PROTOTROPISM IN AMINOPHENOLS AND ANISIDINES: A REINVESTIGATION

RANJIT S. SARPAL and SNEH K. DOGRA†

Department of Chemistry, Indian Institute of Technology, Kanpur 208016 (India)

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Summary

The absorption and fluorescence spectra obtained in various solvents indicate that aminophenols and anisidines act as proton donors in ether and acetonitrile but as proton acceptors in methanol and water in the S_0 state and as proton donors to all the solvents in the S_1 state. Stretched sigmoid curves are observed for the equilibrium between the monocation and the neutral species for all the compounds, except *p*-aminophenol (pAMP) and *p*-anisidine, giving both ground state and excited state pK_a values. For pAMP and *p*-anisidine, proton-induced fluorescence quenching of the neutral species is observed at moderate hydrogen ion concentrations. The values of the quenching constant are 3.3×10^9 dm^3 mol^{-1} s^{-1} and 2.0×10^9 dm^3 mol^{-1} s^{-1} for pAMP and *p*-anisidine respectively. The proton transfer reaction studied in methanol–water systems has indicated that, in low dielectric constant solvents, the excited state equilibrium is not established and thus the ground state pK_a value is observed from fluorimetric titration curves.

1. Introduction

It is now well established that protonation of aromatic amines is preceded by the proton-induced fluorescence quenching of neutral molecules [1 - 13] because, at moderate hydrogen ion concentrations, the rate of protonation of aromatic amines is much slower than that of the fluorescence quenching of neutral amines. This is due to charge migration from the lone pair of the amino group to a particular atom of the ring rather than a scattering of the charge over the complete molecule. This type of quenching is not observed or is very slow compared with the rate of proton transfer if the charge is delocalized over the complete molecule, as, for example, with 3-aminofluoranthene [14]. Further, ANH_3^+ ions are stronger acids in the S_1 state than in the S_0 state. For these reasons, the correspondence between the removal of basic species and the formation of conjugate acidic species is not observed and the fluorimetric curves do not intersect at half of the fluorescence intensity. The pK_a^* value for the equilibrium between the monocation and the neutral species is calculated from the formation fluorescence curve

†Author to whom correspondence should be addressed.

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of the monocation, rather than from the decrease in the relative fluorescence intensity of the basic amine. It has been found that the pK_a^* value calculated by this procedure is not much different from that obtained by time-dependence fluorimetry.

Cowgill [15] has studied the spectral behaviour of *o*-aminophenol (oAMP) and *p*-aminophenol (pAMP) at various pH values to explain the changes in the fluorescence spectrum of 3-aminotyrosin with changing pH. Bridges and Williams [16] have carried out similar studies on various anisidines to correlate the fluorescence spectra observed from the hydroxyindoles. The spectral shifts observed in the absorption and fluorescence spectra of these compounds with changing pH are consistent with the changes observed in the similar compounds. However, the pK_a^* values for the equilibria between the monocation and the neutral species and that between the neutral species and the monoanion, calculated from the fluorimetric titration, resemble the ground state values. Lastly the above study was carried out mostly in ethanol-rich aqueous solutions. As said earlier, this kind of observation is not observed from the fluorimetric titrations of the aromatic amines. This could be due to the small dielectric constant of alcohol and to the fact that the equilibrium process is achieved over a longer time scale. This implies that the lifetimes of the conjugated species are short and thus the equilibrium is not established in the excited state. Ground state pK_a values are also observed from the fluorimetric titrations if the excited state pK_a values fall in the mid pH region. This is because in mid pH regions, the hydrogen ion concentration is such that the rate of protonation cannot compete with the rate of fluorescence. We have reinvestigated the proton transfer reactions of oAMP, *m*-aminophenol (mAMP) and pAMP and *o*-, *m*- and *p*-anisidines in the ground and excited states to resolve the above discrepancy. This study has also been carried out in aqueous and methanolic aqueous media to observe the effects of the solvents.

2. Materials and methods

oAMP, mAMP and pAMP were obtained from Loba–Chemie Indoaustranal Co. and purified as suggested by Cowgill [15]. *m*-Anisidine and *p*-anisidine were crystallized from ethanol, whereas *o*-anisidine was redistilled (boiling point, 223 °C). Analytical grade H_2SO_4 and NaOH were used as such to prepare the acidic and basic solutions. A modified Hammett's acidity scale [17] for H_2SO_4–H_2O and Yagil's basicity scale [18] for NaOH–H_2O were used for the solutions below pH 1 and above pH 13, respectively. Triply distilled water was used for making the aqueous solutions. Spectrograde methanol (B.D.H.) was used as such, whereas analytical grade acetonitrile (E. Merck), ether and cyclohexane (B.D.H.) were further purified as described in the literature [19]. The pH values of the solutions in the range 1 - 13 were measured on a Toshniwal pH meter model CL-44 A.

The absorption spectra were recorded with a Shimadzu spectrophotometer model UV-190, equipped with a U-135 chart recorder. The fluorescence measurements were carried out on a recording spectrofluorimeter, fabricated in our laboratory and described elsewhere [20]. The concentration of the solutions used was of the order of 10^{-4} - 10^{-5} M. The quantum yields of all the compounds were measured from the corrected fluorescence spectra using quinine sulphate in 0.1 N H_2SO_4 as a standard [21]. The bandwidth of the exciting radiation is 8 nm and the wavelengths used for excitation are given in Table 2 (see later). For the fluorimetric titrations, the isosbestic points were chosen as the excitation wavelength to measure the fluorescence intensity at the analytical wavelength. Since some of the compounds were sensitive to the presence of oxygen in the solutions, oxygen-free nitrogen was bubbled through the solutions before the respective compounds were added.

3. Results and discussion

3.1. Effect of solvents on the absorption and fluorescence spectra

The absorption and fluorescence spectra of all the aminophenols (AMPs) and the anisidines have been studied in solvents of various polarities and hydrogen bonding natures. The relevant data are listed in Tables 1 and 2. The respective absorption and fluorescence maxima of all the compounds in ethanol agree with values given in the literature [22]. It is clear from Table 1 that the absorption spectra of all the AMPs are red shifted with increasing polarity of the solvents (from cyclohexane to acetonitrile) but the spectra are blue shifted with increasing proton donor capacity of the solvents. In contrast, the absorption spectra of the anisidines are little affected in the solvents from cyclohexane to acetonitrile but are blue shifted in the proton-donating solvents. The fluorescence spectra of all the compounds are constantly red shifted under similar environments. The fluorescence quantum yields of the molecules are very small in non-polar solvents and decrease with increasing proton donor capacity of the solvents.

The behaviour of the solvents towards these molecules is consistent with the behaviour of these functional groups in the same environments [9, 10]. The red shift observed in the absorption spectra in going from cyclohexane to acetonitrile is due to the dispersive interactions (dipole–dipole, dipole–induced dipole, induced dipole–induced dipole) and the weak proton accepting nature of acetonitrile. However, methanol and water can act as proton donor solvents and thus produce a blue shift in the absorption spectra. As a result of an increased charge transfer from the amino or phenolic group to the ring on excitation, these functional groups act as a better proton donor and thus a continuous red shift is observed in the fluorescence spectra which is due to the dispersive interactions and proton accepting nature of all the solvents. The decrease in the fluorescence quantum yield under the same conditions is due to the increase in the interactions with the solvents, thereby increasing the rate of the radiationless processes.

TABLE 1

Absorption maxima (nm) and log ϵ_{max} of various anilines in various solvents and pH values at 298 K

Compound	*Absorption maxima* (nm) (log ϵ_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)) *for the following conditions*						
	Cyclohexane	*Ether*	*Acetonitrile*	*Methanol*	*Water* pH 7	*Monoanion* pH 12	*Monocation* pH 1
oAMP	211		214 (4.1)	210 (4.2)	204 (4.24)	215 (4.19)	195 (3.97)
							209 (3.81)
	234	238 (3.89)	237 (4.02)	232 (3.84)	230 (3.88)	240 (3.78)	269 (3.35)
	284	291 (3.57)	291 (3.70)	286 (3.52)	281 (3.55)	295 (3.64)	275 (3.29)
mAMP	213	215 (3.38)	216 (4.07)	215 (4.09)	206 (4.19)	216 (4.32)	196 (3.91)
							212 (3.77)
	236	239 (3.82)	240 (3.91)		231 (3.81)	237 (3.91)	270 (3.28)
	286	288 (3.38)	289 (3.42)	284 (3.38)	281 (3.34)	290 (3.53)	275 (3.24)
pAMP	207		208 (4.06)	205 (3.66)	201 (4.18)	204 (3.64)	197 (3.99)
	235	239 (3.93)	240 (3.95)	237 (3.88)	230 (3.90)	263	218 (3.66)
	303	310 (3.51)	310 (3.50)	303 (3.38)	295 (3.46)	308	272 (3.45)
							277 (3.40)

o-Anisidine	212 (3.80)	214 (3.69)	212 (3.86)	212 (3.74)	204 (4.3)	195 (4.03)
	238 (3.79)	239 (3.78)	240 (3.81)	235 (3.74)	232 (3.83)	216 (3.80)
	288 (3.46)	290 (3.55)	289 (3.50)	285 (3.02)	282 (3.45)	269 (3.36)
						275 (3.25)
m-Anisidine	213 (4.17)	219 (3.87)	216 (3.86)	210 (4.25)	207 (4.20)	196 (4.04)
	234 (3.78)	240 (3.82)	240 (3.42)	237 (3.78)	230 (3.88)	219 (3.83)
	285 (3.33)	288 (2.7)	288 (3.35)	286 (3.34)	284 (3.32)	270 (3.24)
						276 (3.17)
p-Anisidine	210	208 (3.82)	208 (3.74)	205 (3.84)	202	196 (4.10)
						220 (3.86)
	236	240 (4.0)	240 (3.93)	236 (3.93)	232 (3.89)	272 (3.16)
	306	308 (3.55)	308 (3.41)	300 (3.34)	296 (3.28)	278 (3.08)

TABLE 2

Fluorescence maxima and quantum yield of various anilines in various solvents and pH values at 298 K

Compound	*Fluorescence maxima* (nm) *(quantum yield) for the following conditions*						
	Cyclohexane	*Ether*	*Acetonitrile*	*Methanol*	*Water* pH 7	*Monocation* $H_0 - 1$	λ_{ex} [a] (nm)
oAMP	325 (0.003)	333 (0.03)	335 (0.02)	335 (0.034)	350	298	300
mAMP	314 (0.08)	322 (0.06)	324 (0.04)	320 (0.05)		296	285
pAMP	344 (0.07)	360 (0.06)	364 (0.05)	364 (0.06)	370 (0.01)	295	300
o-Anisidine	321 (0.07)	326 (0.07)	331 (0.09)	337 (0.04)	350	292	288
m-Anisidine	309 (0.05)	317 (0.04)	323 (0.03)	327 (0.03)	334	296	280
p-Anisidine	337 (0.06)	352 (0.05)	357 (0.06)	361 (0.06)	365 (0.02)	294	298

[a] λ_{ex} is used for calculating ϕ_f for the neutral species.

3.2. *Effect of* pH

The absorption and fluorescence spectra of all six compounds were studied in the H_0–pH–H_- range from −10 to 16. The relevant data are compiled in Tables 1 and 2. The absorption and fluorescence maxima of the various prototropic species of these compounds agree with the values reported in literature [15, 16], within experimental error. Under acidic conditions, a blue shift is observed, in both the absorption and the fluorescence spectra. The band maxima agree with those of phenol [22] and anisole respectively. This clearly indicates that the monocations are formed by protonation of the amino group. This is further manifested by the pK_a values in the ground state, obtained spectrophotometrically, as these values fall in the region where the amino group is protonated [23].

The monoanions of the AMPs, formed by deprotonation of the hydroxyl groups, are non-fluorescent. This is also consistent with the earlier results that, in general, the phenolate ions are not fluorescent [24]. Similarly, the monoanions of the anisidines, formed by deprotonation of the NH_2 group, are also non-fluorescent in the range of H_- values we have studied and the behaviour of the dianions of the AMPs, which can be obtained by deprotonation of the monoanions of the AMPs, is similar.

The fluorimetric titration curves for the various prototropic reactions of oAMP and *o*-anisidine, mAMP and *m*-anisidine and pAMP and *p*-anisidine are given in Figs. 1, 2 and 3 respectively. The fluorimetric titration curves for the neutral species of oAMP, *o*-anisidine and mAMP could not be drawn because of the very weak fluorescence intensities. The behaviour of these fluorimetric titration curves is quite different from those observed by Cowgill [15] and Bridges and Williams [16] (in all six compounds, the ground state pK_a values were observed from the fluorimetric titration in the ethanolic solutions). Stretched sigmoid curves were observed for all the compounds except for pAMP and *p*-anisidine. In all four cases, two inflection points were observed for the monocation curves, one corresponding to the ground state pK_a value and the other to the excited state pK_a value.

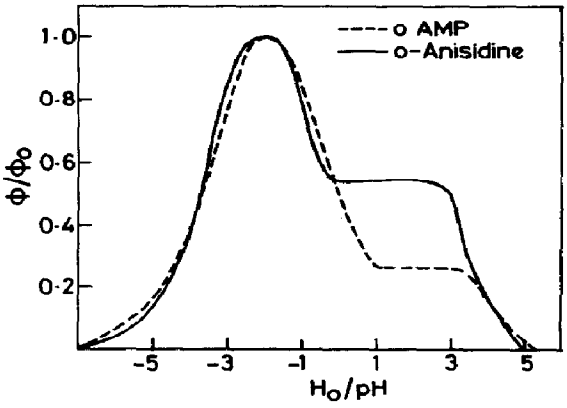

Fig. 1. Plot of ϕ/ϕ_0 *vs.* H_0/pH for the monocation of oAMP (- - - -) and *o*-anisidine (———) at 298 K (λ_{isos} = 272 nm for both).

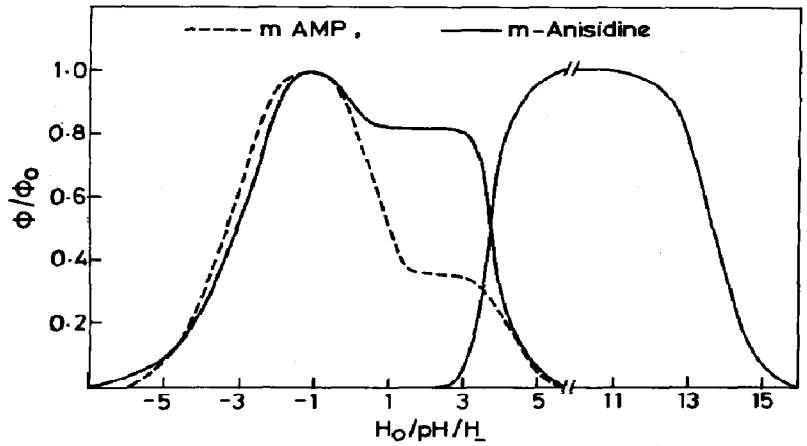

Fig. 2. Plot of ϕ/ϕ_0 *vs.* H_0–pH–H_- of mAMP (- - - -) and *m*-anisidine (——) at 298 K (λ_{isos} = 274 nm for the equilibrium between the monocation and the neutral species and λ_{max} = 281 nm for the equilibrium between the neutral species and the monoanion of *m*-anisidine).

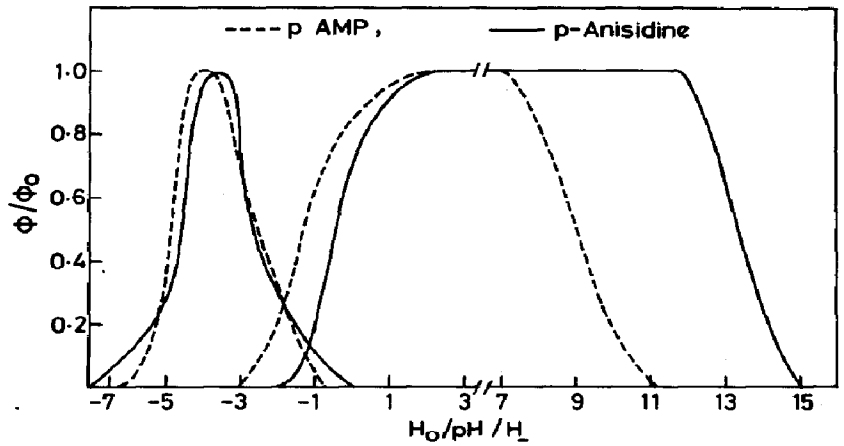

Fig. 3. Plot of ϕ/ϕ_0 *vs.* H_0–pH–H_- of pAMP and *p*-anisidine at 298 K (λ_{isos} = 278 nm for the equilibrium between the monocation and the neutral species of both, λ_{isos} = 308 nm for the equilibrium between the neutral species and the monoanion of pAMP and λ_{max} = 298 nm for the equilibrium between the neutral species and the monoanion of *p*-anisidine).

This kind of behaviour indicates that the equilibrium in the excited state is not complete in the less acidic solution and that the rate of proton transfer in the S_1 state is comparable with the rate of fluorescence. The shapes of the fluorimetric titration curves obtained can be explained on the basis of the kinetics of the excited state proton transfer.

At about $H_0 - 2$, in strong acid, the ϕ/ϕ_0 for the monocation starts to decrease gradually with decreasing hydrogen ion concentration, until a plateau is reached. The stretch of the plateau over the pH region and along the ϕ/ϕ_0 scale depends on the individual compound, as clear from Figs. 1 and 2. The inflection point in this region gives the pK_a* values for the

equilibrium between the monocation and the neutral species. After the plateau, the relative intensity of the monocation decreases to zero through a second inflection point. This point corresponds to the ground state pK_a value. For *m*-anisidine, since the neutral species emits reasonably, the fluorimetric titration curves for the monocation and the neutral species do intersect at $\phi/\phi_0 = \phi'/\phi_0' = 0.5$, for the ground state p$K_a$ value, and then possess another inflection point at an excited pK_a value, without intersection of the two curves. A similar kind of behaviour has been observed for 1- and 2-naphthols [25] and 9-phenanthrol [26].

The shapes of the early part of the curves in Figs. 1 and 2 can be understood on the basis that the reaction

$$AMPH^+ \rightleftharpoons AMP + H^+ \qquad (1)$$

occurs in the excited singlet state. In the plateau region (depending on the molecule) fluorescence is emitted from both $AMPH^+$ and AMP (although very weak). The presence of neutral AMP molecules in considerable amounts is due to the reactions in the S_1 state because, under these pH conditions, the chances of existence of the neutral species are very small in the S_0 state. Further, water molecules are the only species which can accept protons, as the concentration of the hydroxyl ions is very small in this range of pH and moreover the rate of the forward or backward reaction does not depend on the hydroxyl ion concentration. Also, the rate of backward reaction must be very small since this rate does not depend on the hydrogen ion concentration. The latter part of the curves is due to the ground state equilibrium reaction; it is shifted appreciably to the right in the region of the pK_a of $AMPH^+$. As a result, there will be a decrease in the concentration of $AMPH^+$, which in turn leads to $AMPH^{+*}$, and the subsequent increase in the AMP concentration leads to an increase in the AMP* concentration. Figure 4 represents the behaviour of the above reactions. k_1, k_f and k_I are the pseudo-first-order rate constant for deprotonation of $AMPH^+$, the rate constant for fluorescence emission and the rate constant for radiationless processes respectively. The primed values are similar terms for the reactions of AMP.

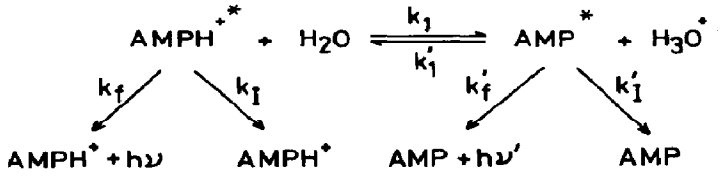

Fig. 4. Reactions of the AMPs.

Using steady state kinetics, Weller [27] has derived expressions for ϕ/ϕ_0 ($AMPH^+$) and ϕ'/ϕ_0' (AMP), given by

$$\frac{\phi}{\phi_0} = \frac{1 + k_1'\tau_0'[H_3O^+]}{1 + k_1\tau_0 + k_1'\tau_0'[H_3O^+]} \qquad (2)$$

$$\frac{\phi'}{\phi_0'} = \frac{k_1\tau_0}{1 + k_1\tau_0 + k_1'\tau_0'[H_3O^+]} \quad (3)$$

where τ_0 and τ_0' are the lifetimes of $AMPH^+$ and AMP respectively. In the plateau region, since the relative quantum yields are independent of pH, the plot of ϕ/ϕ_0 or ϕ'/ϕ_0' *versus* pH should give a horizontal line and a similar behaviour is observed for the four compounds. Equations (2) and (3) reduce to

$$\frac{\phi}{\phi_0} = \frac{1}{1 + k_1\tau_0} \quad (4)$$

$$\frac{\phi'}{\phi_0'} = \frac{k_1\tau_0}{1 + k_1\tau_0} \quad (5)$$

respectively. The values of $k_1\tau_0$ for the four compounds have been calculated, using the plateau value of ϕ/ϕ_0 (from the cation only), as the fluorescence intensity of neutral AMP is too small to have any meaningful plot. These values are tabulated in Table 3. The values of $k_1'\tau_0'$ have been determined from eqn. (2) using various values of ϕ/ϕ_0 at various hydrogen ion concentrations for oAMP and mAMP and these are also listed in Table 3. These values are the averages of four to five such values. The errors for the *o*- and *m*-anisidines are quite large and this could be due to the very small region of the monocation curve. These are not listed as no meaningful values were obtained. Thus from a knowledge of the lifetimes τ_0 and τ_0', k_1 and k_1' and thereby the pK_a^* values can be calculated.

TABLE 3

pK_a values of various prototropic equilibria of the aminophenols and anisidines

Compound	$pK_a(1)$	$pK_a^*(1)$	$k_1\tau_0$	$k_1'\tau_0'$	$pK_a(2)$	$pK_a^*(2)$
oAMP	3.9	−0.3	3	3.0 ± 1	9.9	—
o-Anisidine	3.65	−1.0	0.8	—	>16	—
mAMP	4.2	0.5	1.9	10 ± 2	9.9	—
m-Anisidine	3.8	0.0	0.2	—	>16	13.7
pAMP	3.6	−2.5	—	—	9.35	9.1
p-Anisidine	4.1	−2.7	—	—	>16	13.3

For the anisidines, $pK_a(2)$ is deprotonation of the amino group; for the AMPs it is deprotonation of the hydroxyl group.

The behaviour of pAMP and *p*-anisidine is quite different from that of other isomers and resembles more the similar behaviour of the aromatic amines, *i.e.* the fluorescence intensity of neutral pAMP or *p*-anisidine starts to decrease below pH 2, without the appearance of any other fluorescence band. The monocation fluorescence band only starts to appear when the fluorescence intensity of the neutral species is only about 15% at H_0 −1.5,

whereas under these conditions only monocations are present in the S_0 state. The decrease in fluorescence intensity of the neutral species is due to proton-induced quenching because the SO_4^{2-} ion (produced by the addition of K_2SO_4) of the same concentration, as can be obtained by the addition of H_2SO_4, does not quench the fluorescence. Thus the pK_a^* values for the equilibrium between the monocation and the neutral species of these compounds have been calculated from the formation curve of the monocation rather than from the decrease in the relative intensity of the neutral species. These values are also listed in Table 3. The data of Table 3 clearly indicate that the amino group becomes more acidic on excitation and this behaviour is consistent with the normal behaviour of the aromatic amines.

The fluorescence intensities of the monocations of all six compounds decrease after about H_0 −4. This could be due either to the proton-induced fluorescence quenching of the monocations or to the formation of non-fluorescent dications, by protonation of the hydroxyl or methoxyl groups or the carbon centre of the benzene moiety. In general, the dications formed in this way are fluorescent. It can be concluded that this decrease in fluorescence intensity is due to quenching.

In the highly basic region, the fluorimetric titration curves for pAMP give the ground state pK_a value for the equilibrium between the neutral species and the monoanion, indicating that the lifetimes of the conjugated species are so small that equilibrium cannot be established in the S_1 state. This result is consistent with the behaviour of similar compounds reported earlier. However, the pK_a^* values for the equilibria between the neutral species and the monoanion of the *m*- and *p*-anisidines are calculated from the decrease in the intensities of the neutral species, as the monoanions, formed by deprotonation of the amino group, in general are non-fluorescent with few exceptions. The data are listed in Table 3 and clearly indicate, as expected, that the amino group becomes a stronger acid on excitation.

3.3. Proton-induced fluorescence quenching

As reported earlier no correspondence is found between the decrease in the fluorescence intensity of the neutral species and the increase in the fluorescence intensity of the monocation of pAMP and *p*-anisidine at moderate pH values. By application of the model of Shizuka and Tobita [12] for this behaviour to pAMP and *p*-anisidine, a simple Stern–Volmer plot can be obtained for fluorescence quenching

$$\frac{\phi_0}{\phi} = 1 + k_q\tau[H^+]$$

where ϕ and ϕ_0 are the fluorescence intensities with and without the presence of quencher, k_q is the fluorescence quenching constant and τ is the lifetime of the neutral species. ϕ_0/ϕ *versus* $[H^+]$ is plotted in Fig. 5 and $k_q\tau$ is calculated from the slopes of these plots. These values are found to be 0.66 $dm^3\ mol^{-1}$ and 1.2 $dm^3\ mol^{-1}$ respectively for pAMP and *p*-anisidine. The natural lifetimes τ_{FM} for these species are calculated from the corrected

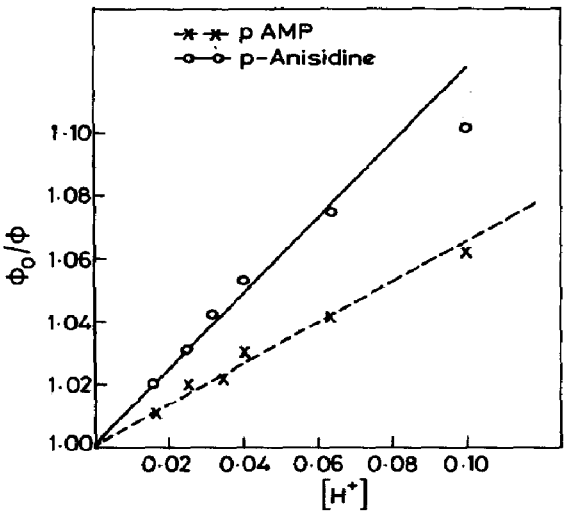

Fig. 5. Plot of ϕ_0/ϕ *vs.* $[H^+]$ for pAMP and *p*-anisidine at 298 K.

fluorescence spectra, as suggested by Strickler and Berg [28]. The lifetimes τ can be calculated from the relation $\tau = \tau_{FM}\phi$, where ϕ is the quantum yield and these values are found to be 0.2×10^{-9} and 0.6×10^{-9} ns. Thus the k_q values obtained are 3.3×10^9 and 2.0×10^9 dm^3 mol^{-1} s^{-1}. These values are of the same order of magnitude as those observed for other aromatic amines [1 - 13].

3.4. Effect of solvents on the equilibrium reaction

The ground state pK_a value was obtained from fluorimetric titrations by Cowgill [15], by studying this reaction in ethanol–water mixtures for pAMP. Similar results were observed by us when we carried out these titrations in methanol–water mixtures, *i.e.* there is a one-to-one correspondence between the decrease in the fluorescence intensity of the neutral species and the increase in the fluorescence intensity of the monocation, and no proton-induced fluorescence quenching of the neutral species was observed. Although nothing can be said quantitatively from our results, a qualitative explanation can be given. Water, having a high dielectric constant as well as a greater proton affinity than methanol [29, 30], will be very effective in promoting the deprotonation of the monocation. Apparently the hydrogen ion exists in methanol–water solutions as the hydronium ion as well as methanol-solvated species. Either species can react with excited pAMP. The decomposition reaction of pAMPH$^+$ is promoted by either methanol or water, but water appears to have a greater proton affinity. Thus the degree of excited state pAMPH$^+$ formation decreases as the water is substituted for methanol. This is clear from the pK_a^* value, and is partially due to the increase in the forward reaction rate with increasing water concentration but is mainly a result of the substantial decrease in the reverse rate. In the absence of water, the forward reaction is quite slow and consequently the system does not rapidly achieve dynamic equilibrium. In the presence of a signif-

icant amount of water, both the forward and the backward reaction rates are fast and the system achieves dynamic equilibrium very rapidly. Thus the formation curve of the monocation represents the establishment of equilibrium. A similar behaviour has been observed in the dynamics of reversible excited state protonation of 2-naphthoic acid in ethanol–water solution [31].

4. Conclusion

In conclusion, the behaviour of oAMP, *o*-anisidine, mAMP and *m*-anisidine is very different from that of pAMP and *p*-anisidine. In the former set of compounds, the stretched sigmoid fluorimetric curves for the monocations are due to a rate of proton transfer in the excited state comparable with the radiative lifetimes. Thus the equilibrium is not established in the excited state. pAMP and *p*-anisidine behave like aromatic amines in moderately acidic solutions.

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