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CHAPTER II

A. Binary Copper β-ketoanilide systems

B. Binary Copper Salicylamide systems

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A. Binary Copper- β-ketoanilide Systems

According to Bjerrum[21] the complex formation is a stepwise reaction as follows :

$$M + L \rightleftharpoons ML \qquad \text{-----(1)}$$

$$ML + L \rightleftharpoons ML_2 \qquad \text{-----(2)}$$

$$ML_{i-1} + L \rightleftharpoons ML_i \qquad \text{-----(3)}$$

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad \text{-----(4)}$$

where M = metal ion and L = ligand. The charges on the metal and ligand have been omitted for clarity. The equilibrium constant governing each step is termed the stepwise formation constant.

Thus, for a complex of the type $[ML_2]$,

$$K_1 = \frac{[ML_1]}{[M][L]} \qquad \text{-----(5)}$$

$$K_2 = \frac{[ML_2]}{[ML][L]} \qquad \text{-----(6)}$$

and $$\beta_2 = K_1 \cdot K_2 = \frac{[ML_2]}{[M][L]^2} \qquad \text{-----(7)}$$

Similarly, for the ligand LH_2 there are two equilibrium constants governing the following stepwise proton-ligand formation constants.

$$L^{2-} + H^{+} \rightleftharpoons LH^{-} \qquad \text{-----(8)}$$

$$LH^{-} + H^{+} \rightleftharpoons LH_2 \qquad \text{-----(9)}$$

The first and second proton-ligand formation constants can be shown as follows :

$$K_2^{\ H} = \frac{[LH_2]}{[LH^-][H^+]} \qquad \text{----(10)}$$

$$K_1^{\ H} = \frac{[LH^-]}{[L^{2-}][H^+]} \qquad \text{----(11)}$$

and $$\beta_2^{\ H} = \frac{[LH_2]}{[L^{2-}][H^+]^2} \qquad \text{----(12)}$$

The formation function, $\bar{n}_H$, can be defined as average number of protons bound per not complex bound ligand. If the total concentration of ligand is $T_L^{\ o}$ and that of metal ion is M, the concentration of the free ligand is equal to $T_L^o - \bar{n}\ T_M^o$, where $\bar{n}$ is the average number of ligands bound per metal ion. For a complex $[ML_2]$ the expression for $\bar{n}$ is as follows :

$$\bar{n} = \frac{K_1[L] + 2K_1 \cdot K_2[L]^2}{1 + K_1[L] + K_1 \cdot K_2[L]^2} \qquad \text{----(13)}$$

It is presumed that the polynuclear complexes and proton bearing complexes do not exist in solution. The free ligand exists in solution, in the form of undissociated molecule LH_2 and the ions LH^- and L^{2-}.

$$T_L^o - \bar{n}\, T_M^o = LH_2 + LH^- + L^{2-} \qquad ----(14)$$

This can be further solved to get the value of pL, i.e. negative logarithm of free ligand ion,

$$- \log L = pL$$

$$= \log \left\{ 1 + \frac{pK_1^{\,H}\,(V^o + V'')}{(T_L^o - \bar{n}\, T_M^o)\, V^o \;.\; \text{antilog } B} + \frac{pK_1^{\,H} \;.\; pK_2^{\,H}\,(V^o + V'')}{(T_L^o - \bar{n}\, T_M^o)\, V^o\, (\text{antilog } B)^2} \right\}$$

$$----(15)$$

Bjerrum has shown[63] that the values of pL at $\bar{n} = 0.5$ and 1.5 correspond to the metal-ligand formation constants, $\log K_1$ and $\log K_2$, respectively. The values are, however, not very precise. Therefore, various computations of $\bar{n}$ and pL values have been attempted to get precise values of the formation constants. Two of the more accurate methods, i.e. the method of least square[64,65] and a computer technique called SCOGS[66] have been used in the present study of Copper. β-ketoanilide complexes.

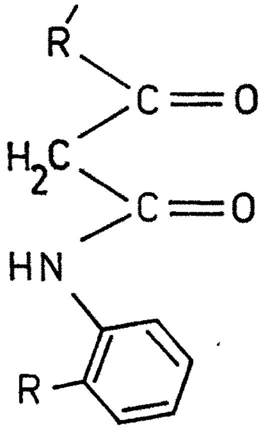
The study of β-ketoanilide complexes of transition and non-transition metals in solution have been reported earlier.[67] Various substitutions were carried out on the phenyl ring to study the effect of the inductive and steric effects on the formation constant values using pH metric and potentiometric techniques on Cu(II) complexes of N,N-dialkyl acetoacetamide and β-ketoanilides by Guenter and coworkers.[68] They[69] have also reported Cu(II) complexes of 2-acetoacetamide pyridines and pyrimidines to study the effect of pyridyl and pyrimidyl substituents. Fe(III)-acetoacetanilide complex formation constants have been studied[70] spectrophotometrically. Calorimetric determination of the stability of Sb(V) β-ketoanilide complexes have also been carried out[71] to see the effect of substituents at the phenyl ring of the ligand on the formation enthalpy values.

The main interest of the present study is to determine the mixed-ligand formation constant K^{CuA}_{CuAL}, where A = 2,2'-dipyridyl, 1,10-phenanthroline, 2-(2'-pyridyl)-benzimidazole or 2-(2'-pyridyl)imidazoline and L = β-ketoanilides. The details of the calculation and discussion on the mixed-ligand formation constants have been presented in the later chapter. However, for obtaining the values of,

$$\Delta \log K = \log K^{CuA}_{CuAL} - \log K^{Cu}_{CuA} \quad \text{-----(16)}$$

the formation constants of binary complexes are required under identical conditions. Hence, in this chapter proton-ligand formation constants of β-ketoanilides and the formation constants of their Cu(II) complexes have been studied by Irving-Rossotti titration technique.[72] Further, a computer programme has been used to determine precise values of such formation constants.

The ligands (LH) selected are :



R = H R' = CH_3 acetoacetanilide (L^1H)
R = CH_3 R' = CH_3 acetoacet-o-toluidide (L^2H)
R = OCH_3 R' = CH_3 acetoacet-o-anisidide (L^3H)
R = H R' = C_6H_5 benzoatoacetanilide (L^4H)

EXPERIMENTAL

Irving-Rossotti titration technique[72] was employed for the determination of the proton-ligand and metal-ligand formation constants in solution. This technique involves the measurement of pH, which was carried out using a glass calomel electrode and pH meter combination. Since, the ligands used in the present study are only sparingly soluble in water, all titrations were carried out in dioxan-water (1 : 1 v/v) mixture. Dioxan was purified by the known method.[73] Throughout this investigation conductivity water was used.

Ligands and other chemicals :

The ligands used were all of A.R. grade, supplied by C and C chemicals division (New York). Their standard solutions were prepared by directly dissolving the weighed quantity in known volume of purified dioxan. Invariably fresh solutions of ligands were prepared in purified dioxan prior to titration, because dioxan on keeping for a longer period develops peroxide.

Sodium hydroxide :

50 gms. of sodium hydroxide (Chemapol Ltd.) was dissolved in 500 ml of conductivity water and was allowed to stand for two days. The solution was filtered through G_4 sintered glass crucible and standardized by titrating against standard oxalic acid solution. This stock solution was stored out of contact with CO_2 using sodalime guard tube and was diluted to get solution of required concentration.

Sodium perchlorate :

The required quantity of sodium perchlorate (A.R., Riedel) was weighed and dissolved in 500 ml of conductivity water for 1M solution.

Perchloric acid solution :

The perchloric acid (Riedel, analysed) supplied was of 80% concentration. A definite volume of the acid was dissolved in 500 ml of conductivity water to get a solution of approximately 0.2M strength. The exact concentration was determined by titrating against standard sodium hydroxide solution.

Copper perchlorate solution :

In order to avoid the complexing tendencies of the anion, the perchlorate of Cu(II) was prepared by dissolving a weighed quantity of copper carbonate in known excess of perchloric acid. By this, the possible hydrolysis of Cu(II) is avoided. This was used as stock solution after estimating the amount of metal present. Required concentration of copper perchlorate was prepared by proper dilution.

Apparata :

All glasswares used were of pyrex glass. The micro burette was calibrated to 0.01, by the method described by Vogel.[74] The measuring vessels such as micropipettes, measuring flasks of various capacities, pipettes etc. were calibrated by using a standard burette.

pH meter and accessories :

An expanded scale pH meter of the type pH 821 of Electronic Corporation of India Ltd., operating on 220-240 volts and 40-60 Hz and designed for the entire pH range was used.

Details of Irving-Rossotti Titration Technique :

All titrations were carried out under nitrogen atmosphere. The titration vessel was designed such that there are inlet holes for the electrode, the burette tip and the glass stirrer. Pure nitrogen gas was obtained by passing the nitrogen gas through pyrogallol (for absorption of oxygen if any in traces), concentrated sulphuric acid (for absorption of moisture) and finally 50% dioxan-water (v/v) solution. Pure nitrogen gas was allowed to pass through the solution by an inlet nozzle fitted at the bottom of the titration vessel.

In all, three sets were prepared as follows :

1. For acid titration-
   0.02M $HClO_4$, 0.180M $NaClO_4$
2. For ligand titration-
   0.02M $HClO_4$, 0.02M ligand and 0.160M $NaClO_4$

3. For Copper-ligand titration-
   0.02M $HClO_4$, 0.02M ligand, 0.002M copper perchlorate and 0.158M $NaClO_4$

In all the cases the total volume was so adjusted that each solution was dioxan-water (1 : 1 v/v). Initially ionic strength of the solution was raised to 0.2M in all the cases by the addition of required amount of sodium perchlorate, a neutral salt.

The titration vessels containing above solutions were allowed to stand for some time (~20 min). After the addition of each portion of alkali, pH was noted. The highest reading which remained steady was recorded in all cases. pH corrections for 50% dioxan medium have been made using the method suggested by Van Uitert and Haas.[75]

The titration data are given in Tables IIA 1 to IIA 3 and Figures IIA 1 to IIA 4.

Determination of Proton-Ligand and Metal-Ligand Stability Constants :

It is seen in the Irving-Rossotti titration curves (Fig. IIA 1 to IIA 4) that in the lower pH range the acid and the ligand curves (1 and 2) overlap each other. In the higher pH range, however, the ligand curve exhibits lower values of pH than the acid titration curve showing the presence of more number of titrable H^+ ions due to the dissociation of the H^+ of enolic hydroxyl.

Calculation of $\bar{n}_H$ and pK_1^H :

The $\bar{n}_H$ values can be calculated by using curves 1 and 2. The horizontal distance between these two curves is used for the calculation of $\bar{n}_H$ at different pH by using the following equation :

$$\bar{n}_H = \frac{(V' - V'')\ (N + E^o)}{(V^o + V')\ T_L^o} + Y \qquad \text{------(17)}$$

where

$\bar{n}_H$ = mean number of protons bound per not complex bound ligand molecule

V^o = initial volume of solutions

V', V'' = volume of alkali required to attain the same pH in the acid and acid + ligand titration curves

E^o = initial concentration of mineral acid

T_L^o = initial total ligand concentration

Y = number of replacable hydrogens from the ligand

The values of proton-ligand stability constant (pK_1^H) were obtained at different pH values using the equation,

$$pH - \log\left[\bar{n}_H / (1 - \bar{n}_H)\right] = pK_1^H \qquad \text{------(18)}$$

The values obtained agree well with the values reported in the literature.[67] The plot of pH against $\log\left[\bar{n}_H / (1 - \bar{n}_H)\right]$

yielded a straight line. The details of $\bar{n}_H$ calculation and the graphs showing linear plot have not been given to save space. The average values obtained are presented in Table IIA 12.

Calculation of Formation Constants of Binary Complexes with Cu(II) :

It is seen that the ligand + Cu(II) curves (3) are separated from the ligand curves (2) at higher pH range. This is due to the liberation of extra hydrogen ions on the coordination of ligand with metal ion. The $\bar{n}$ values have been calculated by measuring horizontal distance in the volume of alkali required to produce the same pH in the metal and ligand titration curves and substituting it in the following equation :

$$\bar{n} = \frac{(V''' - V'') \left[N + E^{o} + T_L^{o} (Y - \bar{n}_H) \right]}{(V^{o} + V'') \, \bar{n}_H \cdot T_M^{o}} \quad \text{----(19)}$$

where

T_M^{o} = initial total metal ion concentration

V'', V''' = volumes of alkali required to attain the same pH in the curves 2 and 3, respectively.

Calculation of pL :

For calculation of pL, equation (15) was used. The pL values have been recorded in Tables IIA 4 to IIA 7.

Since in such systems $K_1 / K_2 < 10^{2.5}$, least square method[64,65] was used to calculate the values of log K_1 and log K_2. The calculations and the values of first and second formation constants ~~values~~ have been recorded in Tables IIA 8. to IIA 11.

The formation constants were refined by using Sayce's computer programme SCOGS[66] (Stability Constants Of Generalized Species). This is capable of calculating simultaneously or individually association constants for any of the species formed in solutions containing upto two metals and two ligands, provided that the degree of formation is pH dependent. In fact, for a mixture of two metals A, B and two ligands S, T association constants may in principle be calculated for any specie j which can be described by a general formula $A_{A_j}\, B_{B_j}\, S_{S_j}\, T_{T_j}\, (OH)_{W_j}$, where A_j, B_j, S_j and T_j are positive integers or zero and W_j is a positive integer (for a hydrolysed specie), zero, or negative integer (for a protonated specie). The practical overall formation constant β_j is given by the expression,

$$\beta_j = \frac{\left[A_{A_j}\, B_{B_j}\, S_{S_j}\, T_{T_j}\, (OH)_{W_j}\right]}{[A]^{A_j}\,[B]^{B_j}\,[S]^{T_j}\,[T]^{T_j}\,\{OH\}^{W_j}} \qquad \text{----(20)}$$

where square brackets denote concentrations and braces denote activities.

A model input data required for the calculation of formation constant in a binary system requires the following details, given in specified format form :

i) the number of ligands (one), number of metals (one) and the number of complex species, including protonated and hydrolysed species, (Five : LH, L, Cu^{2+}, $[CuL]^+$ and $[CuL_2]$)

ii) composition of each species has to be described alongwith its approximate formation constant as the logarithm to base 10

iii) the number of dissociable protons over the ligands

iv) initial concentrations of the metal, ligand, mineral acid ($HClO_4$), titrant base in mole/litre and total initial volume in ml

v) for each titration reading, volume of the titrant base, pH and of INDEX (a quantity which is zero for all but the last reading of the experiment when INDEX = 1)

vi) logarithm to base 10 of the ionic product of water and the activity coefficient of hydrogen ion under the conditions of experiment

vii) the number of constants to be refined and the number of calculation cycles to be repeated to get a convergency in the formation constant values.

viii) the particular constant to be varied, given with serial number as in ii), and the logarithmic increment or decrement to be applied to the formation constant in the numerical differentiation. The refined values of proton-ligand stability constants are fixed i.e. accepted as constants with no variations required further and only the log K_1 and log K_2 are subjected to refinement.

The subroutine COGSNR (Concentration Of Generalized Species by the Newton-Raphson method) is used repeatedly to determine the concentrations of all the selected species in the solution.

The important feature of the SCOGS computer programme is that, after the calculation is over, a systematic output is printed out. This contains the refined values of formation constants along with their standard deviations followed by a table containing for each experimental points the pH, the experimental titre, total concentration of each metal and ligand, the concentration of free metal and free ligand and finally the concentration of each complex species.

The values of K_1^H, log K_1 and log K_2 obtained by the graphical method were fed to the computer for refinement. The refined values of K_1^H, log K_1 and log K_2 obtained by the computer have been presented in Table IIA 12.

Table IIA 1

$N = 0.2M$ $V^o = 50$ ml $T_L^o = 0.02M$

$E^o = 0.02M$ $I = 0.2M$ $T_M^o = 0.002M$ $t = 30\ ^oC$

Acid		L^1		Cu(II) + L^1	
Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B
0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.20	3.00	2.20	3.00	2.20
4.00	2.50	4.00	2.50	4.00	2.50
4.50	2.80	4.50	2.80	4.50	2.80
4.60	2.95	4.60	2.95	4.60	2.95
4.70	3.20	4.70	3.20	4.70	3.20
4.80	3.50	4.80	3.50	4.80	3.50
4.85	3.70	4.90	3.95	4.90	3.65
4.90	3.95	4.95	4.40	4.95	3.75
4.94	4.25	4.98	4.75	5.00	3.85
4.96	4.50	5.00	7.00	5.10	4.05
4.98	4.75	5.02	7.25	5.20	4.25
5.00	7.25	5.05	7.50	5.30	4.55
5.01	8.50	5.10	7.90	5.40	4.85
5.04	9.25	5.20	8.40	5.50	5.15
5.07	9.75	5.30	8.80	5.60	5.40
5.10	10.30	5.40	9.05	5.70	5.65
		5.60	9.35	5.80	5.90
		5.80	9.60	5.90	6.20
		6.00	9.90	6.00	6.55

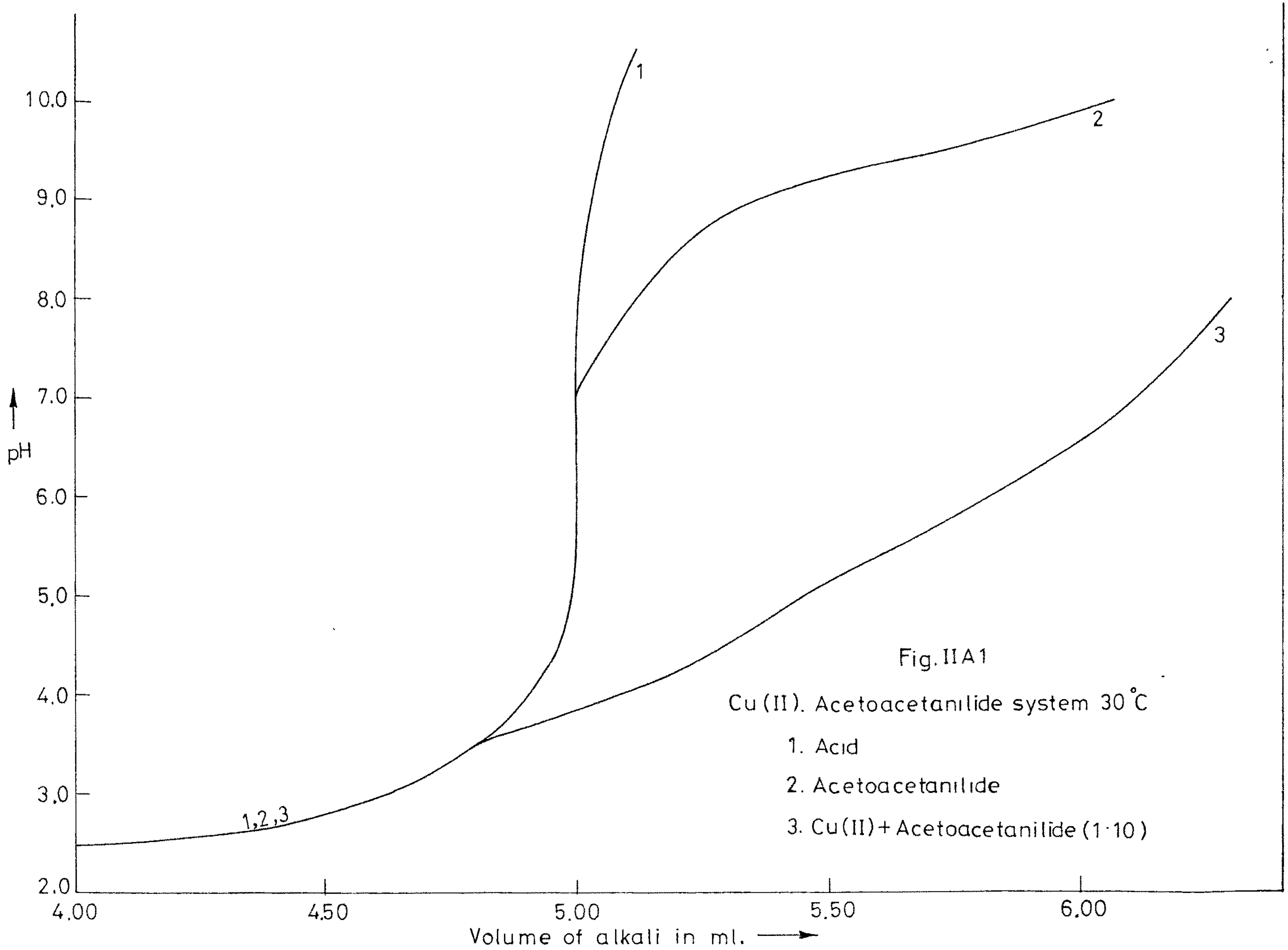


Fig. IIA1

Cu (II). Acetoacetanilide system 30 °C

Table IIA 2

$N = 0.2M$ $V^{o} = 50$ ml $T_{L}^{o} = 0.02M$

$E^{o} = 0.02M$ $I = 0.2M$ $T_{M}^{o} = 0.002M$ $t = 30\ ^{o}C$

Acid		L^2		$Cu(II) + L^2$	
Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B
0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.20	3.00	2.20	3.00	2.20
4.00	2.50	4.00	2.50	4.00	2.50
4.50	2.80	4.50	2.80	4.50	2.80
4.60	2.95	4.60	2.95	4.60	2.95
4.70	3.20	4.70	3.20	4.70	3.20
4.80	3.50	4.80	3.50	4.80	3.50
4.85	3.70	4.90	3.95	4.90	3.80
4.90	3.95	4.95	4.40	5.00	4.00
4.94	4.25	5.00	7.50	5.10	4.20
4.96	4.50	5.05	8.20	5.20	4.45
4.98	4.75	5.10	8.40	5.30	4.70
5.00	7.25	5.20	8.70	5.40	5.00
5.01	8.50	5.30	8.90	5.50	5.25
5.04	9.25	5.40	9.10	5.60	5.55
5.07	9.75	5.50	9.20	5.70	5.85
5.10	10.30	5.60	9.30	5.80	6.15
		5.80	9.50	5.90	6.40
		6.00	9.65	6.00	6.75
		6.15	9.75	6.10	7.05
				6.20	7.40
				6.30	7.80
				6.40	8.20

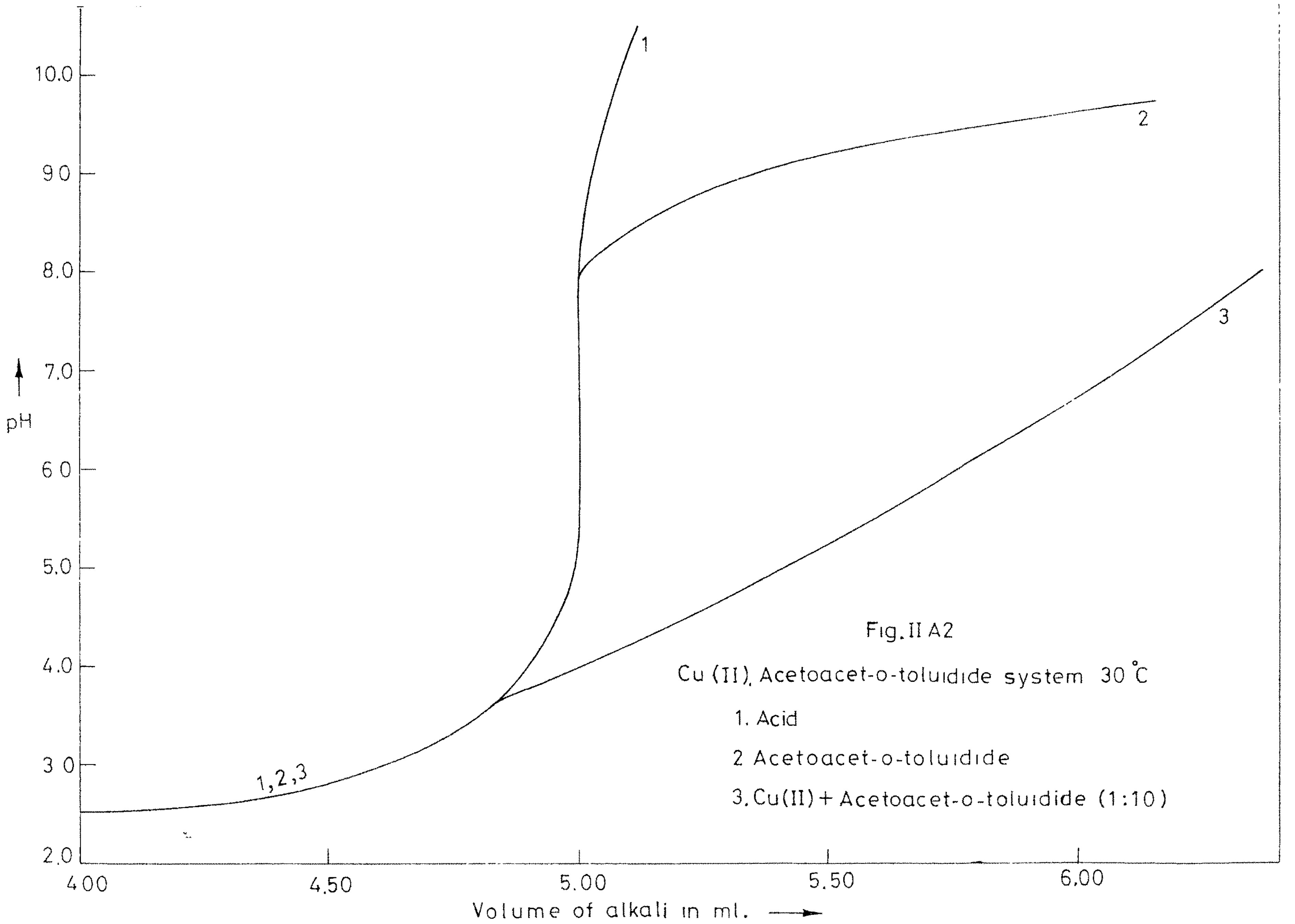


Fig. II A2

Cu (II), Acetoacet-o-toluidide system 30 °C

1. Acid

2 Acetoacet-o-toluidide

3. Cu(II) + Acetoacet-o-toluidide (1:10)

Table IIA 3

$N = 0.2M$ $V^{o} = 50$ ml $T^{o}_{L} = 0.02M$

$E^{o} = 0.02M$ $I = 0.2M$ $T^{o}_{M} = 0.002M$ $t = 30\ ^{o}C$

L^3		Cu(II) + L^3		L^4		Cu(II) + L^4	
Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B
0.00	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20
4.00	2.50	4.00	2.50	4.00	2.50	4.00	2.50
4.50	2.80	4.50	2.80	4.50	2.80	4.50	2.80
4.60	2.95	4.60	2.95	4.60	2.95	4.60	2.95
4.70	3.20	4.70	3.20	4.70	3.20	4.70	3.20
4.80	3.50	4.80	3.50	4.80	3.50	4.80	3.40
4.90	3.95	4.90	3.70	4.90	3.95	4.90	3.55
4.95	4.40	4.95	3.85	4.95	4.40	5.00	3.70
5.00	6.75	5.00	3.95	5.00	6.75	5.10	3.85
5.05	7.35	5.10	4.20	5.05	7.50	5.20	4.00
5.10	7.70	5.20	4.45	5.10	7.80	5.30	4.15
5.20	8.35	5.30	4.75	5.20	8.25	5.40	4.35
5.30	8.75	5.40	5.00	5.30	8.55	5.50	4.55
5.40	9.10	5.50	5.30	5.40	8.75	5.60	4.80
5.50	9.30	5.60	5.70	5.50	8.90	5.70	5.10
5.60	9.45	5.70	6.10	5.60	9.00	5.80	5.40
5.70	9.60	5.80	6.50	5.80	9.20	5.90	5.75
5.80	9.70	5.90	6.90	6.00	9.30	6.00	6.10
6.00	9.85	6.00	7.35	6.20	9.40	6.10	6.45
		6.10	7.90			6.20	6.80
		6.20	8.50			6.30	7.25

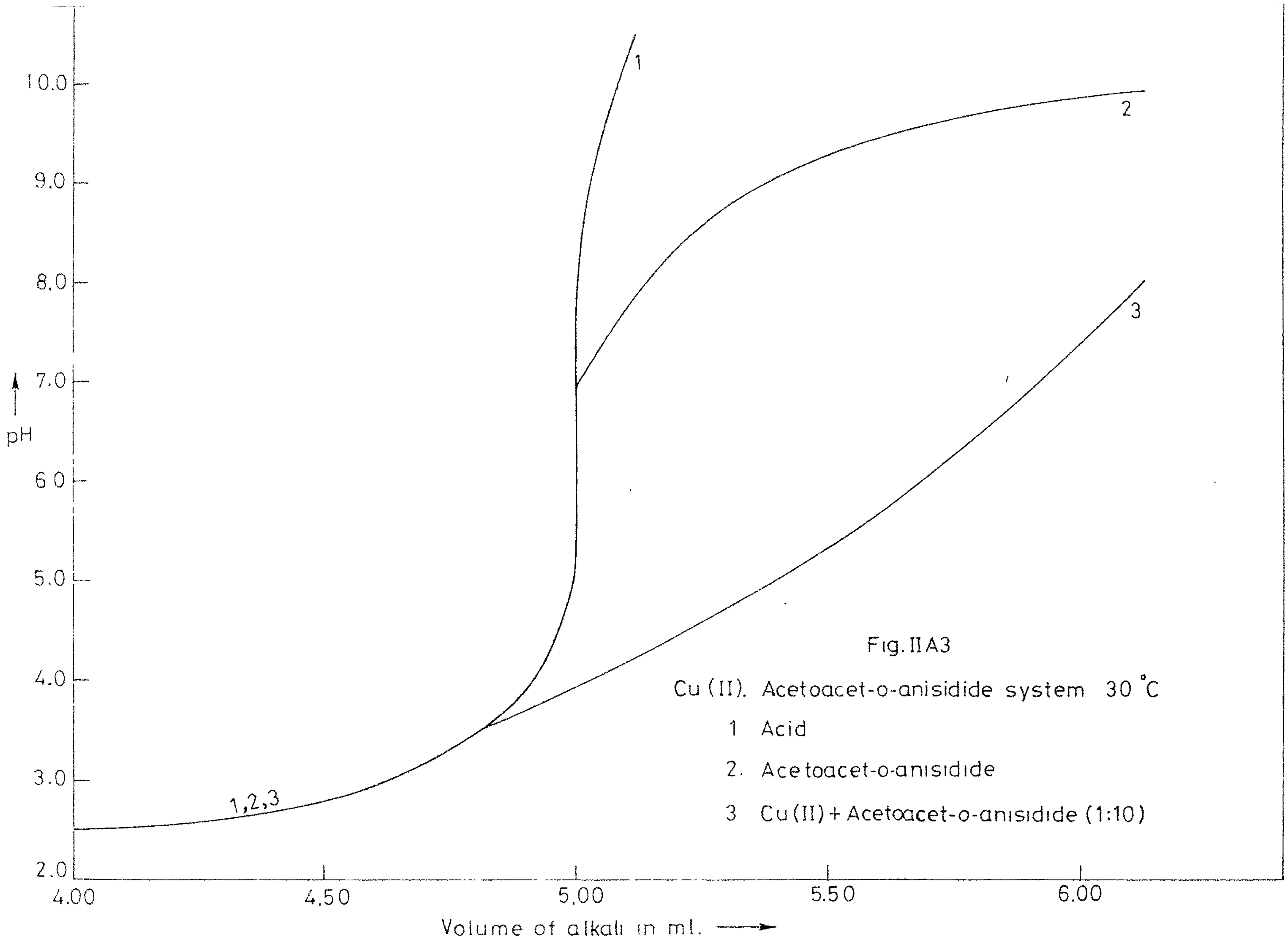


Fig. II A3

Cu (II). Acetoacet-o-anisidide system 30 °C

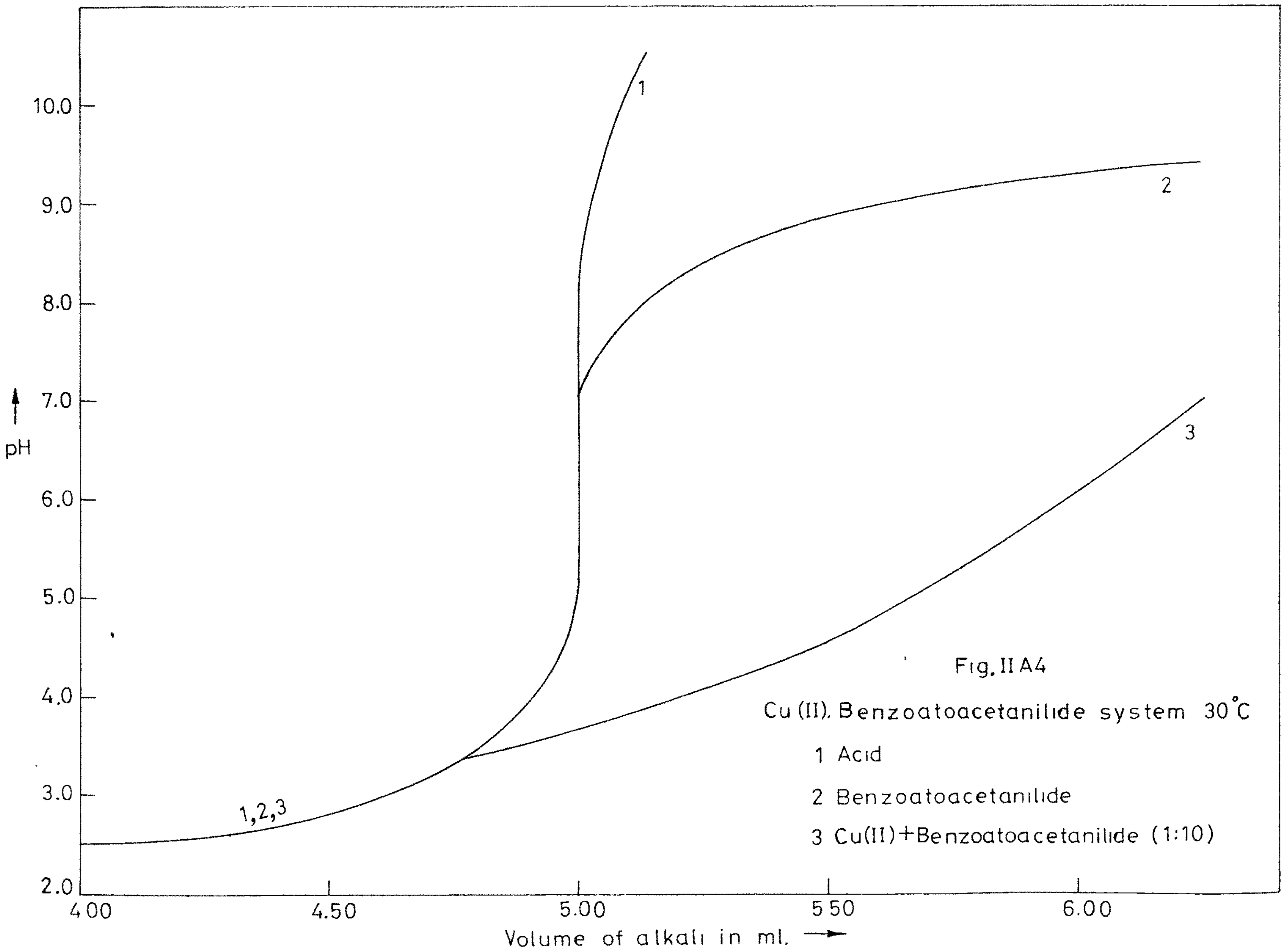


Fig. II A4

Cu (II). Benzoatoacetanilide system 30°C

1 Acid

2 Benzoatoacetanilide

3 Cu(II)+Benzoatoacetanilide (1:10)

Table IIA 4 : $\bar{n}_H$, $\bar{n}$, pL data for Cu(II) + Acetoacetanilide system.

B	$\bar{n}_H$	V"	V"'	V"' - V"	$\bar{n}$	pL
4.85	1.000	4.990	5.400	0.410	0.820	8.527
4.90	1.000	4.990	5.420	0.430	0.860	8.484
4.95	1.000	4.995	5.430	0.435	0.870	8.430
5.00	1.000	5.000	5.450	0.450	0.900	8.381
5.50	1.000	5.000	5.640	0.640	1.280	7.899
5.60	1.000	5.000	5.680	0.680	1.360	7.803
5.70	1.000	5.000	5.720	0.720	1.440	7.707
5.80	1.000	5.000	5.755	0.755	1.510	7.611
5.90	1.000	5.000	5.795	0.795	1.590	7.506

Table IIA 5 : $\bar{n}_H$, $\bar{n}$, pL data for Cu(II) + Acetoacet-o-toluidide system.

B	$\bar{n}_H$	V"	V"'	V"' - V"	$\bar{n}$	pL
5.60	1.000	5.000	5.620	0.620	1.240	7.498
5.65	1.000	5.000	5.640	0.640	1.280	7.450
5.70	1.000	5.000	5.650	0.650	1.300	7.401
5.75	1.000	5.000	5.670	0.670	1.340	7.353
5.80	1.000	5.000	5.685	0.685	1.370	7.304
5.85	1.000	5.000	5.705	0.705	1.410	7.256
5.90	1.000	5.000	5.715	0.715	1.430	7.207
5.95	1.000	5.000	5.740	0.740	1.480	7.160
6.00	1.000	5.000	5.750	0.750	1.500	7.117

Table IIA 6 : $\bar{n}_H$, $\bar{n}$, pL data for Cu(II) + Acetoacet-o-anisidide system.

B	$\bar{n}_H$	V"	V"'	V"' - V"	$\bar{n}$	pL
5.60	1.000	5.000	5.580	0.580	1.160	7.594
5.65	1.000	5.000	5.590	0.590	1.180	7.554
5.70	1.000	5.000	5.610	0.610	1.220	7.494
5.75	1.000	5.000	5.620	0.620	1.240	7.451
5.80	1.000	5.000	5.635	0.635	1.270	7.399
5.85	1.000	5.000	5.645	0.645	1.290	7.352
5.90	1.000	5.000	5.655	0.655	1.310	7.301
5.95	1.000	5.000	5.665	0.665	1.330	7.254
6.00	1.000	5.000	5.680	0.680	1.360	7.204

Table IIA 7 : $\bar{n}_H$, $\bar{n}$, pL data for Cu(II) + Benzoatoacetanilide system.

B	$\bar{n}_H$	V"	V"'	V"' - V"	$\bar{n}$	pL
4.20	1.000	4.940	5.315	0.375	0.750	7.974
4.25	1.000	4.940	5.340	0.400	0.800	7.926
4.30	1.000	4.950	5.380	0.430	0.860	7.877
4.35	1.000	4.950	5.410	0.460	0.920	7.832
4.80	1.000	4.980	5.600	0.620	1.240	7.408
4.90	1.000	4.990	5.640	0.650	1.300	7.301
5.00	1.000	5.000	5.670	0.670	1.340	7.203
5.10	1.000	5.000	5.700	0.700	1.400	7.106
5.20	1.000	5.000	5.730	0.730	1.460	7.009

Table IIA 8 : $\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Cu(II) + Acetoacetanilide system.

$\bar{n}$	pL	$y \cdot 10^8$	$x \cdot 10^{-8}$	log β_2	log K_1	log K_2
0.82	8.53	-15.4373	-1.9109	16.63	8.94	7.69
0.86	8.48	-18.5529	-2.6961	16.62	8.96	7.66
0.87	8.43	-18.0143	-3.2291	16.52	8.83	7.69
0.90	8.38	-21.5879	-4.5859	16.49	8.75	7.74
1.28	7.90	3.6310	3.2374	16.53	8.88	7.65
1.36	7.80	2.3835	2.8178	16.54	8.87	7.67
1.44	7.71	1.6783	2.4818	16.56	8.84	7.72
1.51	7.61	1.2060	2.3587	16.56	8.85	7.71
1.59	7.51	0.8721	2.1473	16.58	8.82	7.76

Average values of : log β_2 = 16.56
log K_1 = 8.86
log K_2 = 7.70

Table IIA 9 : $\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Cu(II) + Acetoacet-o-toluidide system.

$\bar{n}$	pL	$y \cdot 10^7$	$x \cdot 10^{-7}$	log β_2	log K_1	log K_2
1.24	7.50	16.3399	1.0013	15.56	8.24	7.32
1.28	7.45	12.8845	0.9123	15.56	8.26	7.30
1.30	7.40	10.8850	0.9289	15.53	8.30	7.23
1.34	7.35	8.8229	0.8671	15.53	8.30	7.23
1.37	7.30	7.3877	0.8533	15.51	8.32	7.19
1.41	7.26	6.2585	0.7907	15.53	8.30	7.23
1.43	7.21	5.3934	0.8174	15.50	8.34	7.16
1.48	7.16	4.4569	0.7495	15.52	8.31	7.21
1.50	7.12	3.9547	0.7586	15.51	8.33	7.18

Average values of : log β_2 = 15.53
log K_1 = 8.30
log K_2 = 7.23

Table IIA 10 : $\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Cu(II) + Acetoacet-o-anisidide system.

$\bar{n}$	pL	y . 10^7	x . 10^{-7}	log β_2	log K_1	log K_2
1.16	7.59	28.2101	1.3493	15.86	8.84	7.02
1.18	7.55	23.2630	1.2838	15.86	8.84	7.02
1.22	7.49	17.1370	1.1473	15.88	8.82	7.06
1.24	7.45	14.5620	1.1235	15.88	8.82	7.06
1.27	7.40	11.8150	1.0763	15.88	8.82	7.06
1.29	7.35	9.9581	1.0936	15.86	8.84	7.02
1.31	7.30	8.4310	1.1156	15.85	8.86	6.99
1.33	7.25	7.1675	1.1416	15.83	8.88	6.95
1.36	7.20	5.9870	1.1218	15.83	8.88	6.95

Average values of : log β_2 = 15.86
log K_1 = 8.84
log K_2 = 7.01

Table IIA 11 : $\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Cu(II) + Benzoatoacetanilide system.

$\bar{n}$	pL	y . 10^7	x . 10^{-7}	log β_2	log K_1	log K_2
0.75	7.97	-27.9851	-0.5360	15.28	8.16	7.12
0.80	7.93	-34.0425	-0.7050	15.25	8.22	7.03
0.86	7.88	-46.6074	-1.0732	15.37	8.30	7.07
0.92	7.83	-77.7552	-1.9967	15.45	8.45	7.00
1.24	7.41	13.2819	1.2318	15.45	8.29	7.16
1.30	7.30	8.6459	1.1695	15.41	8.31	7.10
1.34	7.20	6.2459	1.2249	15.36	8.39	6.97
1.40	7.11	4.5091	1.1643	15.35	8.39	6.96
1.46	7.01	3.2480	1.1471	15.34	8.41	6.93

Average values of : log β_2 = 15.36
log K_1 = 8.32
log K_2 = 7.04

Table IIA 12 : Stability constants of Copper(II) with β-ketoanilides in dioxan-water (1 : 1 v/v) medium and 0.2M $NaClO_4$ at 30°C.

L	Graphical method			Computer method	
	pK_1^H	log β_1	log β_2	log β_1 ($\sigma\beta$)	log β_2 ($\sigma\beta$)
L^1	11.6	8.86	16.56	8.86 (0.01)	16.56 (0.01)
L^2	11.3	8.30	15.53	8.57 (0.09)	15.74 (0.08)
L^3	11.4	8.84	15.86	9.10 (0.05)	16.09 (0.04)
L^4	10.4	8.32	15.36	8.15 (0.03)	15.24 (0.02)

RESULTS AND DISCUSSION

β-ketoanilides exhibit keto-enol tautomerism. They are characterized by one K^H value, corresponding to the enol form. The proton-ligand stability constants of β-ketoanilides are greater than those of β-diketones.[48] This is due to the additional resonance in the anilide group which supresses the enol form significantly. This in turn lowers the dissociation of proton and results in higher value of K^H.

The order of basicity in case of β-ketoanilides is acetoacetanilide $>$ acetoacet-o-anisidide $\approx$ acetoacet-o-toluidide $>$ benzoatoacetanilide. The methyl and methoxy substituents on the phenyl ring have no significant effect on the K^H values. However, in benzoatoacetanilide the value of K^H is lower due to negative inductive effect of the phenyl ring which results in the ease of proton dissociation.

Although, β-ketoanilides have higher K^H values, they form less stable complexes than β-diketones. The coordination sites in both the cases are two oxygens.[199] The reason for lower stability should, therefore, be sought elsewhere. Stability of β-diketone complexes is due to π delocalization in the pseudoaromatic chelate ring. In β-ketoanilides, π delocalization may be reduced in the metal-ligand chelate ring due to the existence of an adjoining anilide resonance. Further, the lone pair of electrons present on the nitrogen can increase π electron density in the chelate ring which will result in a repulsion between metal $d\pi$ electron and the ligand electrons. Thus, Cu — β-ketoanilide π interaction is less than in Cu — β-diketone complexes. This in turn destabilizes the binary complex and hence, lowers the values of formation constants, log K_1 and log K_2, compared to Cu — β-diketones.

The values of the formation constants follow the order : acetoacet-o-anisidide > acetoacetanilide > acetoacet-o-toluidide > benzoatoacetanilide. The order is not in accordance with the increase in basicities of the ligands. This may be because of the substitution over the phenyl ring of the anilide group which may result in an increase or decrease of the delocalization of the lone pair of electrons of the N atom over the phenyl ring. This in turn affects the Cu — L bond strength and hence the values of the formation constants are not in the order of the increasing basicity of the ligand.

Contrary to expectation, the substitution of an electron releasing group like $-CH_3$ lowers down the value of formation constants in [Cu.acetoacet-o-toluidide] complex. This is because this substituent, with positive inductive effect, increases the electron density over the ligand and this leads to greater repulsion between metal electrons and the ligand electrons. Hence, the M —L bond strength is lowered down. However, methoxy substitution over the phenyl ring increase the formation constant value of the binary complex compared to [Cu.acetoacetanilide] complex. It appears that methoxy group tends to withdraw the electron from the phenyl ring rather than sharing the oxygen lone pair of electrons with the phenyl ring. The net effect is a decrease in electron density over the ligand. Hence, the repulsion between metal and ligand electron is less and this increases the Cu —L bond strength in [Cu.acetoacet-o-anisidide]complex. The formation constant value of [Cu.benzoatoacetanilide] complex also does not show as much lowering as is expected from the lower K_1^H value. This can be attributed to the electron withdrawing tendency of the additional phenyl ring, which lowers the repulsion between metal and ligand electrons. This results in higher values of the formation constants of [Cu.benzoatoacetanilide] complex.

This observation, that the repulsion between metal $d\pi$ electron and ligand π electron affects the formation constants of the complexes, is new. The significance of this factor has been further discussed in the later chapters.

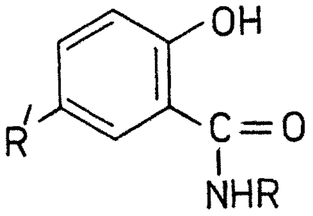
B. Binary Systems of Copper-Salicylamide derivatives

In continuation with the study of β-ketoanilide complexes, analogous substituted phenolic ligands have been selected for further study. The ligands selected are salicylamide, salicylanilide, 5-bromosalicylamide and 5-bromosalicylanilide.

Chakraburtty and coworkers[76] have reported the formation of a complex of salicylamide with uranyl ion which was used for the colorimetric determination. Agren[77] has determined the complexity constants between Fe(III) and salicylamide. Colorimetric and pH metric studies on [Fe(III). salicylamide] complex have been carried out by Ramaiah and coworkers.[78] The stabilities of Mg(II), Be(II) and Al(III) complexes of salicylamide and related ligands have also been studied by Das and Rao.[79] Stability constants and some thermodynamic functions of the complexes of salicylamide with Hg(II), Ce(III) and La(III) have also been reported.[80] The effects of ionic strength and dielectric constant of the medium on the pK and stability constant of the Y(III) complexes with salicylamide and salicylanilide in water-dioxan medium have also been studied.[81]

The main interest in the present study is to see the effect of the presence of aromatic ring and the substitution over the aromatic ring on the mixed-ligand complex formation constant values. However, for comparison the values of binary-complex formation constants are required under identical conditions.

This chapter describes the determination of proton-ligand formation constants, and the constants for the formation of [CuL] and [CuL_2] complexes. Irving-Rossotti titration technique has been used.[72] All these stability constants have been refined by SCOGS[66] computer programme. The ligands (LH) selected are :



R = H R' = H Salicylamide (L^5H)
R = C_6H_5 R' = H Salicylanilide (L^6H)
R = H R' = Br 5-bromosalicylamide (L^7H)
R = C_6H_5 R' = Br 5-bromosalicylanilide (L^8H)

EXPERIMENTAL

Preparation of ligands :

Salicylamide (Riedel) and salicylanilide (BDH) A.R. grade were used. For the preparation of their corresponding bromo derivatives, 5-bromosalicylamide and 5-bromosalicylanilide, a mild brominating agent, N-bromosuccinimide was used.

To a solution of salicylamide/salicylanilide in dimethylformamide (20 ml) was added a solution of N-bromosuccinimide in dimethylformamide (15 ml) in equimolar ratio. The mixture was stirred for an hour at room temperature and the clear solution was poured into ice cold water (300 ml). The resulting solid was filtered, washed with water several times and finally with alcohol. The compounds were then recrystallised from petroleum ether (40-60).

The proton-ligand and binary metal-ligand complex formation constants were determined at 30°C in dioxan-water (1 : 1 v/v) solutions having 0.2M ionic strength.

The details of the various solution sets prepared for titrations, the experimental set up, measurements, of pH, calculations of $\bar{n}_H$, pK_1^H, $\bar{n}$, pL, log K_1 and log K_2 and refinement of all the formation constants by SCOGS computer programme are same as described in Chapter IIA.

The titration data are given in Tables IIB 1 to IIB 3 and the Irving-Rossotti titration curves in Figs IIB 1 to IIB 4. The values of $\bar{n}$ and pL at the selected pH values are recorded in Tables IIB 4 to IIB 7. The formation constants, log K_1 and log K_2, of the binary complexes by least square calculation are presented in Tables IIB 8 to IIB 11. The average values thus obtained are presented in Table IIB 12. Finally, all the computer refined formation constants also have been given in Table IIB 12.

Table IIB 1

$N = 0.2M$ $V^o = 50$ ml $T_L^o = 0.02M$

$E^o = 0.02M$ $I = 0.2M$ $T_M^o = 0.002M$ $t = 30\ ^oC$

Acid		L^5		$Cu(II) + L^5$	
Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B
0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.20	3.00	2.20	3.00	2.20
4.00	2.50	4.00	2.50	4.00	2.50
4.50	2.80	4.50	2.80	4.50	2.80
4.60	2.95	4.60	2.95	4.60	2.95
4.70	3.20	4.70	3.20	4.70	3.20
4.80	3.50	4.80	3.50	4.80	3.50
4.85	3.70	4.90	3.95	4.90	3.80
4.90	3.95	4.95	4.40	4.95	3.95
4.94	4.25	5.00	7.00	5.00	4.10
4.96	4.50	5.05	7.30	5.10	4.40
4.98	4.75	5.10	7.60	5.20	4.80
5.00	7.25	5.20	7.85	5.30	5.25
5.01	8.50	5.30	8.00	5.40	5.70
5.04	9.25	5.40	8.15	5.50	6.10
5.07	9.75	5.50	8.25	5.60	6.45
5.10	10.30	5.60	8.35	5.70	6.75
		5.80	8.50	5.80	7.10
		6.00	8.65	5.90	7.35
		6.20	8.75	6.00	7.60
		6.40	8.85	6.10	7.80

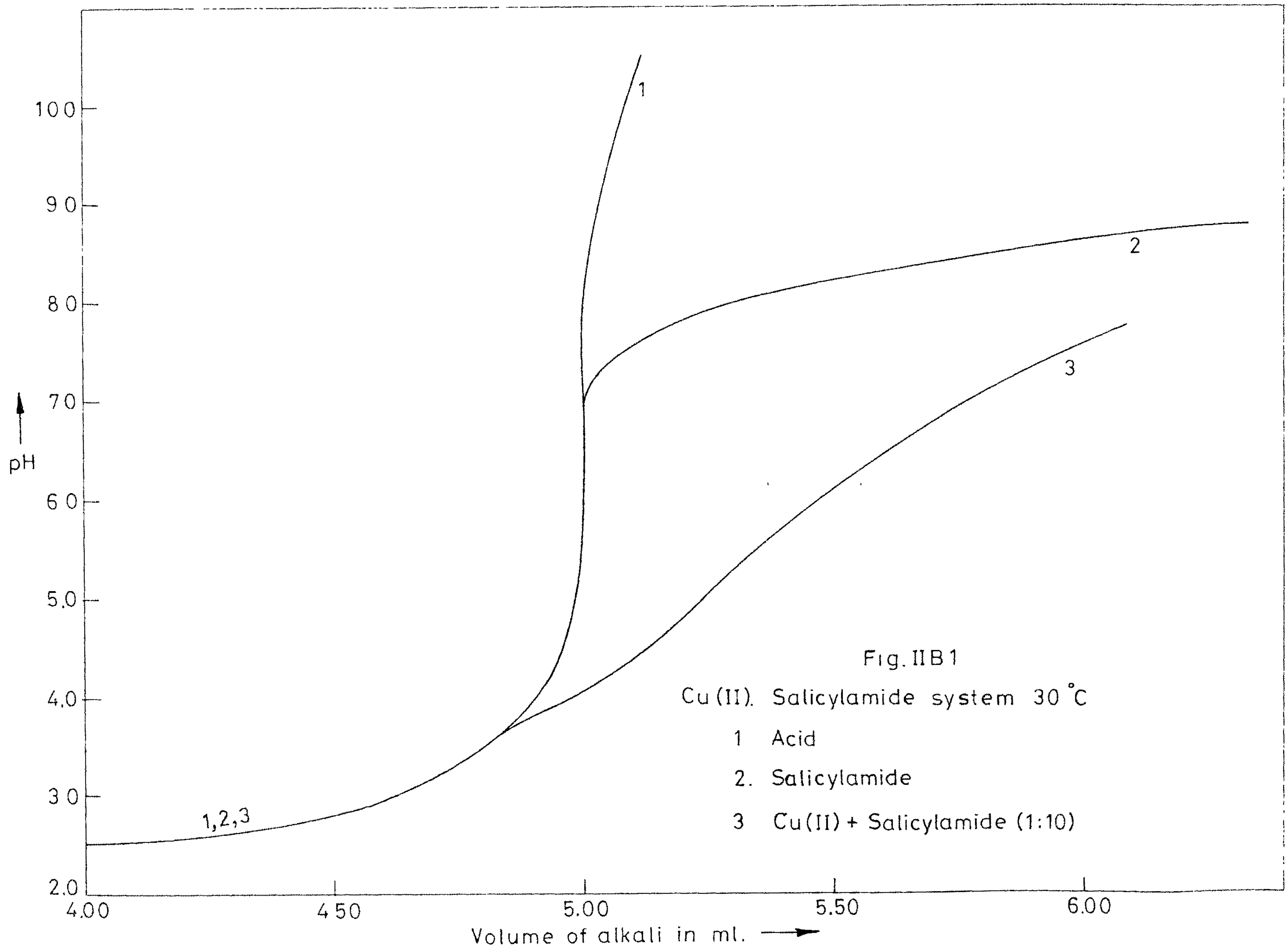


Fig. IIB1

Cu(II). Salicylamide system 30 °C

Table IIB 2

N = 0.2M V^o = 50 ml T^o_L = 0.02M

E^o = 0.02M I = 0.2M T^o_M = 0.002M t = 30 °C

L^6		$Cu(II) + L^6$		L^7		$Cu(II) + L^7$	
Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B
0.00	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20
4.00	2.50	4.00	2.50	4.00	2.50	4.00	2.50
4.50	2.80	4.50	2.80	4.50	2.80	4.50	2.80
4.60	2.95	4.60	2.95	4.60	2.95	4.60	2.95
4.70	3.20	4.70	3.20	4.70	3.20	4.70	3.20
4.80	3.50	4.80	3.50	4.80	3.50	4.80	3.30
4.90	3.95	4.90	3.95	4.90	3.95	4.85	3.40
5.00	6.50	4.95	4.10	5.00	5.60	4.90	3.45
5.05	6.70	5.00	4.25	5.05	5.85	4.95	3.60
5.10	6.90	5.05	4.45	5.10	6.00	5.00	3.75
5.20	7.15	5.10	4.65	5.20	6.20	5.10	4.10
5.30	7.35	5.15	4.85	5.30	6.35	5.20	4.45
5.40	7.50	5.20	5.10	5.40	6.50	5.30	4.80
5.50	7.60	5.30	5.40	5.50	6.65	5.40	5.20
5.70	7.75	5.40	5.65	5.60	6.80	5.50	5.50
5.90	7.90	5.50	5.90	5.70	6.90	5.60	5.80
6.10	8.05	5.60	6.10	5.80	7.05	5.70	6.00
6.30	8.15	5.70	6.35	5.90	7.15	5.80	6.20
6.50	8.25	5.80	6.65	6.00	7.25	5.90	6.40
		5.90	7.00	6.20	7.45	6.00	6.45
		6.00	7.50	6.40	7.60	6.10	6.55

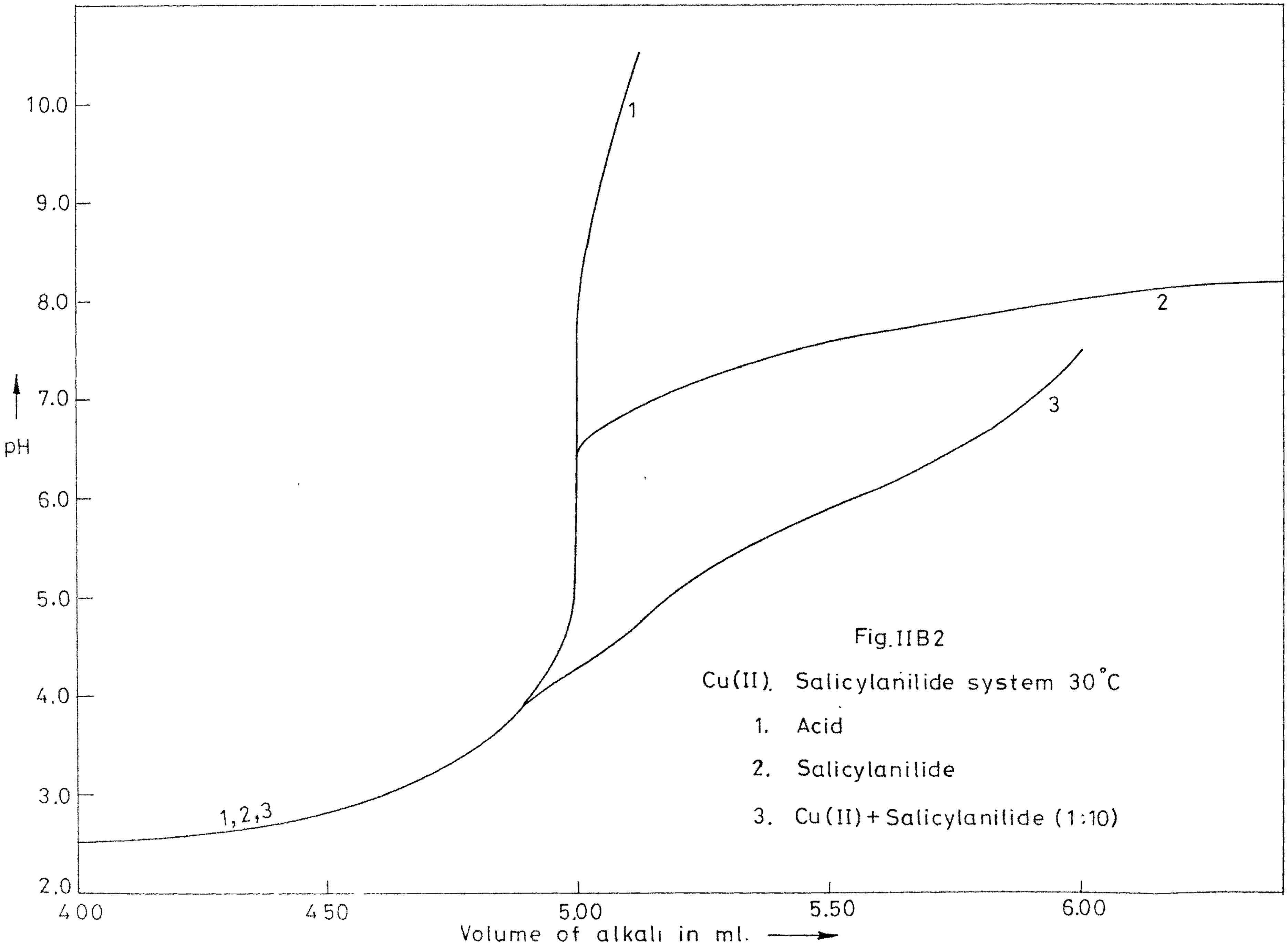


Fig.IIB2

Cu(II). Salicylanilide system 30°C

1. Acid

2. Salicylanilide

3. Cu(II) + Salicylanilide (1:10)

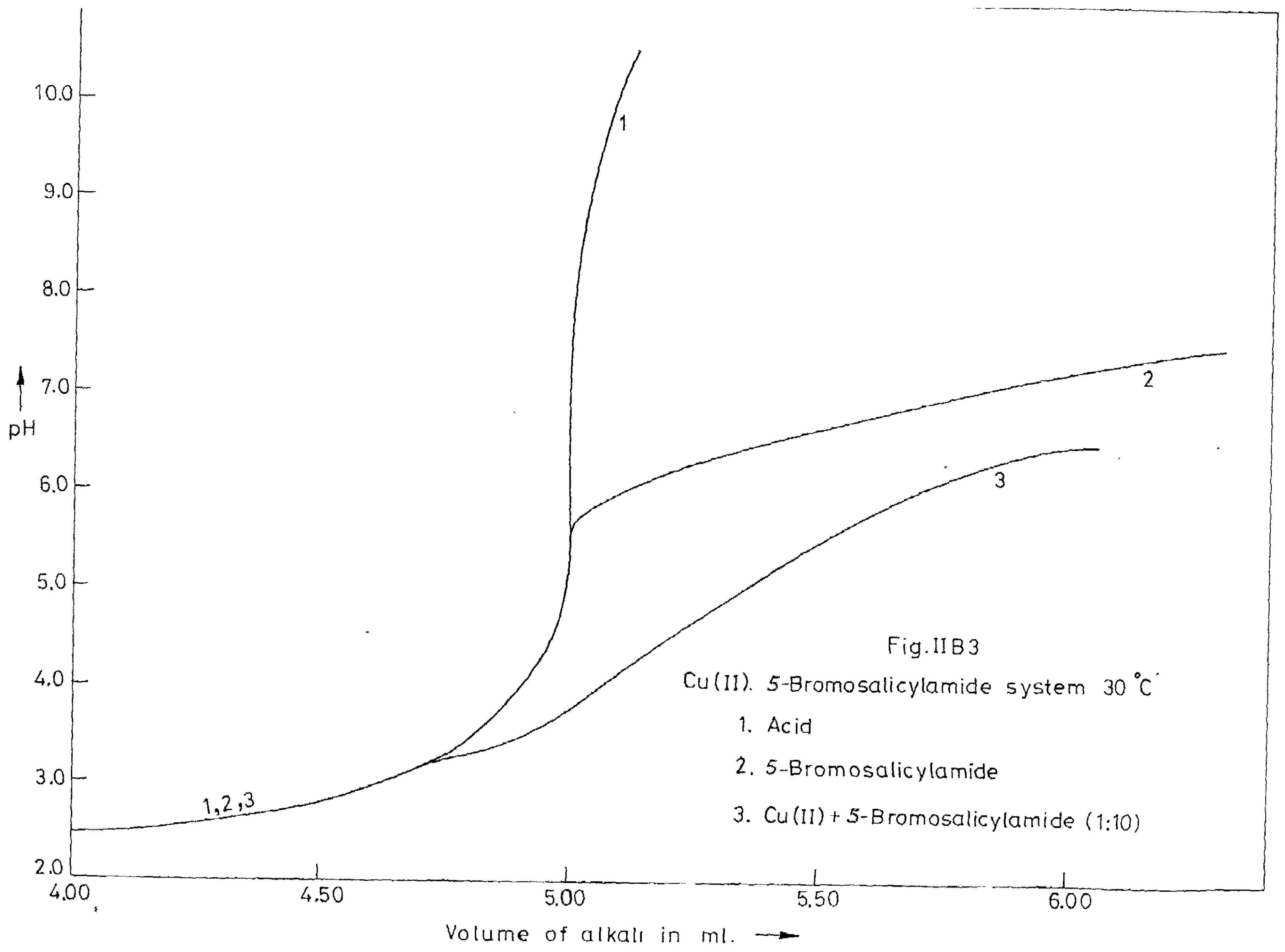


Fig. IIB3

Cu(II). 5-Bromosalicylamide system 30 °C

1. Acid
2. 5-Bromosalicylamide
3. Cu(II) + 5-Bromosalicylamide (1:10)

Table IIB 3

$N = 0.2M$ $V^o = 50$ ml $T^o_L = 0.004M$

$E^o = 0.02M$ $I = 0.2M$ $T^o_M = 0.002M$ $t = 30\ ^oC$

Acid		L^8		Cu(II) + L^8	
Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B	Vol. of alkali (in ml)	B
0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.20	3.00	2.20	3.00	2.20
4.00	2.50	4.00	2.50	4.00	2.50
4.50	2.80	4.50	2.80	4.50	2.80
4.60	2.95	4.60	2.95	4.60	2.95
4.70	3.20	4.70	3.20	4.70	3.20
4.80	3.50	4.80	3.50	4.80	3.50
4.85	3.70	4.90	3.95	4.90	3.95
4.90	3.95	5.00	5.90	4.95	4.85
4.94	4.25	5.05	6.20	5.00	4.50
4.96	4.50	5.10	6.35	5.05	4.75
4.98	4.75	5.15	6.55	5.10	4.95
5.00	7.25	5.20	6.70	5.15	5.15
5.01	8.50	5.30	7.00	5.20	5.35
5.04	9.25	5.40	7.30	5.30	5.60
5.07	9.75	5.50	7.55	5.40	5.85
5.10	10.30	5.60	7.80	5.50	6.10
		5.70	8.00	5.60	6.30
		5.80	8.20	5.70	6.50
		5.90	8.50	5.80	6.70
		6.00	8.80	5.90	6.95
		6.10	9.20	6.00	7.20
		6.20	9.90		

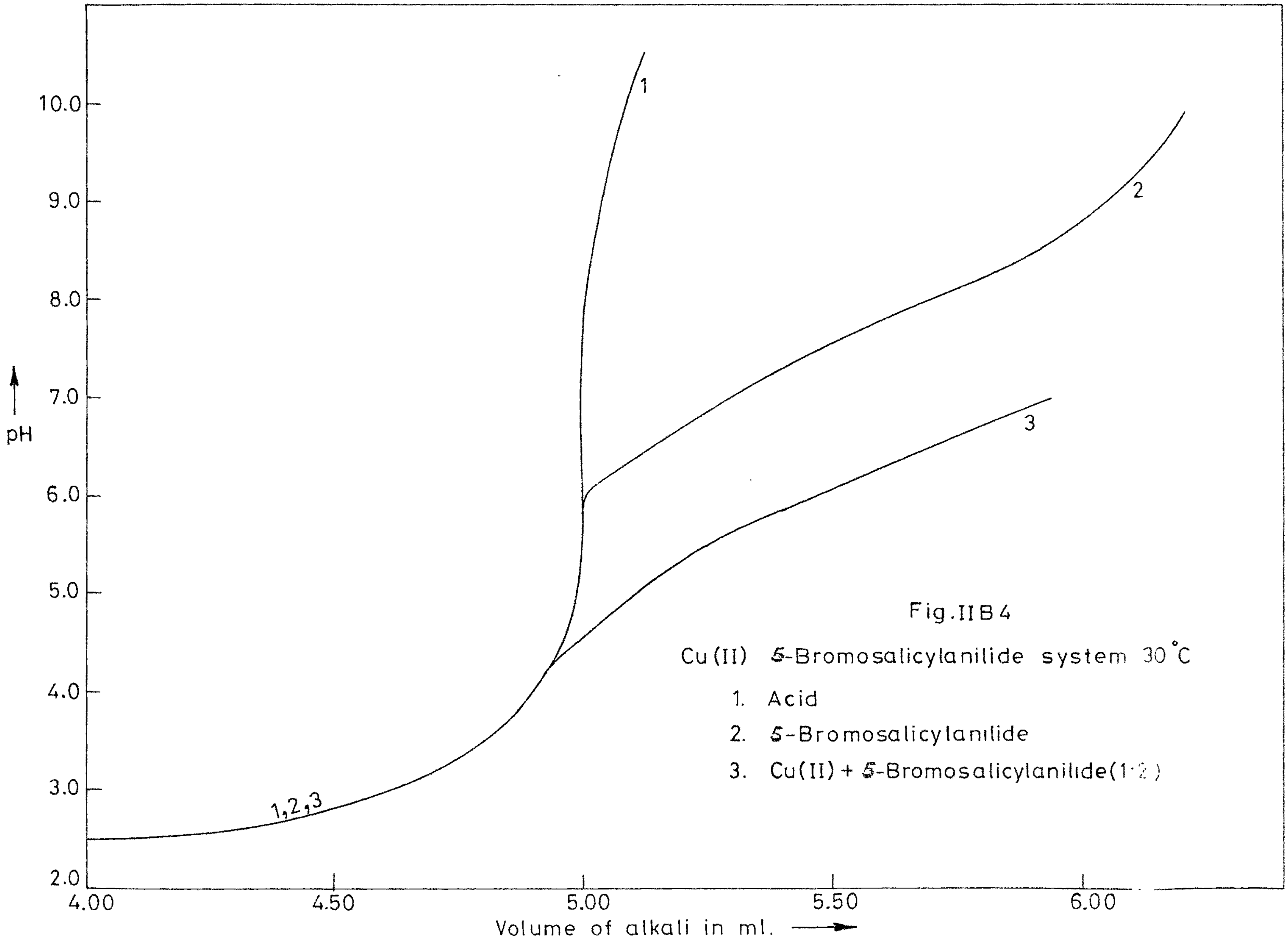


Fig.IIB4

Cu(II) 5-Bromosalicylanilide system 30 °C

1. Acid
2. 5-Bromosalicylanilide
3. Cu(II) + 5-Bromosalicylanilide(1:2)

Table IIB 4 : $\bar{n}_H$, $\bar{n}$, pL data for Cu(II) + Salicylamide system.

B	$\bar{n}_H$	V"	V"'	V"' - V"	$\bar{n}$	pL
5.60	1.000	5.000	5.380	0.380	0.760	5.428
5.70	1.000	5.000	5.400	0.400	0.800	5.330
5.80	1.000	5.000	5.430	0.430	0.860	5.233
6.30	1.000	5.000	5.560	0.560	1.120	4.746
6.40	1.000	5.000	5.590	0.590	1.180	4.650
6.50	1.000	5.000	5.620	0.620	1.240	4.553
6.60	1.000	5.000	5.650	0.650	1.300	4.456
6.70	1.000	5.000	5.680	0.680	1.360	4.359

Table IIB 5 : $\bar{n}_H$, $\bar{n}$, pL data for Cu(II) + Salicylanilide system.

B	$\bar{n}_H$	V"	V"'	V"' - V"	$\bar{n}$	pL
5.40	1.000	5.000	5.300	0.300	0.600	4.920
5.50	1.000	5.000	5.340	0.340	0.680	4.824
5.60	1.000	5.000	5.370	0.370	0.740	4.726
5.70	1.000	5.000	5.410	0.410	0.820	4.631
5.80	1.000	5.000	5.460	0.460	0.920	4.536
6.00	1.000	5.000	5.550	0.550	1.100	4.346
6.10	1.000	5.000	5.600	0.600	1.200	4.251
6.20	1.000	5.000	5.640	0.640	1.280	4.155
6.30	1.000	5.000	5.680	0.680	1.360	4.059
6.40	1.000	5.000	5.730	0.730	1.460	3.965

Table IIB 6 : $\bar{n}_H$, $\bar{n}$, pL data for Cu(II) + 5-Bromosalicylamide system.

B	$\bar{n}_H$	V"	V"'	V"' - V"	$\bar{n}$	pL
5.10	1.000	5.000	5.375	0.375	0.750	4.877
5.20	1.000	5.000	5.400	0.400	0.800	4.780
5.30	1.000	5.000	5.430	0.430	0.860	4.683
5.40	1.000	5.000	5.470	0.470	0.940	4.587
5.70	0.996	5.000	5.570	0.570	1.140	4.297
5.80	0.992	5.000	5.600	0.600	1.210	4.201
5.90	0.985	5.000	5.640	0.640	1.300	4.106

Table IIB 7 : $\bar{n}_H$, $\bar{n}$, pL data for Cu(II) + 5-Bromosalicylanilide system.

B	$\bar{n}_H$	V"	V"'	V"' - V"	$\bar{n}$	pL
5.20	1.000	5.000	5.160	0.160	0.320	4.906
5.30	1.000	5.000	5.190	0.190	0.380	4.822
5.40	1.000	5.000	5.220	0.220	0.440	4.739
5.50	1.000	5.000	5.250	0.250	0.500	4.656
5.60	1.000	5.000	5.300	0.300	0.600	4.587
5.70	1.000	5.000	5.340	0.340	0.680	4.512
5.80	1.000	5.000	5.390	0.390	0.780	4.447
5.90	1.000	5.000	5.420	0.420	0.840	4.369
5.95	1.000	5.000	5.440	0.440	0.880	4.335
6.00	1.000	5.000	5.460	0.460	0.920	4.301

Table IIB 8 : $\bar{n}$, pL, y, x, $\log \beta_2$, $\log K_1$ and $\log K_2$ data for Cu(II) + Salicylamide system.

$\bar{n}$	pL	$y \cdot 10^5$	$x \cdot 10^{-5}$	$\log \beta_2$	$\log K_1$	$\log K_2$
0.76	5.43	- 8.5240	-1.9194	10.07	5.83	4.24
0.80	5.33	- 8.5525	-2.8062	9.91	5.78	4.13
0.86	5.23	-10.4328	-4.7945	9.94	5.79	4.15
1.12	4.75	5.2493	13.0387	9.95	5.81	4.14
1.18	4.65	2.9279	10.1999	9.96	5.80	4.16
1.24	4.55	1.8335	8.9237	9.96	5.79	4.17
1.30	4.46	1.2499	8.0897	9.97	5.78	4.19
1.36	4.36	0.8655	7.7600	9.96	5.79	4.17

Average values of : $\log \beta_2 = 9.97$

$\log K_1 = 5.80$

$\log K_2 = 4.17$

Table IIB 9 : $\bar{n}$, pL, y, x, $\log \beta_2$, $\log K_1$ and $\log K_2$ data for Cu(II) + Salicylanilide system.

$\bar{n}$	pL	$y \cdot 10^4$	$x \cdot 10^{-4}$	$\log \beta_2$	$\log K_1$	$\log K_2$
0.60	4.92	-12.4792	-0.4207	9.02	4.96	4.06
0.68	4.82	-14.0357	-0.6245	8.98	4.95	4.03
0.74	4.73	-15.2855	-0.9024	8.91	4.90	4.01
0.82	4.63	-19.4350	-1.5366	8.87	4.84	4.03
0.92	4.54	-39.8752	-3.8934	8.91	4.91	4.00
1.10	4.35	24.6250	4.0203	8.91	4.91	4.00
1.20	4.25	10.6705	2.2492	8.92	4.89	4.03
1.28	4.16	6.6080	1.7789	8.92	4.90	4.02
1.36	4.06	4.3373	1.5484	8.90	4.92	3.98
1.46	3.97	2.9607	1.2584	8.94	4.86	4.08

Average values of : $\log \beta_2 = 8.93$

$\log K_1 = 4.90$

$\log K_2 = 4.03$

Table IIB 10 : $\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Cu(II) + 5-Bromosalicylamide system.

$\bar{n}$	pL	$y \cdot 10^4$	$x \cdot 10^{-4}$	log β_2	log K_1	log K_2
0.75	4.88	-22.7618	-0.6590	9.11	5.21	3.90
0.80	4.78	-24.0964	-0.9960	8.99	5.15	3.84
0.86	4.68	-29.4057	-1.7010	8.95	5.09	3.86
0.94	4.59	-60.9598	-4.5403	9.01	5.18	3.83
1.14	4.30	16.2467	3.0788	9.00	5.17	3.83
1.21	4.20	9.1314	2.3738	8.99	5.17	3.82
1.30	4.11	5.5828	1.8111	9.04	5.10	3.94

Average values of : log β_2 = 9.01
log K_1 = 5.15
log K_2 = 3.86

Table IIB 11 : $\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Cu(II) + 5-Bromosalicylanilide system.

$\bar{n}$	pL	$y \cdot 10^4$	$x \cdot 10^{-4}$	log β_2	log K_1	log K_2
0.32	4.91	-3.8259	-0.3039	8.41	4.47	3.94
0.38	4.82	-4.0482	-0.3956	8.40	4.46	3.94
0.44	4.74	-4.3171	-0.5070	8.40	4.45	3.95
0.50	4.66	-4.5704	-0.6564	8.37	4.42	3.95
0.60	4.59	-5.8366	-0.8995	8.49	4.50	3.99
0.68	4.51	-6.8770	-1.2746	8.49	4.49	4.00
0.78	4.45	-9.9928	-1.9675	8.55	4.61	3.94
0.84	4.37	-12.3066	-3.0929	8.48	4.48	4.00
0.88	4.34	-16.0432	-4.2663	8.48	4.51	3.97
0.92	4.30	-22.9449	-6.7662	8.47	4.43	4.04

Average values of : log β_2 = 8.45
log K_1 = 4.48
log K_2 = 3.97

Table IIB 12 : Stability constants of Copper(II) with salicylamide derivatives in dioxan-water (1 : 1 v/v) medium and 0.2M $NaClO_4$ at 30°C.

L	Graphical method			Computer method		
	pK_1^H	log β_1	log β_2	pK_1^H ($\sigma\beta$)	log β_1 ($\sigma\beta$)	log β_2 ($\sigma\beta$)
L^5	9.25	5.80	9.97	9.23 (0.01)	5.79 (0.01)	9.90 (0.01)
L^6	8.55	4.90	8.93	8.56 (0.01)	4.95 (0.01)	8.88 (0.01)
L^7	8.20	5.15	9.01	7.86 (0.03)	4.87 (0.01)	8.17 (0.01)
L^8	7.59	4.48	8.45	7.59 (0.02)	-	-

RESULTS AND DISCUSSION

Salicylamide derivatives have only one K^H value corresponding to the dissociation of phenolic hydrogen. The nitrogen of the amide/anilide does not accept any proton from the free mineral acid to form the protonated species above pH 2. This is clearly seen from the titration curves, where the ligand titration curve (2) remains merged with the free acid titration curve (1) in the pH range 2 to 6. If the nitrogen was basic enough to accept a proton, the amount of titrable proton in the ligand solution set would have been less and hence the ligand curve would have been above the acid curve.

The order of basicities of the ligands is salicylamide $>$ salicylanilide $>$ 5-bromosalicylamide $>$ 5-bromosalicylanilide. The phenyl ring of the anilide group can participate in the resonance and withdraws electrons, thereby decreasing the K_1^H value of salicylanilide, compared to salicylamide. As expected, the K_1^H values of the bromo-derivatives decrease due to the electron withdrawing nature of the substituent bromine atom. This facilitates the proton dissociation, thereby reducing their basicities.

The value of the binary complex formation constants follow the order : salicylamide $>$ salicylanilide $>$ 5-bromosalicylamide $>$ 5-bromosalicylanilide. This order is in agreement with the basicities of the ligands. However, the log K_1 value of [Cu.salicylamide] complex is lower than

$\log K^{Cu}_{Cu.salicylaldehyde}$.[42] This can probably mean that in these complexes the coordination takes place from phenolic oxygen and amide/anilide nitrogen, rather than phenolic oxygen and amide/anilide oxygen. The titration curves are, however, smooth showing that coordination sites remain same over the whole pH range. Further, infrared spectral data of the isolated solid complexes (discussed in Chapter IV) confirm that the coordination is from both the oxygen atoms. The alternate reason for lower stability is that $Cu \rightarrow L$ π interaction in these complexes is less than in $[Cu.salicylaldehyde]^+$ complexes.

It is further observed that the extent of lowering in $\log K_1$ values of the binary complexes of the brominated ligands compared to the parent ligands is not as much as the lowering in the K_1^H values. This may be attributed to the decrease in the repulsion between metal $d\pi$ electrons and the ligand electrons due to the electron withdrawal from the phenyl ring by the substituent bromine atom.