

Electronic absorption spectroscopic studies on the red form of methylene blue ion

A S N MURTHY and A P BHARDWAJ

Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India

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Abstract. The nature of the red form of methylene blue has been investigated by electronic absorption spectroscopy. The spectral characteristics of the blue form and red form of methylene blue have been interpreted in terms of a charge-transfer complex equilibria.

Keywords. Red form ; methylene blue ; electronic absorption spectra ; charge-transfer.

1. Introduction

There have been number of studies reported in the literature on the electronic absorption spectra of highly delocalised dye ions (Duff and Giles 1975) in water or alcohol as solvents. In water, for example, in the concentration range of 10^{-6} to 10^{-4} mol dm^{-3} , two major absorption bands appear which are concentration-dependent. The long wavelength band is termed as the monomer (*M*) band and low wavelength band as the dimer band (*D*). As the concentration further increases, another new band or shoulder (*H*-band) appears to the low wavelength side of *D* band. These bands have been interpreted in terms of an equilibrium involving the aggregation of dye ions. Thermodynamic data on the equilibria, as determined by relative variations of the intensities of *M* and *D* bands, are available on a few systems. The forces responsible for such an aggregation have been discussed in terms of hydrogen bonds, van der Waal's forces and hydrophobic bonding (Duff and Giles 1975). Studies in a limited variety of solvents of varying dielectric constants have been interpreted in terms of dye ion and counter ion interactions by McKay and Hillson (1965) and Blandamer *et al* (1967). The special role of water in the aggregation phenomenon has also been emphasised by Blandamer *et al* (1967). It has now been conclusively proved that dimerisation of Methylene Blue cation is strongly favoured in pure water.

During studies on solar photogalvanic cells containing Methylene Blue (MB hereafter) and triethylamine or triethanolamine, Murthy and Reddy (1979) noticed that a pink form of the dye was extracted into a non-aqueous layer from a binary

solvent mixture. We considered it interesting to investigate further this colour change. McKay (1966) observed similar colour changes when MB is dissolved in a few amine solvents and interpreted the "red form" of MB in terms of changes in electronic charge distribution of the dye ion in presence of amine. A new characteristic band has also been reported but the origin of the new electronic transition has not been discussed. Thus McKay's (1966) interpretation is inconclusive and we considered it interesting to make a systematic study of the spectral behaviour of the red form of MB ion. For this purpose, we studied the interaction of MB with *n*-butyl amine, ethylenediamine, ethanolamine, diethylamine, di-*n*-propylamine, di-isopropylamine, di-*n*-butylamine using methanol as solvent by electronic absorption spectroscopy.

2. Experimental

Methylene Blue (Eastman Kodak) was used without further purification. All the amines used in this investigation were kept with KOH pellets overnight and distilled under vacuum. Only middle fractions (at constant temperature) of the distillation were used for making the solutions. Methanol was purified by standard method (Riddick and Bunger 1970).

Electronic absorption spectra were recorded by a Pye Unicam SP 700 recording spectrophotometer. Measurement at other temperatures was carried out by Pye Unicam SP 770 constant temperature cell holder and SP 775 electrical controller. The temperature was kept constant to within $\pm 0.5^\circ\text{C}$. Some spectra were also obtained with Pye Unicam SP 500 Series 2 spectrophotometer. Optically matched 1 cm or 2 cm cells were used. The reference cell always contained the amine of known concentration dissolved in methanol. The stock solutions were freshly prepared and dilutions were carried out in either 25 ml or 10 ml standard flasks covered with black paper to prevent any photochemical decomposition. Also, the spectra were recorded immediately after preparing the solutions.

2. Results and discussion

In methanol, MB shows a high intensity ($\epsilon \sim 10^4$) band around 660 nm due to $\pi \rightarrow \pi^*$ excitation as shown in figure 1. The effect of addition of an amine, e.g., diethylamine to the methanolic solution of MB is also shown in figure 1. As can be seen from the figure, the addition of diethylamine decreases the intensity of 660 nm band and a new band appears at ~ 500 nm. The intensity of ~ 500 nm band increases with increase in concentration of amine. The spectra also show an isoabsorptive point at ~ 560 nm. The appearance of a new band at 500 nm and an iso absorptive point at 560 nm is a definite indication of the existence of a weak interaction between MB cation and amine. Similar spectra were obtained in other amines also.

In figure 2 is shown a plot of the frequency of new band at 500 nm against ionisation potential (I_D) of electron donors employed in this study. The linear dependence between these two further confirms that an interaction occurs between the amines and MB cation. Thus, the colour change upon mixing, the appearance of a new band, and proportionality between ionisation potential and frequency

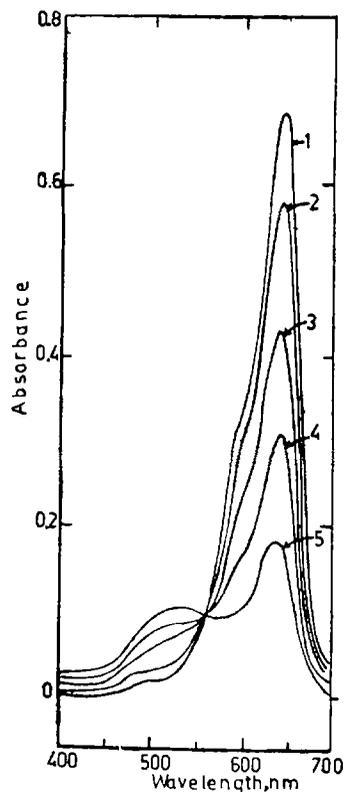


Figure 1. Electronic absorption spectrum of methylene blue ion (1.2×10^{-5} mole dm^{-3}) in methanol with varying concentrations of diethylamine, 1. 0.0 mole dm^{-3} ; 2. 0.01 mole dm^{-3} ; 3. 0.03 mole dm^{-3} ; 4. 0.05 mole dm^{-3} ; 5. 0.08 mole dm^{-3} .

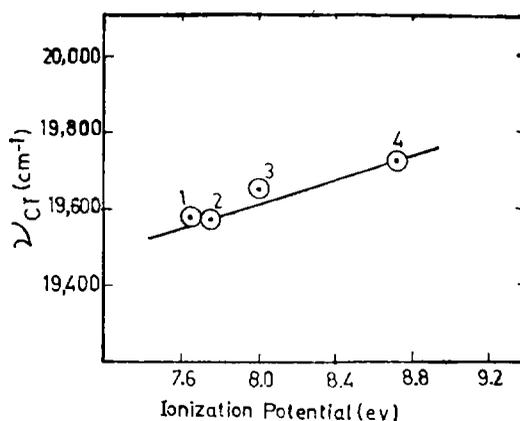


Figure 2. Plot of ionisation potential (eV) of amines against charge transfer frequency (cm^{-1}); 1. Di-*n*-butylamine, 2. Di-isopropylamine, 3. Diethylamine, 4. *n*-Butylamine.

of the new band in MB-donor systems indicate that the interaction is possibly by a charge transfer mechanism and the complex may be termed as a charge transfer complex. One would expect the possibility of such a type of interaction as MB is positively charged and could act as an electron acceptor. The slope of $h\nu_{CT} - I_D$ plot is, however, quite low indicating thereby a weak charge transfer interaction.

If the interaction between MB and amines does involve charge transfer, then according to Mulliken's charge transfer theory, the charge transfer frequencies for a series of electron donors with MB should correlate with frequencies of charge transfer complexes of the same set of donors with a second acceptor molecule. In figure 3 is shown a plot of the frequencies of MB with various donors against the charge transfer maxima of the same donors with I_2 as acceptor. Despite the fact that the solvents are different in both cases, the correlation is good. This demonstrates that charge transfer forces are major contributing forces in the interaction between MB and amines. While charge transfer forces are important, the contribution of electrostatic forces cannot be ruled out in explaining the stability of the dye-amine complex (Person 1973). We could not, however, estimate the relative contributions of both by the present experimental data.

Now considering these systems as charge transfer complexes, we next proceeded to obtain quantitative data on the equilibrium properties of these systems. In all the systems studied, the concentration of the amine was greater than that of MB. From changes in extinction coefficient of the 660 nm band as a function of the concentration of amine, the equilibrium constant was calculated by using the equation of Baba and Suzuki (1961)

$$\frac{1}{(A_f - A)} = \frac{1}{KD(A_f - A_b)} + \frac{1}{(A_f - A_b)}$$

Here A_f is the absorbance of free MB molecule, A is the absorbance for a solution in which the initial concentration of amine is D and A_b is the absorbance of complexed species. A plot of $1/(A_f - A)$ against $1/D$ gave a straight line (figure 4) and equilibrium constants were calculated from the slope and intercept. The equilibrium constants (and $-\Delta G^\circ$) are shown in table 1. The uncer-

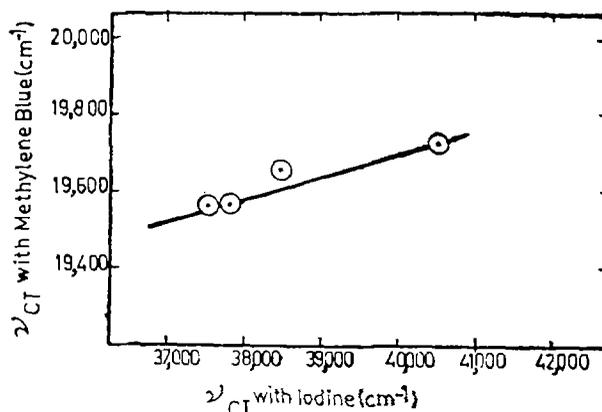


Figure 3. Interrelationship of the frequency of maxima for CT complexes of methylene blue and iodine with the same set of donors.

Table 1. Thermodynamic and spectroscopic data on methylene blue amine systems.

Electron donors	Ionisation ^a potential (eV)	pK_b^b	ν_{CT} (cm^{-1})	K ($\text{dm}^3 \text{mol}^{-1}$)	$-\Delta G^\circ$ (KJ mol^{-1})
<i>n</i> -Butylamine	8.71	3.39	19725	6.50 (24.0° C)	4.65
Ethylenediamine	..	3.94	..	6.20 (21.5° C)	4.50
Ethanolamine	..	4.56	..	1.30 (23.8° C)	0.60
Diethylamine	8.01	2.90	19645	22.50 (28.0° C)	7.80
Di- <i>n</i> -propylamine	..	3.09	..	16.90 (24.0° C)	7.00
Di-isopropylamine	7.73	2.80	19570	14.80 (31.6° C)	6.80
Di- <i>n</i> -butylamine	7.69	3.40	19570	8.00 (27.6° C)	5.20

^a Gold V (1966); ^b Riddick and Burger (1970).

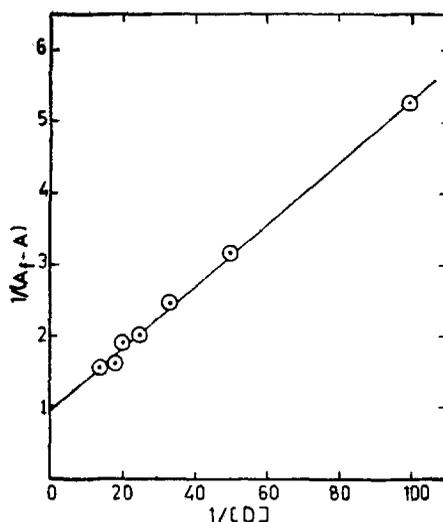


Figure 4. A typical plot for the calculation of equilibrium constant for methylene blue-diethylamine.

tainty in equilibrium constant values is about 5%. The equilibrium constants are low and vary in the range 1.0–22.5 $\text{dm}^3 \text{mol}^{-1}$, thereby indicating that the systems under study are weak charge transfer complexes. A plot of $-\Delta G^\circ$ for the complexes against pK_b values of amine is linear (figure 5) again showing that it is an electron donor-acceptor type interaction with some charge-transfer,

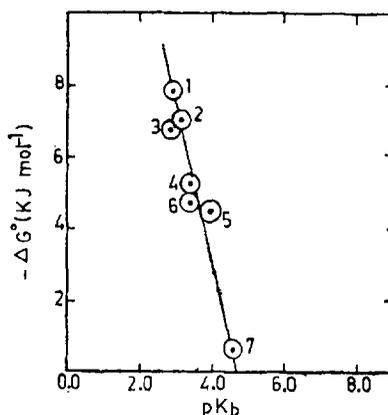


Figure 5. Interrelationship between ΔG° of complexes with pK_b of amines : 1, Diethylamine, 2. Di-*n*-propylamine, 3. Di-isopropylamine, 4. Di-*n*-butylamine 5. Ethylenediamine. 6. *n*-Butylamine. 7. Ethanolamine.

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