



Spectroscopic Behaviour Of 1-Methyl-4-[4-Aminostyryl] Pyridinium Iodide In Cyclodexterins



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ABSTRACT

The electronic absorption and emission spectra of 1-methyl-4-[4-aminostyryl] pyridinium iodide(M-NH₂) were measured in cyclodexterins(CDs) of different cavity sizes. The binding constant k_b of inclusion complex was found to be 67.03 M⁻¹ for (dye- α -CD), 419.7 M⁻¹ for(dye- β -CD) and 1134.8 M⁻¹ for(dye- γ -CD). The fluorescence quantum yield is sensitive to diameters of cyclodextrin and was found to be 0.183, 0.129 and 0.114 in α -CD, β -CD and γ -CD, respectively. The quantum yield of the cis-trans photoisomerization was also determined in CD at pH=1.1 and was found to be Φ_{t-c} =0.62 and Φ_{c-t} =0.37 The ground state and excited state protonation constants were calculated in sodium dodecyl sulphate(SDS) and amounted to 3.95 and -10.24, respectively. © 2007 Trade Science Inc. - INDIA

KEYWORDS

1-Methyl-4-[4-aminostyryl]
pyridinium iodide;
Cyclodextrins;
Effect of acidity;
Fluorescence quantum yield;
Photoisomerization.

INTRODUCTION

Cyclodextrins(CDs) are cyclic oligosaccharides that have a truncated coneshaped structure. Three prototypical and commonly available CDs consisting of 6, 7 or 8 glucose units are designed as α -CD, β -CD and γ -CD, respectively^[1]. These CDs form a hydrophobic cavity with different diameters: α -CD with a 5.7 Å cavity, β -CD with a 7.8 Å cavity, and γ -CD

with a 9.5 Å cavity^[2]. The most remarkable property of cyclodextrins is their ability to form inclusion complexes with a verity of organic and inorganic molecules in aqueous solutions. Geometric rather than the chemical factors are decisive in determining the kind of guest molecules which can penetrate into the cavity.

If the guest is too small, it will easily pass in and out the cavity with little or no bonding at all, complex formation with guest molecules significantly

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larger than the cavity may also be possible but the complex is formed in such a way that only certain groups or side chains of the guest penetrate into the cyclodextrin cavity. The stability of an inclusion complex also depends on the polarity of the guest molecules. Only substrates that are less polar than water can form inclusion complexes with cyclodextrins. The stability of a complex is proportional to the hydrophobic character of the guest molecules^[3]. The high electron density prevailing inside the cyclodextrin cavity can mobilize the electrons of the included guest molecules, resulting in changes of its various spectral properties and also of cyclodextrin itself^[4]. Photophysical properties of various guest molecules have been studied^[5-12]. Merocyanines are well known to function as solvatochromic and photoreactive compounds which are also sensitive to medium acidity^[13]. Due to these properties they are potentially useful in many areas such as solar energy conversion^[14,15], photosensitizers^[16], phototherapy^[17], in laser doublers and as liquid crystals^[18]. Merocyanine dyes are also useful as electrochromic compounds for membrane potentials and high voltage sensitivity^[19,20].

In a previous paper we studied the effect of medium polarity and acidity on the photophysical and photochemical behavior of M-NH₂ dye^[21]. In the present article, it is attempted to study the spectral behaviour of 1-methyl-4-[4-aminostyryl] pyridinium iodide (M-NH₂) in the presence of cyclodextrins

EXPERIMENTAL

1-Methyl-4-[4-aminostyryl]pyridinium iodide was synthesized by refluxing 4-aminobenzaldehyde with 1-methyl-picolinium iodide in ethanol for 2hr. The brown precipitate was filtered and recrystallized several times from water containing traces of KOH. The purity of the dye was checked by thin layer chromatography on silica gel 60, IR and ¹H NMR spectra as well as and by elemental analysis.

Cyclodextrins and sodium dodecyl sulphate (SDS) were fluka, puriss grade and used without further purification. UV-Vis absorption were recorded on a perkin-elmer lambda 17 spectrophotometer using matched 1cm quartz cells. The cell holder was equipped with a variable temperature thermostat by

using julbo thermo-bath U3. Steady state emission spectra were recorded on a Shimadzu RF-5000 spectrofluorophotometer 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 merocyanine dye^[22] in basic media, using λ_{ex} = 380 nm, where the dye has an absorbance less than 0.06 to avoid re-absorption of the emitted photons .

RESULTS AND DISCUSSION

Steady state absorption spectra

The electronic absorption spectra of 3×10^{-5} mol dm⁻³ of M-NH₂ dye were measured in H₂O and 1×10^{-2} mol dm⁻³ of α -, β - and γ -cyclodextrin cavities. An obvious shift in λ_{max} is obtained in the presence of cyclodextrins when going from water (λ_{max} = 402 nm) to α -CD (λ_{max} = 407 nm), β -CD (λ_{max} = 412 nm) and γ -CD (λ_{max} = 404 nm) as shown in figure 1. This indicates that the dye was inserted or partially inserted into the cavities. For γ -CD the absorbance of the dye is nearly the same as in water. This indicates that the dye is included in the cavity and surrounded by more water molecules or perhaps pass in and out of the cavity with little effect. For β -CD a relatively large difference is observed for both wavelength (about 10 nm) and absorbance between the dye in aqueous and in β -CD. This reveals that the dye was more included into the cavity and it exists in a more basic substrate obtained by the high electron density of the non-bonding electron pairs of the glycosidic oxygen

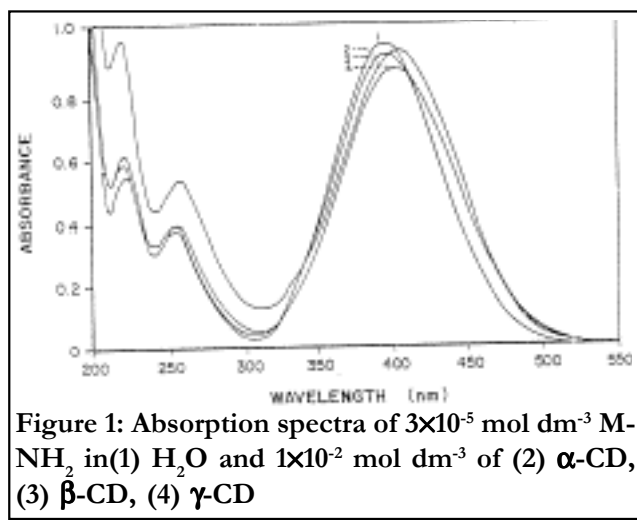
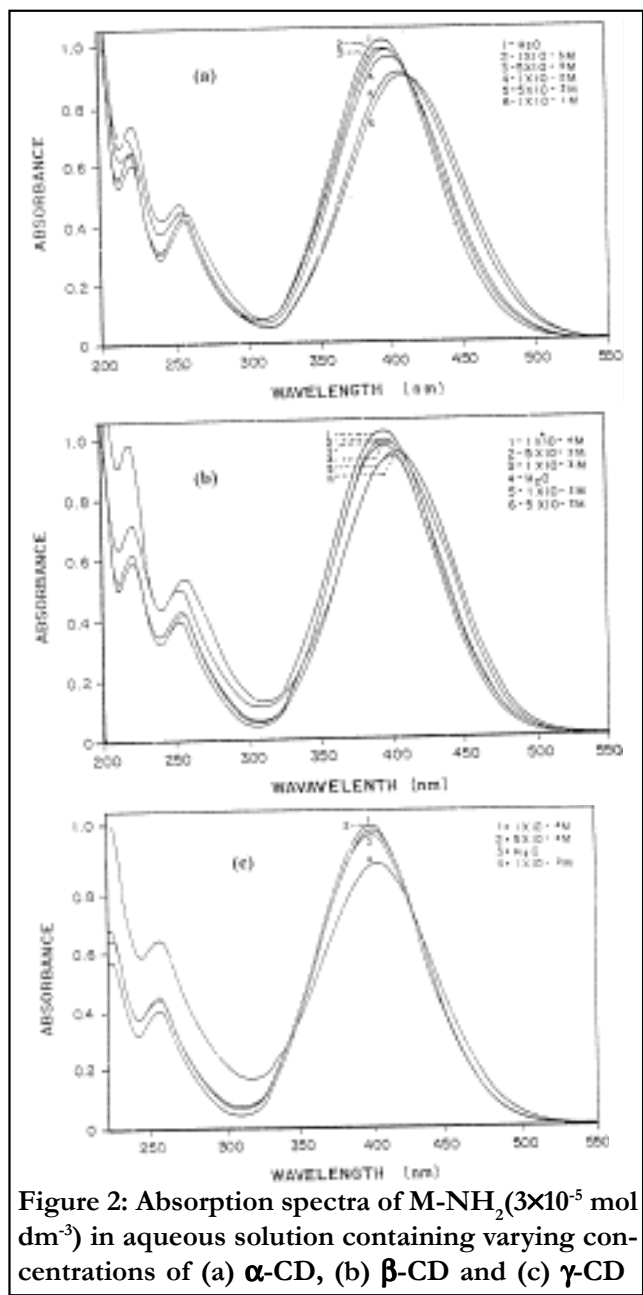


Figure 1: Absorption spectra of 3×10^{-5} mol dm⁻³ M-NH₂ in (1) H₂O and 1×10^{-2} mol dm⁻³ of (2) α -CD, (3) β -CD, (4) γ -CD

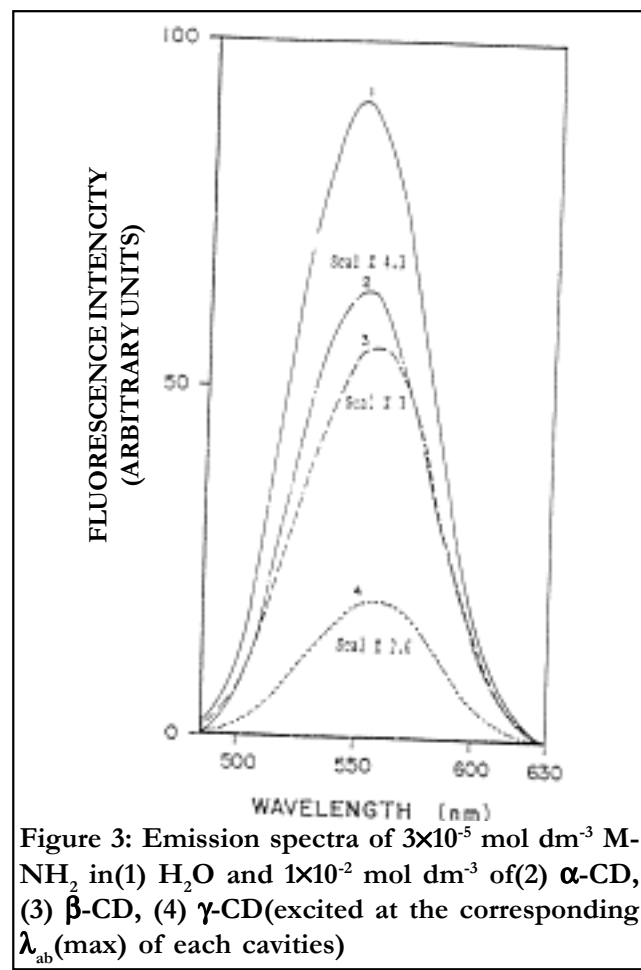


bridges which are directed towards the inside of the cavity. For α -CD there is a slight difference in wavelength (about 5 nm) but the absorbance is less than those of β -CD and γ -CD in aqueous solution. It seems that the M-NH₂ dye is partially inserted into α -CD. Figure 2 illustrates absorption spectra of M-NH₂ dye in aqueous solutions containing varying concentrations of α -, β -, and γ -CDs. As the CD concentration was increased the absorbance decreases and also a peak shift to lower energies was observed in case of α - and β -CDs. The absorption change can be attributed to the formation of inclusion complexes

consisting of M-NH₂ and CDs. Isostasy points were observed for α -, β - and γ -CD indicating that an equilibrium exists between M-NH₂, CDs and their inclusion complexes.

Steady state emission spectra

Figure 3 shows the fluorescence spectra of 3×10^{-5} mol dm⁻³ of M-NH₂ dye in aqueous solutions in the absence and presence of α -, β -, and γ -CD. Only one fluorescence band is observed which is attributed to the M-NH₂ monomer, also the M-NH₂ dye in aqueous solution exhibits a weak fluorescence intensity than that in cyclodextrins. This effect may be ascribed to the polarity of water which increases the polarity of dye and inhibits the delocalization of the lone pair of electron and the conjugation. The transfer of the dye from water to the nonpolar/semi-polar interiors of the cyclodextrin cavities would cause an increase in the fluorescence intensities and a blue shift in λ_{max} . Indeed one observes such enhanced intensities, 2.6 folds in case of γ -CD, 3 folds in case of β -



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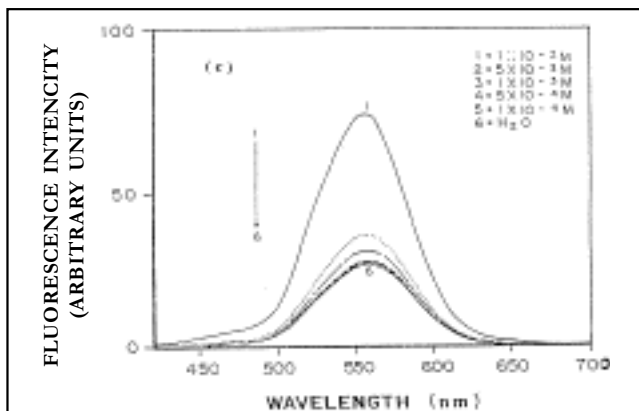


Figure 4: Emission spectra of $3 \times 10^{-5} \text{ mol dm}^{-3} \text{ M-NH}_2$ in aqueous solutions in the presence of γ -CD excited at 402 nm

CD and 4.3 folds in case of α -CD cavities. The fluorescence quantum yields were calculated in water and CD cavities and were found to be 0.043, 0.19, 0.13 and 0.12 in water, α -, β - and γ -CD, respectively. A significant increase of fluorescence quantum yield (ϕ_f) was observed in α -CD this is ascribed to the formation of a stable inclusion complex between M-NH₂ and α -CD. As a result of this the rotational freedom of the amino group is prevented and the polarity is decreased inside the CD cavity hence, the non-radiative rate is retarded in the α -CD cavity. Thus increase in the fluorescence quantum yield of M-NH₂ in the presence of α -CD is observed. The cavity diameter of γ -CD is much higher about 9.5 Å compared to α -CD (about 5.7 Å). So, the possibility of inclusion of M-NH₂ in γ -CD is much higher with respect to the α -CD from the consideration of size. The increase in fluorescence quantum yield on addition of γ -CD to the aqueous solution of M-NH₂ is much less compared to that of α -CD. Figure 4 shows the fluorescence spectra of M-NH₂ in different concentrations of CDs. The stability of the inclusion complex can be described in term of the binding constant k_b as defined by the following equation^[23]

$$1/(F - F_0) = 1/k_b(F_1 - F_0)[CD] + 1/(F_1 - F_0)$$

Where [CD] represents the analytical concentration of CD, k_b is the binding constant, F_0 represents the fluorescence intensity of free M-NH₂, F_1 is the fluorescence intensity of the inclusion complex and F is the observed fluorescence at its maximum. As shown in figure 5 plots of $1/(F - F_0)$ versus $1/[CD]$ for α -, β -, and γ -CD solutions yield straight lines, in-

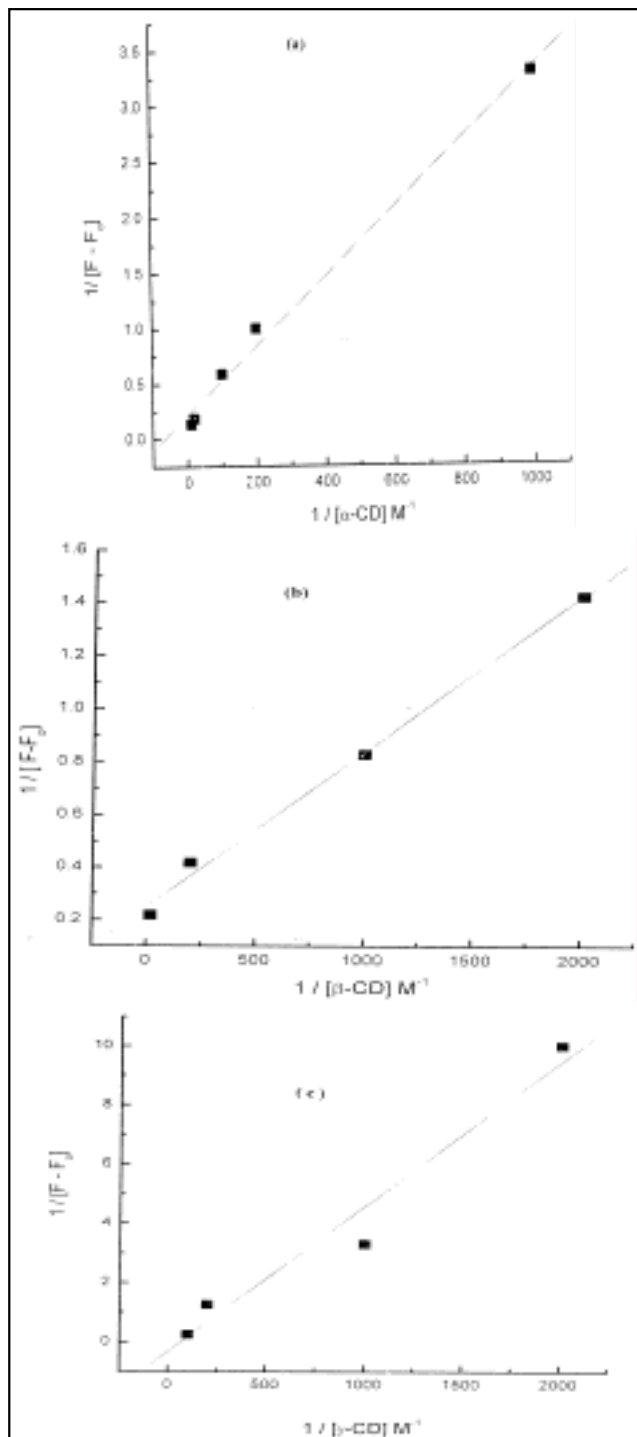


Figure 5: Benesi-Hildebrand plots for the emission of M-NH₂ in (a) α -CD, (b) β -CD and (c) γ -CD solutions

dicating that only 1:1 complexes exist in the system. The k_b values were obtained and found to be to be 67.03 M⁻¹ for (dye- α -CD) system, 417.9 M⁻¹ for (dye- β -CD) system and 1134.7 M⁻¹ for (dye- γ -CD) system. These data indicate that the value of the binding

constant k_b of the inclusion complexes depends markedly on the cavity size of α -, β -, γ -cyclodextrins.

Photoisomerization of M-NH₂

Upon photo irradiation of M-NH₂ dye ($c=3\times 10^{-5}$ mol dm⁻³) in 1×10^{-2} mol dm⁻³ α -CD of pH=1.1 at room temperature ($\lambda_{\text{irr}}=366$ nm, $I_0=5.3\times 10^{10}$ Ein.cm⁻² s⁻¹), the absorption spectra change and show an isosbestic point, finally reaching a photostationary. The long wavelength absorption maximum of photoproduct is displaced to shorter wavelengths than that of the trans-isomer. The photoproduct is assigned to a cis isomer in accordance with the experimental results given in a previous work^[13]. By applying the modified balance and ross method^[24], the quantum yield of trans-cis photoisomerization is calculated as $\phi_{t-c}=0.62$ and $\phi_{c-t}=0.37$. At the photostationary state the proportion of cis to trans was found to be 56:44. In aqueous buffer solution of pH=1.1 the proportion of cis to trans was found to be 64:36^[21]. These findings reveal that the trans form of M-NH₂ becomes more favored in -CD as a result of the tendency of the trans configuration to be stabilized through electrostatic forces in the cavities of α -CD. Steiner^[25] noticed that there is an analogy in the structure of the protonated merocyanine dye and stilbene in their photochemical trans-cis isomerization reaction and in quantum yield. It was suggested that a phantom state is 90° twisted conformation of the excited state by which the deactivation process can occur to either trans or cis ground state

Determination of ground and excited state protonation constants

Solubilization or adsorption of dye molecules in aqueous micellar solutions influences significantly the acid-base properties of the dye. The pKa of acid-base reactions in micellar media is influenced by the effective dielectric constant at the site of solubilization and by the effect of charge distribution of the dye concentrations in double layer. Solubilization of molecules in micellar media can also affect the excited state acid-base equilibria, since the protonation/deprotonation reaction of the excited state is diffusion controlled^[26]. All of these changes have been interpreted as due to the micellar viscosity effect. For this reason the dye in aqueous solution

shows complete equilibrium in the excited state, but in the micellar solutions, such as SDS micelles, only partial equilibrium occurs^[26].

For the determination the ground state pKa value of M-NH₂ dye in aqueous micelles of SDS, the electronic absorption spectra of 3×10^{-5} mol dm⁻³ solutions of the dye were measured in buffer solutions pH ranging from 1 to 5 containing 1×10^{-2} mol dm⁻³ SDS. It was found that the basic form exhibit an absorption band with ($\lambda_{\text{max}}=433$ nm) and the acid form has ($\lambda_{\text{max}}=335$ nm) as shown in figure 6. The pKa value was determined from the pH-absorbance curves by plotting $\log(E-E_{\text{min}})/(E_{\text{max}}-E)$ versus pH value^[27]. The pKa value was found to be 3.95. The protonation constant of the excited state pka^* was calculated using the following relation^[28]

$$pka - pka^* = 2.1 \times 10^{-3} (v'_{\text{BH}^+} - v'_B)$$

The quantities v'_{BH^+} and v'_B represent the wavenumber of pure electronic transitions in the acid and conjugate base, respectively. pka^* for M-NH₂ was found to be - 10.24 indicating the low basicity of M-NH₂ dye in the excited singlet state due to charge transfer from the amino group to pyridinium moiety. The fluorescence spectra of 3×10^{-5} mol dm⁻³ solutions of M-NH₂ dye containing 1×10^{-2} mol dm⁻³ SDS were measured in buffer solutions of varying pH (1 to 5) at an excitation wavelength equals 355 nm. AS can be seen from figure 7, the fluorescence spectra exhibit two broad emission bands with $\lambda_{\text{max}}=405$ nm and 560 nm. A well defined isoemissive point at 500 nm is observed, indicating the existence of an acid-

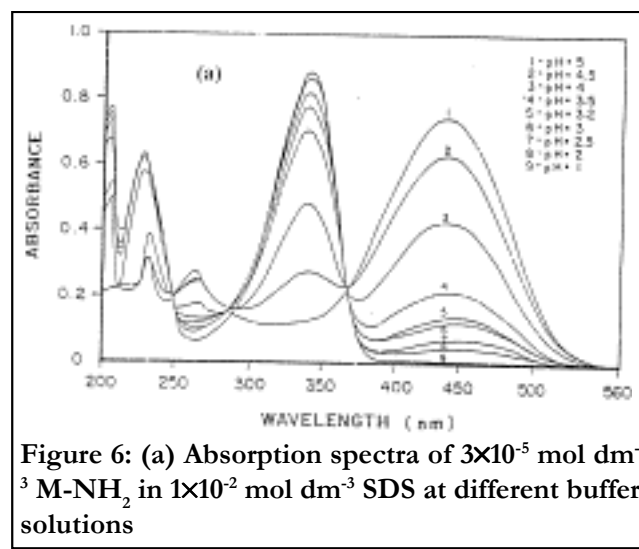


Figure 6: (a) Absorption spectra of 3×10^{-5} mol dm⁻³ M-NH₂ in 1×10^{-2} mol dm⁻³ SDS at different buffer solutions

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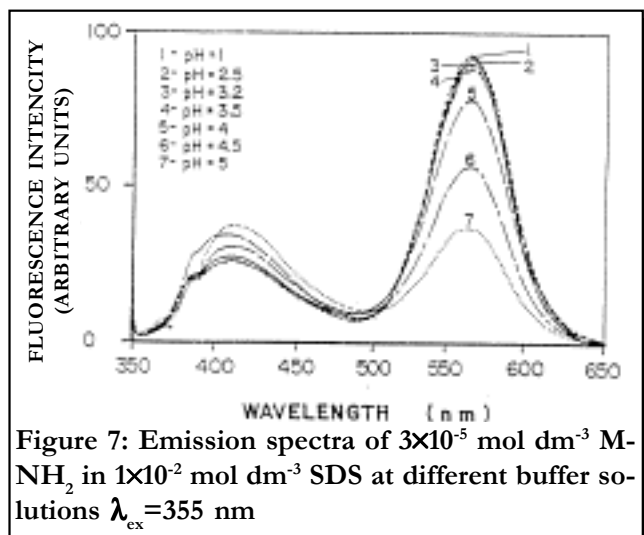


Figure 7: Emission spectra of $3 \times 10^{-5} \text{ mol dm}^{-3} \text{ M-NH}_2$ in $1 \times 10^{-2} \text{ mol dm}^{-3} \text{ SDS}$ at different buffer solutions $\lambda_{\text{ex}} = 355 \text{ nm}$

base equilibrium in the excited state. The intensity of the fluorescence band at 405 nm decreases whereas that of the band at 560 nm increases with decreasing pH value of the medium.

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