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Influence of solvent polarity and medium acidity on the UV–Vis spectral behavior of 1-methyl-4-[4-amino-styryl] pyridinum iodide

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Abstract

Electronic absorption, and excitation spectra of 1-methyl-4-[4-aminostyryl] pyridinum iodide $(M-NH_2)$ were measured in solvents of different polarity. The $(M-NH_2)$ dye exhibits negative solvatochromism, i.e. a hypsochromic band shift as the solvent polarity increases. The fluorescence quantum yield is also sensitive to the polarity and viscosity of the medium. The ground and excited state protonation constants were calculated and amount to 3.35 and 0.62, respectively. The effect of micellization on the emission spectrum of $(M-NH_2)$ are also studied in sodium dodecyl sulphate (SDS). The fluorescence intensity increases as the concentration of SDS increases with an abrupt change at cmc. The quantum yield of the cis trans photoisomerization is also determined in aqueous buffer solution of pH 1.1. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Merocyanine dyes are well known as solvatochromic and photoreactive compounds which are also sensitive to the medium acidity [1]. Due to these properties they are potentially useful in many areas such as solar energy conversion [2,3], photosensitizers [4], phototherapy [5], in laser doublers and as liquid crystals [6]. Merocyanine dyes are also useful as electrochromic compounds for membrane potentials and high-voltage sensitivity [7,8]. In the present article, it is attempted to study the effect of medium polarity, acidity, and viscosity on the UV–Vis spectra and fluorescence quantum yield of a new merocyanine dye, namely 1-methyl-4-[4-aminostyryl] pyridinum iodide (M–NH₂).





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2. Experimental

1-Methyl-4-[4-aminostyryl] pyridinium iodide was synthesized by condensation of 4-aminobenzaldehyde with 1-methyl-picolinium iodide for 2 h. The brown precipitate was filtered and recrystalized several times from water containing traces of KOH. The purity of the dye was checked by thinlayer chromatography on silica gel 60 and by elemental analysis.

Organic solvents (Fluka, puriss) were of spectroscopic grade and used without further purification. For the pK_a determinations, KH_2PO_4 buffer (Merck) and NaOH were used to prepare titrisol buffer according to Britton [9].

UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda 17 Spectrophotometer using matched 1 cm quartz cells; the cell holder was equipped for variable temperature thermostate by using Julbo Thermo-Bath u3. Steady-state emission spectra were recorded on a Shimadzu RF-5000 Spectrofluorometer using 1 cm quartz cells. Fluorescence intensities were measured at right angle to the exciting light. Fluorescence quantum yields (ϕ_f) were measured relative to the merocyanine dye [10] in basic media, using, an absorbance of less than 0.06 to avoid reabsorption of the emitted light. The following relation has been applied to calculate the fluorescence quantum yields relative to those of the merocyanine dye in basic media [11]:

$$\frac{\phi_{\rm f}({\rm s})}{\phi_{\rm f}({\rm r})} = \frac{\int I_{\rm s}(\bar{\nu}) {\rm d}\bar{\nu}}{\int I_{\rm r}(\bar{\nu}) {\rm d}\bar{\nu}} \times \frac{A_{\rm r}}{A_{\rm s}} \times \frac{n_{\rm s}^2}{n_{\rm r}^2}$$

The integral represents the corrected fluorescence peak areas, A is the absorbance at the excitation wavelength, n is the solvent refractive index, the subscripts s and r refer to the sample and reference, respectively.

3. Results and discussion

3.1. Influence of medium polarity and viscosity

The UV–Vis absorption, emission, and excitation spectra of the $(M-NH_2)$ dye were measured at



Fig. 1. UV–Vis absorption spectra of M–NH₂ dye ($c = 3 \times 10^{-5}$ mol dm⁻³) in nine different solvents.

a concentration of $c = 3 \times 10^{-5}$ mol dm⁻³ in 11 solvents of different polarity. As shown in Figs. 1 and 2, the solvent polarity influences strongly the position of the electronic absorption and emission maxima. The hypsochromic band shifts in the electronic absorption and emission spectra of M-



Fig. 2. Emission spectra of M-NH₂ dye ($c = 3 \times 10^{-5}$ mol dm⁻³) in nine different solvents (excited at the corresponding visible absorption maximum λ_{max} of the dye in each solvent).

Table 1 UV-Vis spectral data of $M-NH_2$, measured in 11 solvents and some solvent properties

Solvent	Ζ	β	π*	ΔE_{T}	λ_{\max} (Ab)	λ_{\max} (Em)	$\lambda_{\rm exc.}$
HBD-A							
1. H ₂ O	94.6	0.14	1.09	71.10	402	558	402
2. 1,2-ethandiol	85.1	0.51	0.932	64.67	440	565	440
3. MeOH	83.6	0.62	0.586	63.53	450	565	450
4. 2-propanol	76.3	0.92	0.505	62.15	460	566	460
Aprotic HBA-solvents							
5. DMSO	71.1	0.75	1.000	62.69	456	576	456
6. DMF	68.5	0.61	0.875	63.11	453	571	453
7. Acetone	65.7	0.50	0.683	63.82	448	566	448
HBDA and HBD-solvents							
8. CH ₃ CN	71.3	0.40	0.713	65.72	435	563	435
9. Pyridine	64.0	0.66	0.867	61.22	467	578	476
10. CH_2CI_2	64.2	0.10	0.820	62.69	456	552	456
11. CHCI ₃	63.2	0.10	0.58	64.53	443	523	443

NH₂ with increasing solvent polarity of the medium is expected and reflects a decrease of the ground state dipole moment of the dye molecule upon excitation and an increase of its ground-state dipole moment as a result of solvent polarization [12–14]. Table 1 summarizes the UV–Vis spectral data of M–NH₂. The hydrogen bond acceptor (HBA) basicity of solvents can be described by the Kamlet and Taft's β -scale, whereas the hydrogen bond donor solvents acidity can be empirically described by the coresponding α -scale [13,14].

The plot of the empirical solvent polarity parameter (z) of Kosower [15,16] against the electronic transition energy $(E_{\rm T})$ of the longwavelength Vis absorption band is shown in Fig. 3; the electronic transition energy increases with increasing solvent polarity. The dramatic shifts in electronic absorption spectra observed on going from pyridine ($\pi_{max} = 467 \text{ nm}, z = 64 \text{ kcal mol}^{-1}$) to water $(\mathfrak{X}_{max} = 402 \text{ nm}, z = 94.6 \text{ kcal mol}^{-1})$ results from the solute solvent interaction; the HBD solvents can reduce the delocalization of the amino group lone pair of electrons and hence the bond order of the central bond. It is proposed that one of the main factors causing the solvatochromic behavior is the hydrogen-bonding interaction between the M-NH₂ lone pair of electrons and the HBD solvent molecules. In the HBD solvents such as water and alcohol, the interaction stabilizes the benzenoind structure with a large charge separation. It is expected that the enhancement of the negative solvatochromism of $M-NH_2$ dye results from increasing acidity with decreasing electron donating ability in the order of pyridin < 2-propanol < methanol < 1,2-ethandiol < water. In the presence of the more polar solvent the



Fig. 3. Plot of the transition energy ΔE_{max} vs. Kosower's Z parameter for M–NH₂ in ten different solvents of variable polarity.



Scheme 1.

probability of the conjugation increases and it may decrease with decreasing the polarity [1]. This is indicated by Scheme 1.

For the HBD solvent the dye acts as a proton acceptor at the amino nitrogen group, this is represented by the acid-base equilibrium structures in Scheme 1. Fig. 4 shows the effect of the medium basicity on the behavior of $(M-NH_2)$ dye. A negative solvatochromic behavior was found on decreasing the basicity of the medium. This blue shift increases with increasing solvent polarity and decreasing the basicity indicating that the $S_0 \rightarrow S_1$ transition of $M-NH_2$ dye is of π - π^* character [17].

The effect of solvent polarity and viscosity on the fluorescence quantum yield (ϕ_f) of the M-NH₂ dye was studied. As gathered from Table 2 the fluorescence quantum yield (ϕ_f) of the M-NH₂ dye is strongly quenched in solvent of greater polarity and/or low viscosity. The dramatic decrease in (ϕ_f) of M–NH₂ as the solvent polarity increases, is observed on going from pyridine $(\phi_{\rm f} = 0.24)$ to water $(\phi_{\rm f} = 0.04)$. This indicates clearly that a very efficient non-radiative decay channel opens which is related to the chargetransfer nature of the emitting state and which must involve a further increase in the excited solute dipolarity during the decay [18,19], On the other hand, the fluorescence quantum yield (ϕ_f) increases with increasing viscosity. For example, a $\phi_{\rm f}$ value as high as 0.747 is obtained in 1,2ethandiol ($\eta = 19.9$ cp.) but a low value of 0.155 is obtained in acetone ($\eta = 0.316$ cp.). This can be explained by the effect of the solvent bulk viscosity on the orientation of the dye within the solvation cage which is much effective in hindering molecular twisting [20] in 1,2-ethandiol than that in acetone.

3.2. pK_a and pK_a^* determination

The variation of the electronic absorption spectra ($c = 3 \times 10^{-5}$ mol dm⁻³) of M-NH₂ with pH is represented in Fig. 5a; these spectra exhibit a well-defined isosbestic point, indicating the existence of an acid-base equilibrium between two species of M-NH₂; the first one in which the lone-pair of electrons is free ($\lambda_{max} = 402$ nm) and the second one is the protonated M-N⁺H₃ in



Fig. 4. Linear relationship between $\Delta E_{\rm T}$ and β -scal for M–NH₂ in different solvents 1-2-porpanol. 2-DMSO, 3-Pyridine, 4-MeOH, 5-DMF, 6- 1,2-ethandiol, 7-Acetone, 8-CH₃CN and 9-water.

Table 2 Fluorescence quantum yield (ϕ_f) of (M–NH₂) dye measured in some different solvents

Solvent	$\eta_{(\mathrm{CP})}$	φ _f 0.043	
Water	0.890		
CH ₃ CN	0.345	0.110	
MeOH	0.547	0.120	
Acetone	0.316	0.155	
DMF	0.920	0.193	
Pyridine	0.940	0.246	
DMSO	2.200	0.272	
2-propanol	1.770	0.445	
1,2-ethandiol	19.900	0.747	

which the lone pair of electron is localized with a second positive charge present on the other heterocyclic nitrogen atom ($\pi_{max} = 330$ nm).

The pK_a value has been calculated from the following equation [21].

$$pH = pK_a + \log \frac{E - E_{\min}}{E_{\max} - E}$$

where E_{max} is the maximum absorbance of the protonated form $M-N^+H_3$ or $M-NH_2$ at a given wavelength, E_{min} is the minimum absorption, from the plot of $\log(E-E_{\text{min}}/E_{\text{max}}-E)$ versus pH as shown in Fig. 5b the p K_a was calculated as 3.35.

The effect of medium acidity on the emission spectrum has been studied in aqueous buffer solutions. As shown in Fig. 6, upon increasing the pH value the fluorescence intensity at $\lambda = 440$ nm decreases and the spectral pattern also changes. An isoemissive point is obtained at $\lambda = 400$ nm indicating an acid-base equilibrium in the excited state, the protonation constant of the excited state pK_a^* was calculated as 0.62 by applying the Förster cycle using the following relation [22].

$$pK_a - pK_a^* = 2.1 \times 10^{-3} (\bar{v}_{BH^+} - \bar{v}_B)$$

The quantities \bar{v}_{BH^+} and \bar{v}_B represent the wavenumbers of pure electronic transitions of the acid and conjugate base, respectively.

3.3. Effect of micelle

The emission spectrum of M–NH₂ ($c = 3 \times 10^{-5}$ mol dm⁻³) has been measured at different concentrations of SDS (anionic micelle). The fluorescence intensity increases substantially as the surfactant concentration increases, with a break at a SDS concentration of $c = 8.1 \times 10^{-3}$ mol dm⁻³, that coincides well with the critical micelle concentration (CMC) of SDS [23]. The role of SDS micelles in enhancing fluorescence emission is explained in terms of the increased medium



Fig. 5. (a) UV–Vis absorption spectra of M–NH₂ dye ($c = 3 \times 10^{-5}$ mol dm⁻³) in aqueous buffer solutions (handled only in dark). (b) Determination of pK_a value of M–NH₂ dye ($c = 3 \times 10^{-5}$ mol dm⁻³) in aqueous buffer solutions (λ_{exc} = 330 nm).



Fig. 6. Fluorescence spectra of $M-NH_2$ dye ($c = 3 \times 10^{-5}$ mol dm⁻³) in aqueous buffer solutions $\lambda_{exc.} = 330$ nm).

viscosity accompanying micellization [23] as well as the increased molecular dispersion of the fluorescer with subsequent minimization of molecular aggregation that causes emission quenching.

3.4. Photoisomerization of $M-NH_2$

Upon irradiation of the M–NH₂ dye ($c = 3 \times 10^{-5}$ mol dm⁻³) in aqueous buffer solution of pH 1.1 at room temperature ($\lambda_{irr} = 366$ nm, $I_0 = 5.3 \times 10^{10} E_{in}$ cm⁻² s), the absorption spectrum changes and shows an isosbestic point, finally reaching a photostationary state. The long-wave length absorption maximum of the photoproduct is displaced to shorter wavelengths than that of the trans-isomer. The photoproduct is assigned to the cis-isomer in accordance with the results of a previous work [1], UV–Vis absorption spectra of the trans and cis isomers in aqueous buffer, pH 1.1, are shown in Fig. 7. By using the modified Blance and Ross method [24], the quantum yield of the trans \rightarrow cis photoisomerization is calculated



Fig. 7. UV–Vis absorption spectra of M–NH₂ dye ($c = 3 \times 10^{-5}$ mol dm⁻³) in buffer solution pH 1.1 at different times of irradiation ($\lambda_{irr} = 366$ nm).

as $\phi_{t\to c} = 0.61$ and $\phi_{c\to t} = 0.49$. At the photostationary state the proportion of cis to trans was found to be 64:36, Steiner [25] has noticed that there is an analogy in the structure of the protonated merocyanine dye and stilbene in their photochemical trans \rightarrow cis isomerization reaction and in quantum yield. It was suggested that a phantom state is present in the protonated form at a 90° twisted conformation of the excited state by which the deactivation process can occur to either trans or cis ground state.

References

- S.T. Abdel-Halim, M.K. Awad, J. Phys. Chem. 97 (1993) 3160 (and references there in).
- [2] W. Arden, P. Fromherz, J. Electrochem. Soc. 127 (1980) 372.
- [3] O. Inacker, H. Kuhun, D. Möbius, G. Debuch, Z. Phys. Chem. 101 (1976) 337.
- [4] K. Othmer, Encycl. Chem. Technol. 6 (1985) 122.
- [5] F. Sieber, J.L. Spivak, A. Sutctiffe, Proc. Natl. Acad. Sci. USA 81 (1984) 7584.
- [6] D.J. Williams (Ed.), Nonlinear Optical Properties of Organic and Polymeric Materials. ACS Symposium Series 233, American Chemical Society, Washington DC, 1983.
- [7] A. Grinwald, R.D. Frosting, E. Lieke, R. Hildesheim, Phys. Rev. 8 (1985) 263.

- [8] L.M. Loew, S. Saully, L. Simpson, A.S. Waggoner, Nature 281 (1979) 497.
- [9] H.T.S. Britton, Hydrogen Ions, Second ed., Chapman & Hall, London, 1952.
- [10] M.H. Abdel-Kader, U. Steiner, J. Chem. Educ. 60 (1983) 160.
- [11] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (1971) 1001.
- [12] E. Lippert, F. Moll, Ber. Bunsenges. Phys Chem. 58 (1954) 718.
- [13] M.J. Kamlet, J.L. Abboüd, R.W. Taft, J. Am. Chem. Soc. 100 (1978) 377.
- [14] M.J. Kamlet, J.L. Abboüd, R.W. Taft, J. Am. Chem. Soc. 99 (1977) 6027.
- [15] E.M. Kosower, J. Am. Chem. Soc 80 (1958) 3253.
- [16] E.M. Kosower, An Introduction to physical organic chemisty, Wiley, NY, 1968.

- [17] C. Reichardt (Ed.), Solvents and Solvent Effects in Organic Chemistry, Second ed., VCH, Verlagsgesellschatt, MBH, Weinheim, 1988, p. 285.
- [18] J.D. Cowley, I. Pasha, J. Chem. Soc. Perkin Trans. 2 (1981) 918.
- [19] J.D. Cowley, E. Okame, R.S.T. Todd, J. Chem. Soc. Perkin Trans. 2 (1991) 1495.
- [20] E.M. Ebeid, M.H. Abdel-Kader, R.M. Issa, S.A. El-Daly, Chem. Phys. Lett. 146 (3.4) (1988) 331.
- [21] J. Blance, D.L. Ross, J. Phys. Chem. 72 (1968) 2819.
- [22] S.G. Schulman, in: E.L. Wehry (Ed.), Modern Fluorescence Spectroscopy, vol. 2, Plenum Press, New York, 1976.
- [23] C.A. Bunton, Progr. Solid State Chem. 8 (1973) 293.
- [24] J. Blance, D.L. Ross, J. Phys. Chem. 72 (1968) 2617.
- [25] U. Steiner, M.H. Abdel-Kader, P. Fisher, H.E. Kramer, J. Am. Chem. Soc. 100 (1978) 3190.