CHAPTER-III
RESULTS AND OBSERVATIONS

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✓ The effect of concentration variation of dye complex salt on the absorption spectra has been studied in different alcohols. The results are given table 1-8. The fig 1-8 represent the absorption spectra of complex salt in different alcohols under study in the visible range i.e. 400 nm to 800 nm. The spectra were recorded in the same concentration range $4 \times 10^{-5}M$ to $4 \times 10^{-4}M$ and in the same wave length range i.e. 400 nm to 800 nm at room temperature kept constant at $30^{o}C$, for all alcohols under study. The spectra are seen to exhibit four absorption bands at wavelengths, around 420 nm (λ_1) 525 nm (λ_2), 550 nm (λ_3) and 620 nm (λ_4).

The peaks at λ_2 and λ_3 are corresponding to rose bengal (R.B.) component and that at λ_1 and λ_4 are corresponding to malachite green (MG) component. These results are similar to those reported by Kausha-bayashi et. al.[1]. For comparison, the effect of solvent variation on the absorption spectra of complex, at a concentration of $1.6 \times 10^{-4}M$ is given in table 10.

The absorption intensities at λ_1, λ_2, λ_3 and λ_4 are designated as I_1, I_1, I_3 and I_4 and corresponding extinction coefficient (E) values as E_1, E_2 E_3 and E_4 respectively.

Table (9) shows absorption intensities for pure malachite green (3.2 x 10^{-4}M) and pure rose bengal (1.6 x 10^{-4}M). These concentrations are equivalent to a concentration 1.6 x 10^{-4}M of the complex. It has been reported earlier that the absorption peak of rose bengal around 550 nm (λ_3) is due to its monomeric form, and that around 525 nm to (λ_2) is due to its dimeric form [2]. Malachite green shows absorption peaks near 420 nm (λ_1) and 620 nm (λ_4) [3].

The absorption spectra of the complex salt at different concentrations in a given solvent were studied. Methanol, the lowest homologue of the alcohol series was selected for this purpose. From preliminary experiments, it was observed that below concentration range of about 4 x 10^{-5}M, the absorption spectra were very weak and cannot be recorded in a meaningful way. Similary at concentrations higher than about 4 x 10^{-4}M, the absorption spectra showed very high intensities of absorption (absorbance > 6) and absorption spectra could not be recorded.

Hence, for the present study, concentration of the complex in methanol was selected in the range 4 x 10^{-5}M to 4 x 10^{-4}M . It was further observed that the same range of concentration was suitable for the other solvents under study. The absorption spectra were studied in visible range (400 nm to 800 nm) only and for comparison the absorption spectra of pure components, i.e. malachite green (MG.) and rose bengal (RB.) were recorded in methanol and other solvents for the same concentration and in the same wavelength range as used for the complex under study. Here, we first report our results on absorption studies obtained using methanol as solvent.

3.1 ABSORPTION SPECTRA OF COMPLEX IN METHYL ALCOHOL (METHANOL)

As mentioned above, the concentration range selected for study was 4×10^{-5} M to 4×10^{-4} M. The spectra at different concentrations have been given in fig (1) and the values of absorbance at peak wavelength are given in table (1). From the figure it is observed that the spectra consists of four peaks having wavelength 420 nm (λ_1), 515 nm (λ_2), 545 nm (λ_3) and 618 nm (λ_4), at low concentrations. As the concentration is increased from 4×10^{-5}M to 4×10^{-4}M, the peak wavelength at 515 nm (λ_2) and 545 nm (λ_3) are seen to shift slightly towards higher wavelength (Red shift). The peaks at wavelengths λ_3 and λ_2 are comparatively stronger and above concentration 2×10^{-4}M, the band at λ_3 becomes so pronounced that the asorbance goes

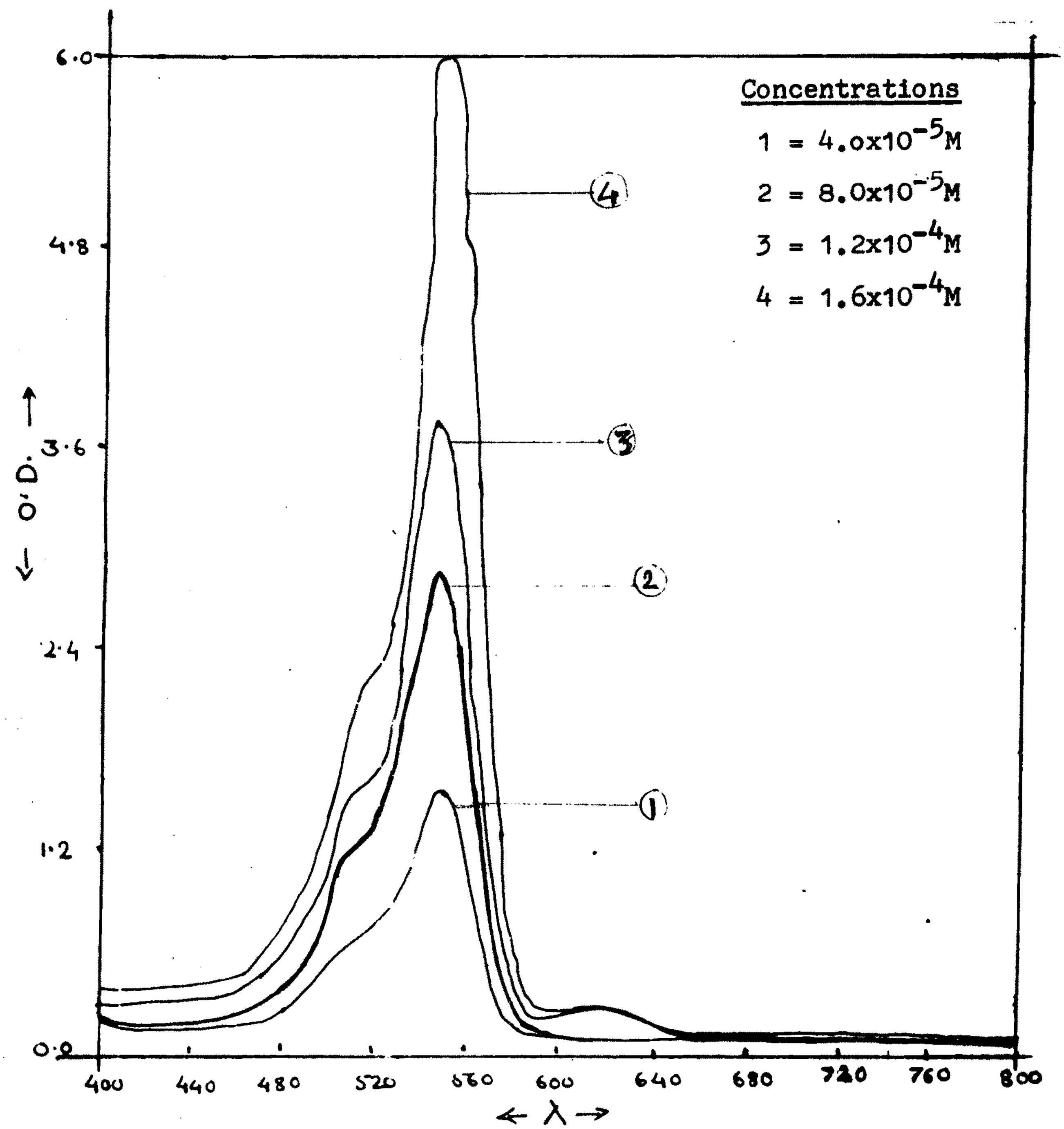

Fig.1 : ABSORPTION SPECTRA OF COMPLEX IN METHYL ALCOHOL (CONCENTRATION VARIATION)

Table - 1

ABSORPTION INTENSITIES OF COMPLEX IN METHYL ALCOHOL (METHANOL)

(CONCENTRATION VARIATION)

CONCENTRATION (M)	ABSORPTION INTENSITIES AT PEAK WAVELENGTHS							
	λ_1	I_1	λ_2	I_2	λ_3	I_3	λ_4	I_4
1) 4×10^{-5}	420	0.18	515	0.72	545	1.56	618	0.01
2) 8×10^{-5}	420	0.20	515	1.26	545	2.88	618	0.01
3) 1.2×10^{-4}	420	0.32	518	1.68	551	4.41	618	0.24
4) 1.6×10^{-4}	420	0.40	518	2.22	551	6.00	618	0.22
5) 2.0×10^{-4}	420	0.54	518	2.46	551	6.00	618	0.42
6) 2.4×10^{-4}	420	0.78	518	2.16	551	6.00	618	0.53
7) 2.8×10^{-4}	420	0.80	518	2.64	551	6.00	618	0.78
8) 3.2×10^{-4}	420	0.90	518	2.82	551	6.00	618	0.84
9) 3.6×10^{-4}	420	0.92	518	3.00	551	6.00	618	0.96
10) 4.0×10^{-4}	420	1.08	520	3.18	552	6.00	618	1.20

beyond measurable limit (greater than 6). But in general, the absorbance at a given wavelength goes on increasing with increasing concentration. It seems that the Beer-Lambert's law is applicable over a very short range of concentration. The results further show that peak wavelengths λ_1 and λ_4 are not much affected by variation of concentration of the complex. However, the peak wavelengths λ_2 (515 nm) and λ_3 (545 nm) seem to be shifting to higher wavelengths.

For comparison, the absorption spectra of pure components (MG. and RB.) in methanol were recorded. For malachite green the concentration selected was 3.2×10^{-4}M and for rose bengal it was 1.6×10^{-4}M. These concentrations are equivalent to concentration of complex as 1.6×10^{-4}M. The absorption spectra of pure components and that of complex at equivalent concentrations are given in fig (9). It is seen that in methanol, malachite green is weakly absorbing with band at 422 nm ($E_1 = 0.75 \times 10^3$) and at 618 nm ($E_4 = 0.34375 \times 10^3$). In case of rose bengal a pronounced peak at 545 nm ($E = 8.687 \times 10^3$) and a shoulder at 520 nm ($E = 4.9375 \times 10^3$) is observed. However, in case of complex, these three peaks are observed with greatly enhanced absorption intensities and in addition to these bands a new band seems to appear at 420 nm. The 'E' values for the complex at peak wavelength λ_2 (518 nm) and λ_3

(551 nm) are E_2 = 13.875 x 10^3 and E_3 = 37.5 x 10^3 respectively. Similarly E values at λ_1 (420 nm) and λ_2(618 nm) are E_1 = 2.5 x 10^3 and E_4 = 1.5 x 10^3 respectively as compared to E values of pure component. (E_1 = 0.75x 10^3 at 420 nm and E_4 = 0.3437 x 10^3 at 618 nm. This comparison of absorption spectra clearly indicates that a definite complex is formed between malachite green and rose bengal and the complex is stable. It is also observed that for complex solution, rose bengal is strongly absorbing in methanol (E_2 = 13.875 x 10^3 & E_3 = 37.5 x 10^3) while malachite green is weakly absorbing (E_1 = 2.5 x 10^3 & E_4 = 1.5 x 10^3)

3.2 ABSORPTION SPECTRA OF COMPLEX IN ETHYL ALCOHOL [ETHANOL]

The absorption spectra of dye complex salt in ethanol was recorded at different concentrations in the range from 4 x 10^{-5}M to 4 x 10^{-4}M in the visible range. The spectra at different concentrations are givewn in fig (2) and the values of absorbance at the peak wave-length are given in table (2). It is seen that the absorption spectra of complex in ethanal is similar to that observed in methanol and it consists of four peaks having wavelengths 420 nm (λ_1), 520 nm (λ_2), 564 nm (λ_3) and 618 nm (λ_4) at low concentration. As the concentration of complex is increased from 4 x 10^{-5}M to

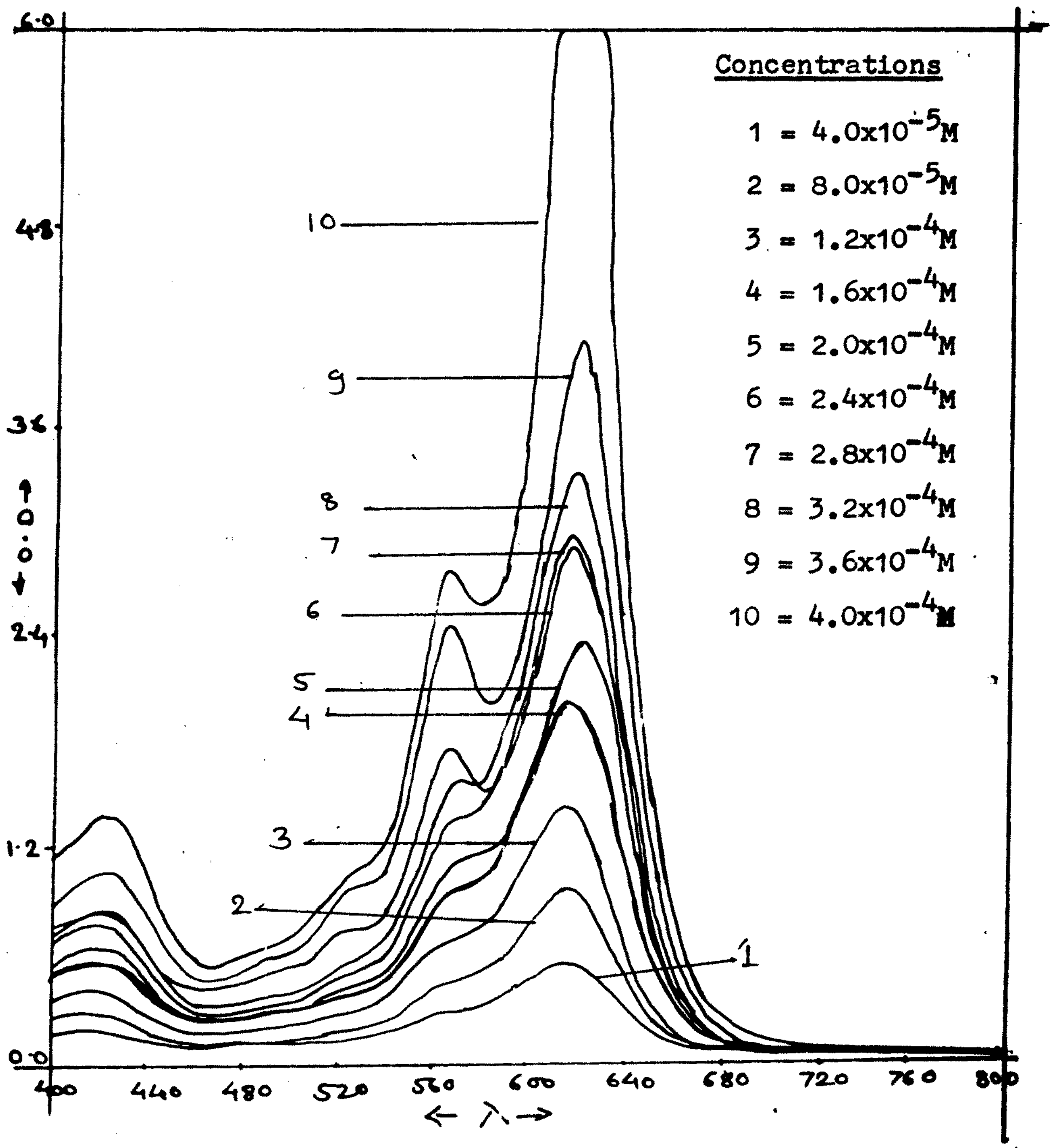

Fig:2 : ABSORPTION SPECTRA OF COMPLEX IN ETHY ALCOHOL (CONCENTRATION VARIATION)

Table - 2

ABSORPTION INTENSITIES OF COMPLEX IN ETHYL ALCOHOL (ETHANOL)

(CONCENTRATION VARIATION)

CONCENTRATION (M)	ABSORPTION INTENSITIES AT PEAK WAVELENGTHS							
	λ_1	I_1	λ_2	I_2	λ_3	I_3	λ_4	I_4
1) 4×10^{-5}	420	0.18	520	0.12	564	0.28	618	0.18
2) 8×10^{-5}	420	0.30	520	0.24	564	0.51	618	0.54
3) 1.2×10^{-4}	420	0.42	520	0.30	566	0.72	618	1.02
4) 1.6×10^{-4}	420	0.57	520	0.36	566	0.96	618	1.47
5) 2.0×10^{-4}	420	0.66	520	0.36	574	1.17	622	2.04
6) 2.4×10^{-4}	420	0.84	520	0.50	568	1.44	620	2.43
7) 2.8×10^{-4}	420	0.90	520	0.60	568	1.62	620	3.09
8) 3.2×10^{-4}	420	0.90	520	0.78	568	1.83	620	3.00
9) 3.6×10^{-4}	420	1.08	520	1.02	568	2.52	620	4.12
10) 4.0×10^{-4}	424	1.41	525	1.08	568	2.82	620	6.00

4×10^{-4}M the wavelength peaks at λ_1 (420 nm), λ_2 (520 nm), λ_3 (564 nm) and λ_4 (618 nm) are seen to shift slightly towards higher wavelength. The peaks at λ_1 and λ_4 seem to be more enhanced than those at λ_2 and λ_3. At concentration 4×10^{-4}M, the band at λ_4 has strong absorption and the absorption intensity is greater than 6.

The comparison of absorption spectra of complex in methanol and ethanol shows that the absorption intensity at λ_2 and λ_3 (RB.) is more in methanol than that observed in ethanol solution, but the absorbance at λ_1 and λ_4 (MG.) is much more in ethanol than that in methanol. Similarly at low concentrations the wavelengths λ_1 and λ_4 are same for both the alcohols, while at higher concentrations λ_1 and λ_4 values are shifted to higher wavelength. The values of λ_2 and λ_4 (RB.) are slightly higher in ethanol than those in methonol at a given concentration. In both the alcohols, with increase in concentration, the values of λ_2 and λ_3 are shifted towards the higher wavelength.

The comparison of absorption spectra at concentration 1.6×10^{-4}M shows that at λ_1 (420 nm) and λ_4 (618 nm) the absorption intensity is much higher in ethanol than that in methanol, though the values of λ_1 and λ_4 are not affected.

The E_1 values in methanol and ethanol are found to be 2.5×10^3 and $3,5625 \times 10^3$ and E_4 values are 1.5×10^3 and 9.18×10^3 respectively. However, in methanol, the E_2 and E_3 values are 13.875×10^3 and 37.5×10^3 respectively. While in ethanol these E values are 2.25×10^3 and 6×10^3 respectively which are appreciably less as compared to those in methanol.

These results clearly show that in methanol, rose bengal is strongly absorbing while malachite green is weakly absorbing. But in ethanol, this order is reversed and it is observed that malachite green is strongly absorbing while rose bengal is weakly absorbing.

3.3 ABSORPTION SPECTRA OF COMPLEX IN n-PROPYL ALCOHOL (1 - PROPANOL)

The absorption spectra of the complex in n-propyl alcohol was recorded in the same concentration range i.e. 4×10^{-5}M to 4×10^{-4}M as used in the study of methanol and ethanol. The spectra at different concentrations are shown in fig. (3) and the values of absorption intensities at peak wavelength are given in table (3). The spectra of complex in 1-propanol is similar to that observed in methanol and ethanol. The

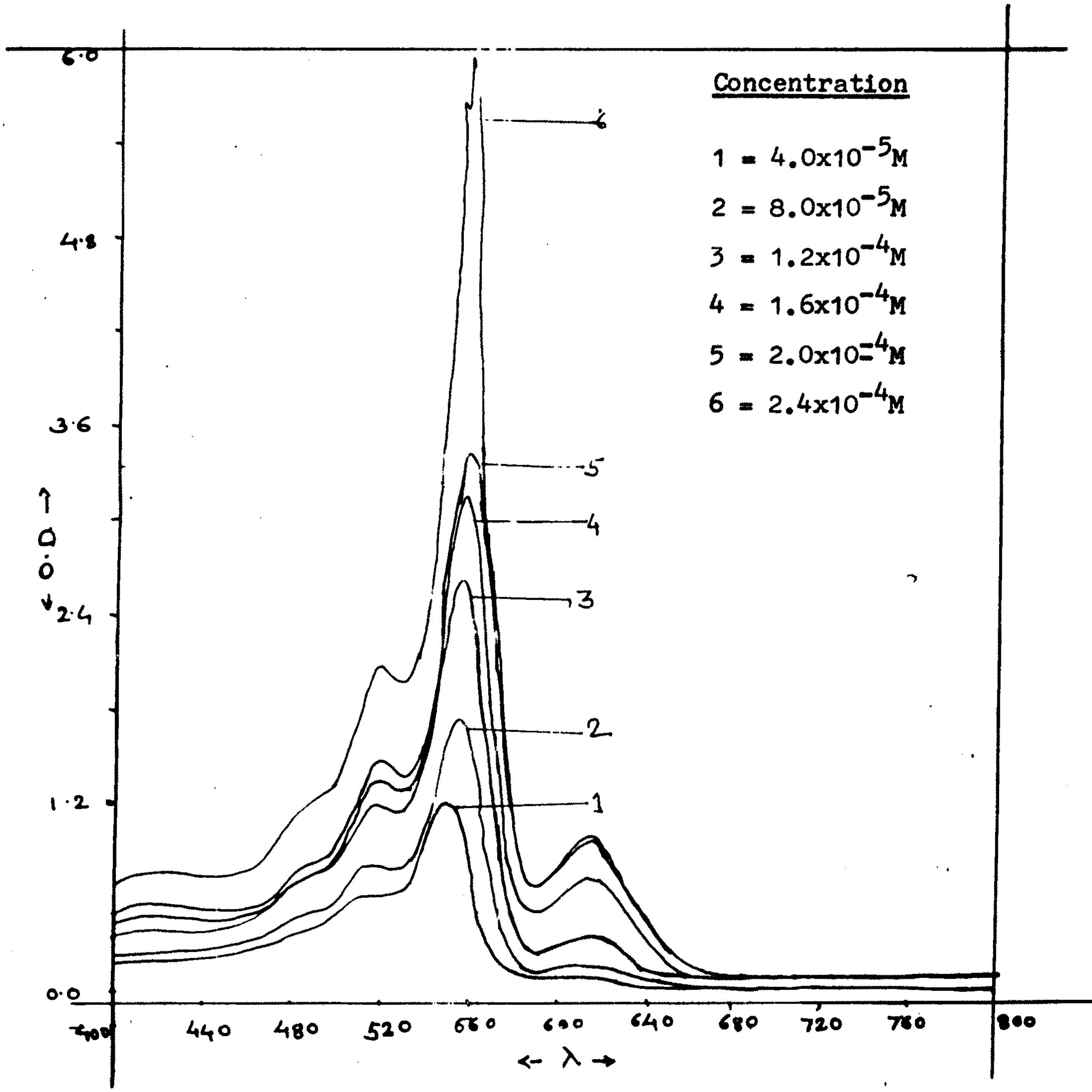

Fig.3 : ABSORPTION SPECTRA OF COMPLEX IN n-PROPYL ALCOHOL (CONCENTRATION VARIATION)

Table - 3

ABSORPTION INTENSITIES OF COMPLEX IN n - PROPYL ALOCOHOL (1 - PROPANOL)

(CONCENTRATION VARIATION)

CONCENTRATION (M)	ABSORPTION INTENSITIES AT PEAK WAVELENGTHS							
	λ_1	I_1	λ_2	I_2	λ_3	I_3	λ_4	I_4
1) 4×10^{-5}	420	0.20	514	0.60	558	1.20	618	0.12
2) 8×10^{-5}	421	0.33	518	0.87	558	1.77	618	0.24
3) 1.2×10^{-4}	421	0.48	519	1.26	560	2.64	618	0.42
4) 1.6×10^{-4}	422	0.54	520	1.38	561	3.18	618	0.75
5) 2.0×10^{-4}	422	0.63	520	1.50	562	3.75	618	1.02
6) 2.4×10^{-4}	422	0.84	521	2.13	562	5.97	618	1.02
7) 2.8×10^{-4}	422	0.84	522	1.74	564	6.00	618	1.86
8) 3.2×10^{-4}	425	1.11	522	2.76	560	6.00	618	1.38
9) 3.6×10^{-4}	425	1.20	523	2.70	560	6.00	618	2.04
10) 4.0×10^{-4}	425	1.10	523	2.07	560	6.00	618	2.70

spectra shows four peaks having wavelength λ_1 (420 nm), λ_2 (514 nm) λ_3 (558 nm) and λ_4 (618 nm) at low concentration. As the concentration is increased from 4 x 10^{-5}M to 4 x 10^{-4}M, it is observed that the values of peak wavelengths are shifted to higher wavelength (Red Shift). The value of λ_1 changes from 420 nm to 425 nm, λ_2 changes from, 514 nm to 523 nm. However, the value of λ_3 is seen to change from 558 nm to 564 nm as the concentration increase to 2.8x10^{-4}M. Beyond this concentration, λ_3 seems to be least affected. The value of λ_4 is constant at 618 nm within the concentration range 4 x 10^{-5}M to 4 x 10^{-4}M. In general the absorbances of all the four bands are seen to increase with increase in concentration.

The comparison of absorption spectra of complex in 1-Propanol with that in methanol at 1.6 x 10^{-4}M of the complex shows following results. (Refer table 10).

The peak wavelength λ_1 (420 nm) and λ_2 (618 nm) are same in all the three alcohols, i.e. methanol ethanol and 1-propanol. The values of λ_2 are 518 nm, 520 nm and 520 nm respectively and those of λ_3 are 551 nm, 566 nm and 561 nm respectively. The comparison of absorption intensities at λ_2 and λ_3 show that rose bengal is strongly absorbing in methanol (E_2 = 13.875 x 10^3 E_3 = 37.5 x 10^3), less absorbing in 1-

propanol (E_2 = 8.625 x 10^3 E_3 = 19.875 x 10^3) and least absorbing in ethanol (E_2 = 2.25 x 10^3 E_3 = 6 x 10^3). On the other hand comparison of absorption intensities at λ_1 and λ_4 clearly indicate that malachite green is very highly absorbing in ehtanol (E_1 = 3.5625 x 10^3 E_2 = 9.18 x 10^3) less absorbing in 1-propanol (E_1 = 3.375 x 10^3 E_4 = 4.6875 x 10^3) and very weakly absorbing in methanol (E_1 = 2.5 x 10^3 E_4 = 1.5 x 10^3).

Further the results also show that in 1-propanol, at any given concentration, rose bengal is strongly absorbing, while malachite green is weakly absorbing.

3.4 ABSORPTION SPECTRA OF COMPLEX IN n-BUTYL ALCOHOL (1-BUTANOL)

The absorption spectra of complex in n-butyl alcohol were recorded in the concentration range from 4 x 10^{-5}M to 4 x 10^{-4}M. The spectra at different concentrations are shown in fig. (4) and the results of absorption intensities at peak wavelengths are given in table (4). The absorption spectra of dye complex salt in 1-butanol is similar to that observed for methanol, ethanol and 1-propanol. It is observed that the spectra consists of four peaks having wavelength λ_1 (420 nm), λ_2 (518 nm), λ_3 (558 nm) and λ_4 (620 nm), at low concentration. As the concentration is increased from 4

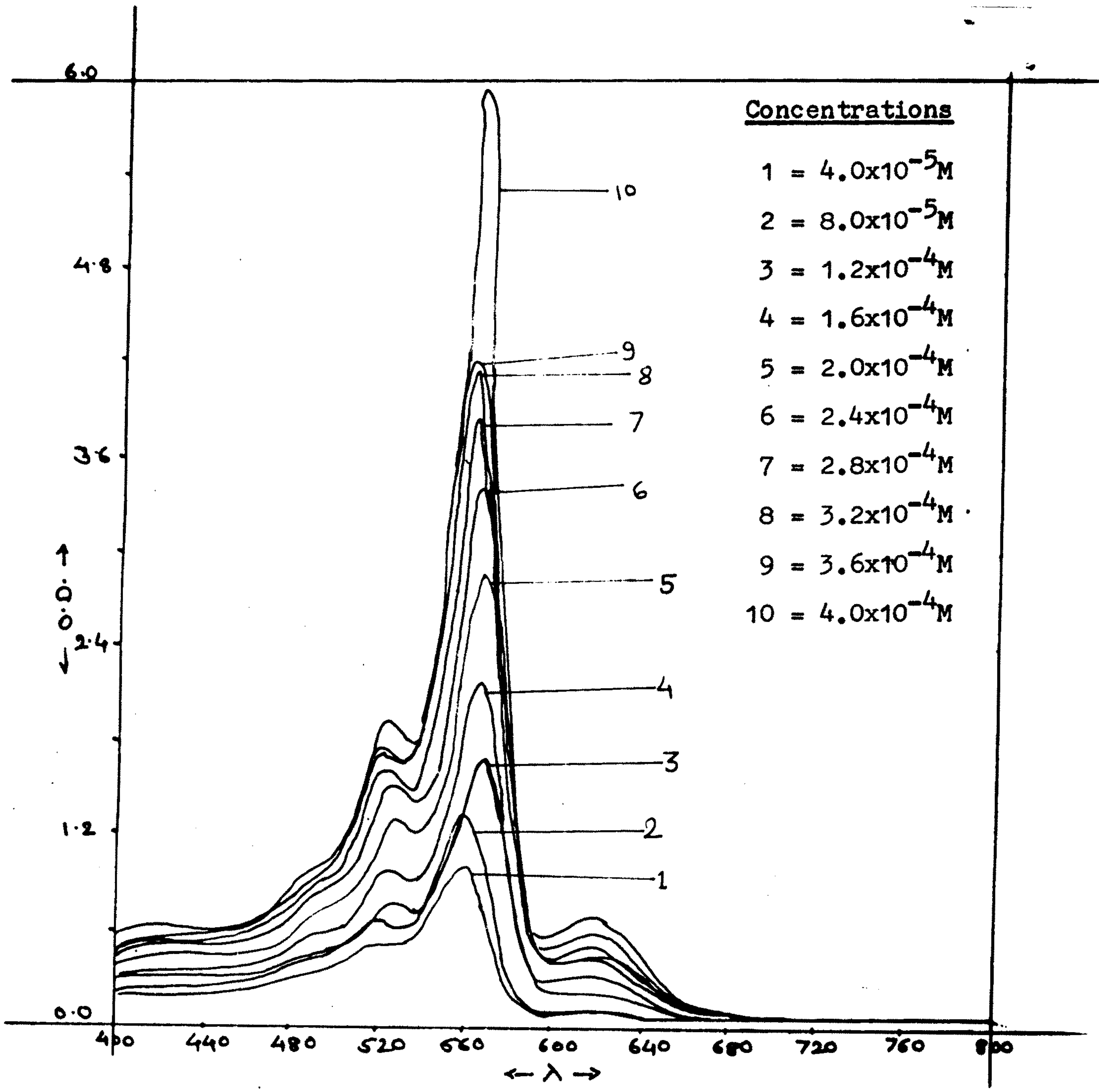

Fig:4 : ABSORPTION SPECTRA OF COMPLEX IN n-BUTYL ALCOHOL (CONCENTRATION VARIATION)

Table - 4

ABSORPTION INTENSITIES OF COMPLEX IN n - BUTYL ALCOHOL (1 - BUTANOL)

(CONCENTRATION VARIATION)

CONCENTRATION (M)	ABSORPTION INTENSITIES AT PEAK WAVELENGTHS							
	λ_1	I_1	λ_2	I_2	λ_3	I_3	λ_4	I_4
1) 4×10^{-5}	420	0.15	518	0.45	558	0.96	620	0.06
2) 8×10^{-5}	420	0.24	518	0.66	558	1.32	620	0.06
3) 1.2×10^{-4}	420	0.31	525	0.78	564	1.68	620	0.36
4) 1.6×10^{-4}	420	0.36	525	0.98	565	2.20	620	0.24
5) 2.0×10^{-4}	420	0.45	525	1.29	565	2.85	620	0.42
6) 2.4×10^{-4}	422	0.48	525	1.50	565	3.39	620	0.42
7) 2.8×10^{-4}	422	0.54	525	1.62	565	3.81	620	0.45
8) 3.2×10^{-4}	422	0.54	525	1.77	565	4.17	620	0.54
9) 3.6×10^{-4}	422	0.58	525	1.77	565	4.23	620	0.58
10) 4.0×10^{-4}	422	0.60	525	1.92	565	5.98	620	0.69

x 10^{-5}M to 1.6 x 10^{-4}M, there is no appreciable change in values of λ_1 and λ_4 . However, the λ_2 is shifted from 518 nm to 525 nm and λ_3 is changed from 558 nm to 565 nm. However, the values of λ_2 (525 nm) and that of λ_3 (565 nm) seem to be least affected by further increase in concentration of the complex. The absorption intensities at all the four bands seem to increase gradually with increase in concentration from 4 x 10^{-5}M to 4 x 10^{-4}M, and absorbance is greater than 6 at 4 x 10^{-4}M of the complex.

The comparison of absorption spectra of complex (C=1.6 x 10^{-4}M) in 1-butanol with that in methanol ethanol and 1-propanol shows that absorbance at λ_1 seems to follow the order as 1-butanol ___ methanol < ethanol __ 1-propanol. Similarly the absorbance at λ_1, at the same concentration of complex seems to follow the order methanol < ethanol < 1-butanol < 1-propanol. However, in case of λ_3 and λ_4, the absorption intensities seem to follow the order, ethanol < 1-butanol < 1-propanol < methanol for λ_3 and methanol ___- 1-butanol < 1-propanol < ethanol for λ_4.

This comparison shows that in 1-butanol rose bengal is strongly absorbing and malachite green is weakly absorbing. These results are similar to those observed for complex solution in methanol and 1-

propanol. However, in case of ethanol reverse observations are obtained.

3.5 ABSORPTION SPECTRA OF COMPLEX IN ISO-PROPYL ALCOHOL (2-PROPANOL)

The absorption spectra of complex in 2-propanol was recorded in the concentration range 4 x 10^{-4}M to 1.6 x 10^{-4}M. Since the absorption intensities beyond concentration 1.6 x10^{-4}M, were very high the absorption spectra could not be recorded in meaningful way. The spectra at different concentrations of complex in 2-propanol are shown in fig.(5) and the results of absorption intensities at peak wavelength are given in table (5). The absorption spectra consists four peaks having wavelength λ_1 (420nm), λ_2 (518nm), λ_3 (550nm) and λ_4 (620nm).

It is observed that as the concentration is increased from 4 x 10^{-4}M to 1.6 x 10^{-4}M, peak position for the four bands seem to be unaffected. However, the absorption intensities at these peaks are seen to increase with increase in concentration.

The absorption spectra of the complex in 2-propanol show a similar trend as in case of 1-propanol. i.e. absorption due to rose bengal is higher than that

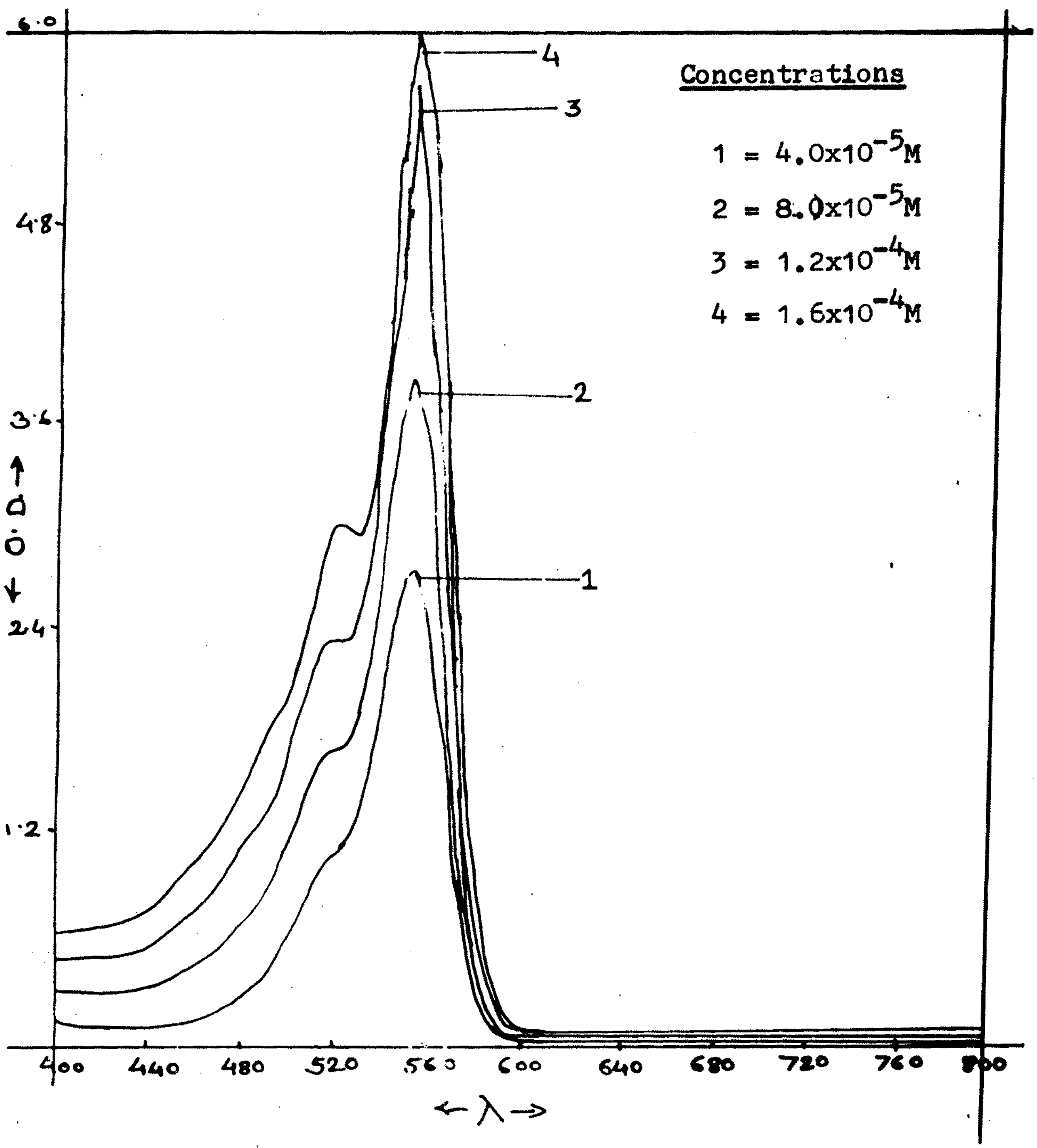

Fig. 5 : ABSORPTION SPECTRA OF COMPLEX IN Iso-PROPYL ALCOHOL (CONCENTRATION VARIATION)

Table - 5

ABSORPTION INTENSITIES OF COMPLEX IN
Iso - PROPYL ALCOHOL (2 - PROPANOL)
(CONCENTRATION VARIATION)

CONCENTRATION (M)	ABSORPTION INTENSITIES AT PEAK WAVELENGTHS							
	λ_1	I_1	λ_2	I_2	λ_3	I_3	λ_4	I_4
1) 4×10^{-5}	420	0.12	518	1.08	550	2.82	620	0.05
2) 8×10^{-5}	420	0.30	518	1.70	550	3.90	620	0.09
3) 1.2×10^{-4}	420	0.54	518	2.34	550	5.70	620	0.12
4) 1.6×10^{-4}	420	0.78	518	3.06	550	6.00	620	0.12

due to malachite green, at any given concentration. The comparison of absorption intensities of complex at .cbconcentration 1.6 x 10^{-4}M in 2-propanol and those in 1-propanol shows that, the molar absorptivities of complex in 2-propanol at λ_2 (518nm) and λ_3 (550nm) are $E_2 = 19.125 \times 10^3$ and $E_3 = 37.5 \times 10^3$ respectively, while those in 1-propanol at λ_2 (520nm) and λ_3 (561nm) are $E_2 = 8.625 \times 10^3$ and $E_3 = 19.875 \times 10^3$. These results clearly show that rose bengal is bettter absorber in 2-propanol than in 1-propanol and the absorption intensities at λ_2 and λ_3 in 2-propanol are nearly twice the absorption intensities in 1-propanol. Similarly, the absorption intensities of complex in 2-propanol at λ_2 (420nm) and λ_4 (620nm) at concentration 1.6 x 10^{-4}M are $E_2 = 4.875 \times 10^3$ and $E_4 = 0.75 \times 10^3$ which are much less than those at λ_2 and λ_3. Comparison of these absorption intensities at λ_1 and λ_4 in 2-propanol with those in 1-propanol ($E_1 = 3.375 \times 10^3$ and $E_4 = 4.8675 \times 10^3$) show that, the absorbance at λ_1 in 2-propanol is enhanced than that in 1-proponol while the absorbance at λ_4 seems to decrease in 2-propanol.

3.6 ABSORPTION SPECTRA OF COMPLEX IN SEC-BUTYL ALCOHOL (2-BUTANOL)

The absorption spectra of complex in 2-butanol

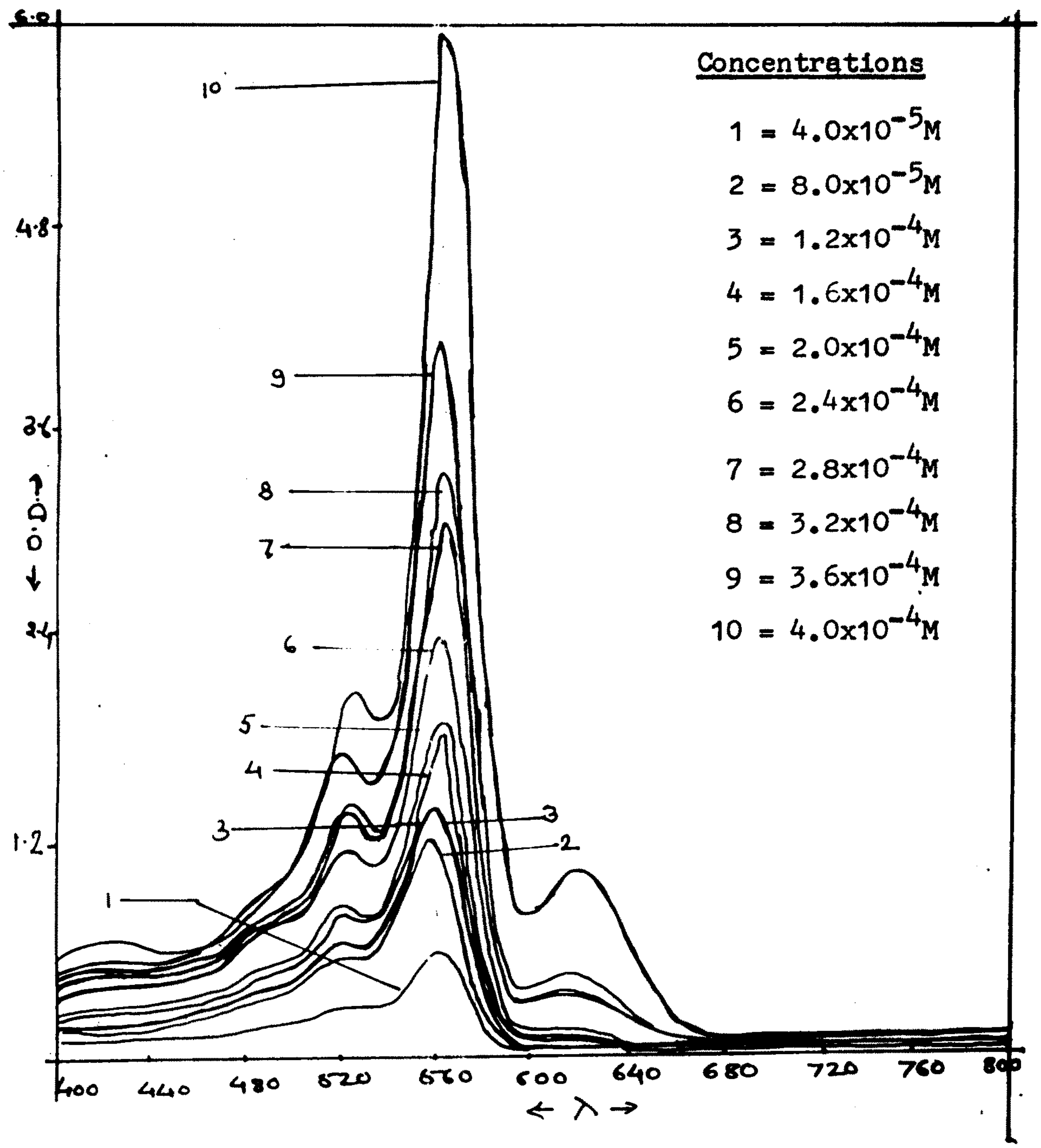

Fig.6 : ABSORPTION SPECTRA OF COMPLEX IN
Sec-BUTYL ALCOHOL (CONCENTRATION VARIATION)

Table - 6

ABSORPTION INTENSITIES OF COMPLEX IN SEC.- BUTYL ALCOHOL (2-BUTANOL) (CONCENTRATION VARIATION)

CONCENTRATION (M)	ABSORPTION INTENSITIES AT PEAK WAVELENGTHS							
	λ_1	I_1	λ_2	I_2	λ_3	I_3	λ_4	I_4
1) 4×10^{-5}	420	0.10	518	0.30	558	0.60	620	0.06
2) 8×10^{-5}	420	0.18	518	0.58	558	1.26	620	0.06
3) 1.2×10^{-4}	420	0.24	520	0.69	558	1.44	620	0.06
4) 1.6×10^{-4}	420	0.30	520	0.90	564	1.86	620	0.12
5) 2.0×10^{-4}	420	0.30	522	0.90	564	1.95	620	0.12
6) 2.4×10^{-4}	420	0.39	522	1.20	564	2.43	620	0.12
7) 2.8×10^{-4}	420	0.48	524	1.29	564	3.00	620	0.30
8) 3.2×10^{-4}	420	0.48	524	1.43	564	3.39	620	0.36
9) 3.6×10^{-4}	420	0.54	524	1.74	564	4.74	620	0.48
10) 4.0×10^{-4}	420	0.72	524	3.33	564	5.94	620	1.08

were recorded in the concentration range 4 x 10^{-5}M to 4 x 10^{-4}M. The absorption spectra of complex at different concentrations is shown in fig. (6) and the results of absorption intensities at peak wave lengths are given in table (6). The absorption spectra of complex in 2-butanol is similar to that in 1-butanol showing four peaks at wave lengths λ_1 (420nm), λ_2(518nm), λ_3(558nm) and λ_4(620nm) at low concentrations. As the concentration is increased from 4 x 10^{-5}M to 4 x 10^{-4}M, the values of λ_1 (420nm) and λ_4 (620nm) are not changed. However, the value of λ_2 is changed from 518 nm to 524 nm during increase in concentration from 4 x 10^{-5}M to 2.8 x 10^{-4}M, and beyond this concentration λ_2 is least affected. Similarly value of λ_3 is changed from 558 nm to 564 nm as concentration is increased from 4 x 10^{-5}M to 1.6 x 10^{-4}M, and beyond this concentration λ_3 (564nm) is constant. The results further, show that as concentration is increased from 4 x 10^{-5}M to 4 x 10^{-4}M, the absorption intensities at λ_1, λ_2, λ_3, and λ_4 are increased. The comparison of absorption spectra of complex in 2-butanol with that in 1-butanol shows that, there is no much difference in absorption intensities at the four peaks. However, the absorbance in 1-butanol is slightly higher than that in 2-butanol. e.g. The absorptivity of complex at concentration 1.6 x 10^{-4}M, in 1-butanol are, E_1 = 2.25 x 10^3, E_2 = 6.125 x 10^3, E_3 = 13.75 x

10^3 and E_4 = 1.5 x 10^3 while these E values corresponding to 2-butanol are, E_1 = 1.875 x 10^3, E_1 = 5.625 x 10^3, E_3 = 11.625 x 10^3 and E_4 = 0.75 x 10^3 respectively.

These results clearly show that in 2-butanol also, rose bengal component is strongly absorbing and malachite green is weakly absorbing.

3.7 ABSORPTION SPECTRA OF COMPLEX IN t-BUTYL ALCOHOL (2-METHYL, 2-PROPANOL)

The absorption spectra of the complex in t-butyl alcohol were recorded in the concentration range 4 x 10^{-5}M to 4 x 10^{-4}M. The spectra of the complex at different concentrations are shown in fig.(7) and the absorption intensities at peak wavelengths are given in table (7). The absorption spectra of the complex in t-butyl alcohol is similar to that observed in n-butyl and Sec-butyl alcohol. The spectram show four peaks at wavelength λ_1 (420nm), λ_2 (522nm), λ_3 (564nm) and λ_4 (618nm) at low concentrations. As the concentration is increased from 4 x 10^{-5}M to 4 x 10^{-4}M, the value of λ_1 is changed from 420 nm to 422 nm but λ_4 is constant at 618 nm. Similarly the value of λ_2 shifts from 522 nm to 524nm but value of λ_3 is changed from 564 nm at 4 x 10^{-5}M concentration to 570 nm at 2.8 x 10^{-4}M

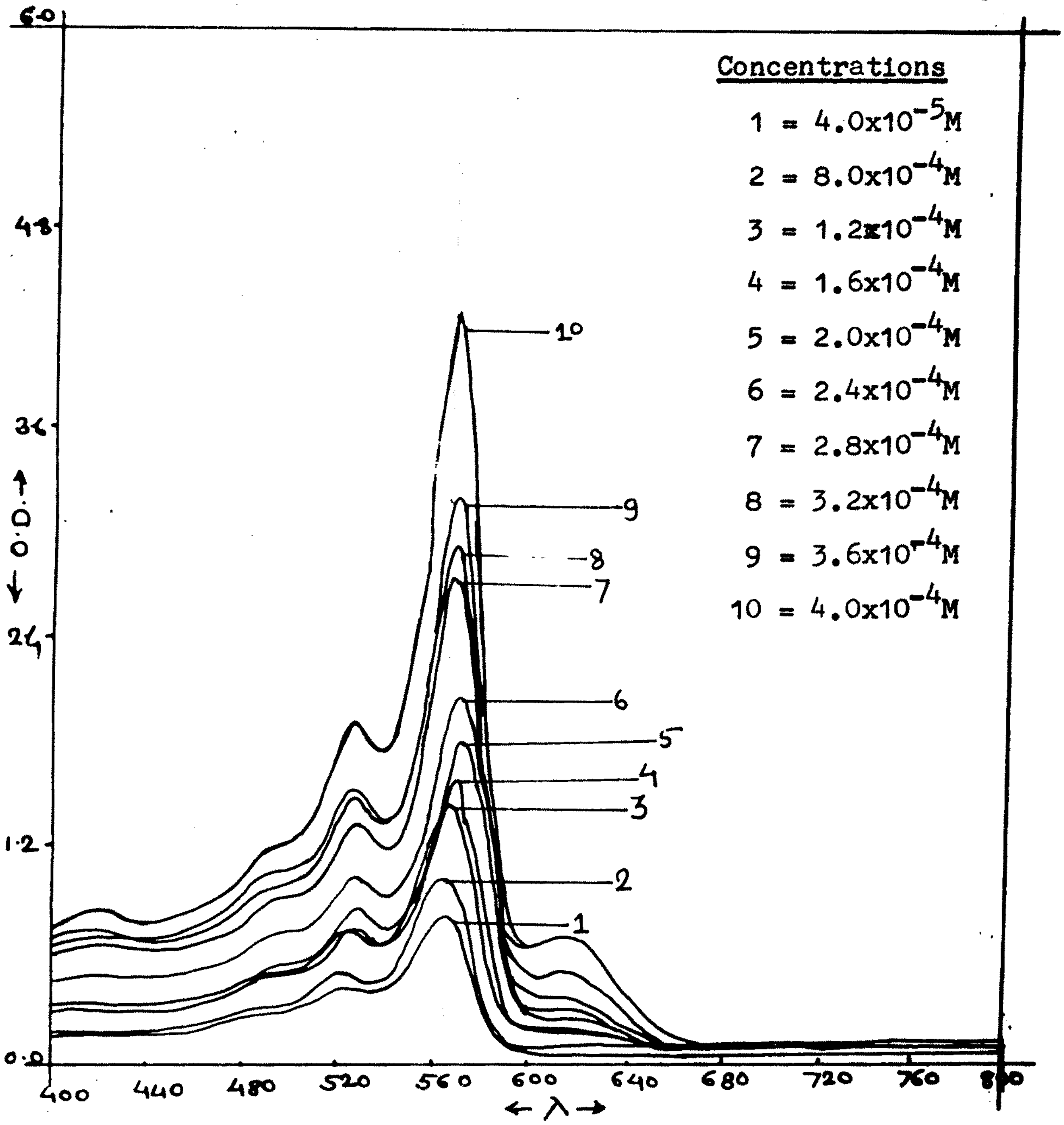

Fig.7 : ABSORPTION SPECTRA OF COMPLEX IN t-BUTYL ALCOHOL (CONCENTRATION VARIATION)

Table - 7

ABSORPTION INTENSITIES OF COMPLEX IN TER.- BUTYL ALCOHOL (2-METHYL - 1 - PROPANOL) (CONCENTRATION VARIATION)

CONCENTRATION (M)	ABSORPTION INTENSITIES AT PEAK WAVELENGTHS							
	λ_1	I_1	λ_2	I_2	λ_3	I_3	λ_4	I_4
1) 4×10^{-5}	420	0.15	522	0.40	564	0.54	618	0.12
2) 8×10^{-5}	420	0.20	522	0.54	565	1.05	618	0.12
3) 1.2×10^{-4}	420	0.27	522	0.70	566	1.44	618	0.12
4) 1.6×10^{-4}	420	0.33	522	0.80	567	1.68	618	0.16
5) 2.0×10^{-4}	420	0.36	522	0.82	567	1.71	618	0.18
6) 2.4×10^{-4}	420	0.48	522	1.02	568	1.98	618	0.24
7) 2.8×10^{-4}	420	0.62	524	1.30	570	2.78	618	0.78
8) 3.2×10^{-4}	420	0.66	524	1.48	570	2.88	618	0.30
9) 3.6×10^{-4}	422	0.63	524	1.48	570	3.18	618	0.66
10) 4.0×10^{-4}	422	0.84	524	1.92	570	4.26	618	0.66

concentration and beyond this it is least affected. However, the absorption intensities at the four peaks are greatly enhanced with increase in concentration.

The comparison of absorption spectra of complex in t-butyl alcohol with that in n-butyl and sec-butyl alcohol shows that at any given concentration the absorption intensities at λ_1, λ_2, λ_3 and λ_4 are nearly the same and there is no much difference. The absorption intensities (E-values) of the complex (C = 1.6×10^{-4}M) in isomeric butyl alcohols at λ_1, λ_2, λ_3 and λ_4 are as below.

	E_1	E_2	E_3	E_4
n-Butyl Alcohol	2.25×10^3	6.125×10^3	13.75×10^3	1.5×10^3
Sec-Butyl Aocohol	1.875×10^3	5.625×10^3	11.625×10^3	0.75×10^3
t-Butyl Aocohol	2.0675×10^3	5.000×10^3	10.05×10^3	1×10^3

It is seen from these results that, E values at λ_2 and λ_3 gradually decrease as we go from n-butyl alcohol to t-butyl alcohol. However, E values at λ_1 and λ_4 seem to be least affected.

In t-butyl alcohol,. the rose bengal component seem to be absorbing better than the malachite green component.

3.8 ABSORPTION SPECTRA OF COMPLEX IN ISO-BUTYL ALCOHOL (2-METHYL, 1-PROPANOL)

The absorption spectra of complex in iso-butyl alcohol at different concentrations are shown in fig. (8) and the results of absorption intensities are given in table (8). The spectra could not be recorded in a meaningful way beyond concentration 2 x 10^{-4}M because the absorption intensity is greater than 6. The spectra of complex in iso-butyl alcohol is similar to that observed in other isomeric butyl alcohols but the absorption intensities are comparatively very high at a given concentration. The spectra again show four peaks at wavelength λ_1 (420 nm), λ_2 (518 nm), λ_3 (552nm) and λ_4 (618 nm) at low concentrations. As the concentration is increased from 4 x 10^{-5}M to 2.4 x 10^{-4}M, λ_1 and λ_4 are not affected and on the other hand λ_2 and λ_3 are seen to exhibit red shift (518 nm to 520 nm and 552 nm to 558 nm respectively)

However, above concentration of 2 x 10^{-4}M, these peak wavelength do not show any shift and remain constant at 520 nm and 558 nm respectively. However, the

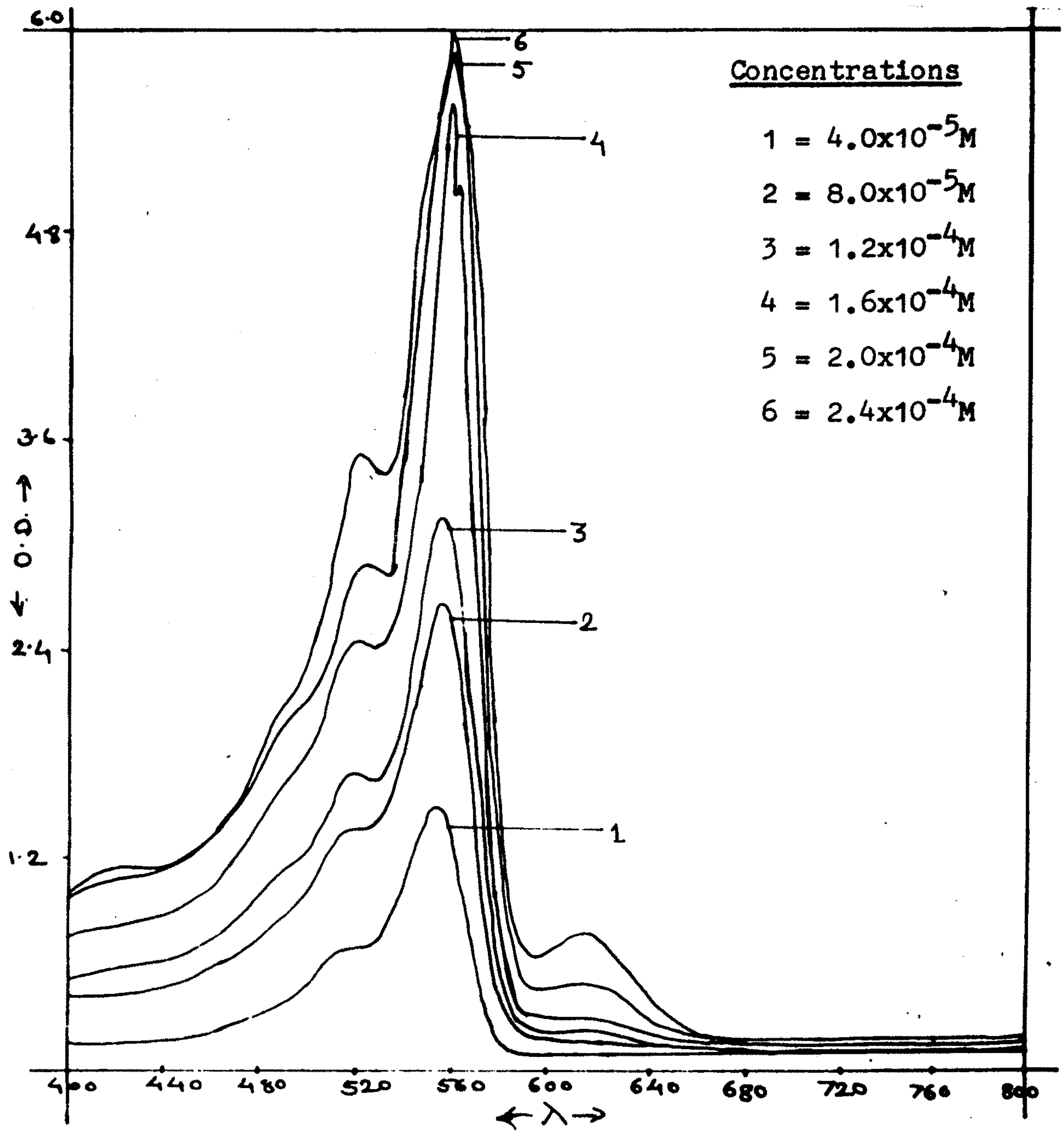

Fig.8 : ABSORPTION SPECTRA OF COMPLEX IN Iso-BUTYL ALCOHOL (CONCENTRATION VARIATION)

Table - 8

ABSORPTION INTENSITIES OF COMPLEX IN
Iso - BUTYL ALCOHOL (2-METHYAL - 1 - PROPANOL
(CONCENTRATION VARIATION)

CONCENTRATION (M)	ABSORPTION INTENSITIES AT PEAK WAVELENGTHS							
	λ_1	I_1	λ_2	I_2	λ_3	I_3	λ_4	I_4
1) 4×10^{-5}	420	0.18	518	0.72	552	1.50	618	0.12
2) 8×10^{-5}	420	0.33	518	1.32	552	2.58	618	0.12
3) 1.2×10^{-4}	420	0.48	518	1.62	556	3.12	618	0.15
4) 1.6×10^{-4}	420	0.72	518	2.34	558	5.50	618	0.18
5) 2.0×10^{-4}	420	0.96	520	2.42	558	5.98	618	0.66
6) 2.4×10^{-4}	420	1.14	520	2.76	558	6.00	618	0.36

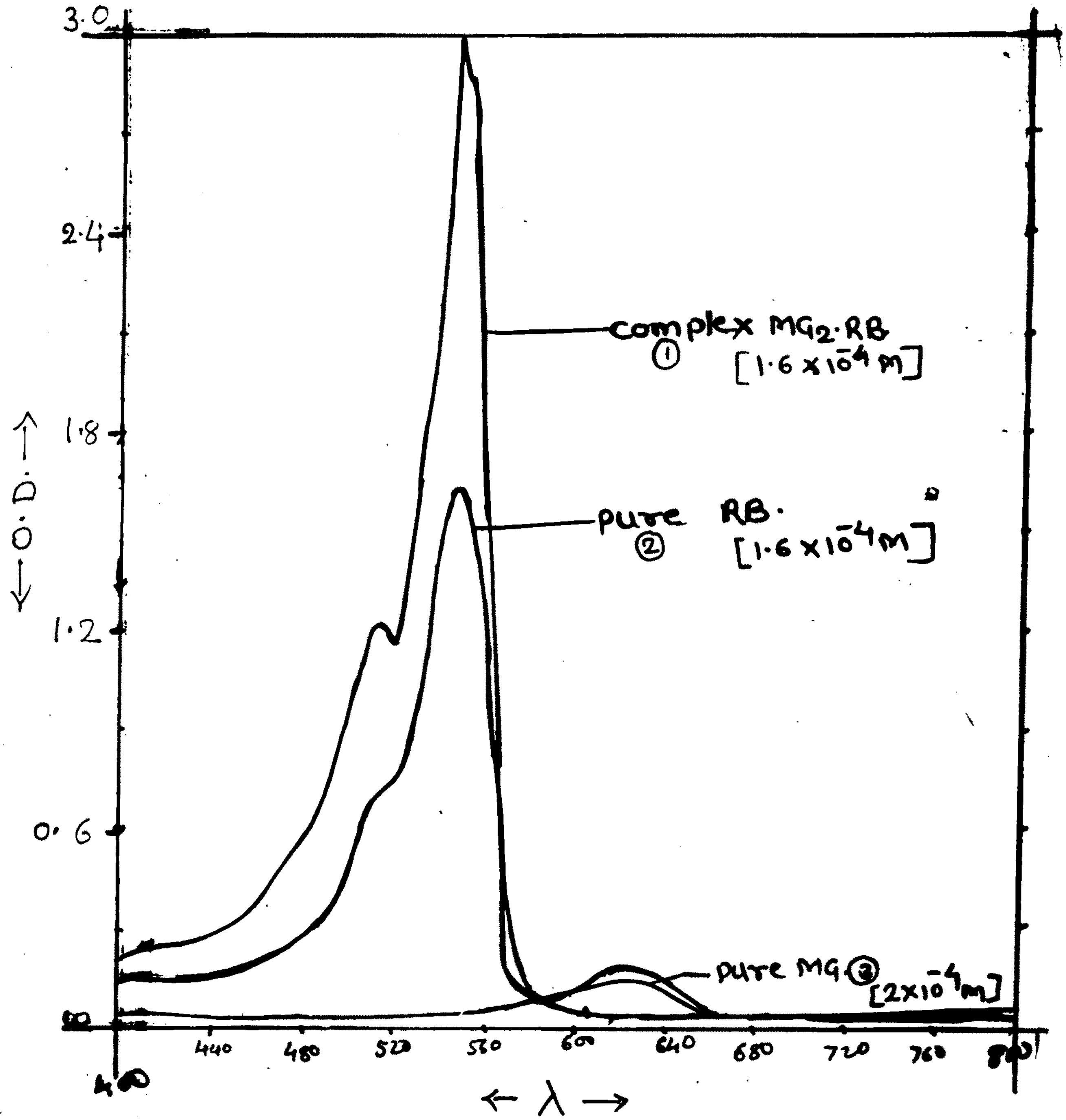

Fig.9 : ABSORPTION SPECTRA OF MG_2.RB COMPLEX, PURE ROSE BENGAL AND MALACHITE GREEN IN METHYL ALCOHOL AT EQUIVALENT CONCENTRATIONS

Table - 9

ABSORPTION INTENSITIES OF PURE ROSE BENGAL (RB.=1.6 X 10^{-4}M)

AND MALACHITE GREEN (MG.=3.2 X 10^{-4}M)

IN DIFFERENT SOLVENTS

(SOLVENT VARIATION.

SOLVENT	ABSORPTION INTENSITIES AT PEAK WAVELENGTHS							
	<-PURE ROSE BENGAL->				<-PURE MALACHITE GREEN->			
	λ_2	I_2	λ_3	I_3	λ_1	I_1	λ_4	I_4
WATER	515	0.22	543	1.38	422	0.054	618	1.08
METHYL ALCOHOL	520	0.79	545	1.39	422	0.24	618	0.110
ETHYL ALCOHOL	512	0.66	550	1.57	420	0.33	618	0.72
n-PROPYL ALCOHOL	514	0.66	551	1.68	422	0.12	620	0.42
Iso-PROPYL ALCOHOL	514	0.54	552	1.22	420	0.05	620	0.055
n-BUTYL ALCOHOL	514	0.63	522	1.56	426	0.42	622	2.10
Sec-BUTYL ALCOHOL	514	0.48	558	1.23	424	0.84	614	0.27
t-BUTYL ALCOHOL	515	0.50	560	1.30	422	0.36	618	0.24
Iso-BUTYL ALCOHOL	512	0.62	550	1.44	422	0.55	618	1.11

Table - 10

**ABSORPTION INTENSITIES OF COMPLEX MG_2 .RB (C = 1.6 X 10^{-4}M)
IN DIFFERENT SOLVENTS (SOLVENT VARIATION)**

SOLVENT	ABSORPTION INTENSITIES AT PEAK WAVELENGTHS							
	λ_{1nm}	I_2	λ_{2nm}	I_3	λ_{3nm}	I_1	λ_{4nm}	I_4
METHYL ALCOHOL	420	0.40	518	2.22	551	6.00	618	0.24
ETHYL ALCOHOL	420	0.57	520	0.36	566	0.96	618	1.47
n-PROPYL ALCOHOL	422	0.54	520	1.38	561	3.18	618	0.75
Iso-PROPYL ALCOHOL	420	0.78	518	3.06	550	6.00	620	0.12
n-BUTYL ALCOHOL	420	0.36	525	0.98	565	2.20	620	0.24
Sec-BUTYL ALCOHOL	420	0.30	520	0.90	564	1.86	620	0.12
t-BUTYL ALCOHOL	420	0.33	520	0.80	567	1.68	618	0.16
Iso-BUTYL ALCOHOL	420	0.72	518	2.34	558	5.50	618	0.18

Table - 11

EXTINCTION COEFFICIENT (E) VALUES FOR MG_2.RB COMPLEX (1.6×10^{-4}M) IN DIFFERENT SOLVENTS (SOLVENT VARIATION)

ALCOHOL	E_1 (AT λ_1)	E_2 (AT λ_2)	E_3 (AT λ_3)	E_4 (AT λ_4)
METHYL ALCOHOL	2.5×10^3	13.875×10^3	37.5×10^3	1.5×10^3
ETHYL ALCOHOL	3.5625×10^3	2.25×10^3	6×10^3	9.18×10^3
n-PROPYL ALCOHOL	3.375×10^3	8.625×10^3	19.875×10^3	4.6875×10^3
n-BUTYL ALCOHOL	2.25×10^3	6.125×10^3	13.75×10^3	1.5×10^3
Iso-PROPYL ALCOHOL	4.875×10^3	1.9125×10^3	37.5×10^3	0.75×10^3
Sec-BUTYL ALCOHOL	1.875×10^3	5.625×10^3	11.625×10^3	0.75×10^3
t-BUTYL ALCOHOL	2.0625×10^3	5.000×10^3	10.5×10^3	1×10^3
Iso-BUTYL ALCOHOL	4.5×10^3	14.625×10^3	34.375×10^3	1.125×10^3

Table - 12

EXTINCTION COEFFICIENT (E) VALUES OF PURE ROSE BENGAL (1.6 X 10^{-4}M) AND MALACHITE GREEN (3.2 X 10^{-4}M) IN DIFFERENT SOLVENTS

(SOLVENT VARIATION)

ALCOHOL	<-PURE ROSE BENGAL->		<-PURE MALACHITE GREEN->	
	E_2 (AT λ_2)	E_3 (AT λ_3)	E_1 (AT λ_1)	E_4 (AT λ_4)
METHYL ALCOHOL	4.9375×10^3	1.0562×10^3	0.75×10^3	0.3437×10^3
ETHYL ALCOHOL	4.125×10^3	9.8125×10^3	1.031×10^3	2.25×10^3
n-PROPYL ALCOHOL	4.125×10^3	10.5×10^3	0.375×10^3	1.312×10^3
n-BUTYL ALCOHOL	3.9375×10^3	9.75×10^3	1.312×10^3	0.6562×10^3
Iso-PROPYL ALCOHOL	3.335×10^3	7.625×10^3	0.1562×10^3	0.1718×10^3
Sec-BUTYL ALCOHOL	3.0×10^3	7.6875×10^3	2.625×10^3	0.8437×10^3
t-BUTYL ALCOHOL	3.125×10^3	8.125×10^3	1.125×10^3	0.75×10^3
Iso-BUTYL ALCOHOL	3.875×10^3	9×10^3	1.7187×10^3	0.3437×10^3

Table - 13

COMPARISON OF CONCENTRATIONS OF RB AND MG COMPONENTS OF COMPLEX IN DIFFERENT SOLVENTS AT MAXIMUM ABSORPTION INTENSITIES

-ALCOHOL	DIELECTRIC CONSTANT	CONCENTRATION OF COMPLEX FOR MAX. ABSORPTION OF RB.	CONCENTRATION OF COMPLEX FOR MAX. ABSORPTION OF MG.
METHYL ALCOHOL	32.63	1.6×10^{-4}	2.4×10^{-4}
ETHYL ALCOHOL	24.3	2.0×10^{-4}	4.0×10^{-4}
n-PROPYL ALCOHOL	20.10	2.4×10^{-4}	4.0×10^{-4}
n-BUTYL ALCOHOL	17.80	4.0×10^{-4}	4.0×10^{-4}
n-PROPYL ALCOHOL	20.10	2.4×10^{-4}	4.0×10^{-4}
Iso-PROPYL ALCOHOL	18.2	4.0×10^{-4}	4.0×10^{-4}
n-BUTYL ALCOHOL	17.80	4.0×10^{-4}	4.0×10^{-4}
Sec-BUTYL ALCOHOL	15.80	3.6×10^{-4}	3.6×10^{-4}
t-BUTYL ALCOHOL	10.10	2.0×10^{-4}	2.0×10^{-4}
Iso-BUTYL ALCOHOL	17.70	4.0×10^{-4}	3.6×10^{-4}

Note:

1. All the 'E' values (extinction coefficient) are in the unit as $M^{-1}cm^{-1}$
2. All the wave length values (/\) are in nm. unit.
3. All the absorption intencities (I values) are in arbitrary units.

absorption intensities are seen to be increasing with concentration.

Comparison of absorption spectra of the complex (c = 1.6 x 10^{-4}M) in iso-butyl alcohol with that in n-butyl, Sec-butyl and t-butyl alcohol reported above, show that iso-butyl alcohol is a better medium for absorption than any other alcohol. In iso-butyl aocohol at λ_1 is E_1 = 4.5 x 10 ^{3} which is much higher than these observed at λ_1 for n-butyl alcohol (E_1 = 2.25 x 10^3), Sec-butyl alcohol (E_1 = 1.875 x 10^3), t-butyl alcohol (E_1 = 2.0625 x 10^3). The absorption intensity at λ_2 for iso-butyl alcohol is (E_2 = 6.125 x 10^3) Sec-butyl alcohol (E_2 = 5.625 x 10^3), t-butyl alcohol (E_2 = 5.0 x 10^3). Similarly the absorption intensity of complex in iso-butyl alcohol at λ_3 is very high (E_3 = 34.375 x 10^3) compared to those observed at λ_3 for n-butyl alcohol (E_3 = 13.75 x 10^3), Sec-butyl alcohol (E_3 = 11.625 x 10^3) and t-butyl alcohol (E_3 = 10.05 x 10^3). However the absorption intensities at λ_4 for all the isomeric butyl alcohol are nearly same and there is no much considerable difference (n-butyl alcohol (E_4 = 1.5 x 10^3), Sec-butyl alcohol (E_4 = 0.75 x 10^3) and t-butyl alcohol (E_4 = 0.75 x 10^3 and iso-butyl alcohol 1.125 x 10^3).

Thus in iso-butyl alcohol the complex solution shows very high absorption at λ_1, λ_2 and λ_3 as compared to that observed for other butyl alcohols. Such higher absorbance is also observed in case of iso-propyl alcohol. This clearly indicates that iso-alkyl group enhances the absorption due to rose bengal and also due to malachite green component of the complex. We have discussed above in section 3.1 to 3.8, the details of results obtained by us, on the absorption spectra of complex MG_2.RB in different alcohols. These results show the following trends in the absorption studies of the complex.

(1) In general absorption spectra of the complex for all the alcohols studied here are similar with some modifications in peak wavelengths and absorption intensities. The absorption bands observed for pure malachite green and rose bengal, are also observed in the spectra of complex. However, the intensities observed are greately enhanced in the complex form.(Fig.9)

(2) Pure rose bengal exists in dimeric form at concentrations above 2 x 10^{-6}M in water and methanol and similar observations are obtained in case of complex in methanol and other alcohols under study.

(3) The bands corresponding to malachite green donot show appreciable red shift but there is a definite red shift observed in case of rose bengal bands. This red shift of rose bengal increases from simplicity to complexity of alcohol molecule.

(4) It is observed that in ethyl alcohol the complex shows abnormal absorption behaviour, especially in case of malachite green bands, higher values of absorptivity (E values) are observed. However, incase of other alcohols malachite green component seems to be less absorbing as compared to rose bengal component. All these results will be discussed in Chapter-IV.

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