

## Absorption and emission spectra of 4-methyl-2,6-diformyl phenol in protic solvents: Interaction with amine bases

REBA ROY, SIVAPRASAD MITRA, RANJAN DAS and SAMARESH MUKHERJEE\*

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

MS received 8 August 1994; revised 10 January 1996

**Abstract.** The interaction of 4-methyl-2,6-diformyl phenol (MFOH) with tributylamine and trioctylamine has been studied quantitatively in protic solvents by means of absorption and fluorescence spectroscopy with special emphasis on proton transfer. It is observed that (a) the intensity of the absorption band in the 430–450 nm region due to the phenolate anion ( $\text{MFO}^-$ ) increases with increasing amine concentration; (b) the change in the intensity of the absorption band in the 350 nm region due to intramolecularly hydrogen bonded MFOH follows inversely the change in intensity of the absorption band due to the anion at 430–450 nm region (c) the intensity of the fluorescence band around 480–520 nm region due to the  $\text{MFO}^-$  anion increases with increase in the added base concentration. The results are interpreted in terms of proton transfer from MFOH to an amine base to yield an anion  $\text{MFO}^-$  both in the ground and excited electronic states. Equilibrium data for the proton transfer reaction between MFOH and amine bases (B) in ethanol, butanol and water as solvents have been obtained and discussed.

**Keywords.** Absorption and emission spectra; equilibrium constant; enthalpy and entropy.

### 1. Introduction

The ultraviolet absorption and fluorescence spectra of the *p*-nitrophenol in the presence of various amine bases in different protic and aprotic solvents of different dielectric constant have been investigated as a function of the amine concentration (Bell and Barrow 1959; Parker and Brody 1963; Scott *et al* 1968; Baba *et al* 1969; Scott and Vinogradov 1969; Murthy and Reddy 1982; Dwivedi *et al* 1986) and the results are interpreted in terms of a tautomeric equilibrium involving a hydrogen bonded complex, a proton transfer complex and a solvent separated ion pair. New discoveries have unfolded the intricacies of solvent effects and ion-pair formation (Caldin and Gold 1975; Bisht *et al* 1990; Smith *et al* 1991; Swinney and Kelley 1991; Syage and Steadman 1991; Timoneda and Hynes 1991). Recently, Syage and Steadman (1990) have presented evidence for the direct detection of ground state ion-pair structure of phenol–amine mixture and showed that the proton transfer in solvent–amine mixture produces contact ion-pairs and not solvent-separated ion-pairs. Mataga *et al* (1956) and Mataga and Tsuno (1957) studied the hydrogen bonding effect on the fluorescence spectra of

---

\*For correspondence

$\beta$ -naphthols and carbonyl compounds as acceptors and concluded that a new hydrogen bonding equilibrium is achieved during the lifetime of the first excited electronic state. On the other hand, in the case of quinoline as proton acceptor, the equilibrium constants of the hydrogen bond formation in the excited state are reported to be practically the same as those in the ground state. In our earlier work (Mitra *et al* 1993) it was shown that in the first excited  $^1(\pi\pi^*)$  state of MFOH, an intramolecular proton transfer takes place accompanied by isomerization to the enol tautomer. The purpose of this work is to study quantitatively the spectral changes in the absorption and the fluorescence of MFOH in the presence of amines and examine the physical and chemical properties of MFOH through the 4-methyl-2,6-diformyl phenolate ion (MFO<sup>-</sup>) formation. The possibility of ionic dissociation and a new equilibrium of the anion formation would be examined through these studies as a function of amine base concentration in butanol, ethanol and water.

## 2. Experimental

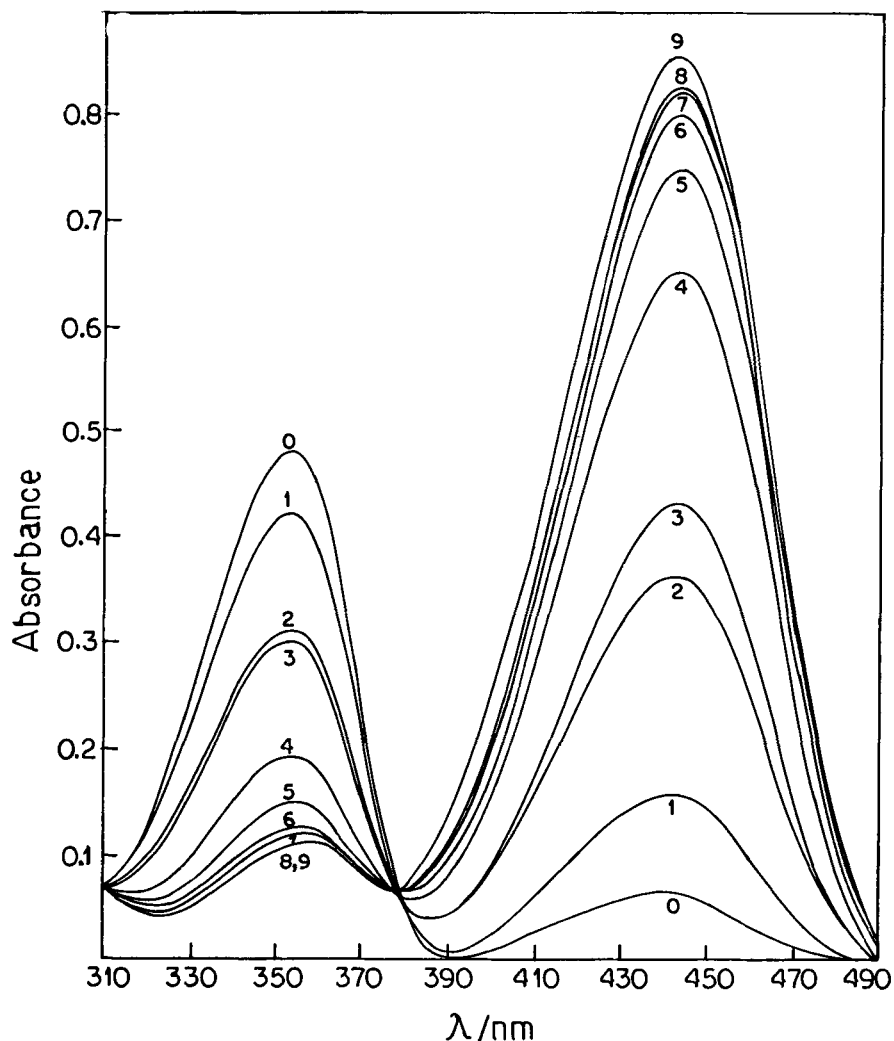
4-Methyl-2,6-diformyl phenol (MFOH) was prepared as reported earlier (Mitra *et al* 1993). Spectroscopic grade ethanol and butanol were distilled before use. Triple-distilled water was used for the preparation of aqueous solutions. Trioctylamine and tributylamine (Aldrich) were kept with anhydrous KOH pellets overnight and then subjected to fractional distillation before use.

The fluorescence and electronic absorption spectra were recorded as described earlier (Mukherjee 1987; Mitra *et al* 1993). Blank runs carried out with solvent alone showed no fluorescence emission in the spectral region of interest. The excitation wavelengths were 380 (isosbestic point) and 360 nm. The concentration of MFOH was maintained at  $1 \times 10^{-4}$  mol dm<sup>-3</sup> and that of amine was varied from 0.35 to  $9.8 \times 10^{-4}$  mol dm<sup>-3</sup>. Equilibrium constants were obtained by using the method of Scott *et al* (1968) and Scott and Vinogradov (1969). The enthalpies of formation ( $\Delta H^0$ ) were calculated from the equilibrium constants at different temperature by plotting  $-\log k$  against  $1/T$ . The free energy change ( $\Delta G^0$ ) and entropy ( $\Delta S^0$ ) values were calculated using the equation  $\Delta G^0 = -RT \ln K$  and from the intercept of the Van't Hoff plot [ $\ln K = \Delta H^0/RT - \Delta S^0/R$ ]. The spectrum of the anion MFO<sup>-</sup> was recorded and verified by addition of an equivalent amount of NaOH to MFOH solution in water.

## 3. Results and discussion

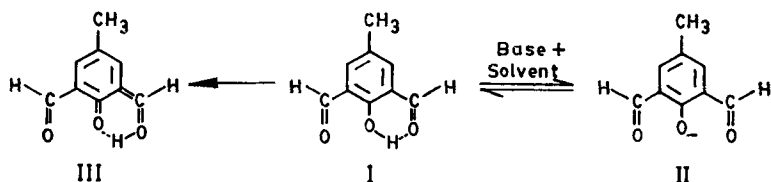
### 3.1 Electronic absorption spectra

The absorption spectra of MFOH show two bands at 350 nm and around the 430–440 nm in ethanol and water, and a single band at 350 nm in butanol. The addition of tributylamine or trioctylamine reduces the intensity of the 350 nm band and simultaneously increases the intensity of the absorption band (430–440 nm) in ethanol and methanol. On the other hand, a new band at 440 nm is formed in butanol by the addition of base. Some typical spectra for the trioctylamine-MFOH system in ethanol at 20°C are shown in figure 1. An isosbestic point is observed around 380 nm. The spectral bands at 350 nm and the red end region may safely be attributed to the intramolecularly hydrogen-bonded species of MFOH (I) and 4-methyl-2,6-diformyl phenolate (MFO<sup>-</sup>) anion (II in scheme 1), respectively in pure solvents (Mukherjee



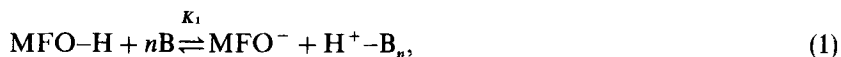
**Figure 1.** Absorption spectra of MFOH + TOA in ethanol at 20°C. [TOA]  $\text{mol dm}^{-3} \times 10^{-4} = 0(0), 1(0.13), 2(0.25), 3(0.3), 4(1.27), 5(2.55), 6(3.82), 7(5.10), 8(6.38), 9(9.57)$ .

1987; Mitra *et al* 1993). The increase in intensity of the 430–440 nm band with a consequent decrease in intensity of the 350 nm absorption band on addition of base is due to increase in concentration of the  $\text{MFO}^-$  ion following subsequent decrease in concentration of the MFOH closed conformer in the ground state. It is pertinent to mention that the intensity of the red band is relatively weak and the  $pK_a$  value for MFOH is low (6.9) (Mukherjee 1987). Hence, this weaker band may also be due to an ortho-quinoid electron arrangement and a tautomeric equilibrium between I and IV (in addition to II). Therefore, it is expected to display spectral absorption of III at a higher wavelength than I. It is noted that the characteristic absorption due to  $\text{MFO}^-$  (II) in water and ethanol is the same as that in butanol and acetonitrile in the presence of amine. In these solvents the maximum intensity of the absorption band due to  $\text{MFO}^-$



Scheme 1.

anion is reached at  $\sim 10^{-2}$  mol dm $^{-3}$  of TEA and both the absorption bands due to dissociated (MFO $^{-}$ ) and undissociated MFOH persist even in the excess of amine ( $10^{-2}$  mol dm $^{-3}$ ). The spectrophotometric data obtained from the titration of MFOH by amine base at a fixed solvent composition are treated assuming simple equilibrium (Scott and Vinogradov 1969),



where B is the amine base. Since equilibrium is constant

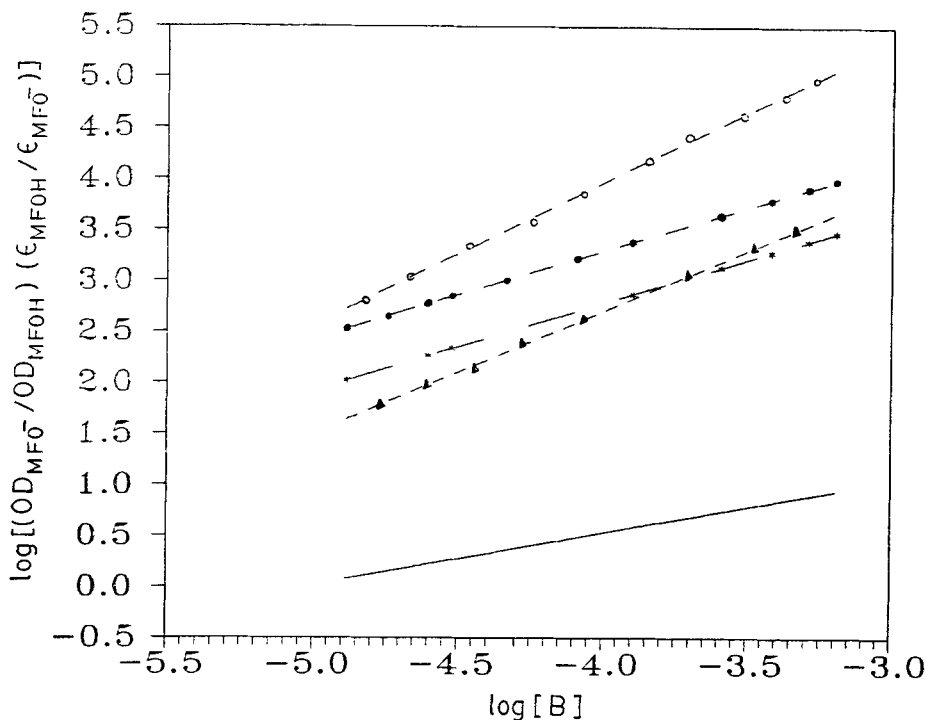
$$K_1 = \frac{[\text{MFO}^{-}]}{[\text{MFOH}][\text{B}]^n}$$

therefore,

$$\log K + n \log C_B = \log \left( \frac{\text{OD}_{\text{MFO}^{-}}}{\text{OD}_{\text{MFOH}}} \times \frac{\varepsilon_{\text{MFOH}}}{\varepsilon_{\text{MFO}^{-}}} \right). \quad (2)$$

where OD is absorbance,  $C_B$  concentration of base and  $\varepsilon$  molar extinction coefficient. The terms on the right hand side of (2) are plotted against  $\log C_B$  and some of the plots are shown in figure 2. Linear plots are obtained with the slope  $n$ . Estimates of  $\log K_1$  are obtained from the intercepts and the results are given in table 1. Addition of an amine base to a solution of MFOH in a protic solvent appears to enhance the ionization of MFOH until the intensity of 430–450 nm region peak reaches a maximum. It is also observed that further addition of the amine reduces the ionization of MFOH with a small decrease in the intensity of the MFO $^{-}$  anion peak. This indicates the apparent decrease of the polarity of solvent at the higher concentration of amine (Scott *et al* 1968). Titration of MFOH with trioctylamine or tributylamine in protic solvent results in an increase in the peak intensity due to MFO $^{-}$  anion and a concomitant decrease in the intensity of the peak due to undissociated MFOH at 350 nm. The data obtained in the spectrophotometric titration of MFOH with amine base may be interpreted on the basis of an equilibrium between MFOH (intramolecularly bonded) and MFO $^{-}$  ion. The presence of an isobestic point at 380 nm is consistent with the assumption of two species (undissociated MFOH and MFO $^{-}$  ions) in equilibrium in the ground state.

The equilibrium constants  $K_1$  in ethanol and water given in table 1 are relatively higher when tributylamine is the base, which is in agreement with the known basicities of tributylamine and trioctylamine in water ( $pK_a = 10.9$  and  $8.2$ , respectively). However,  $K_1$  values obtained are lower when tributylamine is the base in butanol. Although the plots illustrated in figure 2 are linear, it is apparent from the slope and intercept values given in table 1 that the assumption of a 1:1 MFOH-amine complex formation in the present study could be over-simplification. The breakdown of 1:1 stoichiometry



**Figure 2.**  $\text{Log}[(\text{OD}_{\text{MFO}^-}/\text{OD}_{\text{MFOH}}) \times (\epsilon_{\text{MFOH}}/\epsilon_{\text{MFO}^-})]$  vs  $\text{log [B]}$  plots for MFOH-amine systems:  $\circ$  (TOA + butanol) at  $36^\circ\text{C}$ ;  $\bullet$  (TBA + ethanol) at  $27^\circ\text{C}$ ;  $\blacktriangle$  (TBA + water) at  $36^\circ\text{C}$ ;  $*$  (TBA + ethanol) at  $38^\circ\text{C}$ ;  $-$  (TOA + ethanol) at  $35^\circ\text{C}$ .

**Table 1.** Results of spectrophotometric titration of MFOH in the ground state.

Solvent	Amine	$(\text{log}([\text{B}]))^a$	$n$	$\text{log } K^b$	$-\Delta H^c$	$-\Delta G^c$	$\Delta S^d$
Butanol	TBA	4.9	0.94	8.47(20)	9.2	11.43	0.007
		5.2	1.00	8.72(27)	7.1	12.05	0.016
		4.7	1.06	7.22(35)	—	—	—
	TOA	4.5	1.44	9.47(27)	11.03	13.08	6.85
		4.7	1.43	9.45(20)	10.61	12.75	7.31
		4.7	1.39	9.51(35)	—	—	—
Ethanol	TBA	4.6	0.70	6.95(20)	8.0	9.38	4.7
		4.8	0.85	6.69(25)	7.7	9.18	4.9
		4.8	0.85	6.18(35)	—	—	—
	TOA	4.5	0.70	3.09(20)	3.2	4.17	3.3
		4.8	0.50	2.63(27)	2.8	3.63	2.8
		5.1	0.51	2.57(35)	—	—	—
Water	TBA	4.4	1.53	8.20(20)	8.3	11.06	9.42
		4.2	1.19	7.45(35)	6.5	10.56	13.2
		4.6	1.36	5.40(40)	—	—	—

<sup>a</sup> $\text{mol dm}^{-3}$ ; <sup>b</sup> $\text{dm}^3 \text{mol}^{-1}$ ; <sup>c</sup> $\text{kcal mol}^{-1}$ ; <sup>d</sup> $\text{cal K}^{-1} \text{mol}^{-1}$

TBA and TOA stands for tributylamine and trioctylamine, respectively.

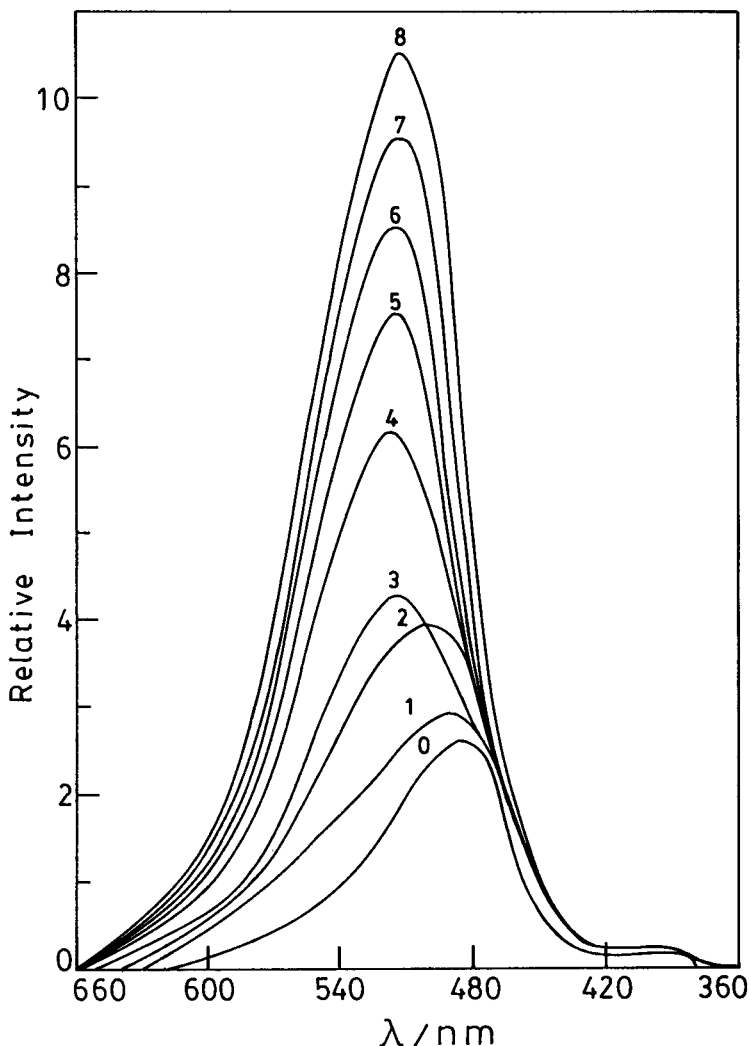
is in agreement with the presence of more than one type of MFOH-amine complex formation. However, the magnitude of the equilibrium constant given in table 1 is of the same order as reported in other earlier studies (Davis 1962; Vinogradov *et al* 1962; Boyles and Evans 1965). A pertinent point to mention is that the alkyl groups in alcohols have a +I effect and are able to release electrons towards its oxygen atom and this fact makes the alcohols proton acceptors. Our results suggest that the proton accepting ability or ionization of MFOH in butanol is relatively weak and MFOH cannot ionize in absence of base. This may be due to the presence of the bulky alkyl group in butanol, which maybe twisted out of plane and exhibit a steric effect. This steric effect will resist the electron-donating ability of butanol. Accordingly, butanol is a weakly proton-accepting solvent and is less basic than ethanol and water. This steric effect should increase the proton transfer barrier as the alkyl group is twisted out of plane in butanol. Another possibility is that in weak proton-accepting solvents like butanol, dimer formation is probable. According to Steadman and Syage (1991) dimerization should prevent MFOH from acting as a proton donor. In this connection it is relevant to mention that phenols, aromatic acids and bases form dimers in solution particularly in weakly polar and nonpolar solvents.

A closer examination of the data in table 1 shows that  $\Delta H$  values are higher in the case of tributylamine. This is to be expected as tributylamine has a higher  $pK_a$  value than trioctylamine. Proton transfer is appreciable when both  $K_1$  and  $\Delta H$  for the anion formation are larger. The general conclusion is that the thermodynamic data obtained in this study indicate that there is some rudimentary kind of relationship between the magnitude of  $K_1$  and  $\Delta H$  and the extent of anion formation.

### 3.2 Fluorescence spectra

It is expected from the absorption spectra that such anions may also be formed due to the interaction between MFOH and amine molecules in the excited state and the fluorescence spectrum may well be influenced accordingly. To get complementary evidence of  $MFO^-$  formation, the fluorescence spectra of MFOH in protic solvents were recorded. The fluorescence spectra of MFOH appeared at 520 nm in water and ethanol and at 480 nm in butanol. It is also observed that the emission spectra of MFOH appears at 520 nm in aqueous alkaline medium. Therefore, the yellow band in water and ethanol can be assigned as due to the  $MFO^-$  anion. The 480 nm emission in butanol which is very close to the anion emission was shifted to 520 nm by the addition of amine base (figure 3). Thus for anion formation addition of base is necessary when butanol is used as solvent. Addition of amine base to a solution of MFOH appears to enhance the ionization of MFOH thereby increasing the intensity of the band and a red shift from 480 nm to 520 nm. The appreciable displacement of the fluorescence band (480 to 520 nm) and gain in intensity of 520 nm band is clearly due to formation of anion (scheme 1). Both intra- and intermolecular hydrogen bonds should provide an efficient nonradiative pathway for energy degradation and, hence, are supposed to decrease the fluorescence intensity. However, the free anion ( $MFO^-$ ) should have enhanced fluorescence intensity due to the absence of any intra- or intermolecular hydrogen bond. From these changes in the fluorescence spectrum, we can calculate the equilibrium constant  $K'$  of anion formation using the same equation as that derived by Mataga *et al* (1956),

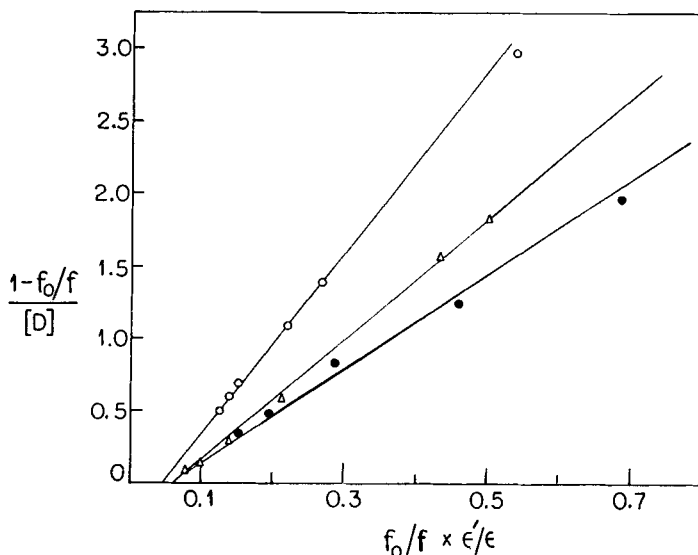
$$1 - (f_0/f)/[D] = K' + K'\alpha(f_0/f) \cdot \epsilon_{MFO^-}/\epsilon_{MFOH} \quad (3)$$



**Figure 3.** Fluorescence spectra of MFOH + TOA in butanol; [TOA] mol dm<sup>-3</sup> × 10<sup>-4</sup> 0(0), 1(0.08), 2(0.19), 3(0.25), 4(1.22), 5(2.55), 6(3.82), 7(6.38), 8(9.57).

where  $f_0$  and  $f$  represent the relative fluorescence intensities of the solution without and with amine,  $[D]$  is the concentration of amine and  $\alpha$  is the ratio of the fluorescence yield of free MFOH to that of the anion. Equation (3) holds under the condition that the extinction coefficients of the closed conformer of MFOH and of the MFO<sup>-</sup> anion are not equal at the wavelength of the exciting radiation. Results obtained from (3) are shown in figure 4. From the slope of the straight line we can calculate the equilibrium constant  $K'$  for the formation of anion in the excited state. Results are given in table 2.

In ethanol and water it is found that the equilibrium constants in the excited state have larger values than those in the ground state. The increase in the ionization of MFOH with the polarity of the medium may be ascribed to the increase in ionizing ability of MFOH by amine in the excited state. It can be concluded that MFOH has



**Figure 4.** Plots of  $(1 - f_0/f)/[D]$  vs  $f_0/f \cdot \epsilon'/\epsilon$  for MFOH-amine system at 28°C. ○(TBA + water); △(TOA + ethanol) and ●(TBA + ethanol).

**Table 2.** MFOH-amine base interaction in the excited state.

Solvent	Amine	$\log K'(\text{dm}^3/\text{mol})$	$\alpha$	$\Delta H'$ kcal/mol
Butanol	TBA	3.4	11.9	88.7
	TOA	4.2	0.2	86.2
Ethanol	TBA	3.4	16.0	86.4
	TOA	3.4	8.8	96.4
Water	TBA	3.6	1.8	118.5

a larger acidity in the first excited singlet state than in the ground state and the excited electronic structure assumes a configuration more attractive to base. The equilibrium constant obtained from fluorescence data is different from that obtained from absorption spectral data when ethanol and water are used as the solvent. Mataga and Tsuno (1957) obtained similar results in the case of  $\beta$ -naphthol and acetic acid in water. They suggested that a new hydrogen bonding equilibrium was achieved during the lifetime of the first excited electronic state and confirmed that the tendency to dissociate is significantly greater in the excited state.

From the lower values of decay rate constant we have earlier shown (Mitra *et al* 1993) that the proton transfer in MFOH is not essentially barrier-free. The enthalpy change ( $\Delta H$ ) may be regarded as representing the potential energy difference between the two potential minima in the ground state. Therefore, the corresponding energy difference in the excited state ( $\Delta H'$ ) can be obtained by combining the  $\Delta H$  value with the excitation energy, as measured at the absorption maxima of the complexes, on the assumption that the positions of the potential minima are approximately the same in the excited state as in the ground state. Results are given in table 2. It can be seen that



the potential energy difference is markedly larger in the excited state. These potential energies are associated with an acid–base system which is present in butanol, ethanol and water. Therefore, the dielectric constants of the solvents should also take part in the stabilization of the anion. This may explain the large  $\Delta H$  values in water. The  $\Delta H$  values in the excited state should be more or less different from the corresponding values in the ground state, since a change will be produced in the dipole moment upon excitation. Moreover the higher stabilization energy in the excited state indicates that the fluorescence originates from the proton-transferred form.

#### 4. Conclusions

In this work the absorption and fluorescence spectra of MFOH are measured in protic solvents both in presence and absence of amine. It is observed that fluorescence intensity becomes stronger on the addition of amine base. In ethanol and water, measurement of the relative spectral intensities established the fact that a new and different equilibrium state of the anion or ion-pair is reached during the lifetime of the excited state. It is possible that the observed extra stabilization of the anion in the excited state is mainly due to the increase of electron delocalization in the excited state. Similar values of equilibrium constant in the ground and excited states in butanol are probably due to the presence of many types of species (e.g. MFOH + donor, butanol + donor, MFOH + butanol etc.) in which solvation effects play an important role.

#### Acknowledgement

A part of this work was supported by the Department of Science and Technology, Government of India.

#### References

- Baba H, Matsuama A and Kokuban H 1969 *Spectrochim. Acta* **25A** 170  
Bell C L and Barrow G M 1959 *J. Chem. Phys.* **31**, 1158  
Bisht P B, Tripathi H B and Pant D D 1990 *Chem. Phys.* **147** 173  
Boyles J W and Evans B 1965 *J. Chem. Soc.* 6984  
Caldin C and Gold V 1975 *Proton-transfer reaction* (New York: Wiley) p. 121  
Davis M M 1962 *J. Am. Chem. Soc.* **89** 3623  
Dwivedi P C, Banga A K and Sharma N 1986 *Spectrochim. Acta* **A42** 623  
Förster T 1950 *Z. Elektrochem.* **54** 42  
Mataga N and Tsuno S 1957 *Bull. Chem. Soc. Jpn.* **30** 368  
Mataga N, Kaifu Y and Koizumi M 1956 *Bull. Chem. Soc. Jpn.* **29** 115  
Mittra S, Das R and Mukherjee S 1993 *Chem. Phys. Lett.* **202** 549  
Mukherjee S 1987 *Indian J. Chem.* **26A** 1002  
Murthy A S and Reddy A R 1982 *Adv. Mol. Relaxation Inter. Processes* **22** 199  
Parker A J and Brody D 1963 *J. Chem. Soc.* 4061  
Scott R and Vinogradov S 1969 *J. Phys. Chem.* **73** 1890  
Scott R, DePalma D and Vinogradov S 1968 *J. Phys. Chem.* **72** 3192  
Smith T P, Zaklika K A, Thakur K, Walker G C, Tominaga K and Barbara P F 1991 *J. Phys. Chem.* **95** 10465  
Steadman J and Syage J A 1991 *J. Phys. Chem.* **95** 10326  
Swinney T C and Kelley D F 1991 *J. Phys. Chem.* **95** 10369  
Syage J A and Steadman J 1990 *Chem. Phys. Lett.* **166** 159  
Syage J A and Steadman J 1991 *J. Chem. Phys.* **95** 2497  
Timoneda J and Hynes J T 1991 *J. Phys. Chem.* **95** 10431  
Vinogradov S, Bell R P and Crookes J E 1962 *J. Chem. Soc.* 3513