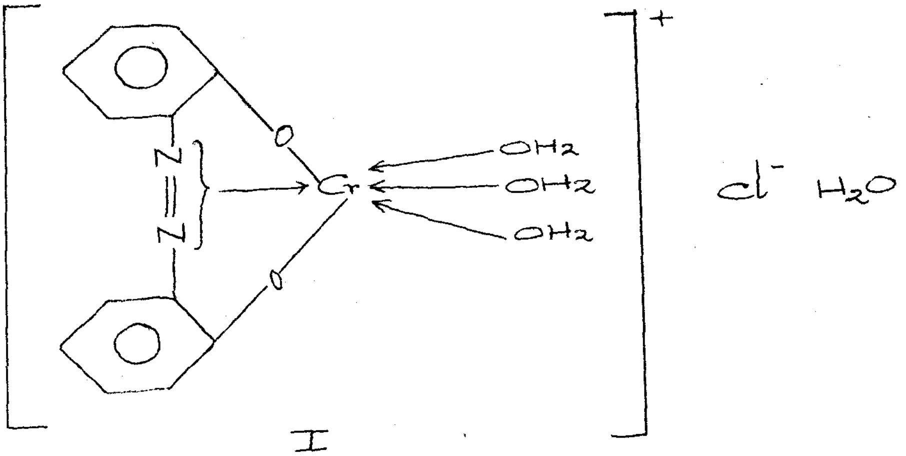
CHAPTER 2

INTERACTION OF COPPER ION WITH SOME FOOD DYES

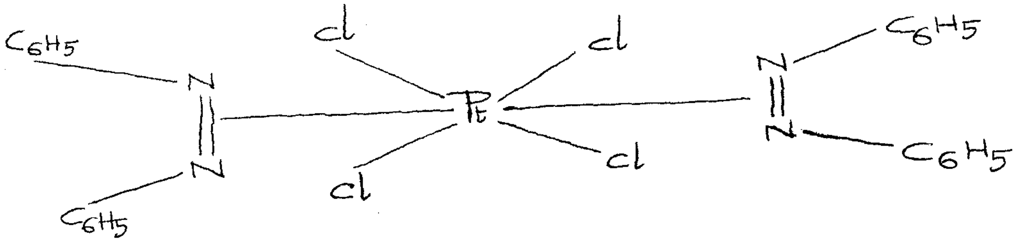
Numerous studies have been made during the last few decades on the azo dyes because of their commercial utility. Azo dyes form complexes with a variety of metals, which themselves are also very important in the dye industry. Of these, transition metal complexes, particularly those of copper, chromium and cobalt, have been studied extensively. The first important 1:1 chromium metallised dye was marketed by Ciba in 1919 (40). In 1930 some 2:1 dye-metal complexes were also introduced (40).

The donor property of the azo group is weak. Its ability to coordinate with metals was originally inferred from the fact that azo compounds having a hydroxyl or an amino group in a position ortho to the azo group form metal complexes, but those having hydroxyl or amino groups in meta or para position do not (41). A number of workers (42-47) examined the reaction of o-hydroxy and o-amino azodyestuffs with metal salts and succeeded in isolating copper, nickel and cobalt complexes of both types of dyestuffs. Drew and Landquist (48) showed that o-hydroxy and o-amino azo compounds formed complexes having 2:1 stoichiometry with divalent copper, nickel and cobalt in which a proton was lost from each molecule of the azo compound. However, the nature of the bond between the azo group and the metal was not clear and as recently as 1952 this uncertainty was indicated (49, 50) by a bracket enclosing the entire azo group (I).



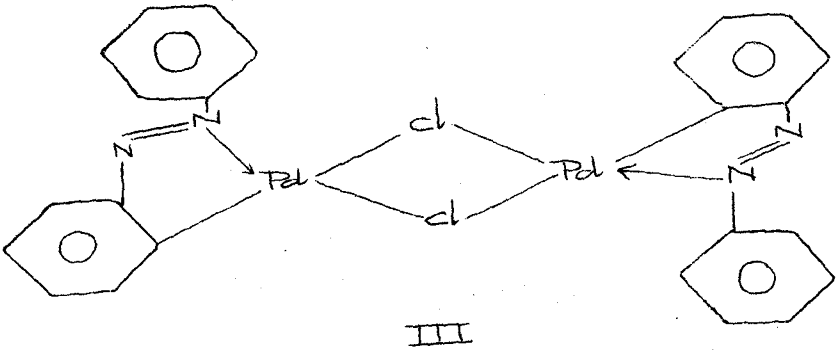
I

In 1936 Kharasch and Ashford (51) isolated a compound which they formulated as $(C_6H_5N : NC_6H_5)_2$ $PtCl_4$ by the interaction of azobenzene and platinic chloride. Werner (52) proposed a π bonded structure for this compound (II). However, recently (53) it has been reported to be a salt derived from hydrazobenzene having the formula $(C_6H_5NHNH_2C_6H_5)_2$ $[PtCl_6].H_2O$.



II

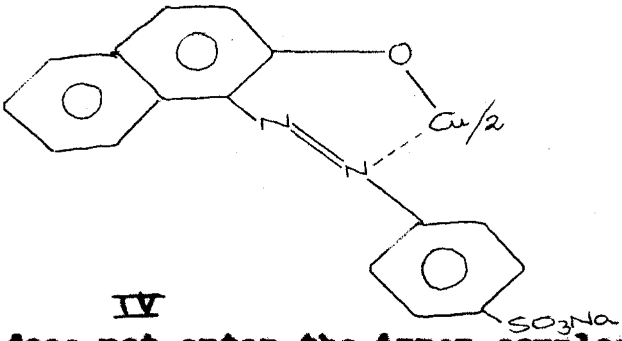
Silver and palladium complexes of azobenzene (54) and 5,6-benzocinnoline (55), which may be compared with cis-azobenzene, have been isolated. No information on the structure of these complexes is available but their formation has effectively demonstrated coordination of the azo group in the absence of other donor groups in the ligand molecules. A number of authors (56-59) have prepared complexes of azobenzene having a metal-carbon bond in a position ortho to the azo group. It is not clear from available evidence which nitrogen atom of the azo group is bonded to the metal in these complexes, e.g. (III), but since metallation occurs with N,N-dimethyl benzylamine (60) but not with N,N-dimethylaniline, Heck (58) concludes, by analogy, that the β-nitrogen atom of the azo group is involved in coordination. Recent X-ray crystal structure determination on the copper complexes of 1-phenylazo-2-napthol and 1-pyrid-2-napthol and also chromium complexes of two o,o′-dihydroxyazo dyestuffs and an o-carboxy-o′-hydroxyazo dyestuff have confirmed that only one nitrogen of the azo group is involved in coordination.



III

In the case of the copper complex of the bidentate azo compound, 1-phenylazo-2-napthol, the β-nitrogen atom of the azo group is bonded to the metal which forms a part of a six-membered chelate ring.

The behaviour of o-hydroxy-azobenzene sulfonic acids towards metallic salts is more complicated than that of the insoluble o-hydroxyazo compounds free from sulfonic groups (61) and is of greater interest since nearly all the technically important mordant azo dyes as well as food dyes contain sulfonic acid groups. With copper salt the sulfonic acids first form the cupric sulfonates. Thus p-sulfobenzene-azo-β-napthol forms an orange-red salt strongly hydrated and somewhat readily soluble in water. On treatment with alkali or alkali acetate, the salt is converted into a brownish-red coordination complex (IV) which is soluble in water with a deep brown colour.



IV

Copper does not enter the inner complex unless the sulfonic group is neutralised by copper or other basic atoms or groups. However, the presence of a single sulfonic group is not sufficient to prevent the formation of an internal complex when there are two hydroxyl groups, both ortho to the azo group.

In contrast to the rather comprehensive literature available on the synthesis of transition metal complexes very little information is available on the spectral behaviour of the metal-azo dye complexes, particularly those containing sulfonic acid groups. Ernsberger and Brode (62) have examined the absorption spectra of a series of phenylazo-p-cresol, β-napthol and β-napthylamine derivatives with methyl, nitro and chloro substituents in the phenyl ring, together with the spectra of their copper, nickel and cobalt compounds. These authors found that apart from the appearance of a new band ascribable to the metal ion, the spectra of metal-azo dye complexes differed very little from those of the azo-dyes.

Some of the azo-dyes, e.g. amaranth, ponceau 4R etc. though not indicators themselves, behave as extremely good indicators when used with Cu^{+2} ions. Thus amaranth solution to which Cu^{+2} has been added may be used as an acid base indicator (63). Obviously this must involve Cu^{+2}-dye complexes. Since no solid complex could be isolated in these cases it was decided to investigate in some detail the nature of Cu^{+2}-complexes of some of the food dyes using spectrophotometric techniques.

Experimental

Copper sulphate, $CuSO_4$, $5H_2O$ (A.R./BDH) was used during the experiment. The dyes, amaranth and sunset yellow, were used after purification chromatographically (40) and were dried in vacuum for 24 hours. Potassium hydroxide and acetic acid buffer was prepared by mixing components in different amounts and solutions of different pH were prepared using Henderson's equation (64). The resulting pH of the buffer solution was measured by Philip's pH meter (PR 9405 M). All the spectral data were taken in Beckman DU2 UV/visible spectrophotometer using 1 cm quartz cell. All solutions were prepared in distilled deionized water.

Results and Discussion

Table 2

Spectrophotometric data on Cu^{+2}-sunset yellow system.

pH of solution = 6
Concentration of sunset yellow = 5.6×10^{-5}M
Concentration of Cu^{+2} = 1.475×10^{-4}M x V
(V = volume of Cu^{+2} solution)
Wavelength used = 500 nm.

V_{ml}	O.D. at 500 nm	$E \times 10^{-3}$	$\frac{E_D - E}{C_M^{2}} \times 10^{-9}$
0	0.89	15.89	
1	0.830	14.82	49.31
2	0.715	12.77	35.94
3	0.601	10.73	26.42
4	0.519	9.27	19.06
6	0.438	7.82	10.33

Table 3

Spectrophotometric data on Cu^{+2}-sunset yellow system

pH of solution = 4.5
Concentration of sunset yellow = 5.6×10^{-5}M
Concentration of Cu^{+2} = V x 3.081×10^{-3}M
(V = volume of Cu^{+2} solution)
Wavelength used = 500 nm.

V_{ml}	O.D. at 500 nm	$E \times 10^{-3}$	$\frac{E_D - E}{C^0_M} \times 10^{-4}$
0	0.890	15.89	
1	0.771	13.77	68.80
2	0.684	12.21	59.72
3	0.618	11.04	52.46
4	0.580	10.36	44.87
6	0.520	9.29	35.70

Table 4

Spectrophotometric data on Cu^{+2}-amaranth system

pH of solution = 5.5

Concentration of amaranth = 4.43×10^{-5}M

Concentration of Cu^{+2} = 5.9×10^{-4} M x V
(V = volume of Cu^{+2} solution)

Wavelength used = 520 nm.

V_{ml}	O.D. at 520 nm	$E \times 10^{-3}$	$\frac{E_0 - E}{C^{0\,2}_{M}} \times 10^{-7}$
0	0.910	20.54	
1.5 ml	0.689	15.55	63.7
2	0.582	13.14	53.1
2.5	0.509	11.49	41.6
3	0.440	9.93	33.86
5	0.292	6.59	16.0
6	0.255	5.76	11.8
7	0.231	5.21	9.0

Table 5

Spectrophotometric data on Cu^{+2}-amaranth system

pH of solution = 4.5
Concentration of amaranth = 4.43×10^{-5}M
Concentration of Cu^{+2} = V x 3.081×10^{-3}M
(V = volume of solution)
Wavelength used = 520 mm.

V_{ml}	O.D. at 520 mm	$E \times 10^{-3}$	$\frac{E_D - E}{C^0_M} \times 10^{-4}$
0	0.910	20.54	
1	0.680	15.35	168.5
2	0.535	12.08	137.3
3	0.448	10.11	112.9
4	0.380	8.58	97.1
5	0.350	7.90	82.1
8	0.280	6.32	57.7

Table 6

Spectrophotometric data on sunset yellow - Cu^{+2} system at different pH

$$X = \frac{\varepsilon - \varepsilon_{MD}}{(\varepsilon - \varepsilon_{M_2D})C_M^0}, \qquad Y = \frac{\varepsilon_D - \varepsilon}{(\varepsilon - \varepsilon_{M_2D})C_M^{0\,2}}$$

pH = 4.5		pH = 5	
$X \times 10^{-2}$	$Y \times 10^{-4}$	$X \times 10^{-3}$	$Y \times 10^{-5}$
3.68	2.82	1.90	2.94
1.89	1.53	0.96	2.34
1.30	1.09	0.65	1.64
1.00	0.81	0.51	1.53
0.71	0.56	0.35	1.10

Values of molar extinctions : $\varepsilon_D = 15.89 \times 10^3$,
$\varepsilon_{MD} = 4.8 \times 10^3$,
$\varepsilon_{M_2D} = 5.85 \times 10^3$.

Table 7

Spectrophotometric data on amaranth -Cu^{+2} system at different pH

$$X = \frac{E - E_{MD}}{(E - E_{M_2D})C_M^0} \quad , \quad \text{and} \quad \frac{E_D - E}{(E - E_{M_2D})C_M^{0\,2}} = Y$$

pH = 4.5		pH = 5.0	
$X \times 10^{-2}$	$Y \times 10^{-4}$	$X \times 10^{-2}$	$Y \times 10^{-5}$
3.70	4.50	9.86	4.80
1.93	2.51	6.83	3.62
1.35	1.77	5.35	3.02
1.07	1.46	4.50	2.68
0.88	1.13	3.91	2.34
0.63	0.75	3.42	1.89

Values of molar extinction used, $E_D = 20.54 \times 10^3$,
$E_{MD} = 1.5 \times 10^3$,
$E_{M_2D} = 3.2 \times 10^3$.

Table 8

Values of $K_1' \ K_2'$ at different pH for Cu^{+2} - sunset yellow system

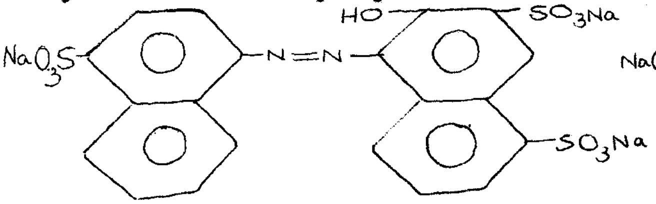
pH	$K_1' \ K_2'$	K_1'	K_2'
4.5	1.3×10^3	0.7×10^2	1.8×10
5.0	4.1×10^4	2.0×10^2	2.0×10^2

Table 9

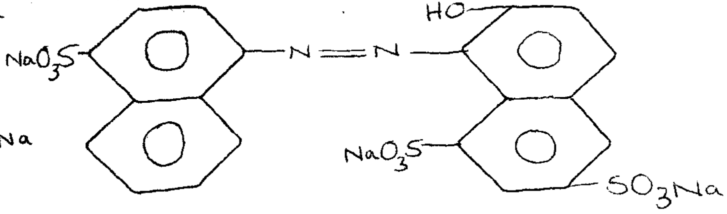
Values of $K_1'.K_2'$ at different pH for Cu^{+2} - amaranth system

pH	$K_1'.K_2'$	K_1'	K_2'
4.5	2.1×10^3	1.2×10^2	1.7×10
5.0	6.5×10^4	4.1×10^2	1.6×10^2

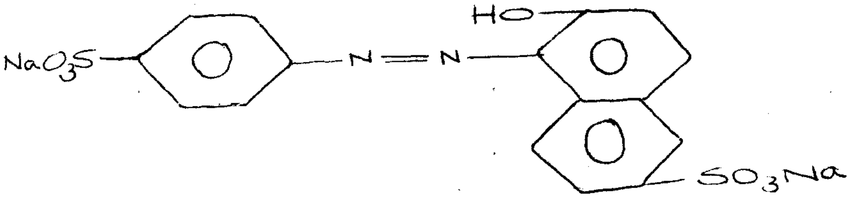
Of the various azo dyes used in food industries, only amaranth (V) ponceau 4R (VI), and sunset yellow (VII) form complexes with Cu^{+2} as evidenced by the change in the colour which accompanies addition of a solution of Cu^{+2} ions to these dyes. This is expected as all these dyes contain an o-hydroxy group. It may be pointed out that other transition metal ions, e.g. Ni^{+2}, Co^{+3}, Fe^{+3}, Zn^{+2}, etc. have no effect indicating very weak donor properties of these dyes.



V Amaranth



VI Ponceau 4 R



VII Sunset yellow

In the case of amaranth as may be seen from Fig. I, addition of Cu^{+2} results in a hypsochromic shift of about 60 nm of the visible absorption with hypochromic effect. The behaviour of ponceau 4R is exactly similer to that of amaranth and need not to be discussed separately. In the case of sunset yellow comparatively small hypsochromic shift occurs, but considerable decrease in absorption intensity in the long wavelength region of the absorption band occurs (Fig. 2). The nature of the absorption spectra of metal-azo dye solutions have been found to be strongly influenced by different factors. These are discussed below.

(i) Effect of pH :

Figs. 3 and 4 show the effect of pH on the absorption spectra of dye-metal solution containing fixed dye/metal concentrations. It will be seen that the colour change is enhanced with the increase of pH, while lowering of pH tends to reverse the colour change. This together with the presence of an isosbestic point in the absorption curves, would indicate a rather simple equilibria of the type :

$$nM^{+2} + D \rightleftharpoons [M_nD']^{+(2n-x)} + xH^{+} \quad \ldots\ldots. \quad (1)$$

However, as has been shown later, such a simple equilibrium cannot quantitatively explain the observed spectrophotometric data.

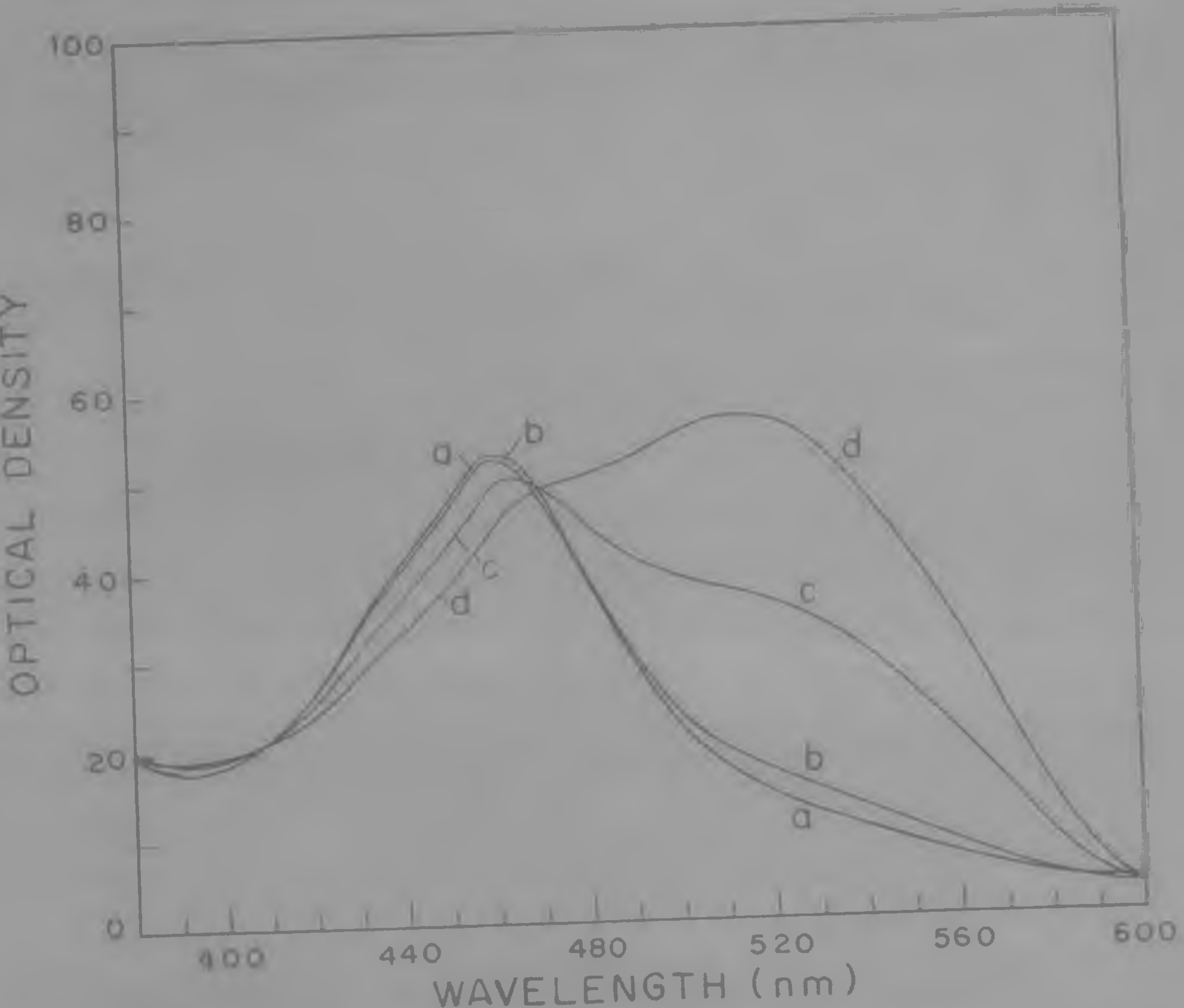


Fig.1. EFFECT OF METAL ION CONCENTRATION (Cu^{+2}) AT A FIXED pH [illegible] ON THE ABSORPTION SPECTRA OF AQUEOUS SOLUTION HAVING CONSTANT CONCENTRATION OF AMARANTH.

a - 8 Cu + 2 D b - 6 Cu + 2 D

c - 2 Cu + 2 D d - 1 Cu + 2 D

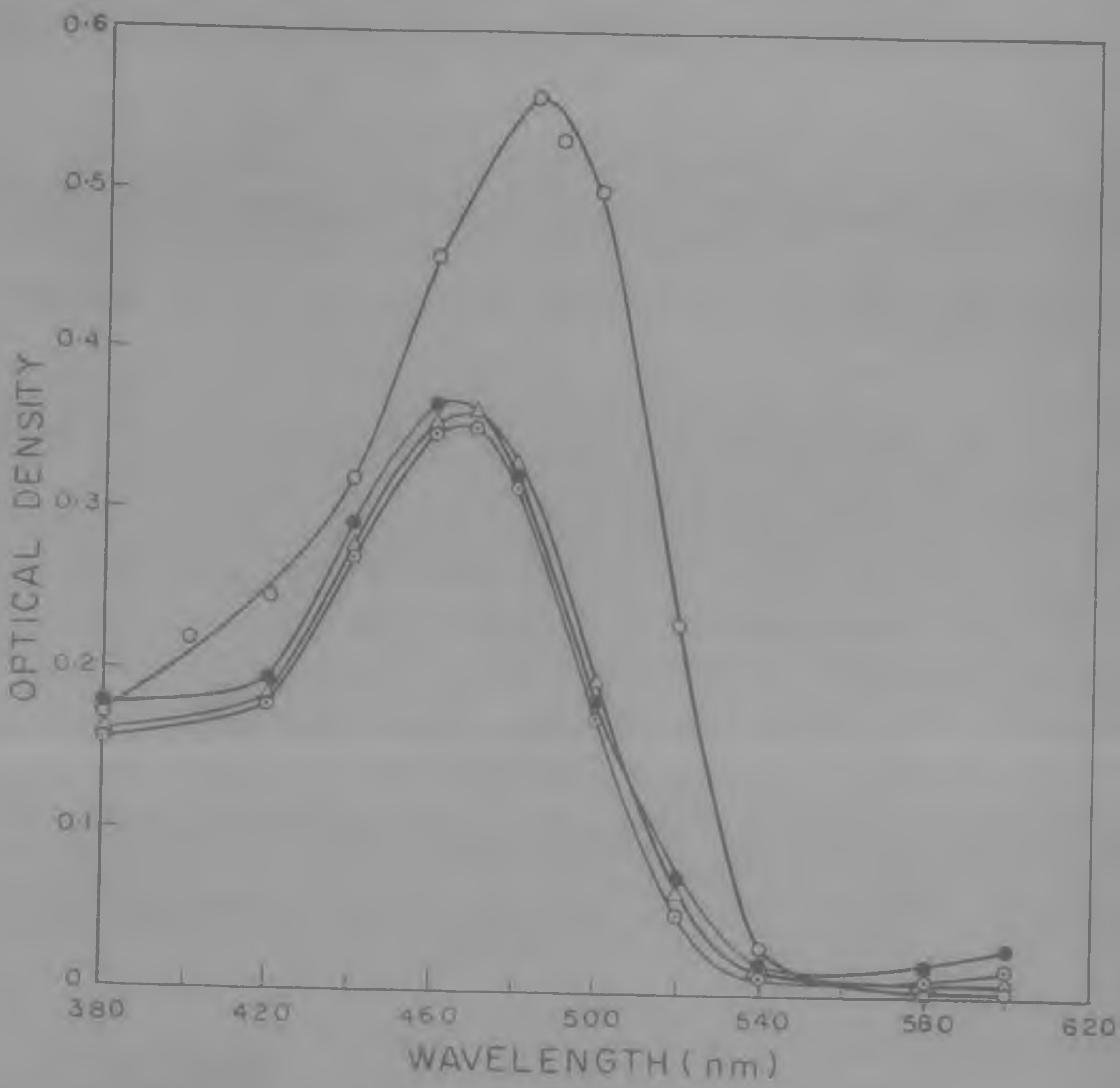


Fig. 2. EFFECT OF METAL ION CONCENTRATION (Cu^{+2}) AT A FIXED pH (5.5) ON THE ABSORPTION SPECTRA OF AQUEOUS SOLUTION HAVING CONSTANT CONCENTRATION OF SUNSET YELLOW.

○ - DYE (D)
⊙ - 4 Cu + 2 D
△ - 2 Cu + 2 D
● - 8 Cu + 2 D

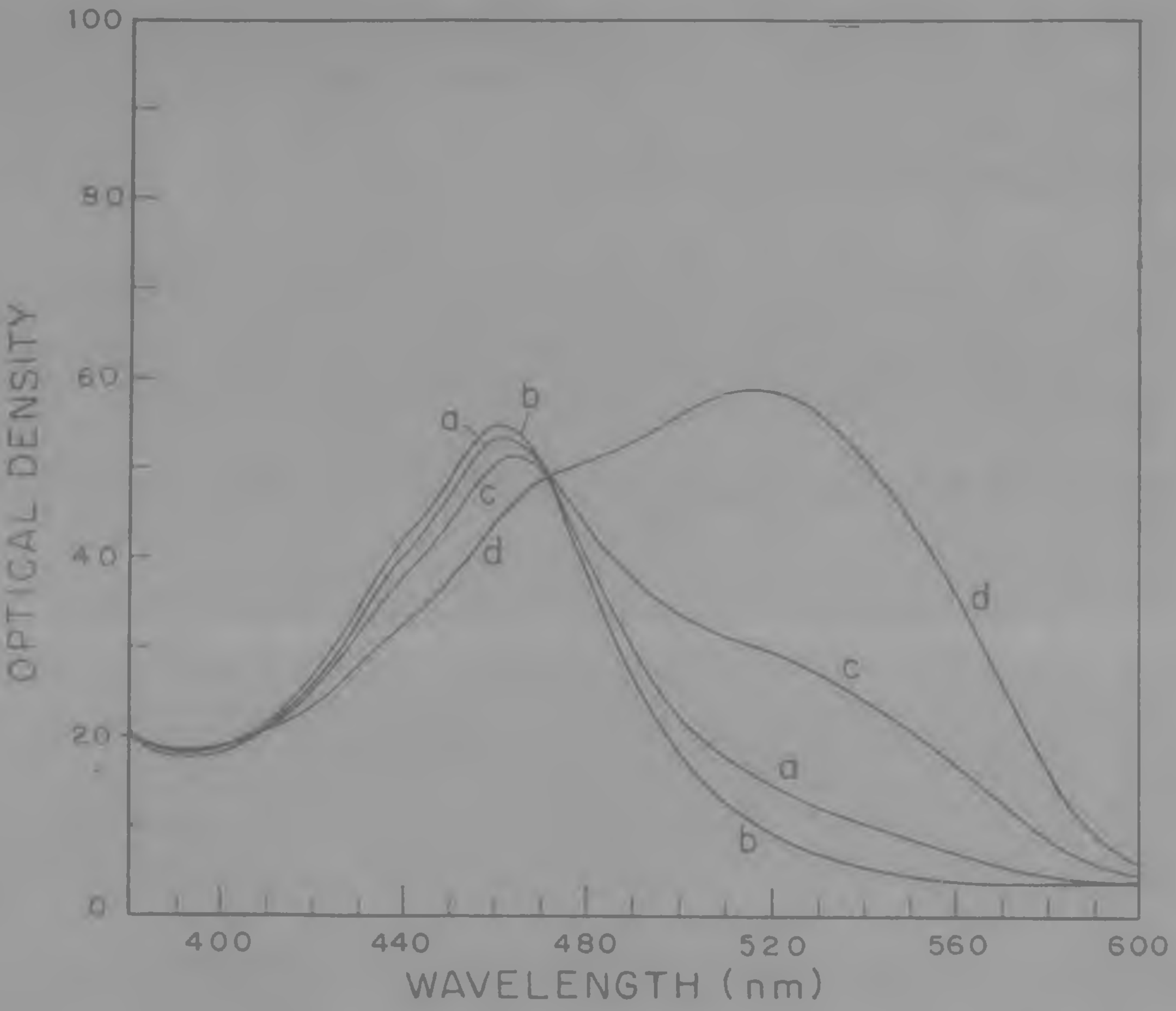


Fig.3. EFFECT OF pH ON THE ABSORPTION SPECTRA OF AMARANTH-METAL SOLUTION CONTAINING FIXED AMARANTH/METAL CONCENTRATIONS.

a - pH 5.5
b - pH 6.00
c - pH 5.00
d - [illegible]

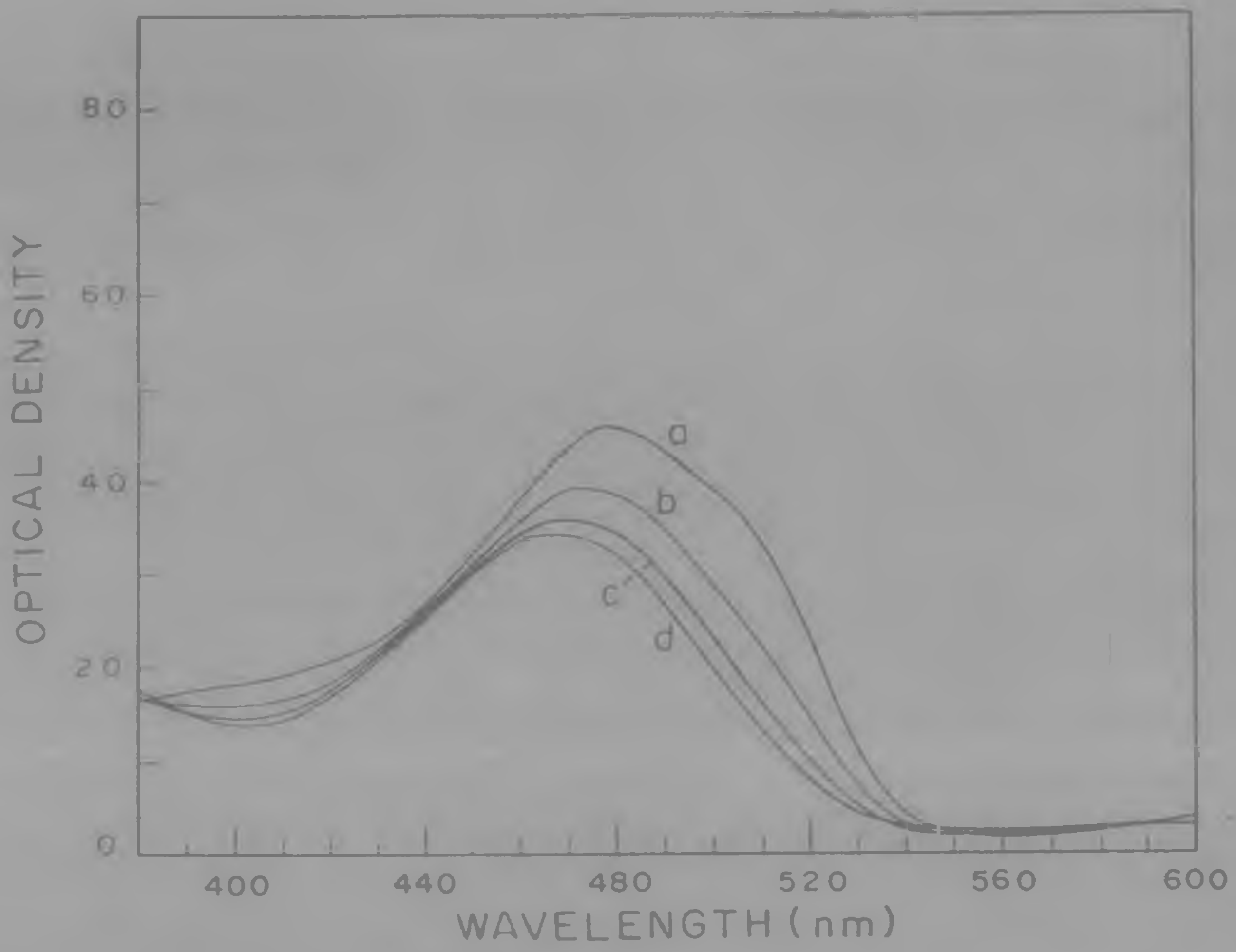


Fig.4. EFFECT [illegible] pH ON THE ABSORPTION SPECTRA OF SUNSET YELLOW - METAL SOLUTION CONTAINING FIXED SUNSET YELLOW/METAL CONCENTRATIONS.

a - pH 4.6 b - pH 5.0

c - pH 5.5 d - pH 6.00

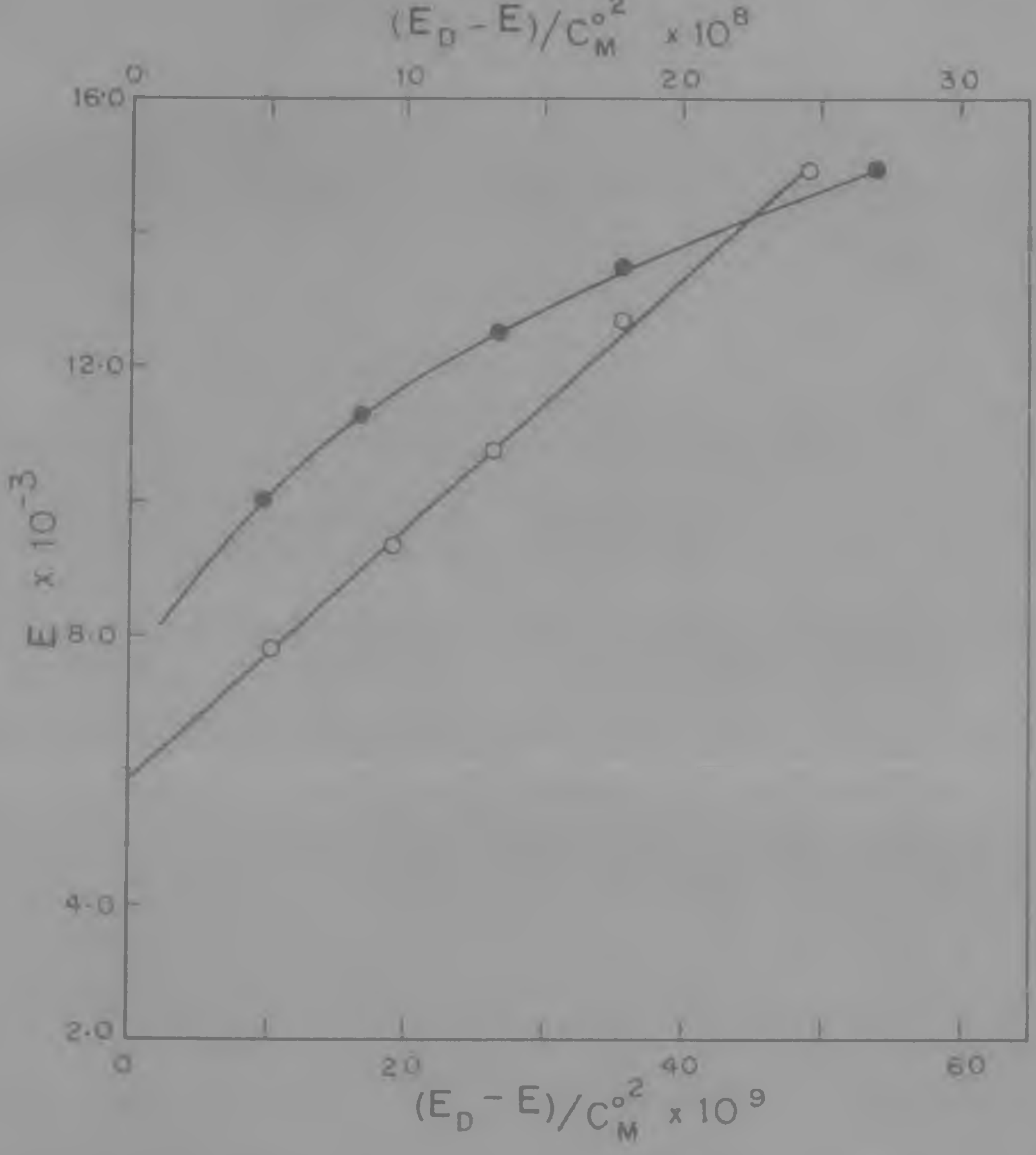


Fig. 5. PLOT OF E V.S. $(E_D-E)/C^{0\,2}$ FOR Cu^{+2}-SUNSET YELLOW SYSTEM AT pH = 5 (●, LOWER SCALE) AND pH = 6 (○, UPPER SCALE).

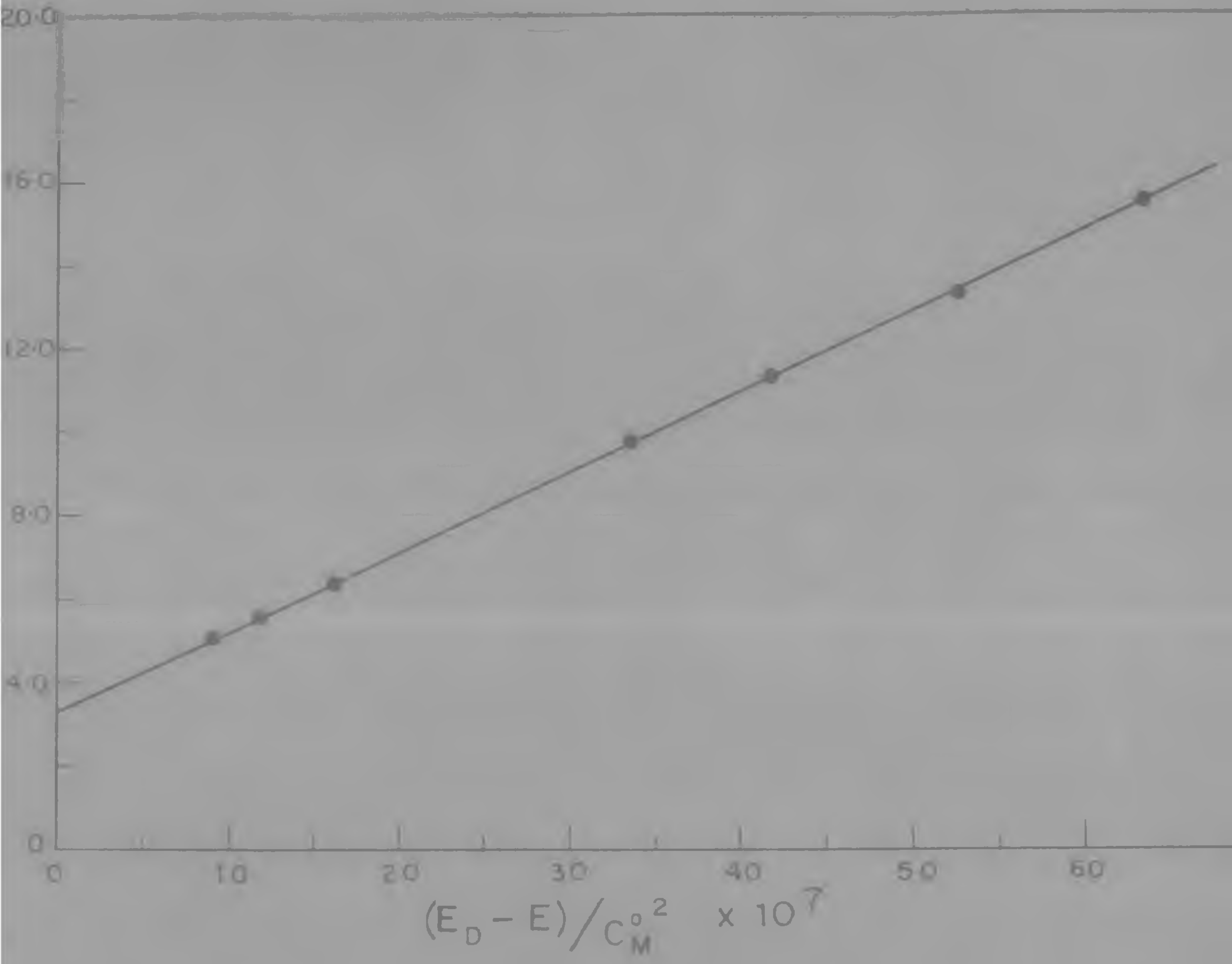


Fig. 6. PLOT OF E VS. $(E_D-E)/C_M^{o\,2}$ AT pH = 5.5 FOR Cu^{+2}-AMARANTH SYSTEM.

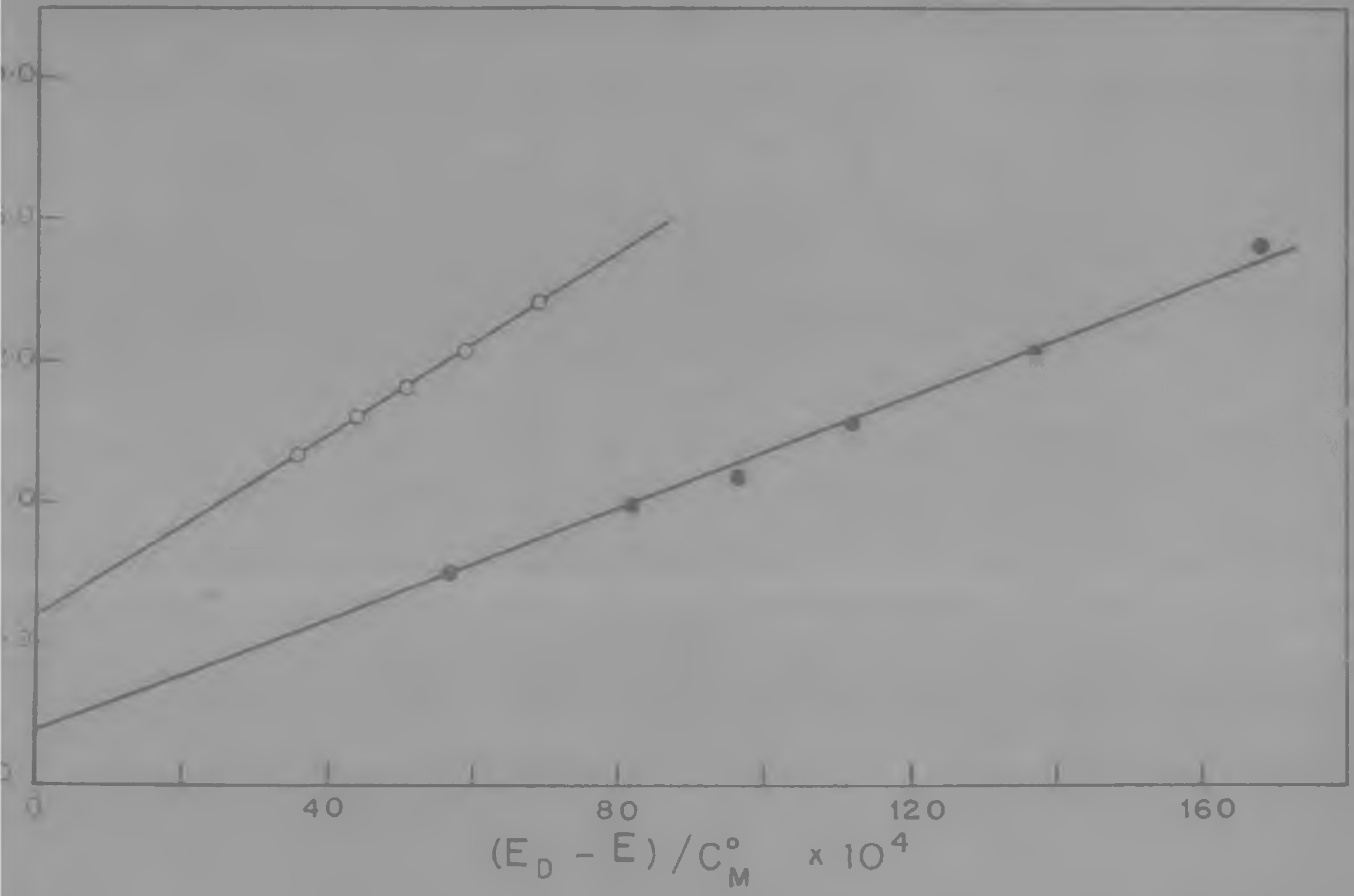


Fig. 7. PLOT OF E VS. $(E_D-E)/C^{o}_M$ FOR DYE - [illegible] SYSTEM AT pH = 4.5.

(○ - SUNSET YELLOW, ● - AMARANTH)

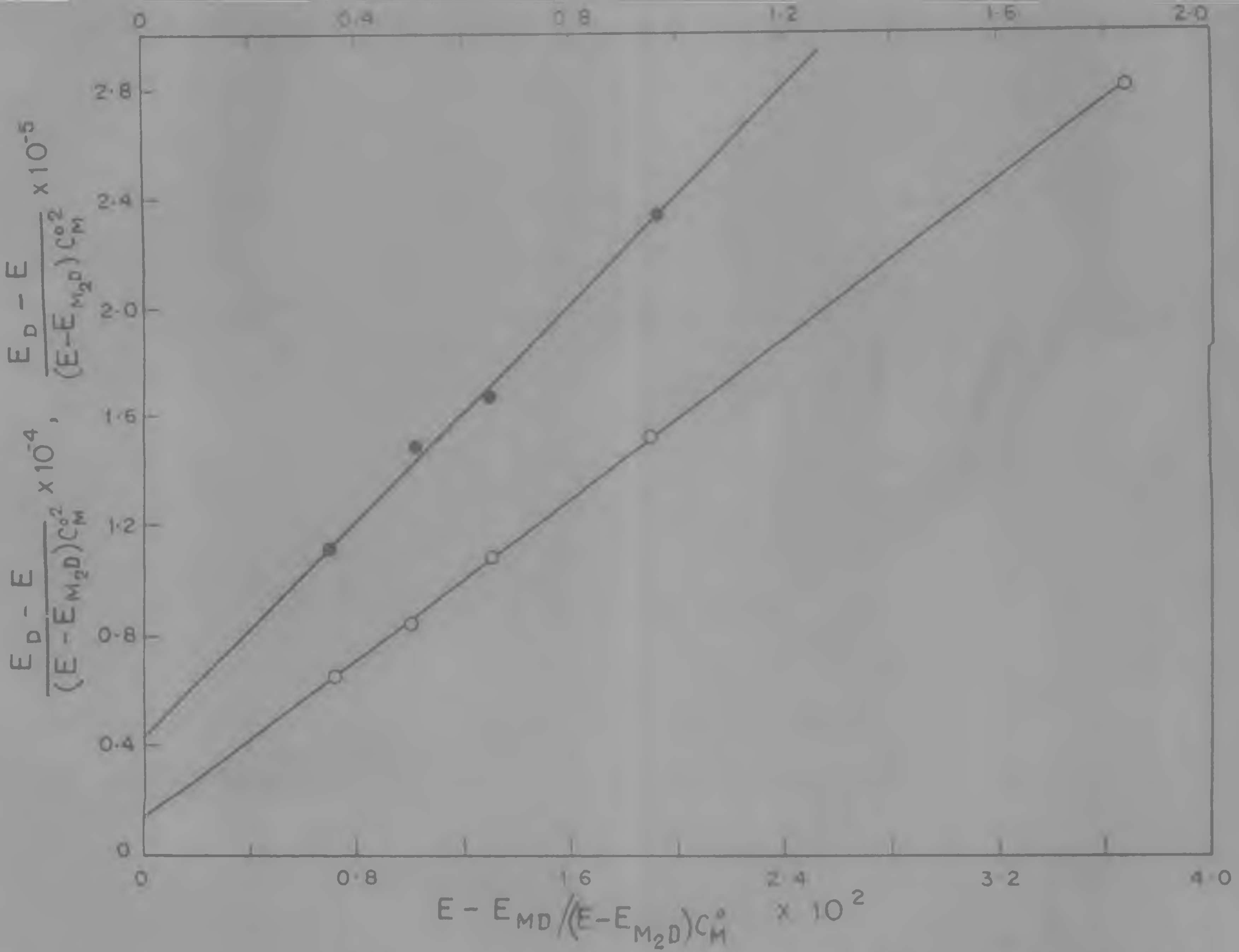


Fig. 8. Plot of $E_D - E/(E - E_{M_2D})C_M^{o\,2}$ (=y) vs. $E - E_{MD}/(E - E_{M_2D})C_M^o$ (=x) for sunset yellow – Cu^{+2} system at pH = 4·5 (○), pH = 5·0 (● , scale in the parenthesis refers to pH = 5·0)

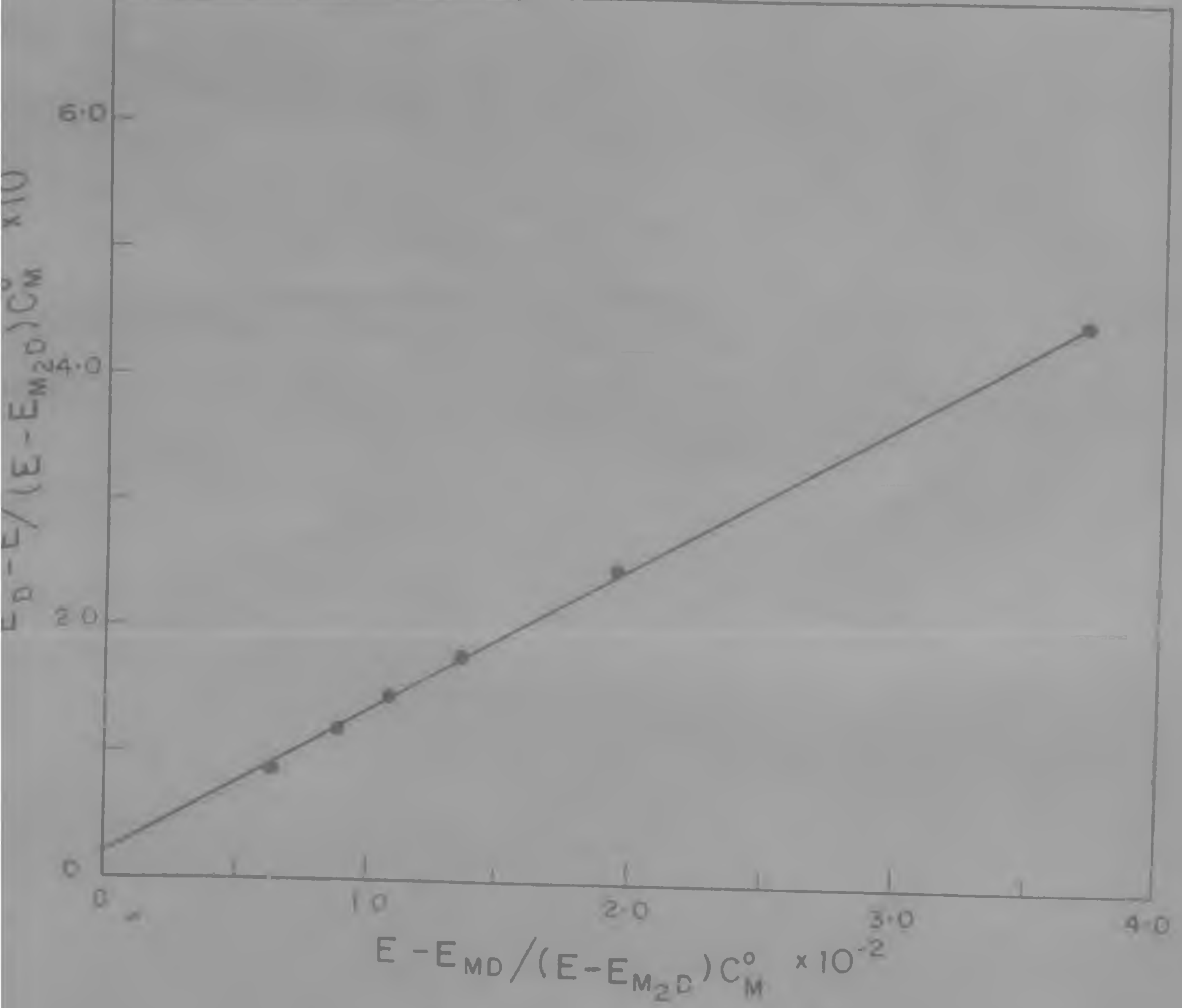


Fig. 9. PLOT OF $\frac{E_D - E}{(E - E_{M_2D})C^0_M}$ (= y) VS. $\frac{E - E_{MD}}{(E - E_{M_2D})C^0_M}$ (= x)

FOR Cu^{+2} - AMARANTH SYSTEM AT pH = 4.5

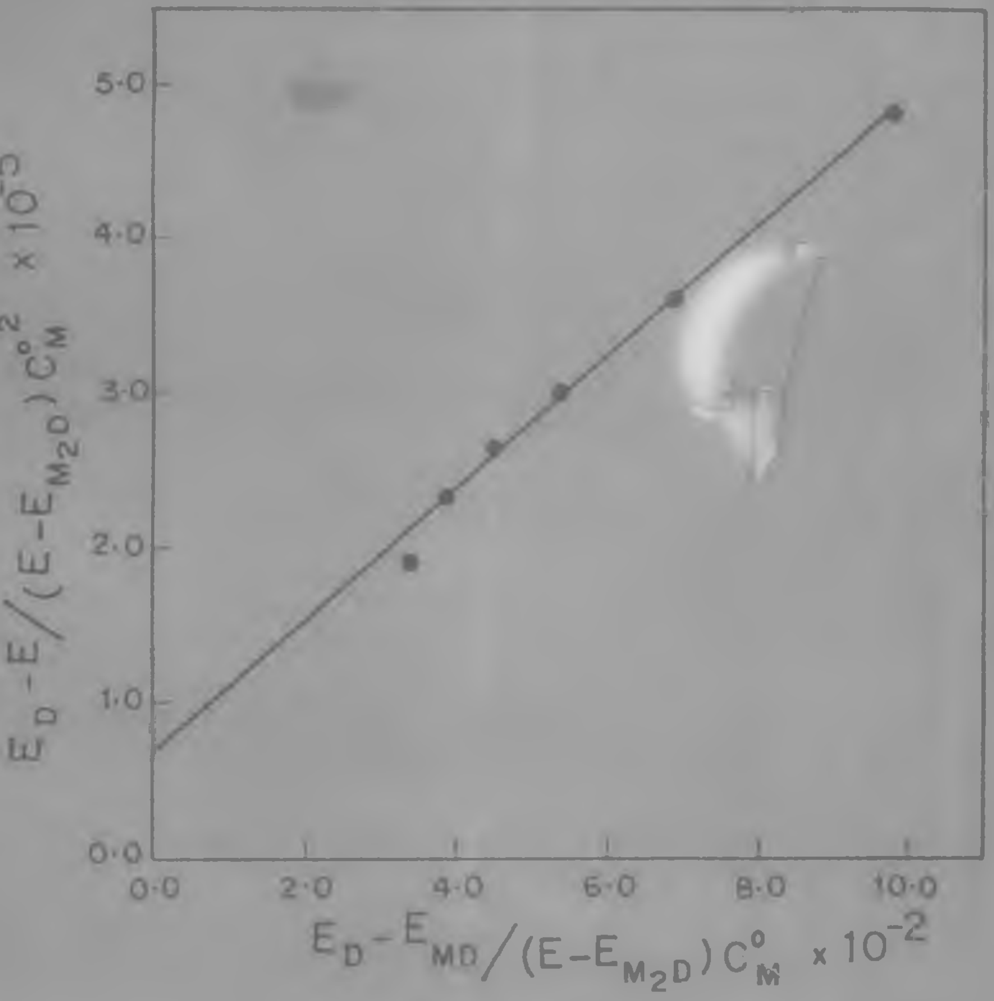


Fig. 10. PLOT OF $\frac{E_D - E}{(E - E_{M_2D}) C_M^{o\,2}}$ (= y) VS. $\frac{E_D - E_{MD}}{(E - E_{M_2D}) C_M^o}$ (= x) FOR Cu^{+2} – AMARANTH SYSTEM AT pH = 5.0

(ii) Effect of metal ion concentration :

Figs. 1 and 2 show the effect of Cu^{+2} concentration at a fixed pH on the absorption spectra of aqueous solution having constant concentration of the dye. As would be expected for a equilibrium of the type (1), increasing metal ion concentration leads to a decrease in the extinction near the absorption maxima of the free dye with the appearance of a new peak at a lower wavelength.

(iii) Effect of buffer solutions :

Interestingly the nature of the buffer solution has a profound effect on dye-Cu^{+2} equilibria. Thus phosphate buffer inhibits the formation of the complex as indicated by the reversal of the colour change by the addition of phosphate buffer to a mixture of dye/Cu^{+2}. However, acetic acid/potassium acetate buffer does not inhibit the complexation and is suitable for use in the present systems. The ability of the phosphate buffer to inhibit the complexation is presumably due to the very weak nature of the Cu^{+2} complex so that phosphate ions are capable of breaking the dye complex by complexing with the Cu^{+2} ions themselves.

Because of considerable overlap between the dye and Cu^{+2}/dye complex absorption bands coupled with the strong absorption of the dye near the absorption maximum of the complex, Job's method (65) was found unsuitable. Similarly, the Slope ratio (66) method was also unsuitable since large concentration of dye could not be employed, though metal : dye ratio could be made quite large. The following method was therefore employed for treatment of the spectrophotometric data.

Consider the equilibrium :-

$$nM^{+2} + D \rightleftharpoons [M_nD]^{+(2n-1)} + xH^{+} \quad \ldots\ldots\ldots\ldots \quad (2)$$

Let C_D^o = Analytical concentration of the dye.

C_D = Equilibrium concentration of the dye.

C_M = Equilibrium concentration of the metal.

C_X = Equilibrium concentration of the metal-dye complex.

and, E_D, E_X be the molar extinctions of the dye and the complex respectively at any given wavelength. Since copper sulphate solution does not absorb in the region of investigation (~400-500 nm), E_M may be neglected. Assuming the validity of Beer's law, one can write :

$$D = E.C_D^o = E_D.C_D + E_X.C_X \quad \ldots\ldots\ldots\ldots \quad (3)$$

where E is the apparent molar extinction of the Cu^{+2} - dye solution.

$$\text{Also, } C_D^o = C_D + C_X \quad \ldots\ldots\ldots\ldots \quad (4)$$

Combining (3) and (4) one gets,

$$\frac{C_X}{C_D} = \frac{E - E_D}{E_X - E} \quad \ldots\ldots\ldots\ldots \quad (5)$$

The equilibrium constant K is given by

$$K = \frac{C_X \cdot C_{H^+}^X}{C_M^n \cdot C_D} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (6)$$

At a fixed pH, C_H^+ is constant, so that using K' for $K/C_{H^+}^X$

$$\frac{C_X}{C_D} = K' . C_M^n \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (6)$$

Equation (5) and (6), when combined leads to :

$$\frac{E - E_D}{E_X - E} = K' . C_M^n$$

$$\text{or} \quad E = E_X + \frac{1}{K'} \frac{E_D - E}{C_M^n} \qquad \ldots\ldots\ldots\ldots\ldots \qquad (7)$$

If the metal concentration, C_M^o, is kept large compared to the dye concentration, then $C_M \approx C_M^o$,

so that $E = E_X + \frac{1}{K'} \cdot \frac{E_D - E}{C_M^{o\,n}}$ $\qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad$ (8)

Thus, a plot E vs. $\frac{E_D - E}{C_M^{o\,n}}$ should give a straight line for any system obeying equilibrium of the type (2).

The spectrophotometric data on amaranth $-Cu^{+2}$ and sunset yellow $-Cu^{+2}$ systems at various pH are given in Tables 2-5. It may be seen from Figs. 5 and 6, that the extinction data beyond pH 5.5, could be explained by an equilibrium of type (2) with n = 2. This is rather unusual, since azo dyes normally form complexes with metals either in 1:1

or 1:2 metal : dye ratio, but not with more than one metal atom per dye molecule.

At lower pH plots E vs. $\frac{E_D - E}{C_M^{o2}}$ do not yield straight lines and at about pH≈4.5, plot of E vs. $\frac{E_D - E}{C_M^o}$ is close to a straight line particularly for low values of C_M^o (Fig. 7) indicating that formation of 1:1 metal dye complex predominates in the lower pH. In view of these observations the equilibria should be represented as :

$$Cu^{+2} + D \rightleftharpoons (CuD')^{+(2-X_1)} + X_1H^+ \quad \ldots\ldots\ldots\ldots \quad 9(a)$$

$$(CuD')^{+(2-X_1)} + Cu^{+2} \rightleftharpoons \left[Cu_2D''\right]^{+(4-X_1-X_2)} + X_2H^+ \quad \ldots\ldots \quad 9(b)$$

The two equilibrium constants K_1 and K_2 are given by :

$$K_1 = \frac{C_{MD} \cdot C_{H^+}^{X_1}}{C_M \cdot C_D} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 10(a)$$

and

$$K_2 = \frac{C_{M_2D} \cdot C_{H^+}^{X_2}}{C_{MD} \cdot C_M} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 10(b)$$

Where C_{MD} and C_{M_2D} represents the equilibrium concentration of the 1:1 and 1:2 dye-Cu^{+2} complexes respectively. Denoting the molar extinctions of the species D, $(CuD')^{+(2-X_1)}$, $\left[Cu_2D\right]^{+(4-X_1-X_2)}$ and that of dye-Cu^{+2} mixture by E_D, E_{MD}, E_{M_2D} and E respectively, one can write :

$$E \cdot C_D^o = E_D \cdot C_D + E_{MD} \cdot C_{MD} + E_{M_2D} \cdot C_{M_2D} \quad \ldots\ldots\ldots\ldots \quad (11)$$

Further :

$$C_D^0 = C_D + C_{MD} + C_{M_2D} \quad \ldots\ldots\ldots\ldots\ldots \quad (12)$$

Substituting C_{MD} and C_{M_2D} in terms of C_D from eqns. 10(a) and (b) and using K_1' and K_2' for $K_1/C_{H^+}^{X_1}$ and $K_2/C_{H^+}^{X_2}$ respectively, eqns. (11) and (12) may be rewritten as :

$$E.\frac{C_D^0}{C_D} = E_D + K_1' \, C_M.E_{MD} + K_1' \, K_2' \, C_M^2 \, E_{M_2D} \quad \ldots\ldots \quad (13)$$

$$\text{and} \quad \frac{C_D^0}{C_D} = 1 + K_1' \, C_M + K_1' \, K_2' \, C_M^2 \, E_{M_2D} \quad \ldots\ldots\ldots\ldots \quad (14)$$

Combining eqns. (13) and (14) one gets after some rearrangement : $E_D - E = K_1' \, C_M(E - E_{MD}) + K_1' \, K_2' \, C_M^2 \, (E - E_{M_2D})$

$$\text{i.e.} \quad \frac{E_D - E}{(E-E_{M_2D})C_M^2} = K_1'.\frac{E - E_{MD}}{C_M(E-E_{M_2D})} + K_1' \, K_2' \quad \ldots\ldots\ldots\ldots \quad (15)$$

As before under experimental conditions $C_M^0 \gg C_D^0$, so that $C_M \simeq C_M^0$ and eqn. (15) may be written as

$$\frac{E_D - E}{(E-E_{M_2D})C_M^{0\,2}} = K_1' \frac{(E - E_{MD})}{(E - E_{M_2D})C_M^0} + K_1' \, K_2' \quad \ldots\ldots\ldots\ldots \quad (16)$$

Thus, a plot of $\frac{E_D - E}{(E-E_{M_2D})C_M^{0\,2}}$ vs. $\frac{E - E_{MD}}{(E-E_{M_2D})C_M^0}$ would yield a straight line for equilibria 9(a) and 9(b).

E_{M_2D} can be determined from the intercepts of the plot of $\frac{(E_D - E)}{C_M^{0\,2}}$ vs. E at higher pH where formation of M_2D

type predominates. Since at lower pH, E gives a linear relation with $(E - E_D)/C_M^o$ (Fig. 7) indicating the formation of 1:1 complex predominantly so that the intercept would be equal to E_{MD} according to eqn. (8). The calculated values of $\frac{E_D - E}{(E - E_{M_2D})C_M^{o\,2}}$ and $\frac{E - E_{MD}}{(E-E_{M_2D})C_M^o}$ for dye-Cu^{+2} systems at different pH values are given in Table 6 and 7 and the plots are shown in Figures 8-10. As can be seen the plots are straight lines within experimental errors confirming the presence of equilibria of the type 9(a) and (b) in Cu^{+2} - dye systems.

Values of K_1', K_2' and K_1' K_2' calculated from the slopes and intercepts of Figs. 8-10 are given in Tables 8 and 9. These values should be regarded as very approximate because of the approximations used for calculating E_{MD} and E_{M_2D}. However, these are probably sufficiently accurate for the determination of the number of protons involved in the equilibria 9(a) and 9(b).

Since K_1' and K_2' are related to hydrogen concentrations as given by eqns. 17(a) and (b), the ratio of the

$$K_1' = \frac{K_1}{C_H^{+x_1}} \quad \ldots\ldots\ldots\ldots\ldots \quad 17(a)$$

$$K_2' = \frac{K_2}{C_H^{+x_2}} \quad \ldots\ldots\ldots\ldots\ldots \quad 17(b)$$

apparent equilibrium constants at two different pH would be given by eqns. 18(a) and 18(b).

$$\frac{(K_1')pH_1}{(K_1')pH_2} = \left(\frac{C_{H_2^+}}{C_{H_1^+}}\right)^{X_1} = 10^{X_1(pH_1 - pH_2)} = 10^{X_1 . \Delta pH} \quad \ldots\ldots \quad 18(a)$$

and similarly,

$$\frac{(K_2')pH_1}{(K_2')pH_2} = 10^{X_2 . \Delta pH} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 18(b)$$

Using the data in Tables 8 and 9, it is easily seen that for both Cu^{+2}-amaranth and Cu^{+2}-sunset yellow systems $X_1 = 1$ and $X_2 = 2$.

The interaction of Cu^{+2} with these dyes may therefore be written as :

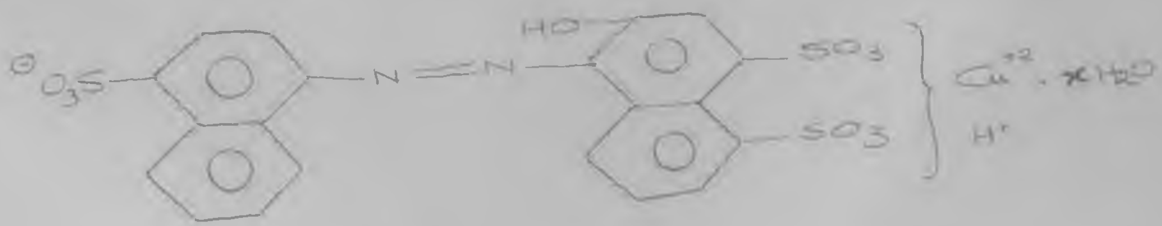
$$Cu^{+2} + D \rightarrow (CuD')^{+} + H^{+} \quad \ldots\ldots\ldots\ldots \quad 19(a)$$

and

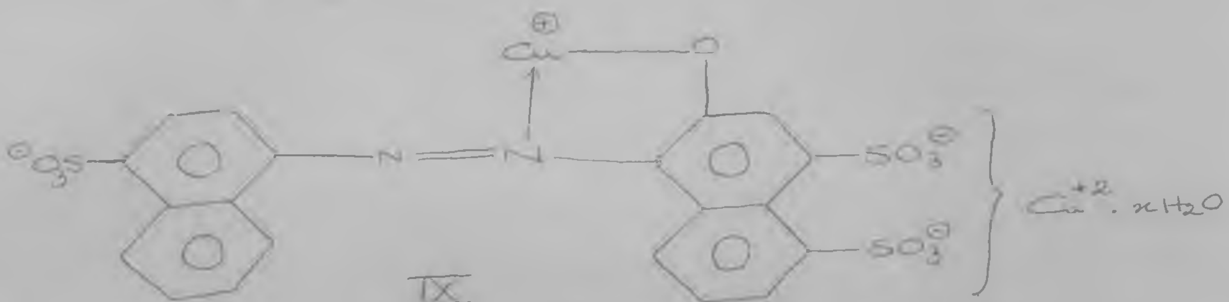
$$Cu^{+2} + (CuD')^{+} \longrightarrow \left[Cu_2D''\right]^{+} + 2H^{+} \quad \ldots\ldots \quad 19(b)$$

The results are both surprising and unexpected since no parallel example is known. These anomalous observations may, however, be rationalised as follows :

In the pH-range investigated some of the sulfonic groups presumably remain in the acid form, i.e., as $-SO_3H$. As is well-known complexation of sulfonated azo-dyes with metal ions occurs only after displacement of the proton of $-SO_3H$ group. The first Cu^{+2} ion thus forms a salt with the sulfonic acid which then complexes with another Cu^{+2} displacing the H^+ of the -OH group as well as another one from $-SO_3H$ group thereby neutralizing the charge.



VIII



IX

The mono and di-copper complexes of amaranth may thus be formulated as VIII and IX respectively. Since the exact location of the salt forming Cu^{+2} ion is not known, this has not been specified in the structures. Similarly the hydration is represented as xH_2O without specifying the site. However, both the species are expected to be hydrated. Similar structures for sunset yellow-Cu^{+2} complexes may be easily written and are therefore not shown separately.

Summary and Conclusion

Results of investigation on the interaction of Cu^{+2} ion with some food dyes have been recorded in this Chapter. The nature of the complexes formed by Cu^{+2} has been studied spectrophotometrically under varied conditions. The results of the present investigation are consistent with the formation of 1:1 metal : dye species in solutions having pH approximately below 4.5 and with 2:1 metal : dye species at higher pH. The latter result is unexpected and surprising since in most cases azo dyes form I:1 or 1:2 metal : dye species and no finding of a transition metal complex having more than one metal per dye molecule has so far been reported. This curious observation has been rationalised in terms of a salt forming Cu^{+2} ion and a coordinated Cu^{+2} ion per dye molecule; tentative structures for these species have also been proposed. It is hoped this unexpected, but justified, finding will stimulate further investigations in the field of metal-dye complexes.
