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Studies of UV Spectra of Methylene Blue Dye

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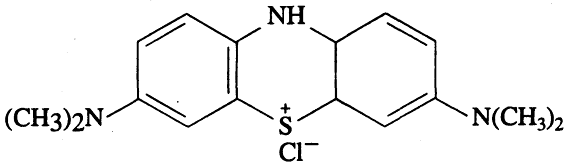
Spectrophotometric studies of methylene blue dye (3,9-bis-dimethyl amino phenazothionium chloride) with solvents like chloroform, water, acetone and amyl alcohol of different polarity have shown the existence, in each case, of a new intense long wave length absorption band in the range of 640–700 nm of the visible region. Such band has been tentatively assigned as charge transfer band due to interaction between Zn ion and phenazothionium ion. The oscillator strength and some spectral characteristics of solute-solvent interaction have also been determined and it has been found that observed red shift of such long wavelength band of methylene blue molecule in solvents in the order of chloroform-water-acetone and amyl alcohol is exactly of the order of their dipole moment values. The oscillator strengths determined seem to be inversely related with the dipole moments.

Key Words: UV-spectrophotometry, Methylene blue dye.

INTRODUCTION

The methylene blue (a class of phenthia zinc dyes) has been known to absorb at 665 nm in almost visible range[1,2]. This typical compound is produced from *p*-aminodimethyl aniline by the action of sodium thiosulphate and sodium dichromate in presence of zinc chloride[3]. The UV spectra of methylene blue in water and with organic solvents differ to such extent that some authors[4–8] could guess of a role of strong hydrogen bonding in shifting of long wavelength absorption band. However, the real position of non-bonding electrons and conjugated system of the molecule is not yet clear. Because of this situation we have tried to measure the effects of four different solvents on the ultraviolet spectrum of methylene blue. Such studies seems to be useful in bringing transitions and ultimately to evaluate the oscillator strength, the probability of electronic transitions and we believe that it provides good evidence of the nature of orbital involved.



METHYLENE BLUE

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EXPERIMENTAL

Methylene blue is an easily soluble compound and we have selected four solvents, *i.e.* chloroform, water, acetone and amyl alcohol for present studies. The solutions of methylene blue of known concentration were prepared by weighing proper amounts of methylene blue and dissolving in the appropriate amount of selected solvents.

A himadzu UV-Vis (model 160 A Japan) double beam spectrophotometer with automatic recording device was used and the spectra scanned through 200 nm to 1100 nm with an accuracy of 0.1 nm at room temperature using silica cell. The spectra were obtained in the shape of broad bands as plots of transmittance against wavelength and the positions of maxima wave absorption (λ_{max}) were estimated from the centre of symmetry of the graph. In case these graphs went beyond the scale the solutions were diluted such that the peak position fall within the desired range.

Extinction coefficients (ε) were calculated of each wavelength using the Beer's law equation. After converting the λ's into wavenumbers (ν cm^{-1}) values of ε were plotted against ν. The area under the curves (ε vs ν) calculated from the product $\varepsilon \times 1/2$ band width gave the value of the integrated absorption intensity I_a for the transition in the molecule. From the ratio $I_{(obs)}/I_{(theo)}$ the values of oscillator strength of the transitions were calculated[9].

RESULT AND DISCUSSION

The spectra of methylene, blue have been recorded in four different solvents, *i.e.*, acetone, water, chloroform and amyl alcohol. The absorption of bands are tabulated be seen in Table-1. A long wavelength band which appears in the range of 658 to 684 nm and another band of the molecule is also observed at 291, 294, 291 and 336 nm in amyl alcohol, chloroform, water and acetone respectively. The solution of methylene blue is known to asorb at 665 nm but in our case methylene blue in water exhibits a strong band at 658 nm and in organic solvents this shifts towards longer wavelengths, *i.e.*, 662, 684 and 693 nm in chloroform, acetone and amyl alcohol respectively. Thus we find that there is an increasing red shift in the order chloroform→water →acetone → amyl alcohol which is exactly the order of the dipole moment values of above solvents *i.e.*, 0.43, 1.85, 2.72 and 2.86 D units[10] of chloroform, water, acetone and amyl alcohol respectively.

TABLE-1
LIST OF BANDS OF METHYLENE BLUE IN SOME SUITABLE SOLVENTS

S. No.	λ_{max} (in nm)	Absorbance	Solvents	Concentration
1.	684	2.494	Acetone	0.048
	336	0.995	Acetone	0.048
2.	668	2.492	Water	0.032
	291	1.793	Water	0.032
3.	652	1.550	Chloroform	0.032
	294	0.791	Chloroform	0.032
4.	658	2.487	Amyl alcohol	0.032
	291	1.715	Amyl alcohol	0.032

TABLE-2
MOLAR EXTINCTION COEFFICENT (ε) AT DIFFERENT FREQUENCIES FOR BANDS OF METHYLENE BLUE IN ACETONE SOLVENT

Concentration (c) = 0.048/473.88 g mole/L
path length (l) = 1 cm and $1/c \cdot l = 473.88/0.048 = 9872.5$ g mol cm^{-1}

$\nu(\text{cm}^{-1})$	$A = \log I_0/I$	$\varepsilon = 1/c. \times \log I_0/I$	$\nu(\text{cm}^{-1})$	$A = \log I_0/I$	$\varepsilon = 1/c. \times \log I_0/I$
For band (a)			For band (b)		
14200	2.075	20487.25	25500	0.100	987.25
14700	2.312	22822.015	26000	0.150	1480.87
15200	2.400	23694.00	26500	0.380	2468.12
15700	2.390	23595.27	27000	0.480	3751.55
16200	2.370	23397.02	27500	0.520	5133.70
17200	1.790	6671.77	28500	0.690	5528.60
17700	0.674	4936.25	29000	0.795	6812.14
18200	0.310	3060.47	29500	0.995	9823.14
			30000	0.975	9629.00
			30500	0.304	3208.56
			31000	0.355	3504.70
			31500	0.223	2209.00

TABLE-3
MOLAR EXTINCTION COEFFICENT (ε) AT DIFFERENT FREQUENCIES (cm^{-1}) FOR THE BAND OF METHYLENE BLUE IN WATER

Concentration (c) = 0.032 g/L = 0.032/473.88 g mole/L
Path length (l) = 1 cm and $1/l \cdot c = 1 \times 473.88/0.32 = 14808.75$ g/mole^{-1} cm^2

$\nu(\text{cm}^{-1})$	$A = \log I_0/I$	$\varepsilon = 1/c \cdot l \times \log I_0/I$	$\nu(\text{cm}^{-1})$	$A = \log I_0/I$	$\varepsilon = 1/c \cdot l \times \log I_0/I$
For bond (a)			For bond (b)		
13300	0.050	740.43	25300	0.075	1110 .65
13800	0.100	1480.87	27300	0.075	1110.65
14300	0.500	7404.37	27800	0.091	1347.59
14800	1.750	25914.00	28300	0.100	1480.87
15000	2.495	36945.96	28800	0.150	2221.31
16300	1.650	24434.48	29300	0.200	2961.75
16800	0.820	12143.17	30300	0.450	6663.93
17300	0.500	7404.37	31300	0.520	7770.55
17800	0.450	6663.93	32300	0.740	10958.47
18300	0.350	5183.06	33300	1.250	18510.93
18800	0.310	4590.71	34300	1.793	26552.08
19300	0250	3702.18	35300	1.200	17770.50
19800	0.190	2813.66	36300	0.490	7256.28
20300	0.150	2221.31	37300	0.250	3709.00
20800	0.100	1480.87	—	—	—

TABLE-4

MOLAR EXTINCTION COEFFICENT (ε) AT DIFFERENT FREQUENCIES (cm^{-1}) FOR BANDS OF METHYLENE BLUE IN CHLOROFORM

Concentration (c) = 0.032 g/l = 0.032/473.88 g mole/L
Path length (l) = 1 cm and $1/c \cdot l = 1 \times 473.88/0.032 = 14808.75$ g/mole^{-1} cm^2

ν(cm^{-1})	A = log I_0/I	$\varepsilon = 1/c. \times \log I_0/I$
14300	0.041	507.28
14800	0.520	7700.55
15300	0.550	22953.56
15800	0.000	14808.75
16300	0.750	11106.56
16800	0.590	8737.16
17800	0.250	3702.18
20000	0.021	310.98
29400	0.081	1199.50
30400	0.220	3257.92
31400	0.250	3702.18
32400	0.310	4590.71
33400	0.490	7256.28
34000	0.791	11713.72
35000	0.230	6071.58
36000	0.230	3406.01
37000	0.210	3109.83

TABLE-5

MOLAR EXTINCTION COEFFICENT (ε) AT DIFFERENT FREQUENCIES (cm^{-1}) BANDS OF METHYLENE BLUE IN AMYL ALCOHOL SOLVENT

Concentration (c) = 0.032 g/L = 0.032/473.88 g mole/L
Path length (l) = 1 cm and $1/c \cdot l = 1 \times 473.88/0.032 = 14808.75$ g/mole^{-1} cm^2

For band (a)			For band (b)		
ν(cm^{-1})	A = log I_0/I	$\varepsilon = 1/c \cdot l \times \log I_0/I$	ν(cm^{-1})	A = log I_0/I	$\varepsilon = 1/c \cdot l \times \log I_0/I$
13900	0.050	740.43	28500	0.150	2222.81
14400	0.190	2813.66	29000	0.240	3556.50
14900	0.480	7108.20	29500	0.310	4590.71
15200	2.487	366829.36	30000	0.420	6219.67
15400	2.120	31394.55	31000	0.500	7404.37
15900	1.210	17918.58	32000	0.710	10514.21
16400	0.750	11114.06	33000	1.010	14956.83
16900	0.420	6228.87	34500	1.715	25395.00
17400	0.250	3704.68	35000	1.240	18362.85
			36000	1.000	14808.75
			37000	0.770	11402.73

It is therefore, concluded that these bands have their origin in the π–π^*transition which leads to highly polar excited state and a consequent strong interactin with the solvent polarity. Qualitatively this may be understood in terms of the following energy level diagram of π–π* molecular orbitals.

The spectra of methylene blue in each solvent show another band in shorter wavelength (UV region). In acetone it appears at 336 nm in water and amyl alcohol at 291 nm and in chloroform at 294 nm respctively. This shows a strong solvent effect in water, chloroform and amyl alcohol with respect to acetone which is in all probability due to hydrogen bonding between solute-sovent interaction. If the transition involved nonbonding electrons of the nitrogen atoms to the π* orbital the ground state would be more stabilized than the excited state leading to blue shift. Water and alcohol are known to have good hydrogen bonding power but acetone does not have. Such explanation is consistent with our observations.

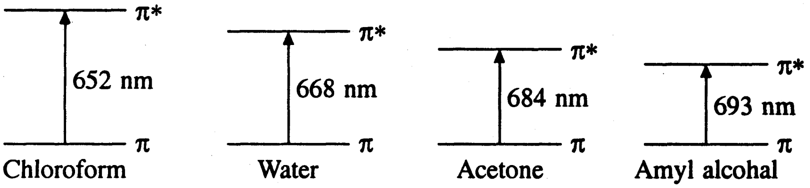

Table 6 gives the values of oscillator strength of methylene blue in different solvents. We have found that the oscillator strength (O.S.) of the compound in chloroform is greater than other solvents. The values of O.S. of methylene blue and the dipole moment values of the solvents are given below from which we can safely conclude that the lesser the dipole moment values of the molecule in the solvent, higher is the oscillator strength.

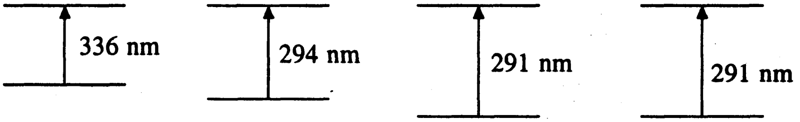

TABLE-6

LIST OF ELECTRONIC ABSORPTION SPECTRA OF METHYLENE BLUE FOR DIFFERENT BANDS IN DIFFERENT SOLVENTS

Sl. No.	Solvents	ν_{max} (cm^{-1})	1/2 ε_{max}	$1/2\varepsilon_{max}\,\Delta\nu \times 10^8$ cm	F = (O.S.) $1 \times 4.315 \times 10^{-9}$
1.	Acetone	16000	3000	0.4800	0.2071
		29500	5000	1.4750	0.6346
2.	Water	15400	3000	0.4620	0.1993
		34300	6500	2.2295	0.9620
3.	Chloroform	15300	3000	0.4590	0.1981
		34300	6700	2.2780	0.9829
4.	Amyl alcohol	15500	1500	0.2325	0.1003
		34300	3000	1.0290	0.4401

	Chloroform	Water	Acetone	Amyl alcohol
O.S.	0.9829	0.9620	0.6346	0.4401
D.M.	0.4300	1.8500	2.7200	2.8600 (DU)

As the magnitude of the oscillator strength for a particular absorption measures this probability of the particular electronic transition, the more probable a given transition the larger is the extinction coefficient. In addition, the probability of transitions is related to the dipole moment[11] of transition of the molecule. We know that absorption of radiation by a molecule is possible only when the dipole moment changes. The more symmetrical the molecule the smaller is the possibility of dipole moment and, therefore, the less likely is the molecule to absorb radiation[12]. But in our case lesser the dipole moment higher is the oscillator strength of the molecule.

Such situation requires critical explanation and needs a new resonance path to be introduced.

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