these effects arise from the interaction of a single cation with the 1-AF solute. Examination of the ground-state Mulliken charge distributions for 1-AF determined using AM1 semiempirical calculations reveals that the carbonyl oxygen, amino nitrogen, and bridging carbon form a pocket of high electron density, as shown below.



This geometry provides an efficient molecular framework for the binding of small cations.

Within such a model, the individual electrolyte effects can be accounted for by considering the geometric constraints of the three-atom pocket. The radius of this pocket is about 2.25 Å. The radii of Li^+ and Na^+ are 0.60 and 0.95 Å, respectively. These cations can fit into the molecular pocket, interacting with the three sites of negative charge density. In contrast, the radius for the tetrabutylammonium molecular cation is 4.15 Å. This cation is too large for this chelation site; therefore, complexation should not occur to any appreciable extent.

Even though both lithium and sodium fit into this chelation site, the experimental results show that lithium perturbs the photophysics slightly more than sodium. Li^+ has a larger charge-to-size ratio than Na^+, which generally results in larger solvation energies.[12,20] Thus, it is not surprising that lithium cations may perturb the electronic structure of 1-AF to a greater extent than sodium cations.

Conclusions

Steady-state and time-resolved spectroscopies are used to characterize the ground-state complexes between cations and 1-AF in acetonitrile–salt solutions. In contrast, no such complexes are observed between salts and the geometric isomer 3-AF. These results demonstrate that small changes in solute structure can dramatically affect intermolecular interactions in electrolyte solutions. Formation of specific complexes between molecular solutes and dissolved salts is found to significantly alter the photodynamics of the solute. In the case of 1-AF, infrared absorption spectroscopy and steady-state and time-resolved emission data support the conclusion that the salt binds to the 1-AF molecule in the vicinity of the intramolecular hydrogen bond.

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(18) Novoa, J. J.; Whangbo, M.-H. *J. Am. Chem. Soc.* **1991**, *113*, 9025.

(19) Baumstark, A. L.; Graham, S. S.; Boykin, D. W. *J. Chem. Soc., Chem. Commun.* **1989**, 767.

(20) Barthel, J.; Iberl, L.; Rossmaier, J.; Gores, H. J.; Kaukal, B. *J. Solution Chem.* **1990**, *19*, 321.