CHAPTER III

VIBRATIONAL AND ELECTRONIC SPECTRA AND IONISATION EQUILIBRIA OF MELLITEIN DYES

3.1 INTRODUCTION

The simplest model of a pair of atoms in a molecule is that of two spherical balls connected by an elastic spring. Such a system can absorb energy leading to increase in inter-atomic distance. With expulsion of energy, the spherical masses come closer together. Several such units consisting of two or more atoms and one or more chemical bonds constitute various functional groups in a molecule. The chemical and spectroscopic behaviour of a molecule depend on such functional units. The aggregate properties therefore can be attributed to the basic properties of individual constituent groups. Even though characteristic properties are expected for functional group, slight variations due to major changes in neighbouring functional groups and atoms can not be overlooked. Hence from a known molecular structure spectroscopic characteristics can be worked out or from a spectrum molecular structure can be assigned on the basis of vibrational energies for organic molecules which lie within 4000 to 600 cm^{-1}. The present chapter explains the infrared absorption spectra of ten fluoromellitein dyes in their neutral form.

In addition to above, when somewhat larger energy is involved in the molecular processes, there is possibility of transfer of

electrons in outer second or third levels undergoing transfer of electrons from one molecular orbital to the other, giving $\sigma^* \leftarrow \sigma$, $\pi^* \leftarrow \pi$ or $\pi^* \leftarrow$ n transitions. There is an absorption of light in the visible region. However more energetic processes result in charge transfer as is exhibited by the mellitein dyes. The charge transfer spectra with one or more isobestic points explain the ionisation of the dyes. This chapter gives an account of vibrational electronic spectra of ten compounds belonging to the class of mellitein dyes.

3.2.1 Vibrational spectra of mellitein dyes

The potassium bromide pellet infrared spectra over the range 4000 to 600 cm^{-1} of all the ten mellitein dyes are given in Fig. 3.1. The molecules are fairly complicated containing as many as more than 60 atoms and therefore are somewhat complicated and difficult to analyse. It can however be said that the spectra exhibit very broad bands pertaining to various forms of water and -OH groups, aromatic and aliphatic groups and also functional groups and the patterns of substitution.

3.2.2 Spectra in terms of appropriate regions

4000 to 3100 cm^{-1}

In this region very broad absorption bands for free water and -OH groups are seen. All the compounds show such broad bands.

3100 to 2000 cm^{-1}

The C-H stretching and vibrational frequency of olefins and aromatic rings absorb in this region [88, 89].

3000 to 2700 cm^{-1}

Below 3000 wave number aliphatic C-H stretching frequency appears. $-CH_3$ groups in cresol show these bands in infrared spectra of cresol fluoromellitein dyes [90-92].

2000 to 1700 cm^{-1}

This is an overtone region. In most cases studied in this chapter a general pattern is of ill-defined very weak bands difficult to identify as different from noise [93]. Weak bands in the region 1715 - 1740 cm^{-1} and 1740 - 1775 cm^{-1} may be attributed to the lactone ring [94, 95].

1800 to 1515 cm^{-1}

Carboxyl frequency is a strong absorption band 1760 cm^{-1} [96, 97].

1700 to 1550 cm^{-1}

Compounds containing C=C absorb in this region [98].

1620 to 1420 cm^{-1}

Aromatic rings show sharp bands near 1615, 1500 and 1416 cm^{-1}. Heterocyclic compounds show the ring absorption band in this region [88, 89].

1500 to 1250 cm^{-1}

C-CH_3 group show an absorption band 1375 cm^{-1} [90-92].

900 to 700 cm^{-1}

Aromatic C-H band, the three adjacent hydrogens and meta substituted groups show bands near 780 cm^{-1}. The two adjacent hydrogen of para substitution show band 820 cm^{-1} and isolated hydrogen atoms near 870 cm^{-1} [99].

830 to 600 cm^{-1}

The C-Cl group absorb at 830 to 570 cm^{-1} [100].

3.2.3 Results and Discussion

As shown above absorption bands are expected to occur at the respective positions. The prominent features of all these structurally similar compounds can be explained in terms of broad -OH and water bands, aromatic ring frequencies, carbonyl frequencies and substitution patterns. Compounds prepared from cresol show bands corresponding to -CH_3 group, while those

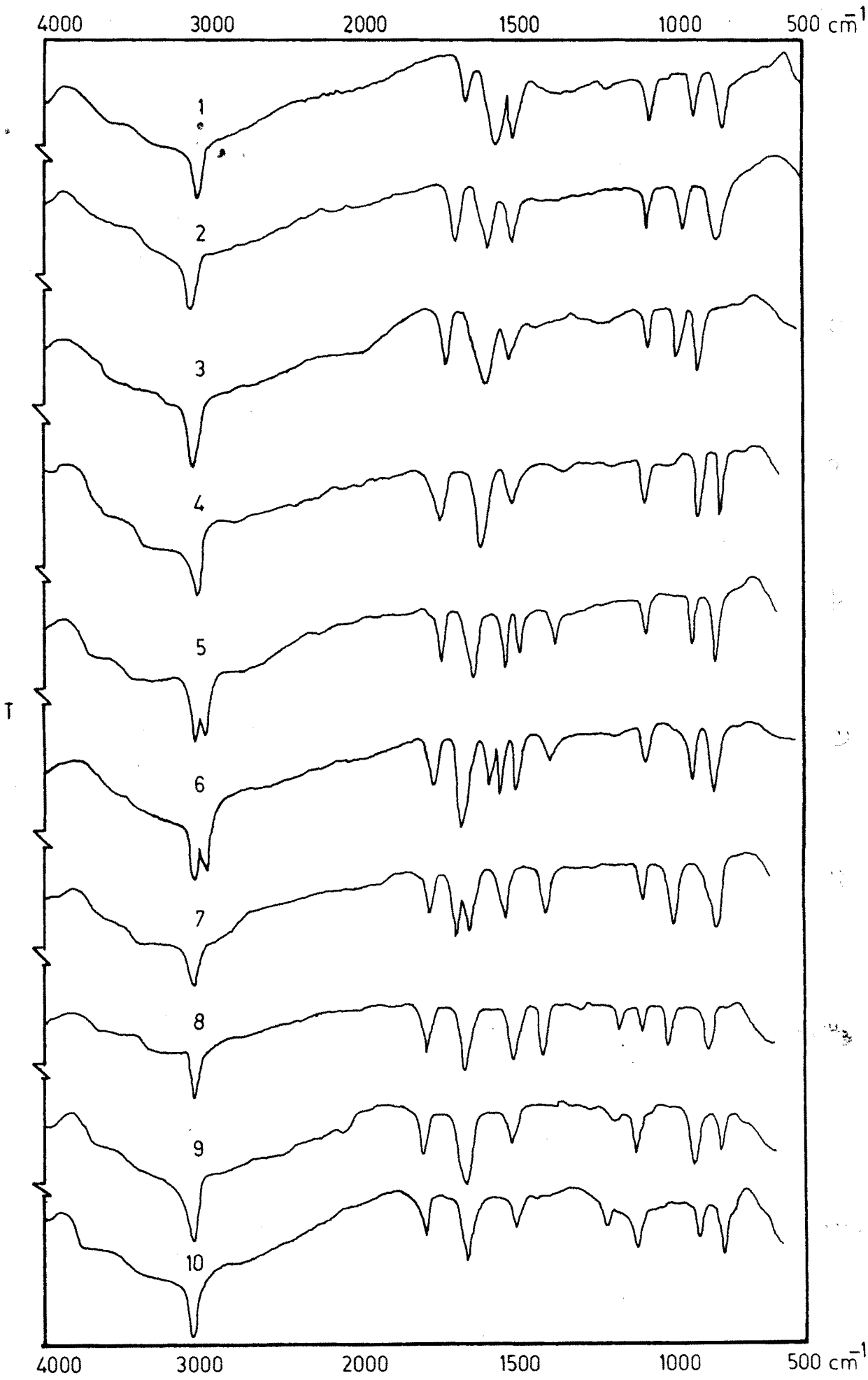

Fig. 3·1 INFRARED SPECTRA OF THE MELLITEIN DYES (1 – 10)

obtained from nitrophenol and chlorophenol show the characteristic frequencies of C-Cl and NO_2. Towards the lower wave-number side, the substitution pattern shows typical bands. The remaining part of the infrared spectra contain a few very weak bands and attempts have not been done to enumerate them. Table 3.1 shows the infrared spectral assignment for compounds under study.

3.2.4 Conclusion

From the above discussion it can be concluded that infrared spectral assignment is straight-forward and since the compounds under investigation are structurally similar, the spectra are comparable. As the molecules contain very large number of atoms it is not possible to account for the large number of very weak and ill-defined bands.

3.3 ELECTRONIC ABSORP TION SPECTRA : RESULTS AND DISCUSSION

3.3.1 General statements

The dyes exhibit strong charge transfer bands in the visible region and due to the pH variation, the proportions of molecular, monoanionic and dianionic species vary [101]. The dynamic equilibrium between these species give rise to a well defined isobestic points. The set of spectra related to a chosen isobestic point can be used for the determination of ionisation constant [102]. It is possible to determine successive ionisation constants from spectra data provided $\triangle$ pK is $\geq$ 4 pH units.

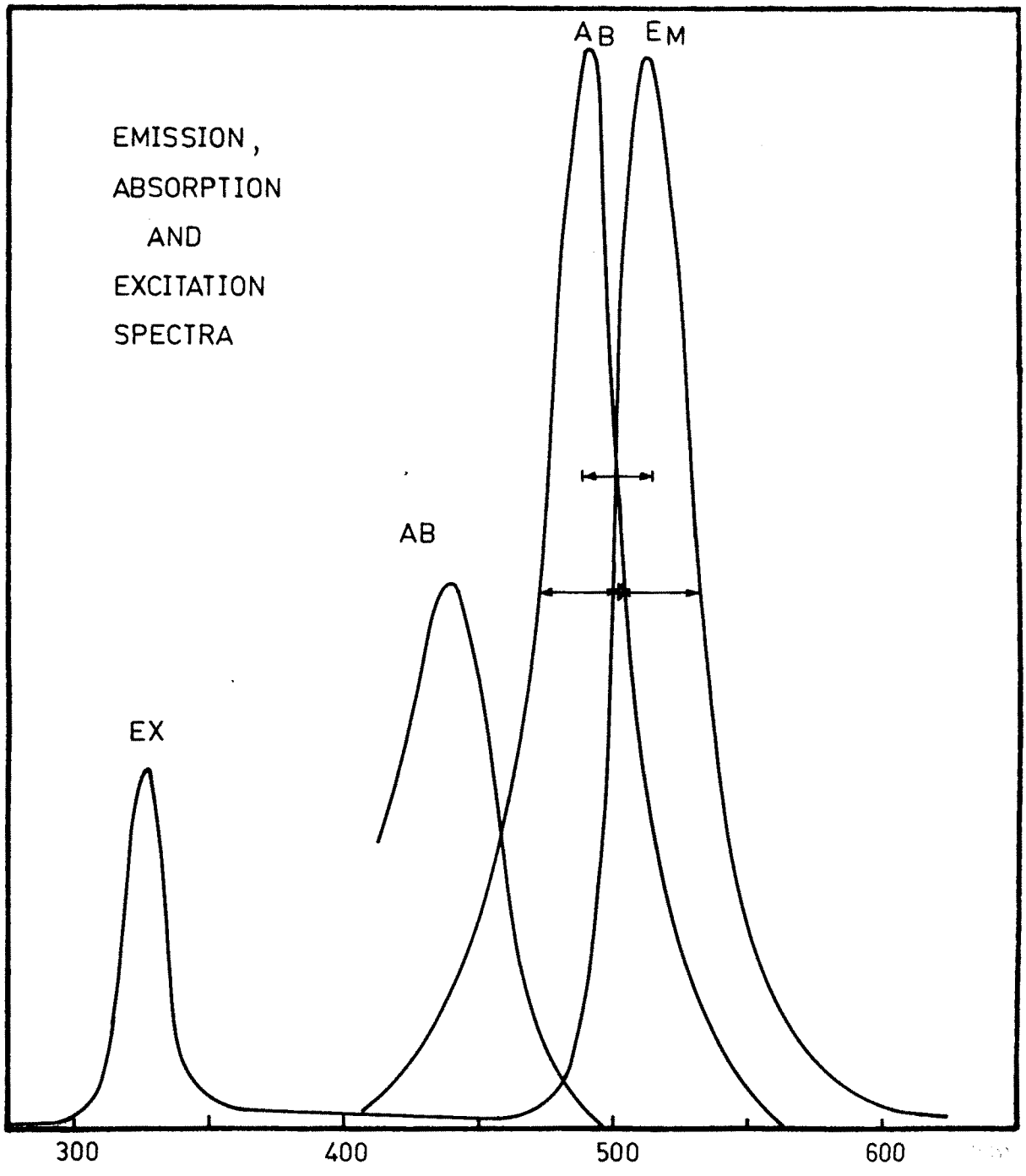

Fig. 3·2 TYPICAL EXCITATION, ABSORPTION AND EMISSION (FLUORESCENCE) SPECTRA.

If the difference is small several species occur simultaneously and the ionization constants are only approximately correct, and the pK values are less reliable. In the present set difference between pK_1 and pK_2 is about four pH units and therefore the values obtained are fairly accurate.

3.3.2 Absorption Spectra

The spectra are recorded over the region 400 to 550 nm. In the acidic medium there is an absorption band in the lower wavelength region and as the pH increases the absorption values are lowered. As the pH increases further a small hump appears in the long wavelength region and with further increase in pH there is increase in absorption in the longer wavelength region with corresponding lowering in absorbance due to acidic species. At high pH long wavelength band is more important. This is repeated in case of monoanionic and dianionic species in dynamic equilibrium. The spectral characteristics are summarised in Table 3.2 and the spectra are shown in Figs. 3.3 to 3.12.

3.3.3 Determination of ionisation constants

Hydrogen ion concentration of the medium is one of the important experimental conditions that governs the rate and the equilibrium of a chemical reaction. The hydrogen ion concentration are generally determined by using the electrochemical or optical methods. The compounds which are used for this purpose by applying optical methods are known as visual acid-

Table 3.2 : Electronic Absorption spectra of Mellitein Dyes

No.	Compound	Acid Medium			Alkaline Medium			Fluorescence
		Colour	λ_{max} in nm	ϵ l $mol^{-1}cm^{-1}$	Colour	λ_{max} in nm	ϵ l $mol^{-1}cm^{-1}$	
1.	Difluoromellitein	orange-yellow		23150	Red	491	39260	Pale green in acidic medium Deepening of green in neutral medium and intense green fluorescence in alkaline medium
2.	Phenolfluoromellitein	"		27170	"	489	44900	
3.	1,2 Dihydroxyfluoro-mellitein	"		31000	"	491	54060	
4.	1,2,3 Trihydroxyfluoro-mellitein	"		19080	"	496	34980	
5.	o-Cresolfluoromellitein	"		28200	"	491	51900	
6.	m-Cresolfluoromellitein	"		18900	"	490	42300	
7.	p-Cresolfluoromellitein	"		24400	"	491	47700	
8.	p-Nitrophenolfluoro-mellitein	"		28800	"	492	34420	
9.	o-Chlorophenolfluoro-mellitein	"		31730	"	491	53520	
10.	p-Chlorophenolfluoro-mellitein	"		37820	"	491	63140	

base indicators. The equilibrium concentration of the highly coloured form or first measured by setting known H^+ ion levels later this data can be used in a reversed order to measure the colour and interpret it in terms of H^+ ion concentration which is an unknown to be found out. The equilibrium expression which can be used conveniently is the equilibrium constant, the ionisation constant or the dissociation constant. It is in fact the pH condition at which half the molecules are dissociated leaving half undissociated [103]. When there is only one replaceable proton in a molecule there is only one pK value but when there are several protons there are equivalent number of ionisation constants when several protons are presents. Some of them have very high and very low ionisation constants. Some have overlapping equilibria and such values can not be measured with simple technique if difference between two ionisation constants is at least 4 pH units there is negligible overlap however overlapping equilibrium can be resolved by using suitable computer programmes or manually by using successive approximations.

An equilibrium associated with an acid HB can be shown as

$$\underset{\text{Acid form}}{HB} \rightleftharpoons H^+ + \underset{\text{Base form}}{B^-}$$

The corresponding equilibrium constant is

$$K_{HB} = \frac{a_{H^+} \cdot a_{B^-}}{a_{HB}}$$

Here a_x represents the activity of the species x. The density of colour during any reaction in presence of HB is given by $[HB]/[B^-]$.

Therefore $$\frac{[HB]}{[B^-]} = \frac{a_{H^+}}{K_{HB}} \cdot \frac{f_{B^-}}{f_{HB}}$$

Here f_x is the activity coefficient of this species x.

Logarithmic form of above equation is

$$- \log a_{H^+} = pH = pK_{HB} + \log \frac{[B^-]}{[HB]} + \log \frac{f_{B^-}}{f_{HB}}$$

The apparent ionisation constant pK' is

$$pK'_{HB} = pK_{HB} + \log \frac{f_{B^-}}{f_{HB}}$$

Here the previous equation can be written as

$$pH = pK'_{HB} + \log \frac{[B^-]}{[HB]}$$

For a set of experiment carried out at very low and constant ionic strength the activity coefficient term will be constant and the colour change which is related to the concentration ratio $[B^-]/[HB]$ will depend only on pH.

Spectrophotometric method can be used to determine the ratio $[B^-]/[HB]$. For most of the visual indicators the extinction coefficients are of the order of 10^4 to 10^5.

The results of measurements on several mellitein dyes are given in Table 3.23 and the values of individual compounds are given in Tables 3.3 to 3.22.

Ionisation constants of difluoromellitein
Conc. 10.00 mg/l, Temp. 25.0°;
Path length 10.01 mm,

Table 3.3

Analytical wavelength 440 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.42$ $d_I = 0.22$

pH	d	$d-d_I$	d_M-d	$\log \frac{d-d_I}{d_M-d}$	pK_1	Mean pK_1
2.80	0.23	0.01	0.19	$\bar{2}.7212$	1.62	
2.71	0.24	0.02	0.18	$\bar{1}.0457$	1.76	
2.62	0.245	0.025	0.175	$\bar{1}.1551$	1.78	1.82
2.30	0.28	0.06	0.14	$\bar{1}.6321$	1.93	
2.10	0.30	0.08	0.12	$\bar{1}.8235$	1.92	
1.62	0.35	0.13	0.07	0.2686	1.89	

Table 3.4

Analytical wavelength 490 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.70$ $d_I = 0.20$

pH	d	d_I-d	$d-d_M$	$\log \frac{d_I-d}{d-d_M}$	pK_2	Mean pK_2
7.22	0.62	0.08	0.42	$\bar{1}.2799$	6.50	
6.70	0.53	0.17	0.33	$\bar{1}.7119$	6.42	
6.49	0.45	0.25	0.25	0.0000	6.49	6.40
6.30	0.43	0.27	0.23	0.0697	6.37	
5.90	0.36	0.34	0.16	0.3274	6.23	
5.62	0.27	0.43	0.07	0.7882	6.41	

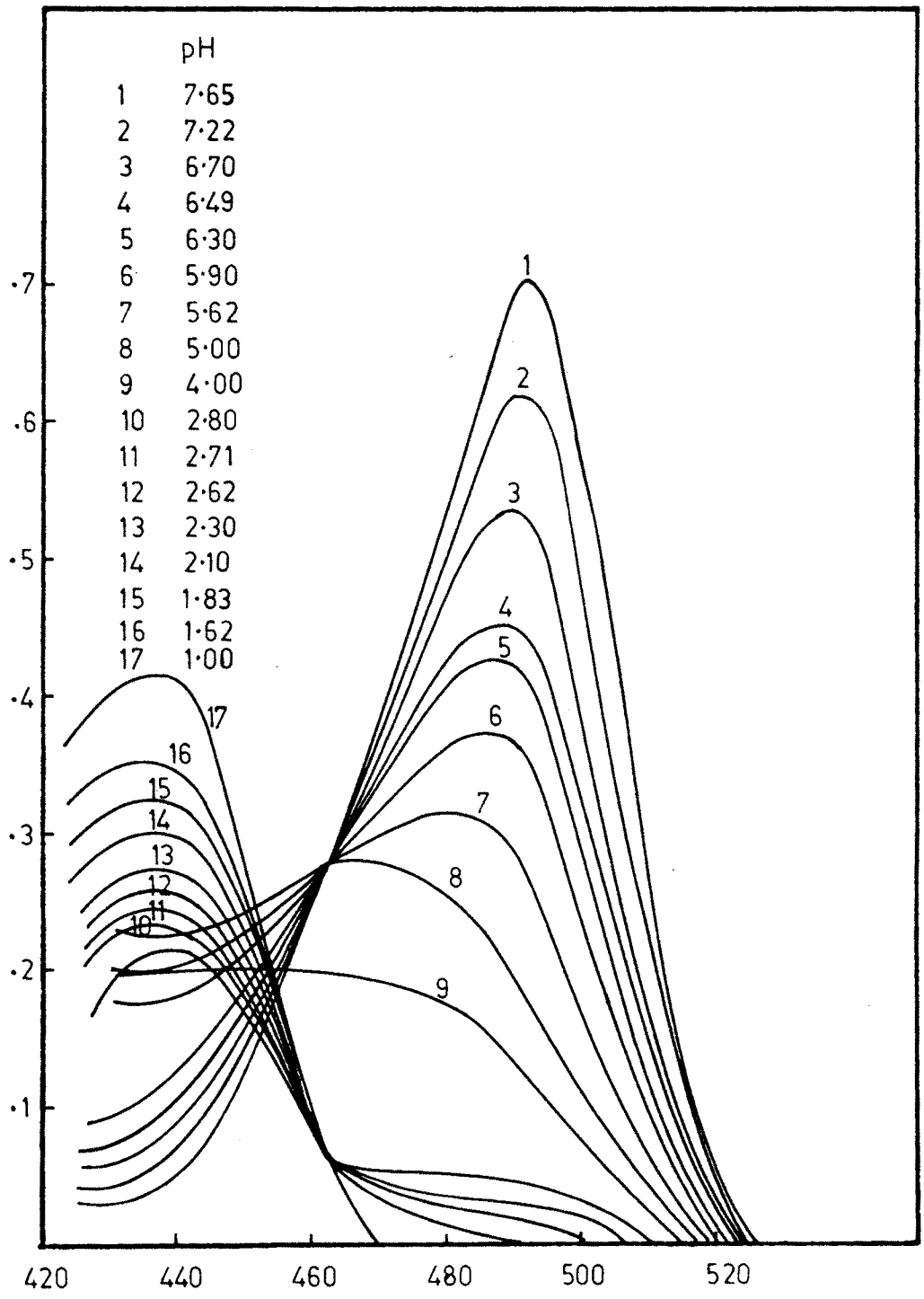

Fig. 3·3 ABSORPTION SPECTRA OF DIFLUOROMELLITEIN .
(CONC. 10 µg ml^{-1})

Ionisation constants of phenol fluoromellitein
Conc. 10.00 mg/l, Temp. 25.0°;
Path length 10.01 mm;

Table 3.5

Analytical wavelength 440 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.47$ $d_I = 0.24$

pH	d	$d-d_I$	d_M-d	$\log \frac{d-d_I}{d_M-d}$	pK_1	Mean pK_1
2.40	0.29	0.05	0.18	$\bar{1}.8426$	1.84	
2.10	0.32	0.08	0.15	$\bar{1}.7270$	1.83	
2.00	0.33	0.09	0.14	$\bar{1}.8080$	1.81	1.83
1.90	0.35	0.11	0.12	$\bar{1}.9622$	1.86	
1.63	0.38	0.14	0.09	0.1914	1.82	
1.25	0.42	0.18	0.05	0.5563	1.81	

Table 3.6

Analytical wavelength 490 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.22$ $d_I = 0.78$

pH	d	d_I-d	$d-d_M$	$\log \frac{d_I-d}{d-d_M}$	pK_2	Mean pK_2
7.22	0.67	0.11	0.45	$\bar{1}.3882$	6.61	
7.00	0.60	0.18	0.38	$\bar{1}.6755$	6.68	
6.65	0.52	0.26	0.30	$\bar{1}.9379$	6.59	6.63
6.30	0.42	0.18	0.10	0.2553	6.56	
6.00	0.33	0.45	0.11	0.6117	6.61	
5.61	0.26	0.52	0.04	1.1139	6.72	

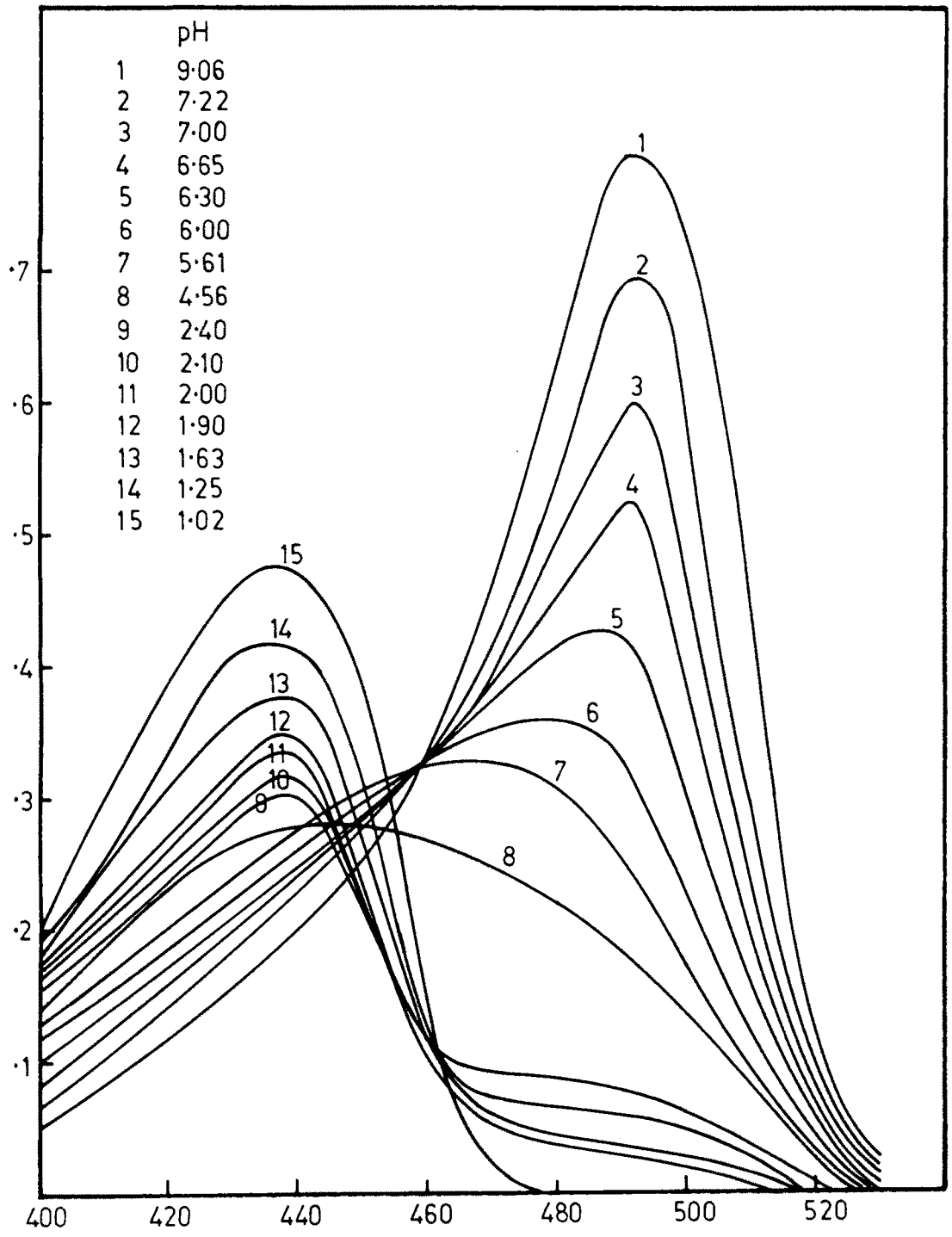

Fig. 3·4 ABSORPTION SPECTRA OF PHENOL FLUOROMELLITEIN.
(CONC. 10 μg ml^{-1})

Ionisation constants of 1,2 dihydroxy phenol fluoromellitein
conc. 10.00 mg/l, Temp. 25.0°;
Path length 10.01 mm;

Table 3.7

Analytical wavelength 440 nm;
Solvent 50 % ethanol-water v/v;
d_M = 0.60 d_I = 0.25

U

pH	d	$d-d_I$	d_M-d	log $\frac{d-d_I}{d_M-d}$	pK_1	Mean pK_2
2.95	0.30	0.05	0.30	$\bar{1}$.2219	2.17	
2.76	0.32	0.07	0.28	$\bar{1}$.3979	2.16	
2.42	0.35	0.10	0.25	$\bar{1}$.6021	2.02	2.08
2.23	0.40	0.15	0.20	$\bar{1}$.8751	2.11	
2.00	0.43	0.18	0.17	0.0249	2.02	
1.49	0.52	0.27	0.08	0.5283	2.02	

Table 3.8

Analytical wavelength 490 nm;
Solvent 50 % ethanol-water v/v;
d_M = 0.24 d_I = 0.92

pH	d	d_I-d	$d-d_M$	log $\frac{d_I-d}{d-d_M}$	pK_2	Mean pK_2
6.95	0.75	0.17	0.51	$\bar{1}$.5228	6.48	
6.81	0.63	0.29	0.39	$\bar{1}$.8713	6.68	
6.42	0.53	0.39	0.29	0.1287	6.55	6.53
5.83	0.38	0.54	0.14	0.5863	6.42	
5.32	0.28	0.64	0.04	1.2041	6.52	

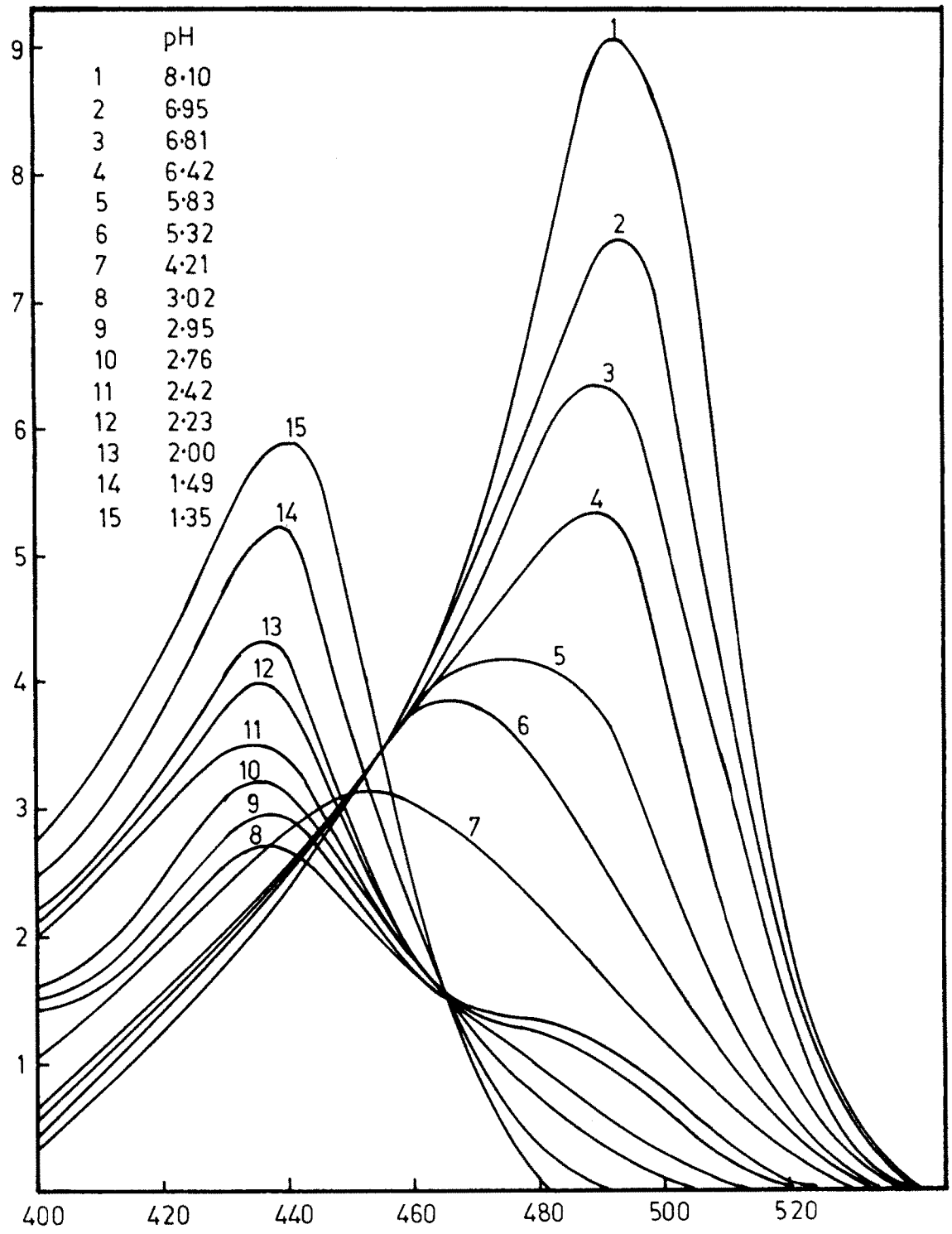

Fig.3·5 ABSORPTION SPECTRA OF 1,2 DIHYDROXYPHENOL FLUOROMELLITEIN.
(CONC. 10 μg ml^{-1})

Ionisation constants of 1,2,3 trihydroxyphenol fluoromellitein
Conc. 10.00 mg/l, Temp. 25.0°;
Path length 10.01 mm;

Table 3.9

Analytical wavelength 440 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.37$ $d_I = 0.18$

pH	d	$d-d_I$	d_M-d	$\log \frac{d-d_I}{d_M-d}$	pK_1	Mean pK_1
2.5	0.21	0.03	0.16	$\bar{1}.2729$	1.77	
2.33	0,22	0.04	0.15	$\bar{1}.4260$	1.75	
2.22	0.24	0.06	0.13	$\bar{1}.6643$	1.88	1.83
2.00	0.26	0.08	0.11	$\bar{1}.8617$	1.86	
1.85	0.28	0.10	0.09	0.0458	1.90	
1.6	0.30	0.12	0.07	0.2330	1.83	

Table 3.10

Analytical wavelength 490 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.18$ $d_I = 0.57$

pH	d	d_I-d	$d-d_M$	$\log \frac{d_I-d}{d-d_M}$	pK_2	Mean pK_2
6.80	0.46	0.15	0.28	$\bar{1}.5941$	6.39	
6.70	0.44	0.13	0.26	$\bar{1}.6990$	6.40	
6.25	0.38	0.19	0.20	$\bar{1}.9778$	6.23	6.41
6.10	0.28	0.29	0.10	0.4624	6.56	
5.25	0.20	0.37	0.20	1.2672	6.52	

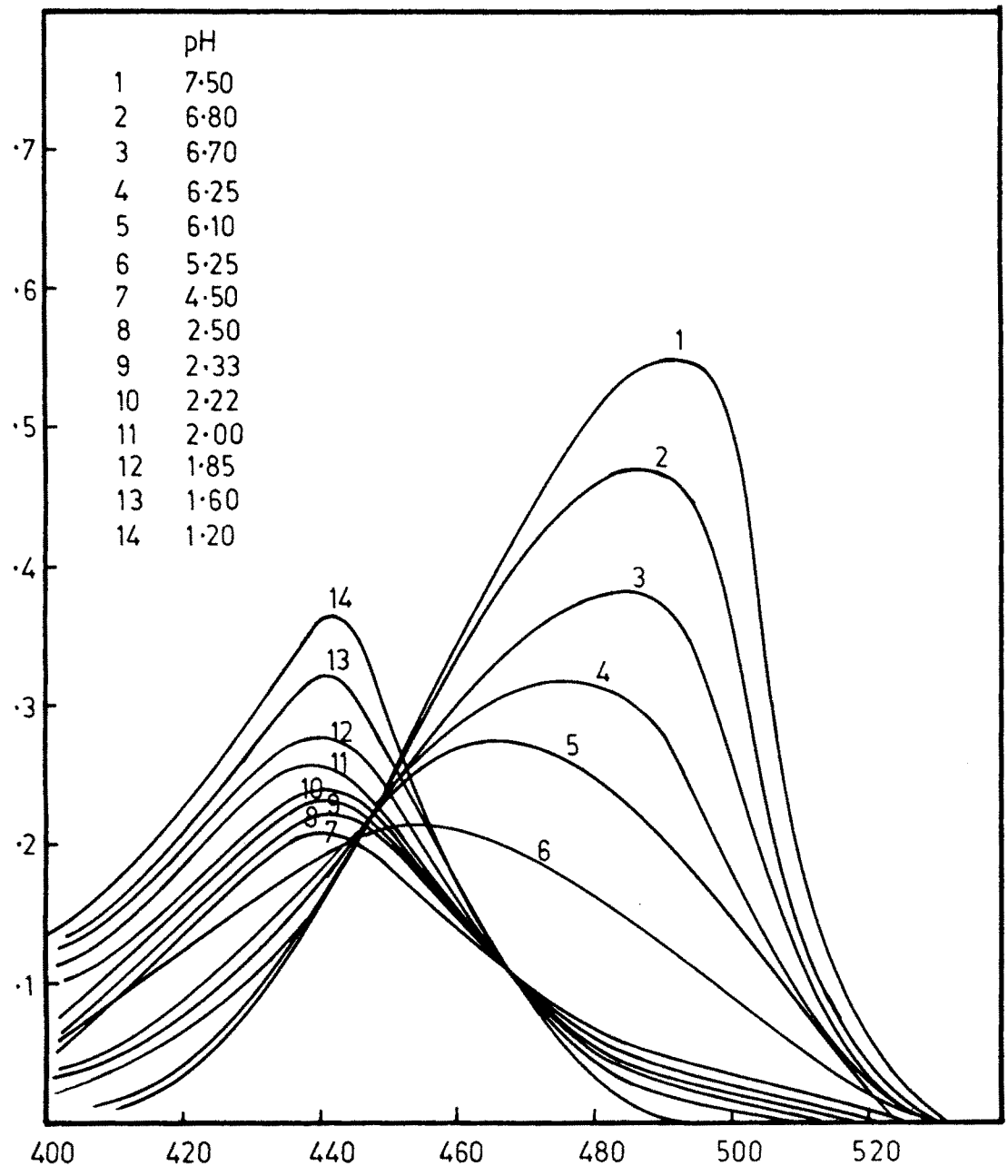

Fig.3·6 ABSORPTION SPECTRA OF 1,2,3 TRIHYDROXYPHENOL FLUOROMELLITEIN
(CONC. 10 µg ml^{-1})

Ionisation constants of o-cresol fluoromellitein
Conc. 10.00 mg/l, Temp. 25.0°;
Path length 10.01 mm;

Table 3.11

Analytical wavelength 440 nm;
Solvent 50 % ethanol-water v/v;
d_M = 0.49 d_I = 0.23

pH	d	$d-d_I$	d_M-d	$\log \frac{d-d_I}{d_M-d}$	pK_1	Mean pK_1
2.75	0.27	0.04	0.22	$\bar{1}$.2596	2.01	
2.15	0.34	0.11	0.15	$\bar{1}$.8653	2.02	
1.7	0.40	0.17	0.09	0.2742	1.97	2.01
1.5	0.43	0.20	0.06	0.5224	2.02	
1.35	0.35	0.12	0.04	0.4771	1.83	
1.10	0.47	0.24	0.02	1.0792	2.18	

Table 3.12

Analytical wavelength 490 nm;
Solvent 50 % ethanol-water v/v;
d_M = 0.20 d_I = 0.83

pH	d	d_I-d	$d-d_M$	$\log \frac{d_I-d}{d-d_M}$	pK_2	Mean pK_2
7.48	0.70	0.13	0.50	$\bar{1}$.4179	6.90	
7.25	0.65	0.18	0.45	$\bar{1}$.6020	6.85	
7.00	0.60	0.23	0.40	$\bar{1}$.7597	6.76	6.77
6.85	0.52	0.31	0.32	$\bar{1}$.9863	6.83	
6.55	0.40	0.43	0.20	0.3324	6.88	
6.00	0.325	0.505	0.125	0.6064	6.41	

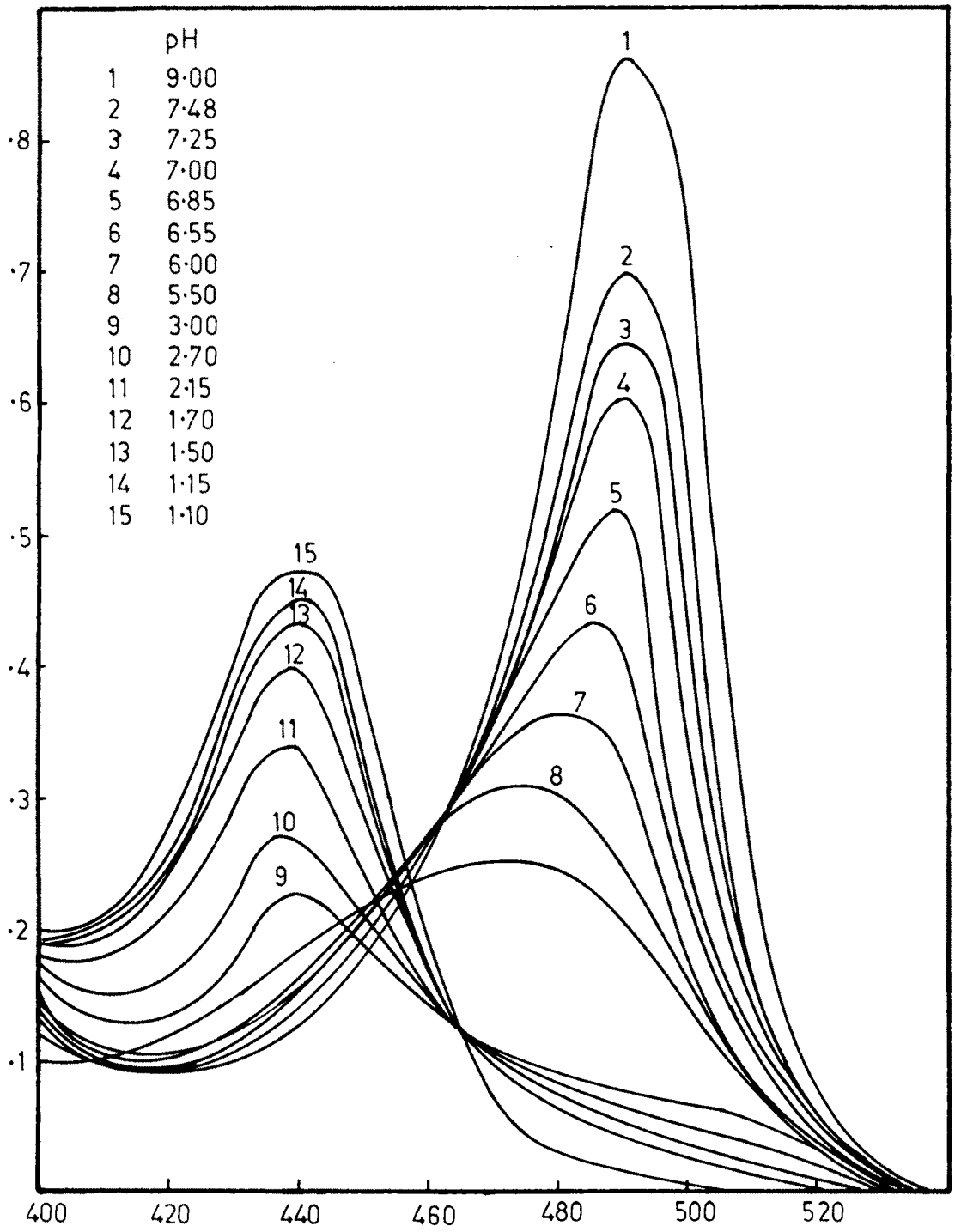

Fig.3·7 ABSORPTION SPECTRA OF O-CRESOL FLUOROMELLITEIN.
(CONC. 10 $\mu g\ ml^{-1}$)

Ionisation constants of m-cresol fluoromellitein
Conc. 10.00 mg/l, Temp. 25.0°;
Path length 10.01 mm;

Table 3.13

Analytical wavelength 440 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.34$ $d_I = 0.20$

pH	d	$d-d_I$	d_M-d	$\log \frac{d-d_I}{d_M-d}$	pK_1	Mean pK_1
2.50	0.22	0.02	0.12	$\bar{1}.2217$	1.72	
2.00	0.25	0.05	0.09	$\bar{1}.7443$	1.74	
1.70	0.27	0.07	0.07	0.0000	1.70	1.78
1.62	0.28	0.08	0.06	0.1249	1.74	
1.50	0.30	0.10	0.04	0.3979	1.89	
1.10	0.32	0.12	0.02	0.7782	1.88	

Table 3.14

Analytical wavelength 490 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.17$ $d_I = 0.74$

pH	d	d_I-d	$d-d_M$	$\log \frac{d_I-d}{d-d_M}$	pK_2	Mean pK_2
6.95	0.62	0.12	0.45	$\bar{1}.8500$	6.80	
6.75	0.56	0.18	0.39	$\bar{1}.9059$	6.74	
6.65	0.50	0.24	0.33	$\bar{1}.9600$	6.61	6.61
6.50	0.40	0.34	0.23	0.0490	6.56	
6.22	0.31	0.43	0.14	0.1312	6.35	

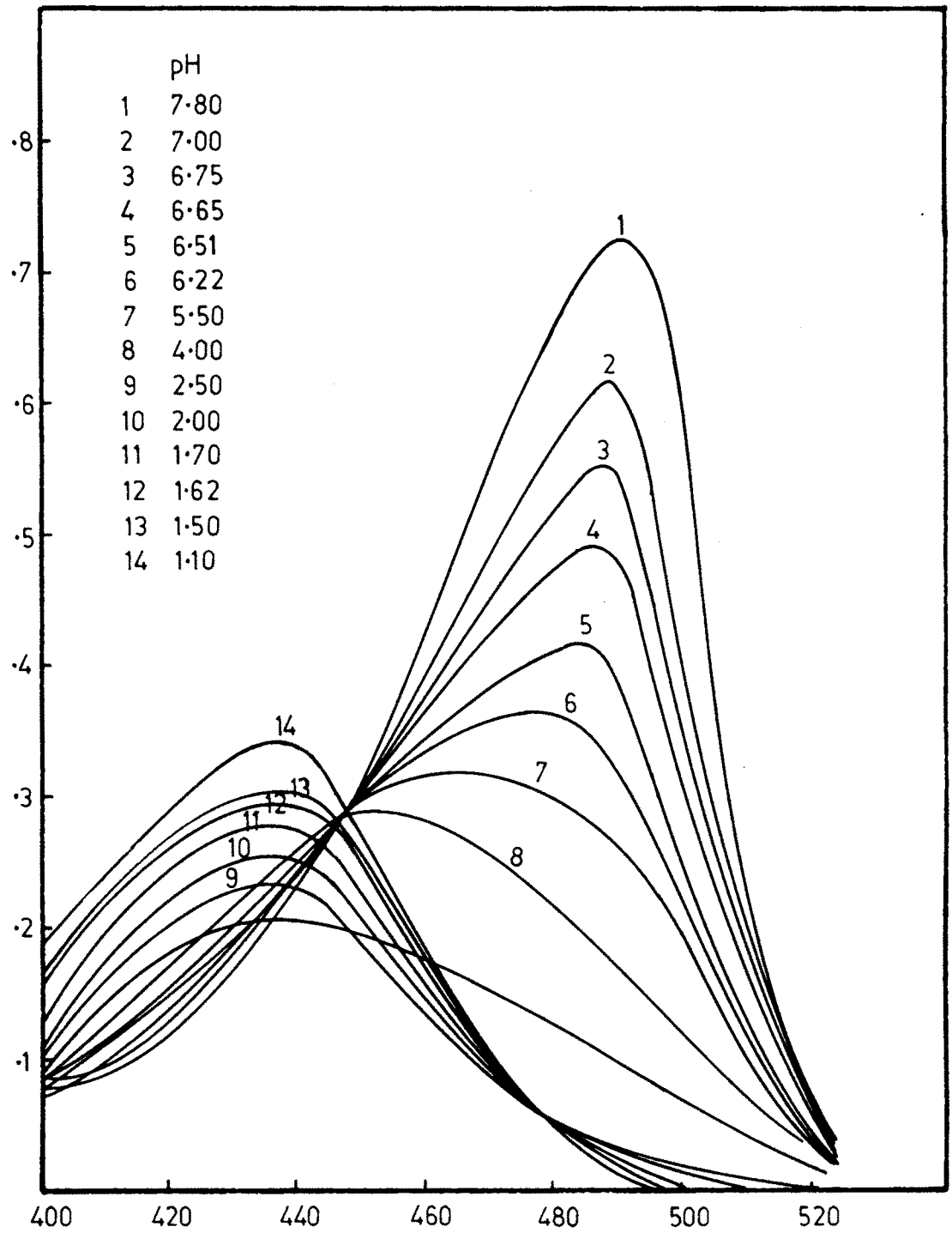

Fig.3·8 ABSORPTION SPECTRA OF m-CRESOL FLUOROMELLITEIN.
(CONC. 10 μg ml^{-1})

Ionisation constants of p-cresol fluoromellitein
Conc. 10.00 gm/l, Temp. 25.0°;
Path length 10.01 mm;

Table 3.15

Analytical wavelength 440 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.50$ $d_I = 0.25$

pH	d	$d-d_I$	d_M-d	$\log \frac{d-d_I}{d_M-d}$	pK_1	Mean pK_1
2.75	0.39	0.04	0.21	$\bar{1}.2799$	2.03	
2.50	0.32	0.07	0.18	$\bar{1}.5898$	2.08	
2.30	0.34	0.09	0.16	$\bar{1}.7501$	2.05	2.04
2.00	0.37	0.12	0.13	$\bar{1}.9653$	1.97	
1.70	0.42	0.17	0.08	0.3273	2.03	
1.50	0.45	0.20	0.05	0.6021	2.10	

Table 3.16

Analytical wavelength 490 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.20$ $d_I = 0.85$

pH	d	d_I-d	$d-d_M$	$\log \frac{d_I-d}{d-d_M}$	pK_2	Mean pK_2
7.34	0.70	0.15	0.50	$\bar{1}.4771$	6.82	
7.05	0.66	0.19	0.46	$\bar{1}.6160$	6.67	
6.94	0.59	0.26	0.39	$\bar{1}.8239$	6.76	6.64
6.42	0.50	0.35	0.30	0.0670	6.49	
6.10	0.40	0.45	0.20	0.3522	6.45	

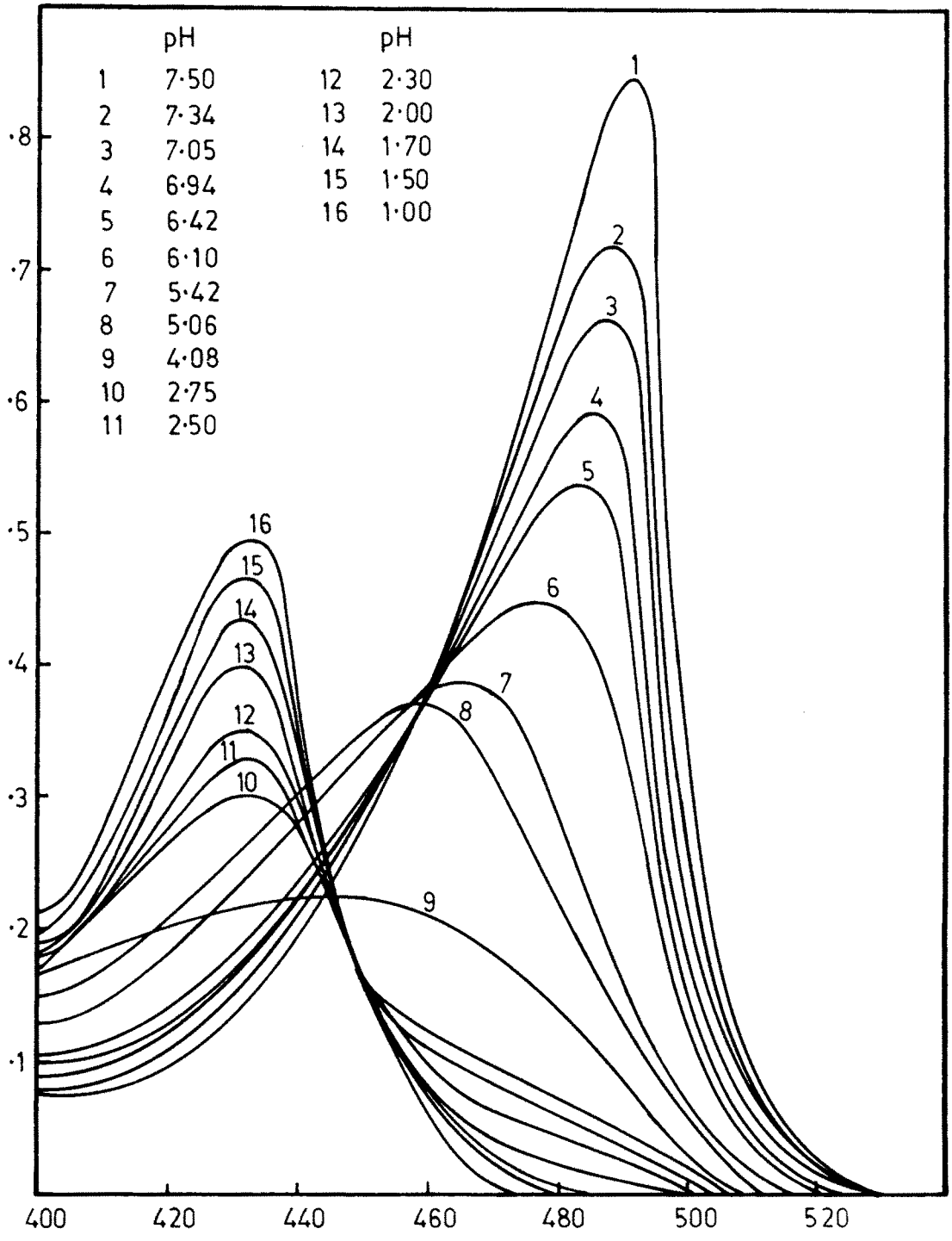

Fig.3·9 ABSORPTION SPECTRA OF P-CRESOL FLUOROMELLITEIN.
(CONC 10 μg ml^{-1})

Ionisation constants of p-Nitrophenol fluoromellitein
Conc. 10.00 gm/l, Temp. 25.0°;
Path length 10.01 mm;

Table 3.17

Analytical wavelength 440 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.48$ $d_I = 0.22$

pH	d	$d-d_I$	d_M-d	$\log \frac{d-d_I}{d_M-d}$	pK_1	Mean pK_1
2.75	0.25	0.03	0.23	$\bar{1}.1154$	1.87	
2.20	0.30	0.08	0.18	$\bar{1}.6478$	1.85	
2.00	0.32	0.10	0.16	$\bar{1}.7959$	1.80	1.87
1.87	0.35	0.13	0.13	0.0000	1.87	
1.52	0.40	0.18	0.08	0.3521	1.87	
1.10	0.45	0.23	0.03	0.8842	1.98	

Table 3.18

Analytical wavelength 490 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.20$ $d_I = 0.60$

pH	d	d_I-d	$d-d_M$	$\log \frac{d_I-d}{d-d_M}$	pK_2	Mean pK_2
7.05	0.50	0.10	0.30	$\bar{1}.5229$	6.57	
6.65	0.42	0.18	0.22	$\bar{1}.9129$	6.56	
4.42	0.37	0.23	0.17	0.1313	6.55	6.57
6.10	0.32	0.28	0.10	0.4472	6.55	
5.31	0.22	0.38	0.20	1.2788	6.58	

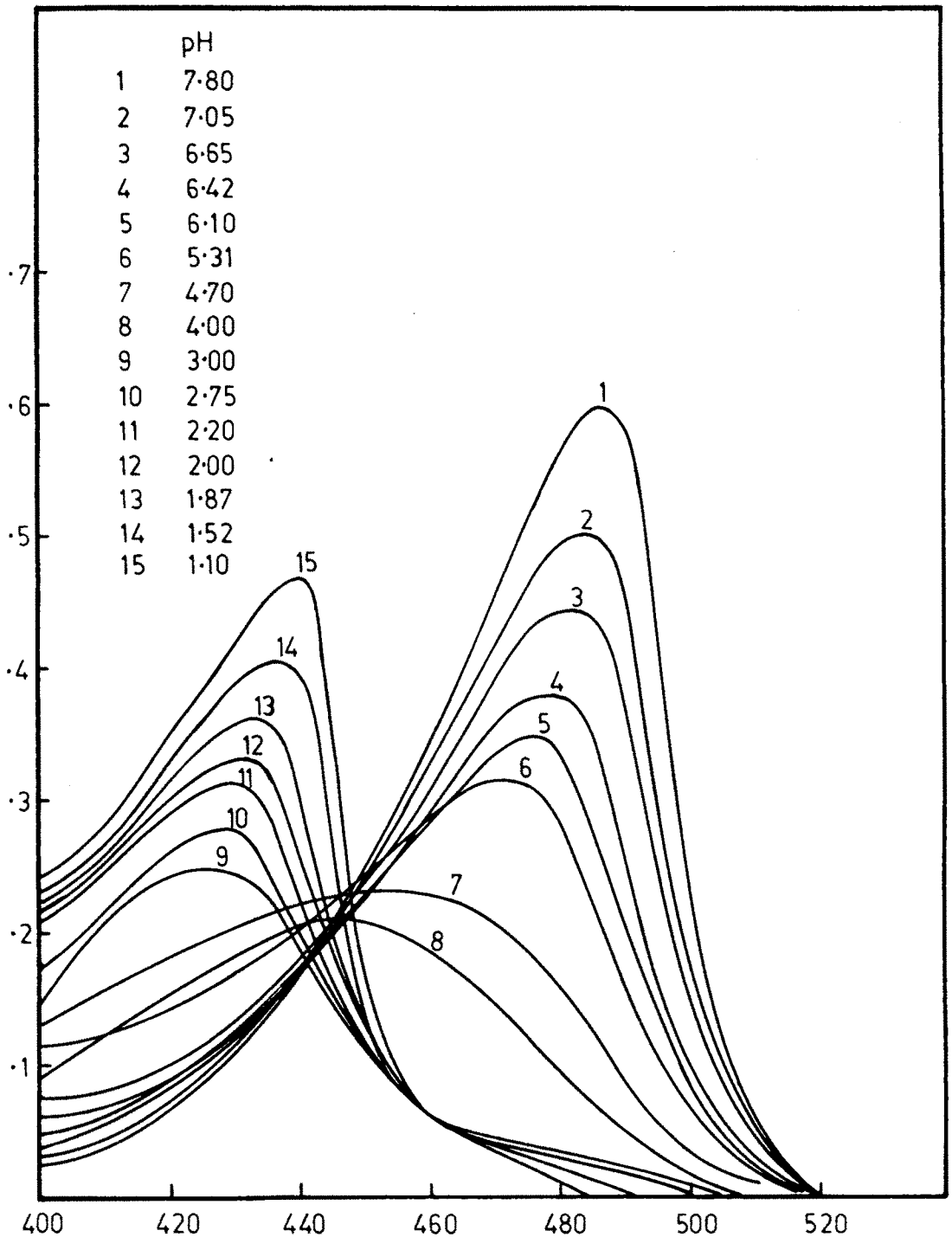

Fig. 3·10 ABSORPTION SPECTRA OF P-NITROPHENOL FLUOROMELLITEIN. (CONC. 10 $\mu g\ ml^{-1}$)

Ionisation constants of o-chlorophenol fluoromellitein
Conc. 10.00 mg/l, Temp. 25.0°;
Path length 10.01 mm;

Table 3.19

Analytical wavelength 440 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.50$ $d_I = 0.28$

pH	d	$d-d_I$	d_M-d	$\log \frac{d-d_I}{d_M-d}$	pK_1	Mean pK_1
2.90	0.30	0.01	0.10	$\bar{1}.0000$	1.90	
2.60	0.32	0.02	0.09	$\bar{1}.3468$	1.94	
2.40	0.34	0.03	0.08	$\bar{1}.5740$	1.97	1.93
2.15	0.36	0.04	0.07	$\bar{1}.7570$	1.91	
1.65	0.42	0.07	0.04	0.2430	1.89	
1.4	0.46	0.09	0.02	0.6532	2.00	

Table 3.20

Analytical wavelength 490 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.25$ $d_I = 0.90$

pH	d	d_I-d	$d-d_M$	$\log \frac{d_I-d}{d-d_M}$	pK_2	Mean pK_2
7.0	0.72	0.18	0.47	$\bar{1}.5832$	6.58	
6.71	0.64	0.26	0.39	$\bar{1}.8239$	6.53	
6.42	0.54	0.36	0.29	0.0939	6.51	6.52
6.21	0.47	0.43	0.22	0.2911	6.50	
5.70	0.34	0.56	0.09	0.7940	6.49	

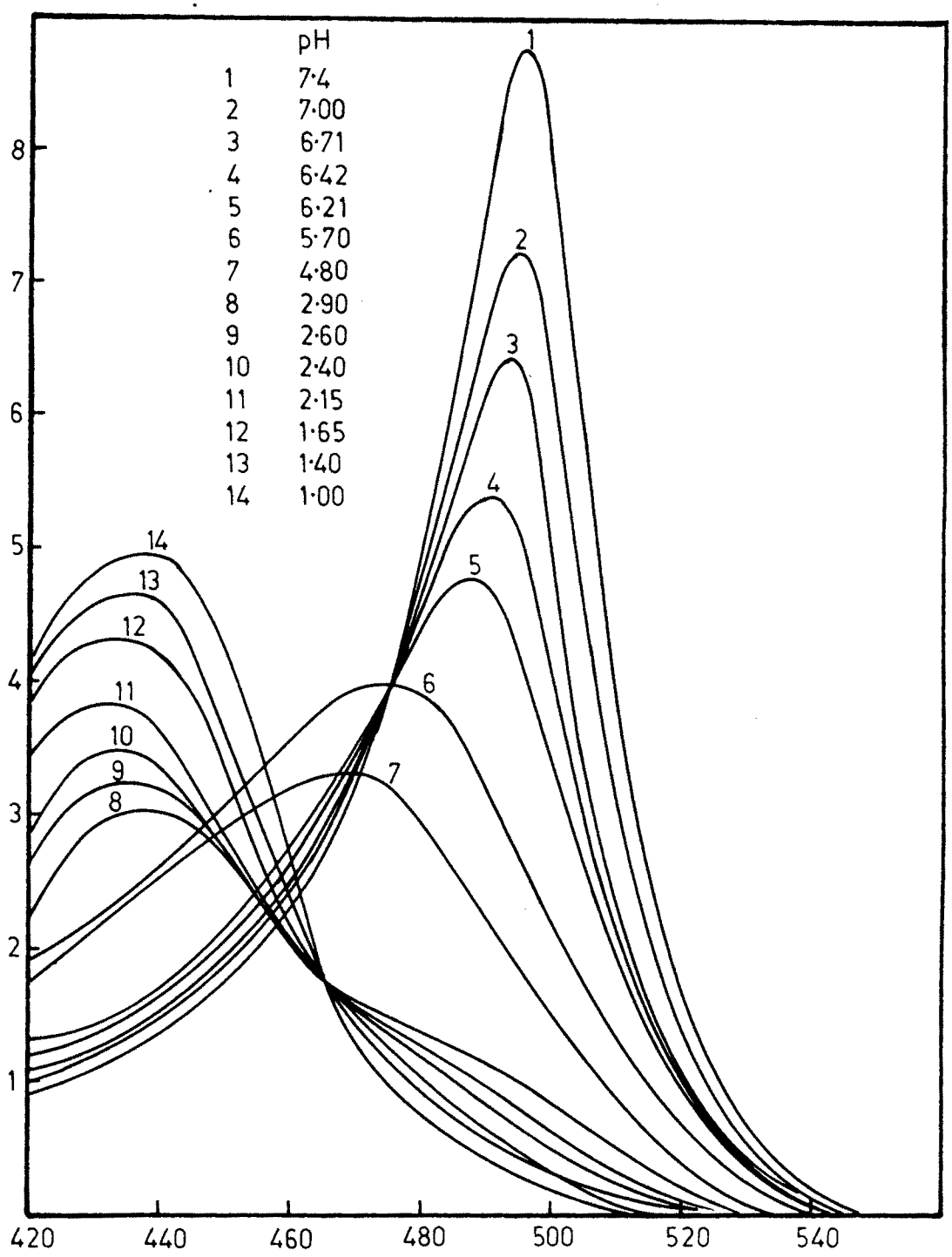

Fig. 3·11 ABSORPTION SPECTRA OF O-CHLOROPHENOL FLUOROMELLITEIN. (CONC. $\mu g\ ml^{-1}$)

Ionisation constants of p-chlorophenol fluoromellitein
Conc. 10.00 mg/l, Temp. 25.0°;
Path length 10.01 mm;

Table 3.21

Analytical wavelength 440 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.68$ $d_I = 0.35$

pH	d	$d-d_I$	d_M-d	$\log \frac{d-d_I}{d_M-d}$	pK_1	Mean pK_1
2.90	0.36	0.01	0.32	$\bar{2}.4949$	1.39	
2.35	0.40	0.05	0.28	$\bar{1}.2518$	1.50	
1.90	0.45	0.10	0.23	$\bar{1}.6383$	1.54	1.56
1.80	0.49	0.14	0.19	1.8673	1.67	
1.50	0.53	0.18	0.15	0.0795	1.58	
1.20	0.60	0.25	0.08	0.4949	1.69	

Table 3.22

Analytical wavelength 490 nm;
Solvent 50 % ethanol-water v/v;
$d_M = 0.30$ $d_I = 1.20$

pH	d	d_I-d	$d-d_M$	$\log \frac{d_I-d}{d-d_M}$	pK_2	Mean pK_2
6.90	0.85	0.07	0.11	$\bar{1}.8037$	6.70	
6.70	0.75	0.45	0.45	0.0000	6.70	
6.50	0.65	0.55	0.35	0.1963	6.70	6.66
6.2	0.54	0.11	0.04	0.4393	6.64	
5.9	0.45	0.75	0.15	0.6990	6.60	

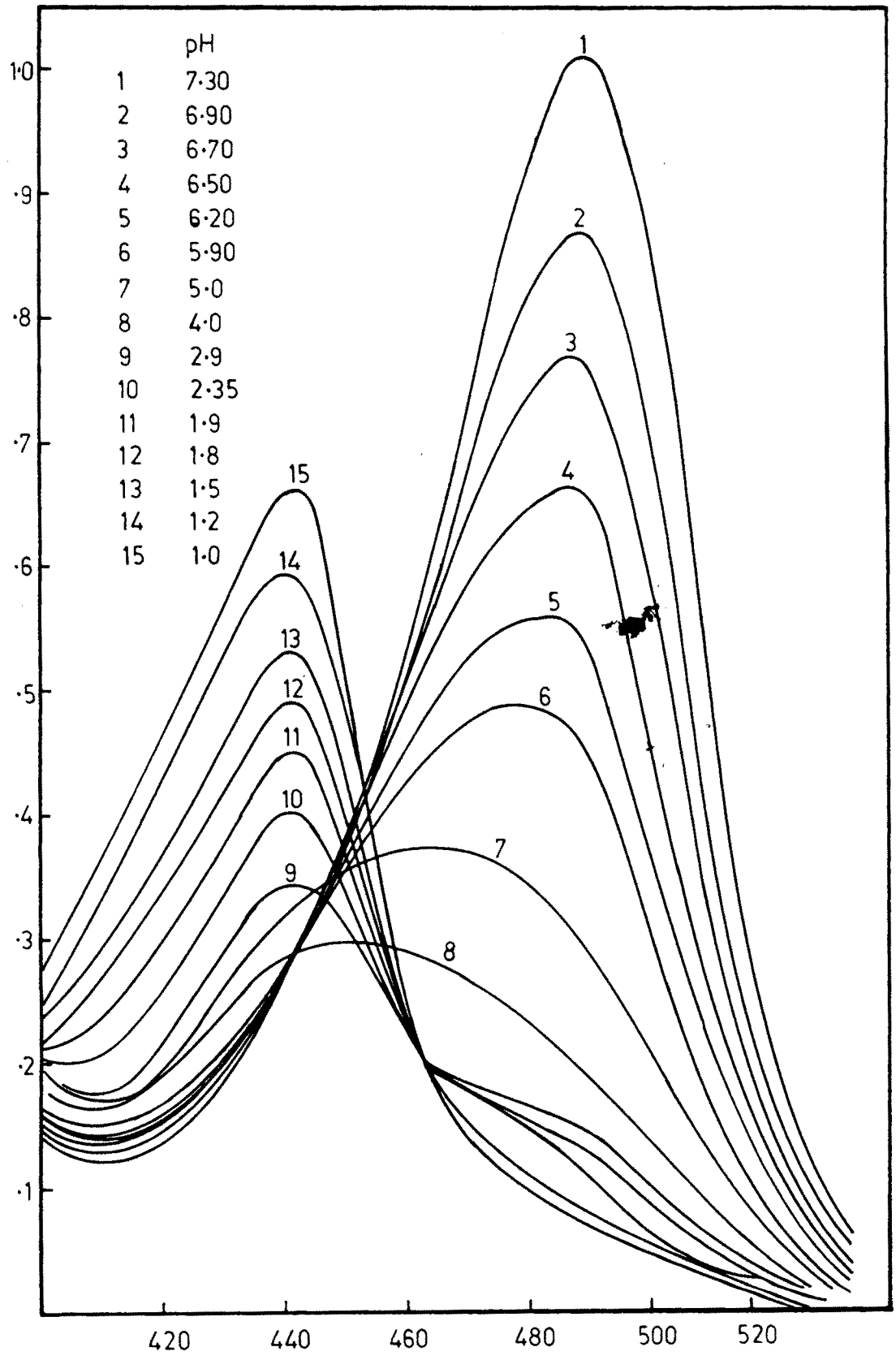

Fig. 3·12 ABSORPTION SPECTRA OF P-CHLOROPHENOL FLUOROMELLITEIN.
(CONC. 10 $\mu g\ ml^{-1}$)

3.3.4 Substituent Effect

The effect of substituent on ionisation constant has been extensively studied and the variation in ionisation constant by various substituent can be profitable exploited, when the acid-base indicators in the form of mellitein dyes are to be used for photometric determination of neutralisation reaction [104]. These indicators can be chosen on the basis of pH transition interval. In case of mellitein dyes the nature of fluorescence is the same of that of fluorescein to account for a large number of very weak and ill-defined bands. In the variation in the acid-base behaviour both form colour change and appearance of fluorescence can be used. The spacial feature of the compounds reported in this world is that pK values differ considerably but nature of fluorescence are remaining the same. Such series of compounds may be quite useful.

The substituent effect in mellitein dyes is summarised in Table 3.23. For assessing the substituents effect phenol fluoromellitein has been assumed to be the molecule in which substitution takes place and this substitution of groups leads to variation of the ionisation constants. It is well known that Hammett equation is applicable to simpler molecules with substitution is meta or para position [105]. If there is ortho substitution the correlation becomes difficult and although σ ortho values are reported there application is not straight forward [106]. When there are several substituents attempts have been made to use sums of σ values to assess the substituent effect but the success is limited. In addition to this the applicability

Table 3.23 : Effect of substitution on ionisation constants

No.	Compound	σ ortho	σ meta	σ para	$\sum\sigma$	pK_1	pK_2
1.	Difluoromellitein	-	0.10*	-	0.10	1.82	6.40
2.	Phenolfluoromellitein	-	-	-	-	1.83	6.63
3.	1,2 Dihydroxyfluoromellitein	1.22**	-	-	1.22	2.08	6.53
4.	1,2,3 Trihydroxyfluoromellitein	1.22	0.10	-	1.32	1.83	6.41
5.	o-Cresol fluoromellitein	0.29	-	-	0.29	2.01	6.77
6.	m-Cresolfluoromellitein	-	-0.07	-	-0.07	1.56	6.66
7.	p-Cresolfluoromellitein	-	-	-0.17	-0.17	1.78	6.61
8.	p-Nitrophenolfluoromellitein	-	-	0.78	0.78	1.93	6.52
9.	O-Chlorophenolfluoromellitein	1.28	-	-	1.28	2.04	6.64
10.	p-Chlorophenolfluoromellitein	-	-	0.23	0.23	1.87	6.57

* See Ref. 133

** See Ref. 134

of Hammett equation to complicated large molecular with ambiguous ionisation is also doubtful. On this account the very bulky mellitein molecule with remoute substitution may not be giving a very happy picture. The plot of Σ_{σ}Vs pK_1 and pK_2 is given in Fig. 3.13.

It can be seen from the structure of a representative mellitein dye that it will undergo changes in several successive steps as shown in Fig. 3.14, which is self explanating. The dye molecule has at least four replaceable protons and we expect four pK values or more for such dyes it will be noted that the presence of two -COOH groups and two -OH groups in the molecule may have possibility of deprotonation to the extent of only two protons over the normal pH range and one deprotonation may be very difficult. Since it has been lowered very much and the other one equally difficult since it has been raised to much. We therefore expect that in the normal case the indicator in the solid state may exist as already deprotonated and on of the -OH group cannot be deprotonated in the normal basic range. It is therefore possible that what we recorded as pK_1 and pK_2 are actually deprotonation processes for one -COOH and one -OH group in the mellitein molecule. Since there is a difference of about 3.5 pH units in the two pK values. We presume that the ionisation constant may be fairly correct. These values will be useful while assessing their uses as visual acid-base indicators. In the present study our aim is to evaluate there role with respect to fluorescent character. Our concern here with the various

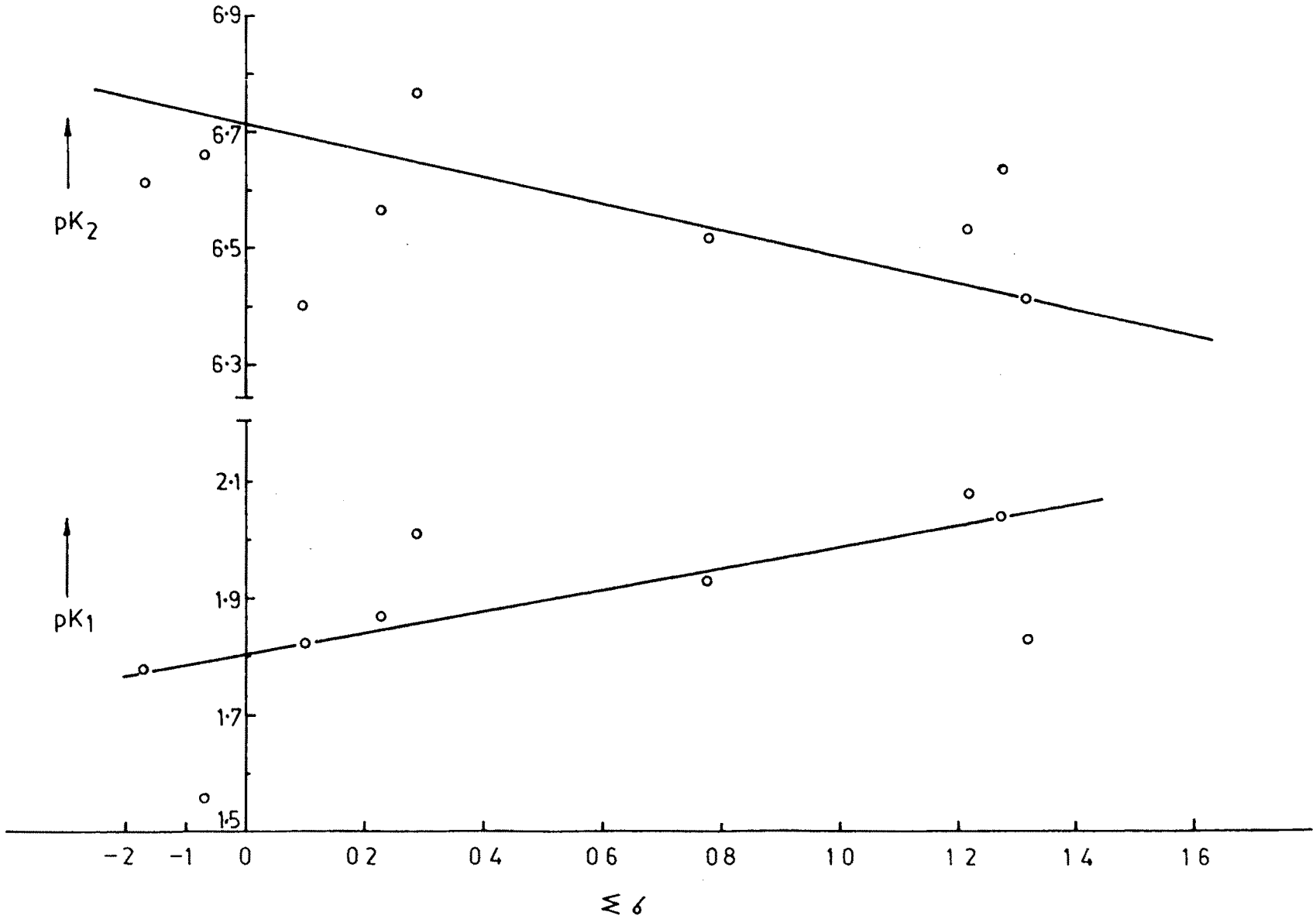

Fig 3.13 PLOT OF $\Sigma\sigma$ vs pK_1 AND pK_2

substituted dyes lies in an enquiry into the role of change of pK in deciding the strength of weak bond and its relation to the fluorescence possessed by the alkaline solution of the dye.

Fig. 3.14 shows the possible changes on successive deprotonation and the possible way in which deprotonation may proceed is A $\longrightarrow$ B $\longrightarrow$ C $\longleftrightarrow$ (D $\longleftrightarrow$ D') $\longrightarrow$ E $\longrightarrow$ F' $\longrightarrow$ G rather than A $\longrightarrow$ B' $\longrightarrow$ C $\longrightarrow$ (D $\longleftrightarrow$ D') $\longrightarrow$ E $\longrightarrow$ F' $\longrightarrow$ G. This speculation is based on the behaviour of phenolphthalein.

3.3.5 Conclusion

The electronic spectra of mellitein dyes show that a series of structurally related phthalein dyes with fairly constant. Fluorescent characteristics and various ionisation constant has been developed and combine property of fluorescence and variable pH transition interval and corresponding colour changes can be utilised in acid-base titration. However the series of compounds find better applications in which these fluorescence characteristics are main use.