Application of the Continuous Variation Method to Systems Involving Stable Stepwise Complexes: Ni(II)-1,10-Phenanthroline & Cu(II)-Ethylenediamine Systems

K. A. PRAKAS, P. S. RAMANATHAN & CH. VENKATESWARLU

Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085

Expressions relating the concentrations of complexes [as well as the corrected absorbance values (ΔE)] in systems of stable stepwise complexes, with X values (mole fraction of the ligand) in the continuous variation method in equimolar solutions are presented, from which the nature of continuous variation curve at any wavelength can be obtained. These are comprehensive and complementary to those of Vosburgh and Cooper. Interesting typical continuous variation curves in nickel-phenanthroline and copper-ethylenediamine systems at different wavelengths are given. A brief account of the former system at higher acidities up to 10N is also included.

VOSBURGH and Cooper[1] were the first to describe an extension of the continuous variation (c.v.) method[2] in equimolar solutions. Taking Ni-phenanthroline (phen) system as a representative case, in which three coloured stepwise complexes exist, they demonstrated the possibility of selection of suitable wavelengths at which the c.v. curves would exhibit X_{max} corresponding to the compositions of the complexes. Subsequently, several workers have critically evaluated the applicability of the c.v. method to systems involving multiple equilibria[3-6]. Recently, van der Linden and Beers[7] have shown that in some systems involving two stable stepwise complexes, c.v. plots can be obtained in which the existence of intermediate complexes is obscured. However, their discussions do not cover all interesting aspects observable in such systems.

The purpose of the present communication is, therefore, to describe the nature of the c.v. curves and X_{max} expected at any arbitrarily chosen wavelength, in systems in which very stable stepwise complexes exist. Besides this, a brief account of the results obtained in the spectrophotometric studies of Ni-phen system at higher acidities is also given.

Theory

Expressions relating the concentrations of complexes as well as ΔE, with X — When a single stable complex is exclusively formed in a system, its concentration in solution with any value of $X[=C_A/(C_M+C_A)]$ can easily be computed. When two or three very stable complexes form in a system*, the expressions for the concentrations of the stepwise complexes (C_1, C_2 and C_3) in solutions of various X values will be as indicated in Table 1. Typical

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*The systems considered are such that each complex forms exclusively and quantitatively (for all practical purposes) when the metal and ligand are in the appropriate stoichiometric amounts.
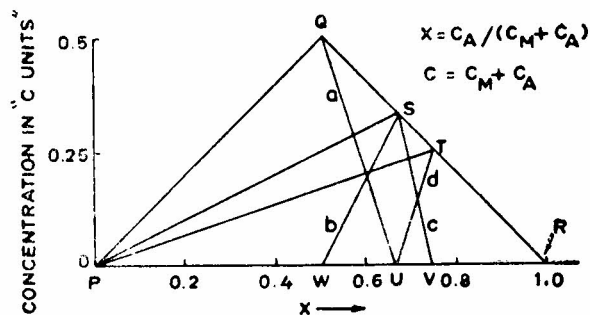

Fig. 1 — C.v. curves (concentration vs X) for systems involving stable stepwise complexes [(i) Curve PQUR: C_1 vs X in systems with two and three stepwise complexes; (ii) curve PWSR: C_2 vs X in a system with two stepwise complexes; (iii) curve PWSVR: C_2 vs X in a system with three stepwise complexes; and (iv) curve PUTR: C_3 vs X in a system with three stepwise complexes]

theoretical c.v. curves (correlating C_1, C_2 or C_3 with X) are shown in Fig. 1.

When spectrophotometry is employed to study the system, the measured E and ΔE values (E values of the mixtures corrected for absorption due to metal and ligand, assuming no reaction) can be expressed in terms of ϵ of the species involved and X, as shown in Table 2.

Based on the treatment of Katzin and Gebert[3] it can be shown that, in systems of the type considered above, the X_{max} in c.v. curves will not show any observable shift from stoichiometric values, in spite of the formation of successive complexes.

From Tables 1 and 2 it can be seen that C_1, C_2, C_3, E and ΔE are all linear functions of X in the appropriate regions. In other words, c.v. curves (concentration or ΔE vs X) will be composed of linear segments. The maximum number of linear segments in a c.v. curve will be $n+1$ for a system involving n stepwise complexes.

TABLE 1 — EXPRESSIONS FOR THE CONCENTRATIONS IN TERMS OF X

X	(M)	(A)	C_1	C_2	C_3	Curve in Fig. 1
		SYSTEM INVOLVING MA AND MA_2				
0·00-0·50	$C(1-2X)$	0·0	CX	0·0	—	PQUR (MA)
0·50-0·67	0·0	0·0	$C(2-3X)$	$C(2X-1)$	—	PWSR (MA_2)
0·67-1·00	0·0	$C(3X-2)$	0·0	$C(1-X)$	—	
		SYSTEM INVOLVING MA, MA_2 AND MA_3				
0·00-0·50	$C(1-2X)$	0·0	CX	0·0	0·0	PQUR (MA)
0·50-0·67	0·0	0·0	$C(2-3X)$	$C(2X-1)$	0·0	PWSVR (MA_2)
0·67-0·75	0·0	0·0	0·0	$C(3-4X)$	$C(3X-2)$	—
0·75-1·00	0·0	$C(4X-3)$	0·0	0·0	$C(1-X)$	PUTR (MA_3)

$$C = C_M + C_A; \quad X = C_A/C.$$

TABLE 2 — EXPRESSIONS FOR E AND ΔE VALUES OF DIFFERENT METAL-LIGAND MIXTURES

X	E	ΔE
	SYSTEM INVOLVING MA AND MA_2	
0·00-0·50	$\epsilon_M C + CX(\epsilon_1 - 2\epsilon_M)$	$CX(\epsilon_1 - (\epsilon_M + \epsilon_A)) = S_1.CX$
0·50-0·67	$(2\epsilon_1 C - \epsilon_2 C) + CX(2\epsilon_2 - 3\epsilon_1)$	$(2\epsilon_1 C - \epsilon_2 C - \epsilon_M C) + CX((2\epsilon_2 + \epsilon_M) - (3\epsilon_1 + \epsilon_A) = I_1 + S_2.CX$
0·67-1·00	$(\epsilon_2 C - 2\epsilon_A C) + CX(3\epsilon_A - \epsilon_2)$	$(\epsilon_2 C - 2\epsilon_A C - \epsilon_M C) + CX(2\epsilon_A + \epsilon_M - \epsilon_2) = I_2 + S_3.CX$
	SYSTEM INVOLVING MA, MA_2 AND MA_3	
0·00-0·50	$\epsilon_M C + CX(\epsilon_1 - 2\epsilon_M)$	$CX(\epsilon_1 - \epsilon_M - \epsilon_A) = S_{11}.CX$
0·50-0·67	$\epsilon_1 C(2-3X) + \epsilon_2 C(2X-1)$	$(2\epsilon_1 C - \epsilon_2 C - \epsilon_M C) + CX(2\epsilon_2 + \epsilon_M - 3\epsilon_1 - \epsilon_A) = I_{11} + S_{22}.CX$
0·67-0·75	$\epsilon_2 C(3-4X) + \epsilon_3 C(3X-2)$	$(3\epsilon_2 C - 2\epsilon_3 C - \epsilon_M C) + CX(3\epsilon_3 + \epsilon_M - 4\epsilon_2 - \epsilon_A) = I_{33} + S_{44}.CX$
0·75-1·00	$\epsilon_3 C(1-X) + \epsilon_A C(4X-3)$	$(\epsilon_3 C - 3\epsilon_A C - \epsilon_M C) + CX(3\epsilon_A + \epsilon_M - \epsilon_3) = I_{44} + S_{55}.CX$

ϵ_M, ϵ_A, ϵ_1, ϵ_2 and ϵ_3 are the molar absorbances of the metal, ligand and the three complexes in that order.

In spectrophotometric studies the sign of the slope of each segment will depend upon the n values of the complexes and the ϵ values of the absorbing species involved in that region. Excepting in certain special cases, a " break " or extremum will be found in the c.v. curve, corresponding to the maximum concentration of each of the complexes forming in the system. From the X values corresponding to these breaks/extrema, the compositions of the complexes forming in the system can be arrived at.

The above-mentioned conclusions are put to test by applying the c.v. method to Cu(II)-ethylenediamine(en) and Ni(II)-phen systems, which involve two and three coloured stable stepwise complexes respectively.

Materials and Methods

All the chemicals used were of AR grade. Absorbance measurements were made with a Beckman spectrophotometer, model DU, employing corex cells of 10 mm path length.

Results and Discussion

Cu-en system at pH 5·5 — In Fig. 2 the slope determining functions S_1, S_2 and S_3 of Cu-en system
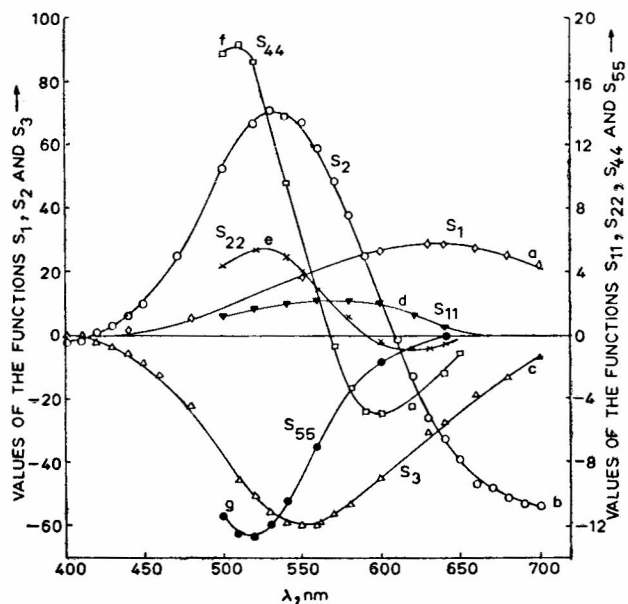

Fig. 2 — Variation of the values of slope determining functions with wavelength [(i) Curves a-c: S_1, S_2 and S_3 of Cu-en system; (ii) curves d-g: S_{11}, S_{22}, S_{44} and S_{55} of Ni-phen system]

TABLE 3 — FEATURES OF C.V. CURVES OF Cu-en SYSTEM AT DIFFERENT WAVELENGTHS

Wavelength region	Sign/magnitude of			X^*_{max}	Break*	Exptl curve in Fig. 3
	S_1	S_2	S_3			
GENERAL CASES						
400	+ve	—ve	—ve $S_3 \neq S_2$	0·50	0·67	—
430-600	+ve	+ve $S_2 \neq S_1$	—ve	0·67	0·50	a (550 nm)
610-700	+ve	—ve	—ve $S_3 \neq S_2$	0·50	0·67	b (650 nm)
SPECIAL CASES						
410	+ve	—ve	—ve $S_3 = S_2$	0·50	No break at 0·67	—
415	+ve	0·0	—ve	Steady region between 0·50 and 0·67	Breaks at 0·50 and 0·67	—
425	+ve	+ve $S_2 = S_1$	—ve	0·67	No break at 0·50	—
590	+ve	+ve $S_2 = S_1$	—ve	0·67	do	c
605	+ve	0·0	—ve	Steady region between 0·5 and 0·67	Breaks at 0·50 and 0·67	d
635	+ve	—ve	—ve $S_3 = S_2$	0·50	No break at 0·67	e

*Anticipated from sign/magnitude of S_1, S_2 and S_3.

have been plotted as functions of wavelengths in the 400-700 nm region (curves a, b and c). The sign and magnitude of these three functions at any chosen wavelength decide not only the nature of the c.v. curves but also the X_{max}/break obtained experimentally. Table 3 summarizes the features of c.v. curves of Cu-en system at different wavelengths. A few experimental curves are included in Fig. 3 to illustrate the conclusions arrived at.

Ni-phen system at pH 3·0— Curves d-g in Fig. 2 represent respectively the variation of the functions S_{11}, S_{22}, S_{44} and S_{55} of Ni-phen system with wavelength in the 500-650 nm region. The features of c.v. curves expected in Ni-phen system at different wavelengths are summarized in Table 4. A few experimental curves are included in Fig. 4 to demonstrate the validity of the conclusions arrived at.

C.v. curves of higher complexes (MA_2 *and* MA_3), *obtained by varying a lower complex* (MA *or* MA_2) *and ligand* — In systems of the type discussed above, the composition of MA_2 can be arrived at by carrying out the c.v. experiment, varying MA and A continuously. Similarly, the composition of MA_3 can be deduced from c.v. curves obtained by varying either MA or MA_2 and A. In all these cases the lower complex takes the place of metal ion. One can easily derive expressions relating E or ΔE and X in these cases as well. The expressions relevant to these cases are listed in Table 5.
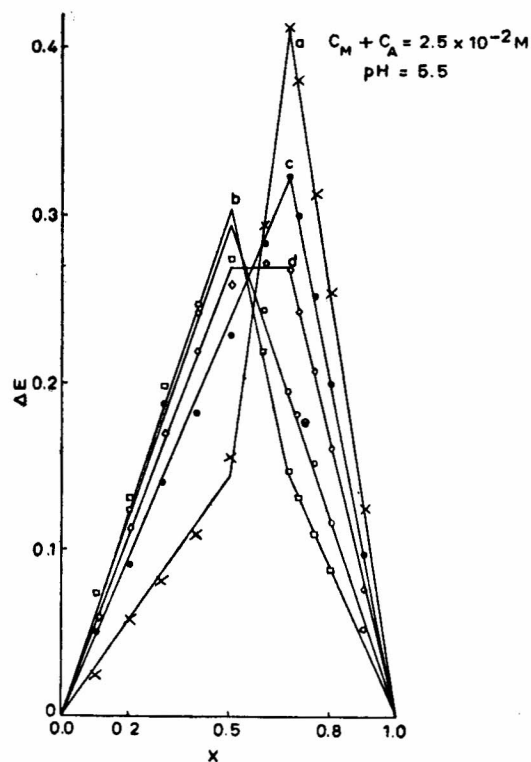

Fig. 3 — C.v. curves of Cu-en system at different wavelengths [a, 550; b, 650; c, 590; d, 605; e, 635 nm]

TABLE 4 — FEATURES OF C.V. CURVES OF Ni-phen SYSTEM AT DIFFERENT WAVELENGTHS

Wavelength region	Sign/magnitude of				X^*_{max}	Break*	Exptl curve in Fig. 4
	S_{11}	S_{22}	S_{44}	S_{55}			
GENERAL CASES							
500-560	+ve	+ve $S_{22} \neq S_{11}$	+ve $S_{44} \neq S_{22}$	—ve	0·75	0·50, 0·67	a (520 nm)
570-590	+ve	+ve $S_{22} \neq S_{11}$	—ve	—ve $S_{55} \neq S_{44}$	0·67	0·50, 0·75	b (575 nm)
600-620	+ve	—ve	—ve $S_{44} \neq S_{22}$	—ve $S_{55} \neq S_{44}$	0·50	0·67, 0·75	c (600 nm)
630-650	+ve	—ve	—ve $S_{44} \neq S_{22}$	—ve	0·50 and X_{min} at 0·75	0·67	d (640 nm)
SPECIAL CASES							
550	+ve	+ve $S_{22} \neq S_{11}$	+ve $S_{22} = S_{44}$	—ve	0·75	0·50 No break at 0·67	?
565	+ve	+ve $S_{22} = S_{11}$	0·0	—ve	Steady region between 0·67 and 0·75. Breaks at 0·67 and 0·75 but no break at 0·50		f
580	+ve $S_{22} \neq S_{11}$	+ve	—ve $S_{44} = S_{55}$	—ve	0·67	0·50 No break at 0·75	g
590	+ve	0·0	—ve	—ve $S_{55} \neq S_{44}$	Steady region between 0·50 and 0·67 with breaks at 0·50, 0·67 and 0·75		h

*Anticipated from the sign/magnitude of S_{11}, S_{22}, S_{44} and S_{55}.

TABLE 5 — EXPRESSIONS FOR E AND ΔE FOR DIFFERENT COMPLEX-LIGAND MIXTURES

K	E	ΔE
EXPERIMENTS IN WHICH MA AND A ARE VARIED*		
0·00-0·50	$\epsilon_1 C + CK(\epsilon_2 - 2\epsilon_1)$	$CK(\epsilon_2 - \epsilon_1 - \epsilon A) = CX.T_1$
0·50-0·67	$(2\epsilon_2 C - \epsilon_3 C) + CK(2\epsilon_3 - 3\epsilon_2)$	$(2\epsilon_2 C - \epsilon_3 C - \epsilon_1 C) + CX(2\epsilon_3 + \epsilon_1 - 3\epsilon_2 - \epsilon A) = J_1 + CX.T_2$
0·67-1·00	$(\epsilon_3 C - 2\epsilon_A C) + CK(3\epsilon_A - \epsilon_3)$	$(\epsilon_3 C - 2\epsilon_A C - \epsilon_1 C) + CX(2\epsilon_A + \epsilon_1 - \epsilon_3) = J_2 + CX.T_3$
EXPERIMENTS IN WHICH MA$_2$ AND A ARE VARIED†		
0·00-0·50	$\epsilon_2 C + CX(\epsilon_3 - 2\epsilon_2)$	$CX(\epsilon_3 - \epsilon_2 - \epsilon A) = CX.T_4$
0·50-1·00	$(\epsilon_3 C - \epsilon_A C) + CX(2\epsilon_A - \epsilon_3)$	$(\epsilon_3 C - \epsilon_A C - \epsilon_2 C) + CX(\epsilon_2 + \epsilon_A - \epsilon_3) = J_3 + CX.T_5$

*$X = C_A/(C_{MA} + C_A)$; $E = E_{mixture} - (E_{MA} + E_A)$, calculated assuming no reaction.
†$X = C_A/(C_{MA_2} + C_A)$; $E = E_{mixture} - (E_{MA_2} + E_A)$, calculated assuming no reaction.

The discussions given in earlier sections concerning the dependence of the nature of c.v. curves and the X_{max} on ϵ values of the species involved in the equilibria (in the different regions of the c.v. curve) is equally applicable in these cases as well. This becomes obvious from the expressions given in Table 5 for the E and ΔE values.

To illustrate the points from the practical point of view, data of Ni-phen system can be made use of. In Fig. 5, the slope determining functions (T_1 to T_5) are plotted as functions of wavelengths in the 500-650 nm region (curves a-e). Table 6 summarizes the features of c.v. curves obtained (at different wavelengths) by varying MA and A as well as MA$_2$ and A. A few experimental curves are shown in Fig. 6.

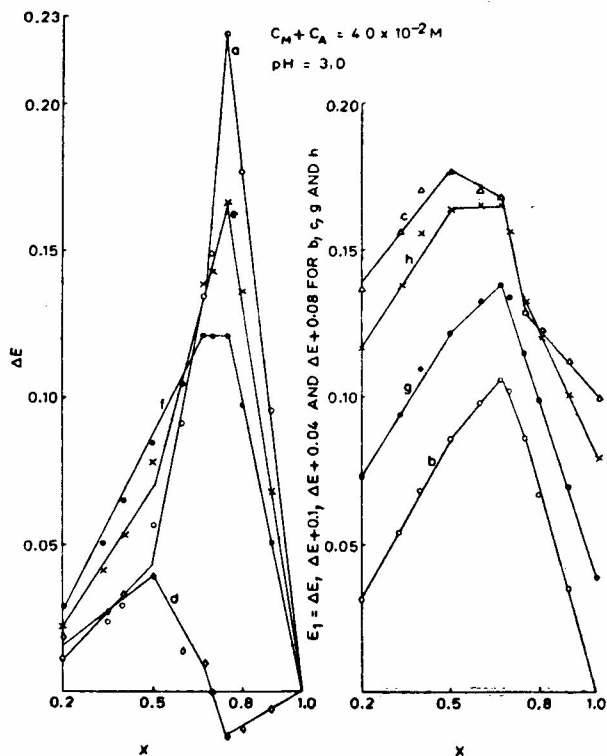*Studies on Ni-phen system at higher acidities (pH 2·0 to 10N)*— The spectra of mixtures of Ni and

Fig. 4 — C.v. curves of Ni-phen system at different wavelengths [a, 520; b, 575; c, 600; d, 640; e, 550; f, 565; g, 580; h, 590 nm]
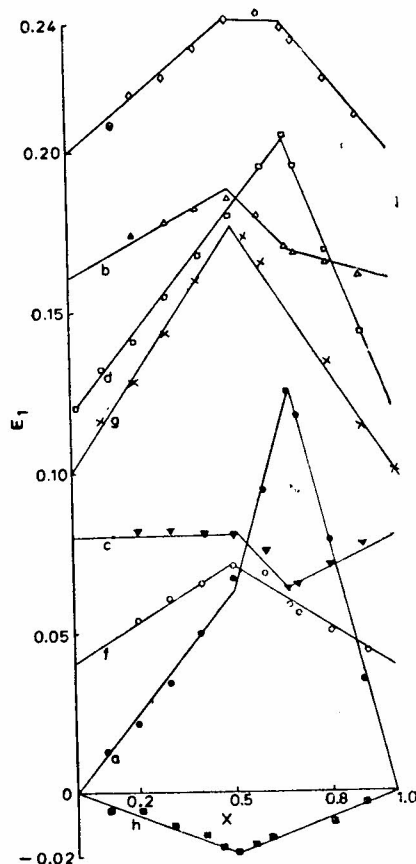

Fig. 5 — Variation of the values of the slope determining functions T_1-T_5 with wavelength [(i) Curves a-c: T_1, T_2 and T_3 (variation of MA and A); and (ii) curves d and e: T_4 and T_5 (variation of MA_2 and A)]

Fig. 6 — C.v. curves obtained by varying one complex and ligand [Variation of MA and A: a, 520; b, 585; c, 620; d, 550; e, 570; f, 580 nm; $E_1 = \Delta E$ for a; $\Delta E + 0.16$ for b; $\Delta E + 0.08$ for c; $\Delta E + 0.12$ for d; $\Delta E + 0.20$ for e and $\Delta E + 0.04$ for f. Variation of MA_2 and A: g, 520; h, 620 nm; $E_1 = \Delta E + 0.10$ for g and ΔE for h]
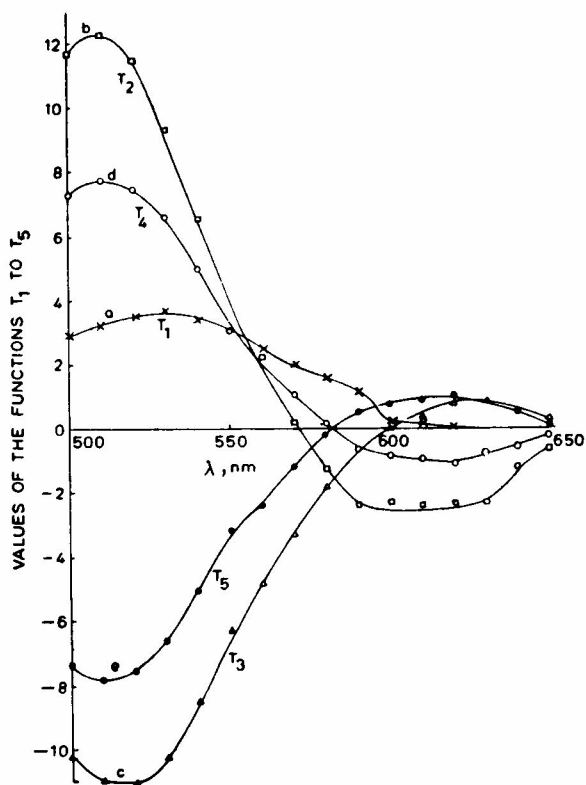
phen (1:1, 1:2, 1:3 and 1:5), scanned at different acidities (pH 2·0 to 10N) in the region 500-680 r.m are shown in Fig. 7. From the change in the nature of spectra it becomes obvious that the higher complexes dissociate to lower ones with increase in acidity. Colour saturation curves support this contention (Fig. 8).

A close inspection of the spectra of the complexes formed at lower and higher acidities does reveal some differences in their nature. These spectral changes may be attributed to the formation of either protonated (or sulphato) complexes at higher acidities. During the study of the mechanism of dissociation of the 1:1 complex in acid solution, Margerum *et al.*[8] have also reported the formation of a protonated complex species as an intermediate one. Protonated complexes have been reported in ferrous-phen system as well[9].

Interestingly enough, even at 5N acidity, the c.v. curves at 620, 580 and 520 nm show X_{max} corresponding to the compositions 1:1, 1:2 and 1:3. At 10N acidity, however, formation of the 1:3 complex is not indicated. Even the formation of the lower complexes cannot be unambiguously established, owing to the broad maxima exhibited by the c.v. curves at higher wavelengths. The
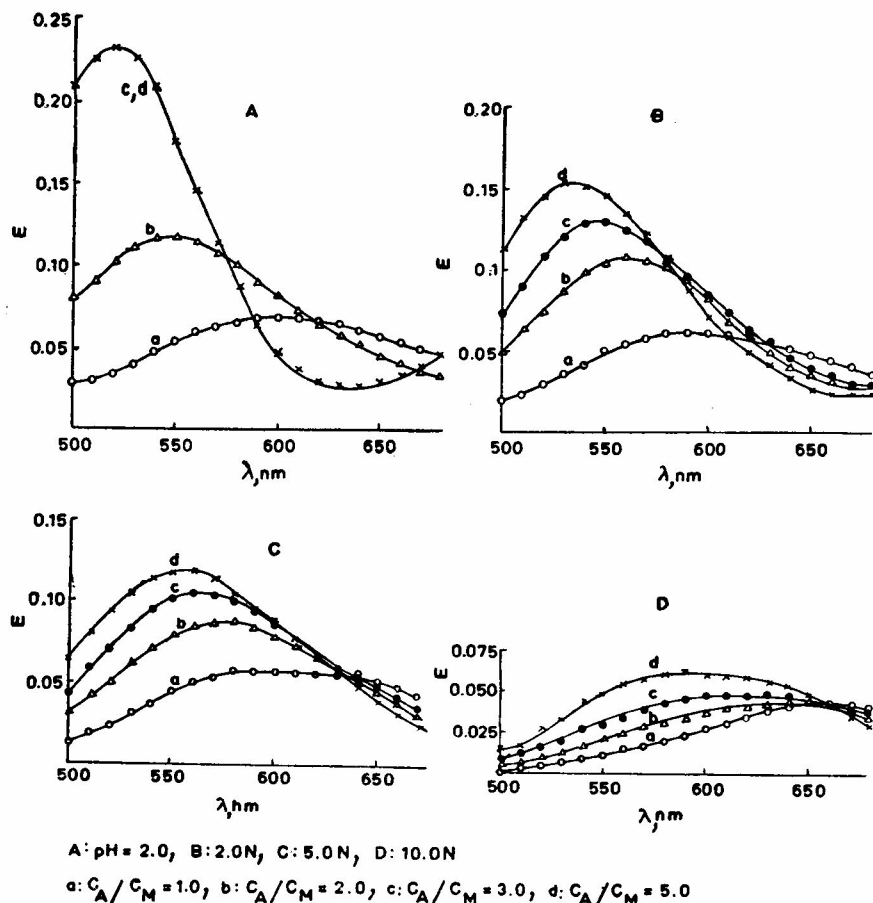
Fig. 7 — Spectra of Ni-phen system at different acidities [A, $pH = 2 \cdot 0$; B, $2N$; C, $5N$; D, $10N$; a, $C_A/C_M = 1 \cdot 0$; b, $C_A/C_M = 2 \cdot 0$; c, $C_A/C_M = 3 \cdot 0$; $C_A/C_M = 5 \cdot 0$]

A: pH = 2.0, B: 2.0N, C: 5.0N, D: 10.0N

a: $C_A/C_M = 1.0$, b: $C_A/C_M = 2.0$, c: $C_A/C_M = 3.0$, d: $C_A/C_M = 5.0$

TABLE 6 — FEATURES OF C.V. CURVES IN Ni-phen SYSTEM AT DIFFERENT WAVELENGTHS
(VARIATION OF A LOWER COMPLEX AND LIGAND)

Wavelength range	Sign/magnitude of			X^*_{max}	Break*	Exptl curve in Fig. 6
	T_1	T_2	T_3			
VARIATION OF MA AND A: GENERAL CASES						
500-565	+ve	+ve $T_1 \neq T_2$	—ve	0·67	0·50	a (520 nm)
570-595	+ve	—ve	—ve $T_2 \neq T_3$	0·50	0·67	b (585 nm)
600-650	0·0	—ve	+ve	X_{min} at 0·67	Up to $X = 0·50$ the curve coincides with X-axis	c (620 nm)
SPECIAL CASES						
550	+ve	+ve $T_1 = T_2$	—ve	0·67	No break at 0·50	d
570	+ve	0·0	—ve	Steady region between 0·50 and 0·67	Breaks at 0·50 and 0·67	e
580	+ve	—ve	—ve $T_2 = T_3$	0·50	No break at 0·67	f
VARIATION OF MA$_2$ AND A						
500-575	+ve†	—	—ve‡	0·50	—	g (520 nm)
585-650	—ve†	—	+ve‡	X_{min} at 0·50	—	h (620 nm)
582	0·0†	—	0·0‡	C.V. curve merges with X-axis	—	—

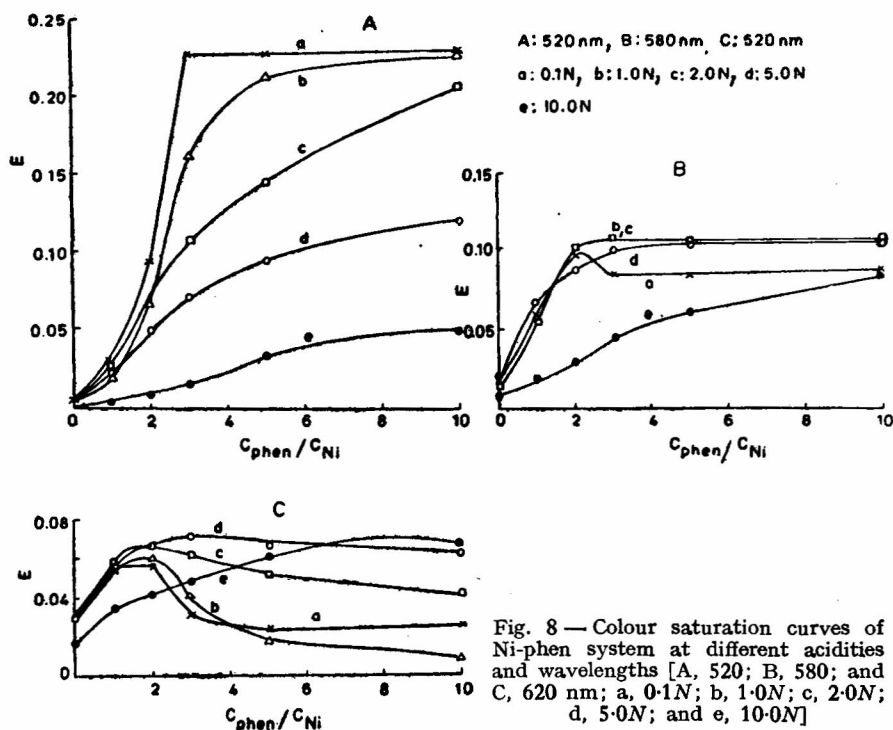*Anticipated from sign/magnitude of T_1, T_2 and T_3. ‡T_5. †T_4.

Fig. 8 — Colour saturation curves of Ni-phen system at different acidities and wavelengths [A, 520; B, 580; and C, 620 nm; a, $0.1N$; b, $1.0N$; c, $2.0N$; d, $5.0N$; and e, $10.0N$]

curves at higher wavelengths show a distinct shoulder below $X = 0.50$. Even those curves which exhibit a broad X_{max} around 0.50 are not symmetrical in nature. These experimental observations indicate the possible formation of one or more new complex species in the Ni-phen system at higher acidities.

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