well with previously held generalizations and with solution behavior. The threshold shapes have been analyzed.

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Proton Exchange and Hydration in Photoexcited Naphthylamines and Naphthylammonium Ions

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Abstract: The lack of reciprocity between the fluorometric pH titration curves of the naphthylamines and their conjugate acids is shown to be the result of static quenching of the cation emissions, resulting from hydration of the cations in the ground electronic state. The excited hydrated cations are shown to undergo protolytic dissociation, their extremely short-lived lowest excited singlet states notwithstanding.

The conversion of the blue fluorescence of 2-naphthylamine to the ultraviolet fluorescence of the corresponding naphthylammonium ion, in a pH region different from that in which the absorption spectrum of the neutral molecule was converted to that of the cation, was one of the earliest recorded examples of proton exchange in the lowest excited singlet state.[1] Subsequent studies of the pH dependencies of the fluorescence spectra of 2-naphthylamine[2,3] and 1-naphthylamine[3] indicated that excited-state proton exchange in these compounds was not simple, as suggested by the reaction

$$BH^{+*} + H_2O \underset{k^-}{\overset{k^-}{\rightleftharpoons}} B^* + H_3O^+ \qquad (1)$$

because the sums of the relative quantum yields of fluorescence of BH^{+*} and B^* did not equal unity at all points in the fluorometric titrations. Rather, the fluorescences of the neutral molecules were quenched with decreasing pH, without the concomitant appearance of the fluorescences of the cations. The fluorescences of the cations appeared, to a significant extent, only in moderately concentrated mineral acid solutions where the fluorescences of the neutral molecules were unobservable. Moreover, the absorption spectra of the cations did not change appreciably in this region of Hammett acidity. It was hypothesized that quenching,[2] possibly due to the formation of hydrated exciplexes of the naphthylammonium ions[3] was responsible for this unusual fluorometric titration behavior.

In order to further elucidate the nature of the anomalous fluorometric pH titration behavior of the naphthylamines and the naphthylammonium ions, the present reinvestigation of the pH and Hammett acidity dependences of their fluorescence spectra was undertaken.

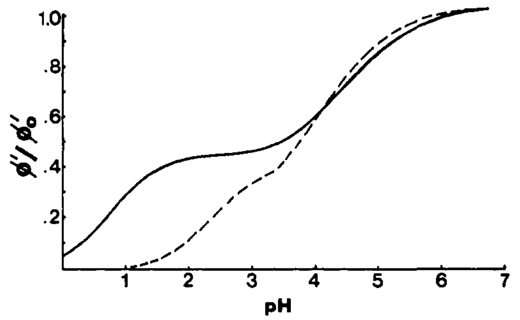

Figure 1. Variations of the relative fluorescence efficiencies (ϕ'/ϕ_0') of 1-naphthylamine (- - -) and 2-naphthylamine (—) with pH.

Experimental Section

1-Naphthylamine and 2-naphthylamine were purchased from Eastman Organic Chemicals, Inc., Rochester, N.Y., and were each triply recrystallized from 95% ethanol. Fluorescence spectra were taken on a Perkin-Elmer MPF-2A fluorescence spectrophotometer at ambient temperature (26 °C). pH measurements were made on on Orion Model 801 pH meter with a Corning glass–silver–silver chloride combination electrode. Fluorescence decay times >1.6 ns were measured on a TRW Model 31B decay-time fluorometer interfaced with a Tektronix 556 dual-beam oscilloscope employing two 1A2 plug-in amplifiers. The source employed in the decay-time instrument was an 18-W deuterium lamp. Fluorescence spectra were taken on solutions 5.00×10^{-6} M in 1-naphthylamine or 2-naphthylamine in aqueous sulfuric acid or perchloric acid. For solutions of pH <1, the corrected Hammett acidity scales of Jorgenson and Hartter[4] and of Yates and Wai[5] were employed to calibrate the sulfuric acid and perchloric acid solutions, respectively. All solutions were purged for 5 min with dry nitrogen, immediately prior to the taking of the fluorescence spectrum, in order to minimize fluorescence quenching by dissolved oxygen. Fluorescence was excited at an isosbestic point in each case, in order to directly translate the normalized fluorescence intensities measured, into relative fluorescence efficiencies.

Results and Discussion

The variations of the relative fluorescence efficiencies of the naphthylamines with pH and of the naphthylammonium ions with Hammett acidity are shown in Figures 1 and 2, respectively. Essentially identical fluorometric titration curves were obtained whether the solutions contained sulfuric acid or perchloric acid.

Although the formal acid concentrations in sulfuric and perchloric acid solutions of the same Hammett acidity differ, the activity of free water is the same in either acid, at the same Hammett acidity.[5,6] This indicated that the variations of the fluorescence efficiencies of the naphthylammonium ions with water activity would also be identical in sulfuric and in perchloric acids and suggested that the hydration of the anhydrous or poorly hydrated cations might be responsible for the decrease in cation fluorescence in solutions too acidic to observe excited-state dissociation. The hypothesis of hydration-quenching was supported when it was found that making moderately concentrated perchloric acid solutions 0.1 F in HSO_4^- (with $NaHSO_4$) or moderately concentrated sulfuric acid solutions 0.1 F in ClO_4^- (with $NaClO_4$) failed to produce appreciable quenching of the fluorescences of the cations. Moreover, in neutral aqueous solutions, 0.1 F SO_4^{2-} (from Na_2SO_4) and 0.1 F ClO_4^- (from $NaClO_4$) failed to appreciably quench the fluorescences of the neutral amines. Hence, it is a safe assumption that the species derived from the acids, themselves, are not responsible for the anomalous fluorometric titration behavior of the naphthylamines or their conjugate acids, and it is the increase in water activity resulting from dilution of the mineral acid solutions that results in quenching of the cation fluorescences.

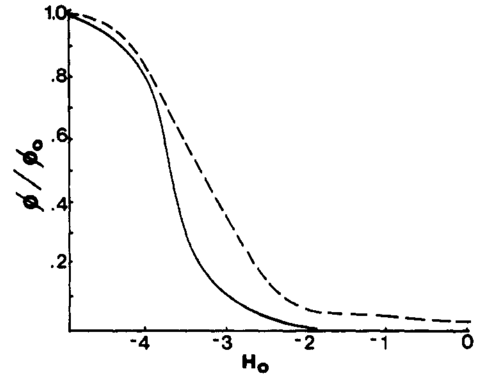

Figure 2. Variations of the relative fluorescence efficiencies (ϕ/ϕ_0) of 1-naphthylammonium ion (- - -) and 2-naphthylammoniun ion (—) with Hammett acidity in either sulfuric acid or perchloric acid.

Measurements of the fluorescence decay times, T_0, of the naphthylammonium ions, each at six different Hammett acidities along the fluorometric titration curves, indicated that the lifetimes of the excited naphthylammonium ions (Table I) were essentially unchanged as the apparent quantum yields decreased. This suggests that the quenching of the naphthylammonium ion fluorescence is static, resulting from hydration of the cations in their ground electronic states. The hydration reaction may be formulated as follows

$$BH^+ + nH_2O \rightleftharpoons BH^+(H_2O)_n \qquad (2)$$

The overall equilibrium constant for this reaction may be written

$$K = (BH^+(H_2O)_n)/(BH^+)(H_2O)^n \qquad (3)$$

If BH^+ is fluorescent and $BH^+(H_2O)_n$ is not, eq 3 may be rewritten, in terms of the relative fluorescence efficiency, ϕ/ϕ_0, of BH^+

$$K = \frac{(1 - \phi/\phi_0)}{(\phi/\phi_0)(H_2O)^n} \qquad (4)$$

or, in logarithmic form

$$\log (1 - \phi/\phi_0)/(\phi/\phi_0) = n \log (H_2O) + \log K \qquad (5)$$

Hence, a plot of $\log (1 - \phi/\phi_0)/(\phi/\phi_0)$ vs. $\log (H_2O)$ should yield a straight line of slope n and intercept $\log K$. Plots of this type were constructed, for the 1- and 2-naphthylammonium ions, utilizing the data represented in Figure 2 and the activities of water in aqueous sulfuric acid, published in ref 6. These plots, shown in Figure 3, indicate that upon passing from moderately concentrated to very dilute acid, the 1-naphthylammonium ion is hydrated by three water molecules while the 2-naphthylammonium ion is hydrated by four water molecules. The overall equilibrium constants for the hydrations of the cations are presented in Table I.

Let us now consider the problem of proton exchange in the lowest excited singlet states of the naphthylamines and the naphthylammonium ions. Weller[7] has shown that if proton exchange is the only bimolecular process competing with fluorescence and the unimolecular radiationless deactivation processes, in the lowest excited singlet state, and if all of the exciting radiation is absorbed only by the photodissociating acid, the relative fluorescence efficiency of the excited acid is given, to a fair approximation, by

$$\phi/\phi_0 = \frac{1 + k^{\leftarrow}\tau_0'[H_3O^+]}{1 + k^{\rightarrow}\tau_0 + k^{\leftarrow}\tau_0'[H_3O^+]} \qquad (6)$$

where $k^{\rightarrow}$ and $k^{\leftarrow}$ are the rate constants for pseudo-first-order proton abstraction, by the solvent, from the excited acid and the second-order rate constant for reprotonation of the excited

Table I. Lifetimes of the Lowest Excited Singlet States (T_0), Hydration Numbers (n), and Overall Hydration Equilibrium Constants (K) Associated with Transfer of the Naphthylammonium Ions from Concentrated Mineral Acid to "Pure" Water

	T_0, ns	n	K
1-Naphthylamine	4.1 ± 0.3	3.0	21 ± 1
2-Naphthylamine	5.0 ± 0.3	4.0	220 ± 10

conjugate base by H_3O^+, respectively, and τ_0 and τ_0' are the respective lifetimes of the lowest excited singlet states of acid and conjugate base. The relative fluorescence efficiency of the excited conjugate base is given by

$$\phi'/\phi_0' = \frac{k^{\rightarrow}\tau_0}{1 + k^{\rightarrow}\tau_0 + k^{\leftarrow}\tau_0'[H_3O^+]} \qquad (7)$$

The problem that arises in the case of the naphthylamines is that in the pH region 0-3, where excited-state proton-exchange is fluorometrically observed, the exciting radiation is absorbed by at least two distinct cations. Since the activity of water is unity, in this pH region, and the molar absorptivities of the anhydrous and hydrated cations are identical, the fraction of anhydrous or poorly hydrated naphthylammonium cations absorbing is $1/(1 + K)$, while the fraction of fully hydrated cations absorbing is $K/(1 + K)$. If the anhydrous cations, which have reasonably long-lived excited states, are alone responsible for photodissociation, the relative fluorescence efficiencies of the excited cations should vary with, pH according to

$$\phi/\phi_0 = \frac{1 + k^{\leftarrow}\tau_0'[H_3O^+]}{1 + k^{\rightarrow}\tau_0 + k^{\leftarrow}\tau_0'[H_3O^+]}\,\frac{1}{1 + K} \qquad (8)$$

while the relative fluorescence efficiencies of the neutral amines should vary with pH according to

$$\frac{\phi'}{\phi_0'} = \frac{k^{\rightarrow}\tau_0}{1 + k^{\rightarrow}\tau_0 + k^{\leftarrow}\tau_0'[H_3O^+]}\,\frac{1}{1 + K} \qquad (9)$$

On the other hand, if the fully hydrated cations, which have very short-lived excited states, are alone responsible for photodissociation, the relative fluorescence efficiencies of the excited cations should vary according to

$$\frac{\phi}{\phi_0} = \frac{1 + k^{\leftarrow}\tau_0'[H_3O^+]}{1 + k^{\rightarrow}\tau_0 + k^{\leftarrow}\tau_0'[H_3O^+]}\,\frac{K}{1 + K} \qquad (10)$$

and those of the excited neutral molecules, according to

$$\frac{\phi}{\phi_0'} = \frac{k^{\rightarrow}\tau_0}{1 + k^{\rightarrow}\tau_0 + k^{\leftarrow}\tau_0'[H_3O^+]}\,\frac{K}{1 + K} \qquad (11)$$

Since the observable cation fluorescences are very weak at pH 0-3 and, therefore, measurements of their variations will be imprecise, we shall concentrate on the variations of neutral amine fluorescence, with pH, related by eq 9 and 11.

According to Figure 1, the values of ϕ'/ϕ_0', resulting from excited-state dissociation go as high as about 0.4 in both naphthylamines. In order for excited state dissociation to be easily observable the term $k^{\rightarrow}\tau_0/(1 + k^{\rightarrow}\tau_0 + k^{\leftarrow}\tau_0'[H_3O])$ must lie between, approximately, 0.05 and 0.95. Now for 1-naphthylamine $1/(1 + K) = 0.046$ and for 2-naphthylamine $1/(1 + K) < 0.0045$. Hence, if the anhydrous cations are solely responsible for photodissociation, it would be impossible to realize values of ϕ'/ϕ_0' as high as those observed in Figure 1. However, $K/(1 + K) = 0.96$ for 1-naphthylamine and 1.0 for 2-naphthylamine. Consequently, it must be concluded that the dissociations of the directly excited, fully hydrated cations, derived from the naphthylamines, are principally or entirely responsible for the high fluorescence efficiencies of the neutral amines at low pH. Although the lifetimes of the hydrated cations in their lowest excited singlet states are so short that no fluorescence is observed from them, it is apparent that the rates of photodissociation in these species are at least comparable to the rates of the nonradiative processes deactivating their excited states.

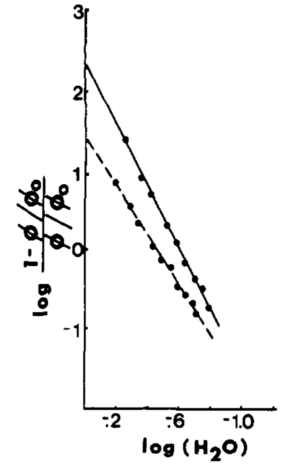

Figure 3. Estimation of the stoichiometry of hydration (n) and the corresponding overall equilibrium constants (K) of 1-naphthylammonium ion (- - -) and 2-naphthylammonium ion (—) from the logarithmic plot of $K = (1 - \phi/\phi_0)/(\phi/\phi_0)(H_2O)^n$.

In order to evaluate the kinetic parameters associated with protolytic reactivity in the excited naphthylamines, it was first necessary to correct the apparent relative fluorescence efficiencies of 1-naphthylamine (Figure 1) for the fraction of directly excited naphthylamine molecules. This was necessary in the case of 1-naphthylamine because the pH region in which 1-naphthylamine fluorescence resulted from photodissociation of $BH^+ (H_2O)_n$ overlapped part of the pH region in which 1-naphthylamine fluorescence also resulted from direct excitation (pH ~ pK_a). This correction was made by multiplying each value of ϕ'/ϕ_0', taken from the fluorometric titration curve for 1-naphthylamine, in Figure 1, by the fraction (f_c) of directly excited cation

$$f_c = \epsilon_c[H_3O^+]/(\epsilon_c[H_3O^+] + \epsilon_n K_a) \qquad (12)$$

where ϵ_c and ϵ_n are the molar absorptivities of the cationic and the neutral molecules, respectively, and K_a is the ground-state dissociation constant ($K_a = 1.20 \times 10^{-4}$) of the 1-naphthylammonium ion. Since, excitation was effected at an isosbestic point, $\epsilon_c = \epsilon_n$ and

$$f_c = [H_3O^+]/([H_3O^+] + K_a) \qquad (13)$$

For 1-naphthylamine, we then have

$$\frac{\phi'}{\phi_0'}(f_c) = \frac{0.96k^{\rightarrow}\tau_0}{1 + k^{\rightarrow}\tau_0 + k^{\leftarrow}\tau_0'[H_3O^+]} \qquad (14)$$

which can be rearranged to

$$\frac{1}{[H_3O^+]} = \frac{0.96 - (\phi'/\phi_0')f_c}{(\phi'/\phi_0')f_c[H_3O^+]}\,k^{\rightarrow}\tau_0 - k^{\leftarrow}\tau_0' \qquad (15)$$

A plot of $1/[H_3O^+]$ vs. $[0.96 - (\phi'/\phi_0')f_c]/(\phi'/\phi_0')f_c[H_3O^+]$ (Figure 4), for 1-naphthylamine, yielded a straight line of slope $k^{\rightarrow}\tau_0$ and ordinate intercept $-k^{\leftarrow}\tau_0'$. These values are presented in Table II.

For 2-naphthylamine, no correction for direct excitation of the neutral molecule was necessary, because most of the region where excited-state proton-exchange was observed was well removed from the region of ground state ionization. Hence, the variation of ϕ'/ϕ_0' with $[H_3O^+]$, in 2-naphthylamine, is well represented by eq 7. However, the flat region observed in the fluorometric titration of 2-naphthylamine, in Figure 1,

Table II. Kinetic Parameters of Proton Exchange in the Lowest Excited Singlet States of the Naphthylamines

	$k^{\rightarrow}\tau_0$	$k^{\leftarrow}\tau_0'$, M^{-1}	τ_0, ns	τ_0', ns	$k^{\rightarrow}$, s^{-1}	$k^{\leftarrow}$, $M^{-1}\ s^{-1}$	pK_a^*
1-Naphthylamine	0.55	340	<0.20	25.3 ± 0.4	$>2.8 \times 10^9$	1.4×10^{10}	<0.7
2-Naphthylamine	0.79	15	<0.023	23.9 ± 0.4	$>3.5 \times 10^{10}$	6.3×10^8	<−1.7

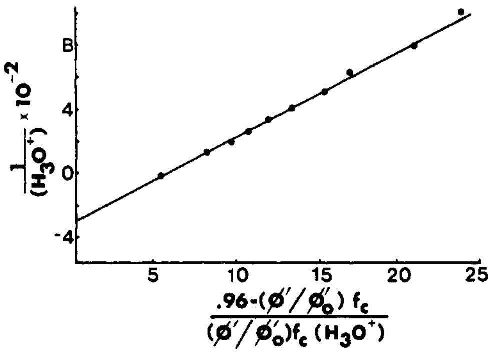

Figure 4. Estimation of $k^{\rightarrow}\tau_0$ and $k^{\leftarrow}\tau_0'$ for 1-naphthylamine and its conjugate acid from graphical representation of $1/[H_3O^+] = \{[0.96 - (\phi'/\phi_0')f_c]/(\phi'/\phi_0')f_c[H_3O^+]\}\ k^{\rightarrow}\tau_0 - k^{\leftarrow}\tau_0'$, where f_c is the fraction of directly excited cations at any value of $[H_3O^+]$ and 0.96 is the fraction of directly excited 1-naphthylammonium trihydrates in dilute aqueous solution.

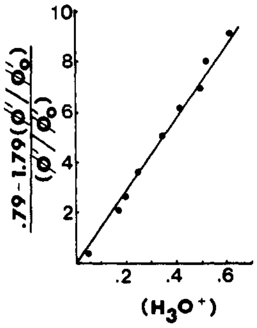

Figure 5. Estimation of $k^{\leftarrow}\tau_0'$ for 2-naphthylamine from graphical representation of $[k^{\rightarrow}\tau_0 - (1 + k^{\rightarrow}\tau_0)(\phi'/\phi_0')]/(\phi'/\phi_0') = k^{\leftarrow}\tau_0'[H_3O^+]$, where $k^{\rightarrow}\tau_0 = 0.79$, was previously estimated from the pH-independent portion of the fluorometric titration curve in Figure 1.

indicates that for the higher pH section of the fluorometric titration ϕ'/ϕ_0' is independent of $[H_3O^+]$. This results from the negligibility of the term $k^{\leftarrow}\tau_0'[H_3O^+]$, at high pH, in eq 7 due to the absence of appreciable reprotonation of the neutral molecule, during the lifetime of its excited state. In this case, we may write

$$(\phi'/\phi_0')_{\text{const}} = k^{\rightarrow}\tau_0/(1 + k^{\rightarrow}\tau_0) \quad (16)$$

Since $(\phi'/\phi_0')_{\text{const}} = 0.44$ for 2-naphthylamine we find immediately, that $k^{\rightarrow}\tau_0 = 0.79$. Hence, for 2-naphthylamine eq 7 becomes

$$\phi'/\phi_0' = \frac{0.79}{1.79 + k^{\leftarrow}\tau_0'[H_3O^+]} \quad (17)$$

which may be rearranged to

$$\frac{0.79 - 1.79(\phi'/\phi_0')}{\phi'/\phi_0'} = k^{\leftarrow}\tau_0'[H_3O^+] \quad (18)$$

A plot of $[0.79 - 1.79(\phi'/\phi_0')]/(\phi'/\phi_0')$ vs. $[H_3O^+]$ for 2-naphthylamine is shown in Figure 5 and has a slope of $k^{\rightarrow}\tau_0$, the value of which is listed in Table II. Also presented in Table II are the fluorescence decay times of the neutral 1- and 2-naphthylamines, from which $k^{\leftarrow}$ was calculated, in each case. Since the fully hydrated cations were not observably fluorescent, $k^{\rightarrow}$ could not be calculated. However, if it is assumed that the relative fluorescence efficiencies of the anhydrous cations in dilute acid (when the activity of water is unity) which are equal to $1/(1 + K)$, represent an approximate upper limit to the ratio of the quantum yields of fluorescence of the hydrated and anhydrous cations, and if the natural lifetimes of the hydrated and unhydrated cations are taken to be identical (their absorption spectra are), then the lifetimes of the excited hydrated cations, τ_0, are related to the lifetimes of the excited anhydrous cations, T_0, by

$$\tau_0 < T_0[1/(1 + K)] \quad (19)$$

These very approximate upper limits to the lifetimes of the excited hydrated cations as well as the lower limits of $k^{\rightarrow}$, calculated from the former and $k^{\rightarrow}\tau_0$, and the upper limits of pK_a^* (the equilibrium constant of excited state proton exchange), calculated from $pK_a^* = \log k^{\rightarrow}/k^{\leftarrow}$ are listed in Table II.

The considerably greater rate constant, $k^{\leftarrow}$, for reprotonation of 1-naphthylamine, in the excited state, relative to that of 2-naphthylamine is not anticipated because the nitrogen atom of 1-naphthylamine in the ^1L_a state (the lowest excited singlet state of 1-naphthylamine) should be more electron deficient than that of 2-napthylamine in the ^1L_b state (the lowest excited singlet state of the 2-isomer).[8-10] Possibly, this discrepancy is related to the nature of the solvent cages about the amino groups in the excited molecules. The fact that the upper limits of the pK_a^* values of the naphthylamines are considerably lower than their ground state pK_a's is in qualitative agreement with the observed blue shifting of their absorption[3] and fluorescence[3] spectra, accompanying protonation.[11]

Solvation-desolvation phenomena in mineral acid media may also influence the fluorescence yields of other aromatics[12] and may be of great consequence in the optimization of solution conditions in the construction of pH-tunable dye lasers.[13,14]

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