****
****

CHAPTER III

Ternary Systems of Copper(II), 2,2'-dipyridyl, 1,10-phenanthroline, 2-(2'-pyridyl)benzimidazole or 2-(2'-pyridyl)imidazoline and β-ketoanilides or Salicylamide derivatives

****
****

In a system containing a metal and two ligands A and L, if the complexing tendencies of the two ligands do not differ very much, following types of reactions take place leading to the formation of mixed-ligand complex.[82]

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

$$M + A \rightleftharpoons MA \; ; \quad MA + L \rightleftharpoons MAL \qquad \text{---(2) \& (3)}$$

$$M + L \rightleftharpoons ML \; ; \quad ML + A \rightleftharpoons MLA \qquad \text{---(4) \& (5)}$$

$$MA_2 + ML_2 \rightleftharpoons 2MAL \qquad \text{---------(6)}$$

Charges on the ions have been omitted for clarity.

The various species present in solution in such systems, therefore, will be MA, MA_2, ML, ML_2 and MAL, in addition to the protonated or hydroxo species of ligands and complexes. Extensive studies have been carried out on such systems.[17-19,82-89]

However, if the complexing tendencies of the two ligands are significantly different, or if the two ligands are combining with the metal ion in two different pH ranges, the formation of the mixed-ligand complex will take place in two distinctly separated steps as follows :

$$M + A \rightleftharpoons MA \qquad \text{---------(7)}$$

$$MA + L \rightleftharpoons MAL \qquad \text{---------(8)}$$

In such cases where the formation of [MA] complex is complete at a lower pH range and it remains stable upto a

higher pH range where the second ligand (L) combines with the metal ion, the mixed-ligand complex formation constant which characterises the reaction, as represented by equation (8), is,

$$K^{MA}_{MAL} = \frac{[MAL]}{[MA][L]}$$

The major species present in solution will be M , [MA] and [MAL].

Exhaustive studies of formation of such mixed-ligand complexes have been reported, particularly of complexes with tertiary amines as primary ligands.[25-42]

Martell and coworkers[23,24] have suggested a pH-metric method for the determination of mixed-ligand complex formation constants of the systems [CuAL], where A = dipyridyl, o-phenanthroline or tetramethylene diamine and L = ligands coordinating through anionic oxygen atoms (Tiron, Salicylic acid or Chromotropic salt). They have considered that Cu(II) forms 1 : 1 chelate with bidentate amines and the second ligand combines with the preformed $[CuA]^{2+}$.

The above explanation also holds good in the cases where the first ligand is a polydentate amino acid. Martell and coworkers[90,91] and also Thompson and Lorass[92] determined the formation constants of the complexes of the type [M.aminopolycarboxylate.L] considering the reaction to be MA + L $\rightleftharpoons$ MAL.

An extension of Irving-Rossotti titration technique for binary complexes[72] to the systems [M.dipyridyl.L] [26] and [M.aminopolycarboxylate.L] [93] systems has been successfully developed by Chidambaram and Bhattacharya. It is presumed that the preformed [M.dipyridyl] or [M.aminopolycarboxylate] behave as the metal ion and combine with the secondary ligand, mimicing binary systems. Using the above method, formation constants of mixed-ligand complexes, [MAL], where A = 2,2'-dipyridyl or 1,10-phenanthroline and L = ions from aminoacids, polyhydroxy phenols, thioacids, diamines, β-diketones, orthohydroxy aromatic aldehydes or ketones, have been reported from our laboratory.[34-40,42,48,94]

Sigel and coworkers[9,25,95] have determined the formation constants of mixed-ligand complexes by considering the reaction to be taking place in steps and also by considering all possible species in solution using Zajicek's iteration technique.[96]

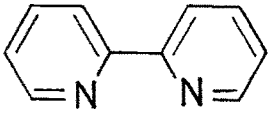
Abbott and coworkers[97-99] used SCOGS computer programme to determine the formation constants of mixed-ligand complexes involving tertiary amines.

In the present chapter, studies of the mixed-ligand complexes of the type $[CuAL]^+$, where A = 2,2'-dipyridyl (A^1), 1,10-phenanthroline (A^2), 2-(2'-pyridyl)benzimidazole (A^3) or 2-(2'-pyridyl)imidazoline (A^4) and L = anion of acetoacetanilide (L^1), acetoacet-o-toluidide (L^2), acetoacet-o-anisidide (L^3), benzoatoacetanilide (L^4), salicylamide (L^5),

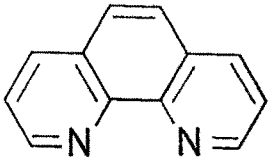
salicylanilide (L^6), 5-bromosalicylamide (L^7) or 5-bromosalicylanilide (L^8), have been described.

The formation constant values have been determined by using the extension of Irving-Rossotti titration technique[26] and have been further refined by computer programme SCOGS,[66] considering the reaction to be strictly of the type $CuA + L \rightleftharpoons CuAL$ and also by considering all possible species to be present in solution. The latter considers simultaneous coordination of both the ligands and the formation of the ternary complex proceeding through the reactions as represented by equations (1) to (6).

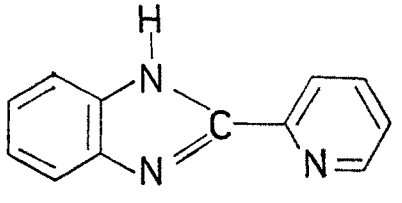
The primary ligands used are similar, coordinating through two N atoms and having delocalized π electrons and their structures are as follows :



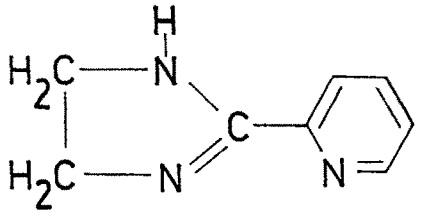
2,2'-dipyridyl (A^1)



1,10-phenanthroline (A^2)



2-(2'-pyridyl)benzimidazole (A^3)



2-(2'-pyridyl)imidazoline (A^4)

EXPERIMENTAL

Materials :

2,2'-dipyridyl and 1,10-phenanthroline (Merck, pure) were of A.R. grade. The secondary ligands (L^1 to L^8) were of the same quality as detailed in the Chapter II. 2-(2'-pyridyl)benzimidazole and 2-(2'-pyridyl)imidazoline were prepared by a known method.[100] Standardization of all the required solutions of metal perchlorate, sodium hydroxide perchloric acid and the instruments used were done in the same way as detailed in Chapter II.

The mixed-ligand formation constants were determined at 30 ^{o}C in dioxan-water (1 : 1 v/v) of ionic strength 0.2M $NaClO_4$. Dioxan was purified by the known procedure[73] and pH corrections were done by the method suggested by Van Uitert and Haas.[75]

Extension of Irving-Rossotti's Titration Technique :

The formation constant K^{CuA}_{CuAL}, constant for the reaction CuA + L $\rightleftharpoons$ CuAL, have been calculated by using a modified form of Irving-Rossotti titration technique (Method I = m_1).[26] To apply the above method following five sets of solutions were prepared in every case for titration against standard alkali :

1. 0.02M $HClO_4$ and 0.180M $NaClO_4$
2. 0.02M $HClO_4$, 0.002M primary ligand and 0.178M $NaClO_4$
3. 0.02M $HClO_4$, 0.002M primary ligand, 0.002M Copper perchlorate and 0.176M $NaClO_4$
4. 0.02M $HClO_4$, 0.002M secondary ligand and 0.178M $NaClO_4$
5. 0.02M $HClO_4$, 0.002M primary ligand, 0.002M secondary ligand, 0.002M Copper perchlorate and 0.174M $NaClO_4$

The solutions for titrations were allowed to stand for some time (20-25 min) and all the titrations were carried out in an inert atmosphere. Pure nitrogen gas, obtained by passing successively through pyrogallol, sulphuric acid and 50% dioxan-water, was bubbled through the solution during titrations. After the addition of each portion of alkali, pH was noted.

The titration data are given in Tables III 1 to III 21 and Figures III 1 to III 32. In every case the concentrations of various reagents taken have been shown

on the top of the tables.

The horizontal distance between curves (4) and (5) was measured and used for the calculation of $\bar{n}$, where $\bar{n}$ is the average number of secondary ligands associated with one molecule of $[CuA]^{2+}$. The values of $\bar{n}$ and pL were calculated in the pH range 4 to 6.5 using the same equations as for binary systems[72] and are recorded in Tables III 22 to III 53. At $\bar{n} = 0.5$ in the formation curve, pL Vs $\bar{n}$, $pL = \log K^{CuA}_{CuAL}$. However, this will be only one point and may involve experimental error. More precise values were obtained by plotting pL at each point against $\log \left[(1 - \bar{n})/ \bar{n}\right]$ and obtaining a straight line (Figures III 33 to III 40). At each point on the straight line,

$$\log K^{CuA}_{CuAL} = pL - \log \left[(1 - \bar{n})/ \bar{n}\right]$$

The average values were thus calculated and have been presented along with $\bar{n}$ and pL values (Tables III 22 to III 53).

Computer calculations of mixed-ligand formation constants :

The formation constants of mixed-ligand complexes, obtained by the modified Irving-Rossotti titration technique were subjected to refinement by using the computer programme SCOGS.[66] The values of K^{CuA}_{CuAL} were obtained in two ways :

i) by considering the species present in the solution to be LH, L^-, $[CuA]^{2+}$ and $[CuAL]^+$ (Method II = m_2). This gives directly the value of $\log K^{CuA}_{CuAL}$.

ii) taking into account all possible species to be present in the solution i.e., LH, L^-, AH_2^{2+}, AH^+, A, $[CuL]^+$, $[CuL_2]$, $[CuA]^{2+}$, $[CuA_2]^{2+}$ and $[CuAL]^+$ (Method III = m_3). This gives the value of $\log K^{Cu}_{CuAL}$ from which $\log K^{CuA}_{CuAL}$ was calculated as follows :

$$\log K^{CuA}_{CuAL} = \log K^{Cu}_{CuAL} - \log K^{Cu}_{CuA}$$

The refined values of pK_1^H, $\log K^{Cu}_{CuL}$ and $\log K^{CuL}_{CuL_2}$, as obtained in Chapter II were used. The values of $\log K^{Cu}_{CuA}$ and $\log K^{CuA}_{CuA_2}$ were obtained from literature.[101]

In Method II the value of pK_1^H was supplied as a fixed parameter and the $\log K^{CuA}_{CuAL}$ value obtained by Irving-Rossotti method was refined over five cycles.

In Method III the values of pK_1^H, $\log K^{Cu}_{CuL}$, $\log K^{CuL}_{CuL_2}$, $\log K^{Cu}_{CuA}$, $\log K^{CuA}_{CuA_2}$ were used as fixed parameters and the value of $\log K^{Cu}_{CuAL}$ was refined. The stepwise refinement gave proper convergency for the mixed-ligand formation constants of all the complexes.

However, in cases of $[CuA^3L]^+$ and $[CuA^4L]^+$, calculation of mixed-ligand formation constants considering all possible species (Method III) could not be used. This is because the formation of $[CuA^3]^{2+}$ or $[CuA^4]^{2+}$ are complete at very low pH and hence the values of $K^{Cu}_{CuA^3}$ and $K^{Cu}_{CuA^4}$ could not be determined by pH-metric method. The formation constants of mixed-ligand complexes were, therefore,

determined only by presuming complete formation of $[CuA^3]^{2+}$ or $[CuA^4]^{2+}$ (Method II).

The mixed-ligand formation constants determined by Method I, II and III are given in Tables III 54 and III 55. These tables also include $\Delta \log K$ values.

The concentration of the species as a percentage of total Cu^{2+} at different pH have been plotted from the computer output. Figures III 41 and III 42 show the curves for the two representative systems, $(Cu^{2+} + A^1 + L^1)$ and $(Cu^{2+} + A^1 + L^5)$, respectively.

Table III 1

N = 0.2M V^{o} = 50 ml T_A^o = 0.002M

E^{o} = 0.02M I = 0.2M T_M^o = 0.002M t = 30 °C

Acid		A^1		Cu(II) + A^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	2.25	3.00	2.20	
4.00	2.50	4.00	2.65	4.00	2.50	
4.50	2.80	4.50	3.25	4.50	3.00	
4.60	2.95	4.60	3.40	4.60	3.10	
4.70	3.20	4.70	3.65	4.70	3.20	
4.80	3.50	4.80	4.00	4.80	3.50	
4.85	3.70	4.90	4.55	4.90	3.95	
4.90	3.95	4.95	5.20	4.95	4.40	
4.94	4.25	4.98	5.70	4.98	4.75	
4.96	4.50	5.00	7.50	5.00	6.00	
4.98	4.75	5.01	8.50	5.02	6.20	
5.00	7.25	5.04	9.25	5.04	6.30	
5.01	8.50	5.07	9.75	5.10	6.50	ppt
5.04	9.25	5.10	10.30	5.20	6.80	
5.07	9.75			5.30	7.05	
5.10	10.30			5.40	7.40	
				5.50	8.10	
				5.60	9.00	

Table III 2

$N = 0.2M$ $V^o = 50$ ml $T_A^o = 0.002M$ $T_L^o = 0.002M$

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

L^1		$Cu(II) + A^1 + L^1$		L^2		$Cu(II) + A^1 + L^2$	
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
4.70	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	3.50
4.90	3.95	4.90	3.85	4.90	3.95	4.90	3.80
4.95	4.40	4.95	3.95	4.95	4.40	4.95	3.95
5.00	7.50	5.00	4.15	5.00	7.60	5.00	4.05
5.02	8.50	5.05	4.30	5.02	8.60	5.05	4.20
5.05	8.75	5.10	4.45	5.05	8.85	5.10	4.40
5.10	9.20	5.20	4.75	5.10	9.25	5.20	4.80
5.20	10.00	5.30	5.20	5.20	10.00	5.30	5.30
5.30	10.60	5.40	5.60	5.30	10.65	5.40	5.80
		5.50	6.05			5.50	6.35
		5.70	7.00			5.70	7.90
		5.90	8.05				

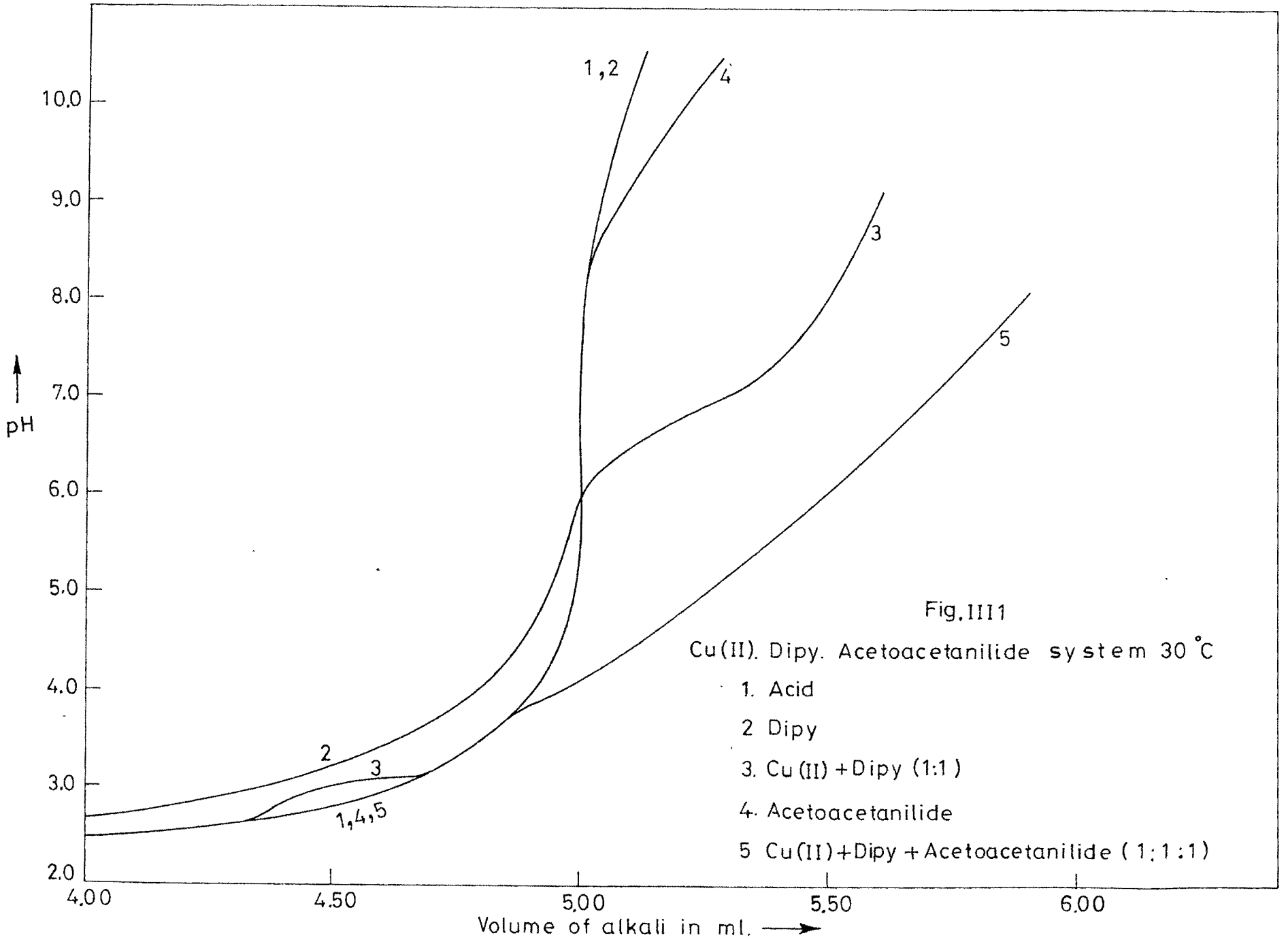


Fig. III 1

Cu(II). Dipy. Acetoacetanilide system 30 °C

1. Acid
2. Dipy
3. Cu(II) + Dipy (1:1)
4. Acetoacetanilide
5. Cu(II) + Dipy + Acetoacetanilide (1:1:1)

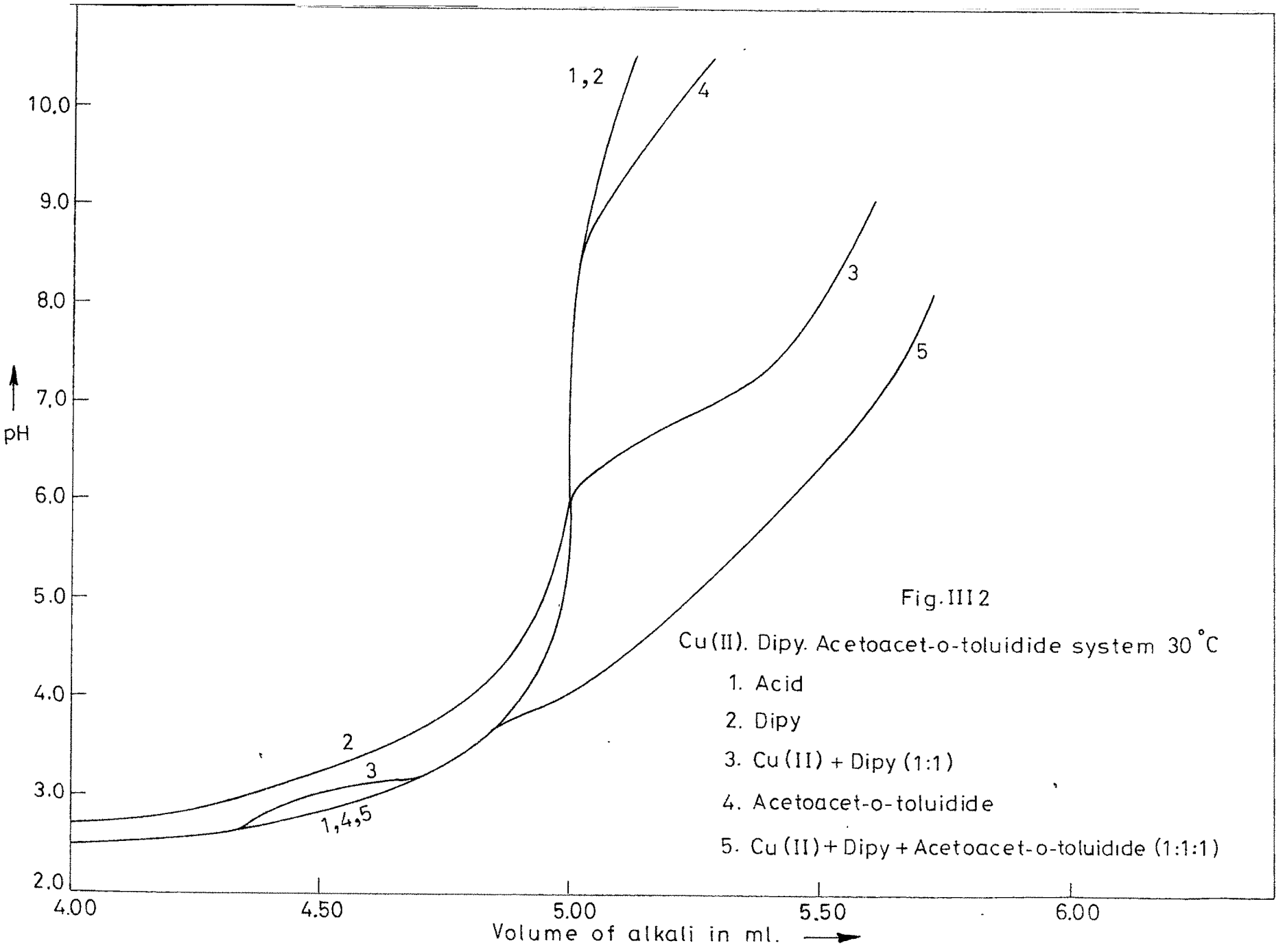


Fig. III 2

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

1. Acid
2. Dipy
3. Cu(II) + Dipy (1:1)
4. Acetoacet-o-toluidide
5. Cu(II) + Dipy + Acetoacet-o-toluidide (1:1:1)

Table III 3

$N = 0.2M$ $V^o = 50$ ml $T_A^o = 0.002M$ $T_L^o = 0.002M$

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

L^3		$Cu(II) + A^1 + L^3$		L^4		$Cu(II) + A^1 + L^4$	
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
4.70	3.20	4.70	3.20	4.70	3.20	4.70	3.20
4.80	3.50	4.80	3.40	4.80	3.50	4.80	3.30
4.90	3.95	4.90	3.60	4.90	3.95	4.90	3.50
4.95	4.40	4.95	3.70	4.95	4.40	4.95	3.60
5.00	7.70	5.00	3.85	5.00	7.25	5.00	3.70
5.02	8.25	5.05	4.00	5.02	8.25	5.05	3.80
5.05	8.65	5.10	4.15	5.05	8.60	5.10	3.90
5.10	9.25	5.20	4.45	5.10	9.05	5.20	4.15
5.20	10.20	5.30	4.85	5.20	9.70	5.30	4.40
5.30	10.80	5.40	5.30	5.30	10.20	5.40	4.90
		5.50	5.85	5.40	10.60	5.50	5.65
		5.70	7.20			5.70	8.20
		5.90	9.50				

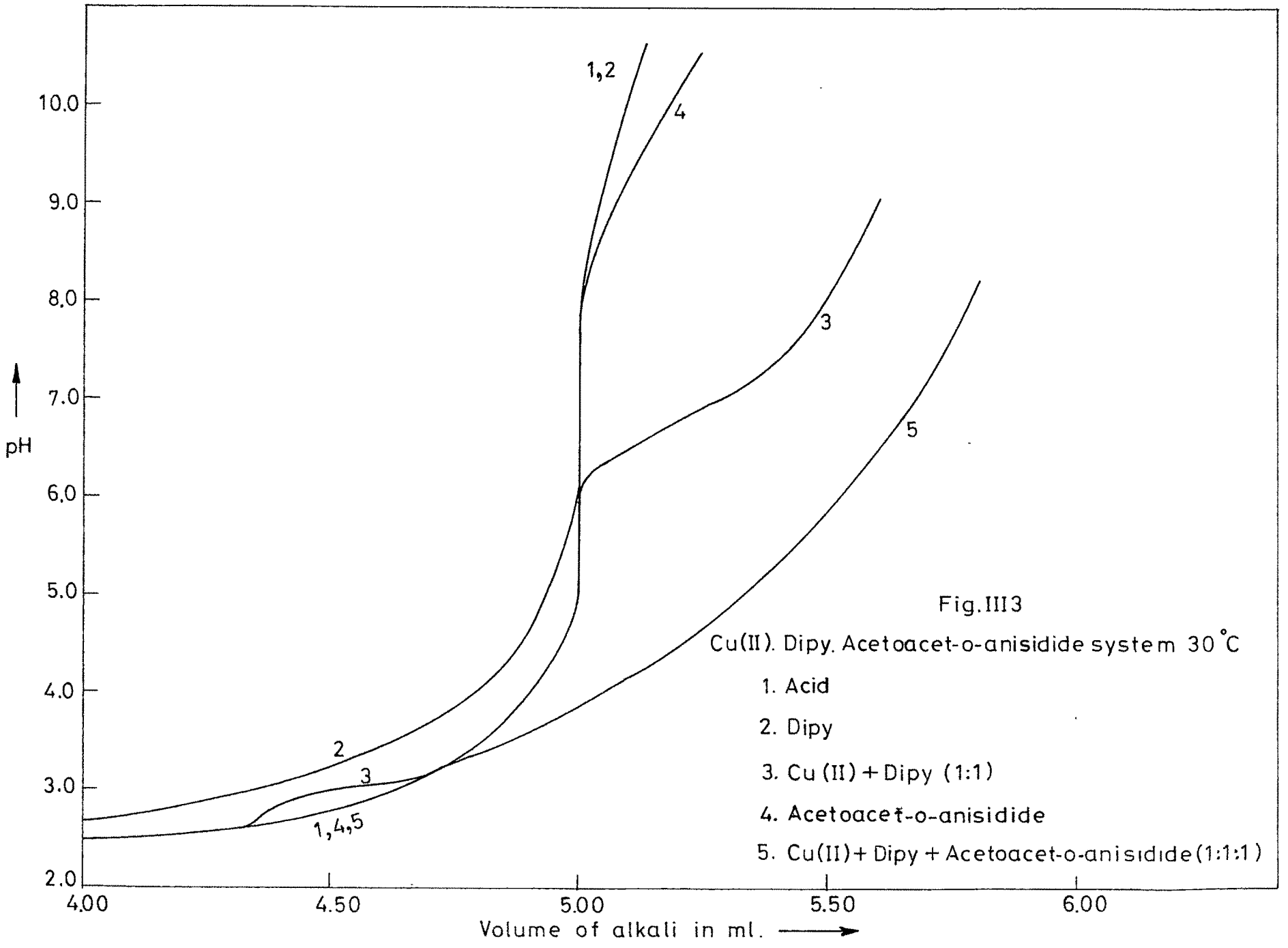


Fig. III3

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

1. Acid
2. Dipy
3. Cu (II) + Dipy (1:1)
4. Acetoacet-o-anisidide
5. Cu(II) + Dipy + Acetoacet-o-anisidide (1:1:1)

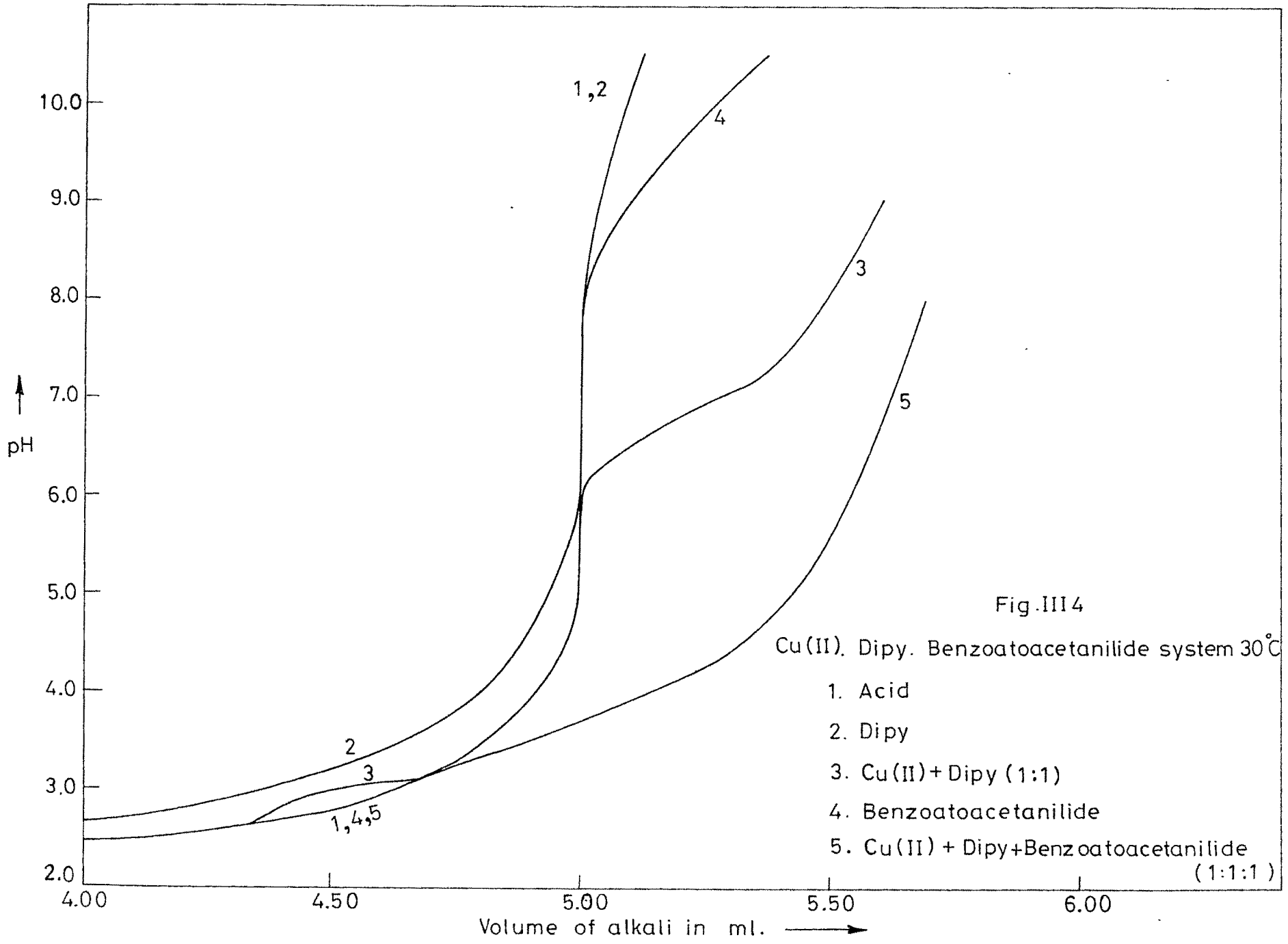


Fig.III4

Cu(II). Dipy. Benzoatoacetanilide system 30°C

1. Acid
2. Dipy
3. Cu(II)+Dipy (1:1)
4. Benzoatoacetanilide
5. Cu(II) + Dipy+Benzoatoacetanilide (1:1:1)

Table III 4

N = 0.2M V^{o} = 50 ml T_{A}^{o} = 0.002M T_{L}^{o} = 0.002M

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

L^5		Cu(II) + A^1 + L^5		L^6		Cu(II) + A^1 + L^6	
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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.95
4.95	4.40	4.95	4.30	4.95	4.40	4.95	4.40
5.00	7.50	5.00	4.45	5.00	6.75	5.00	4.70
5.02	7.85	5.05	4.70	5.02	7.25	5.05	4.90
5.05	8.20	5.10	4.90	5.05	7.55	5.10	5.15
5.10	8.55	5.20	5.45	5.10	7.90	5.20	5.75
5.20	9.00	5.30	6.00	5.20	8.35	5.30	6.35
5.30	9.35	5.40	6.65	5.30	8.65	5.40	6.90
5.40	9.60	5.50	7.60	5.40	8.90	5.50	7.45
5.50	9.80			5.50	9.05	5.60	8.20

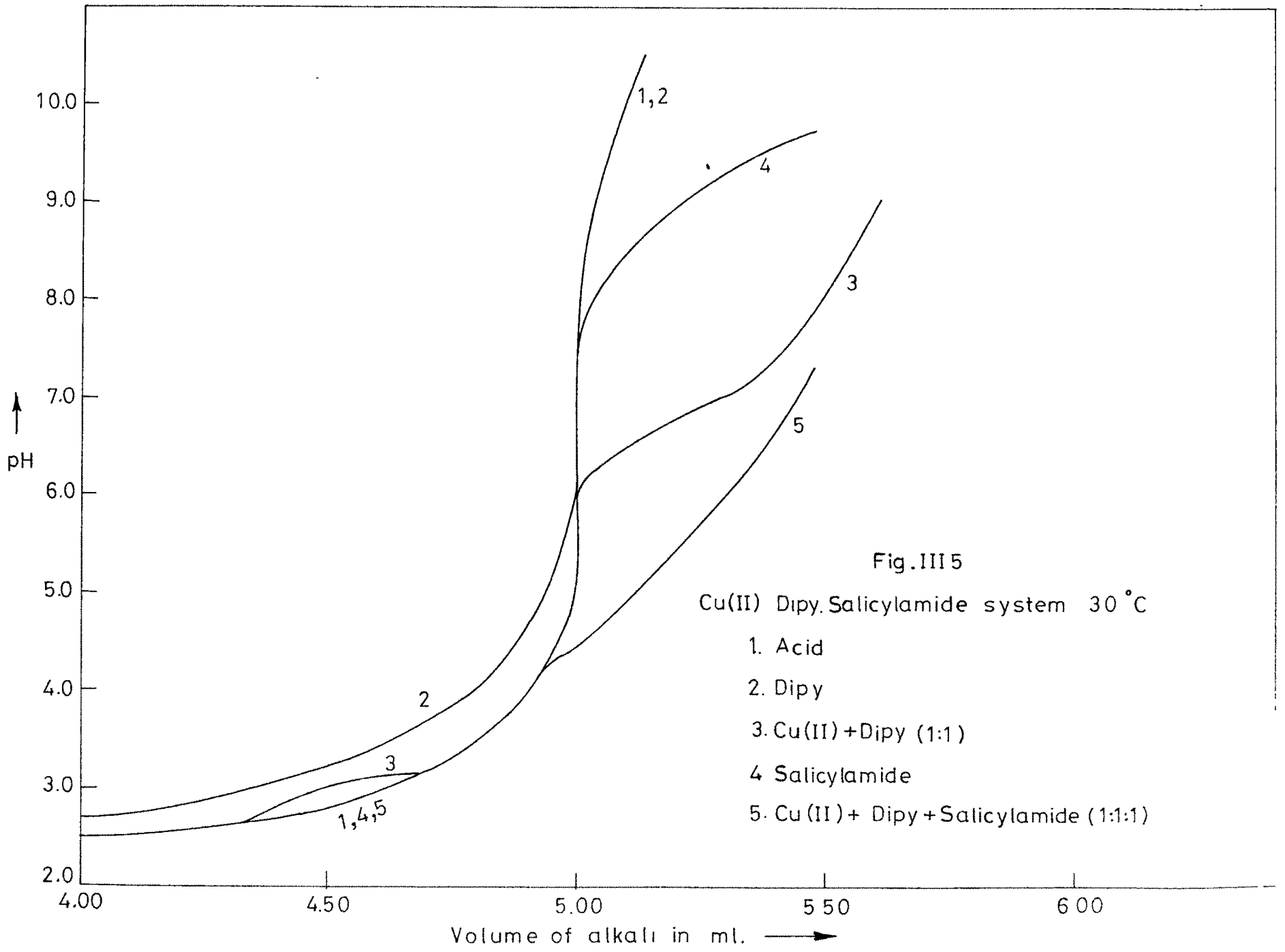


Fig. III 5

Cu(II) Dipy. Salicylamide system 30 °C

1. Acid
2. Dipy
3. Cu(II) + Dipy (1:1)
4. Salicylamide
5. Cu (II) + Dipy + Salicylamide (1:1:1)

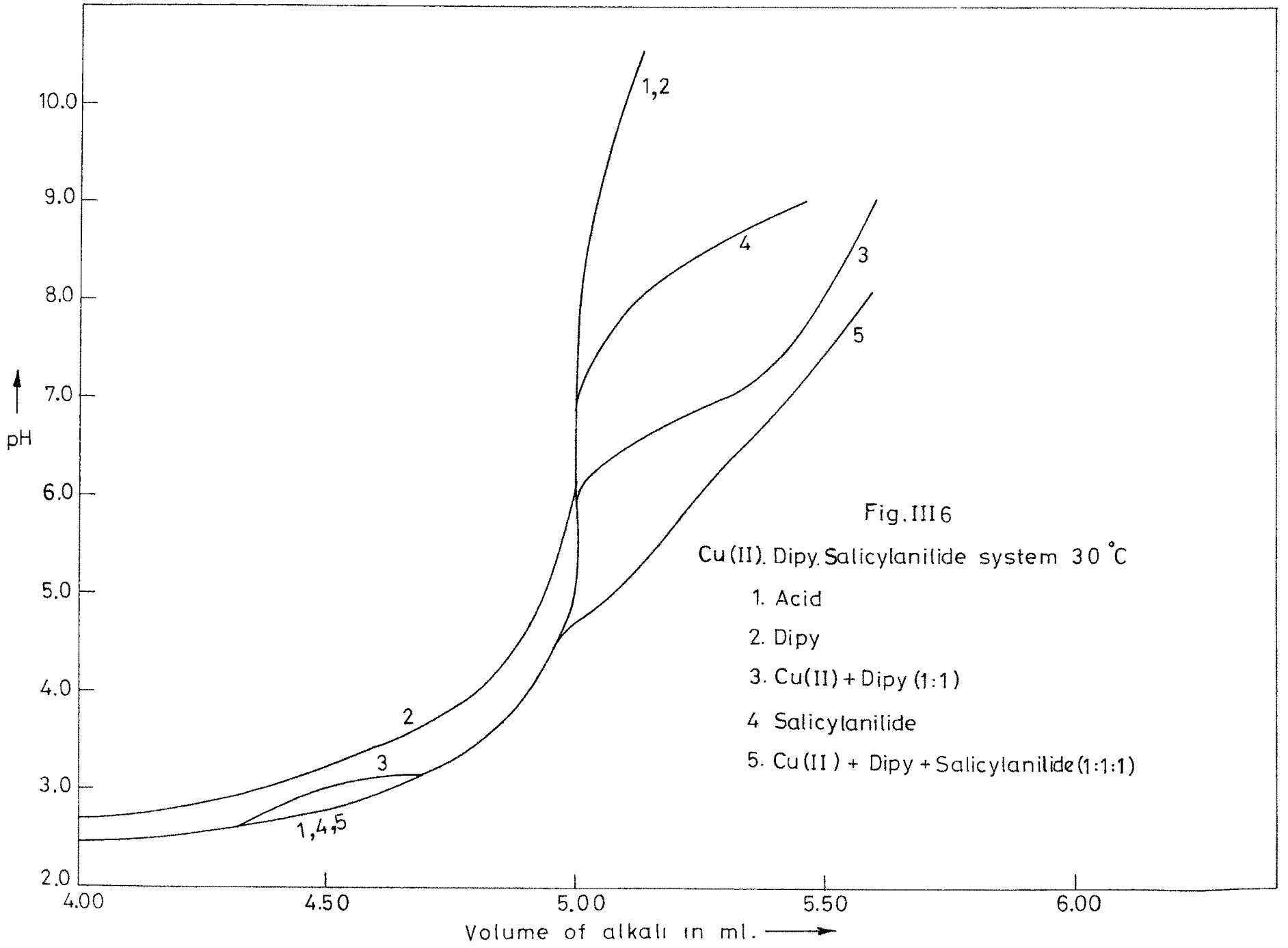


Fig. III 6

Cu(II). Dipy. Salicylanilide system 30 °C

1. Acid
2. Dipy
3. Cu(II) + Dipy (1:1)
4. Salicylanilide
5. Cu(II) + Dipy + Salicylanilide (1:1:1)

Table III 5

$N = 0.2M$ $V^o = 50$ ml $T_A^o = 0.002M$ $T_L^o = 0.002M$

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

L^7		$Cu(II) + A^1 + L^7$		L^8		$Cu(II) + A^1 + L^8$	
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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.90
4.95	4.40	4.95	4.15	4.95	4.40	4.95	4.10
5.00	6.10	5.00	4.35	5.00	6.00	5.00	4.30
5.02	6.60	5.05	4.60	5.02	6.30	5.05	4.55
5.05	6.90	5.10	4.85	5.05	6.45	5.10	4.80
5.10	7.30	5.20	5.50	5.10	6.75	5.20	5.35
5.20	7.85	5.30	6.15	5.20	7.35	5.30	5.95
5.30	8.40	5.40	7.00	5.30	7.85	5.40	6.65
5.40	8.80	5.50	7.80	5.40	8.30	5.50	7.35
5.50	9.25			5.50	8.75	5.60	8.30
				5.60	9.40		

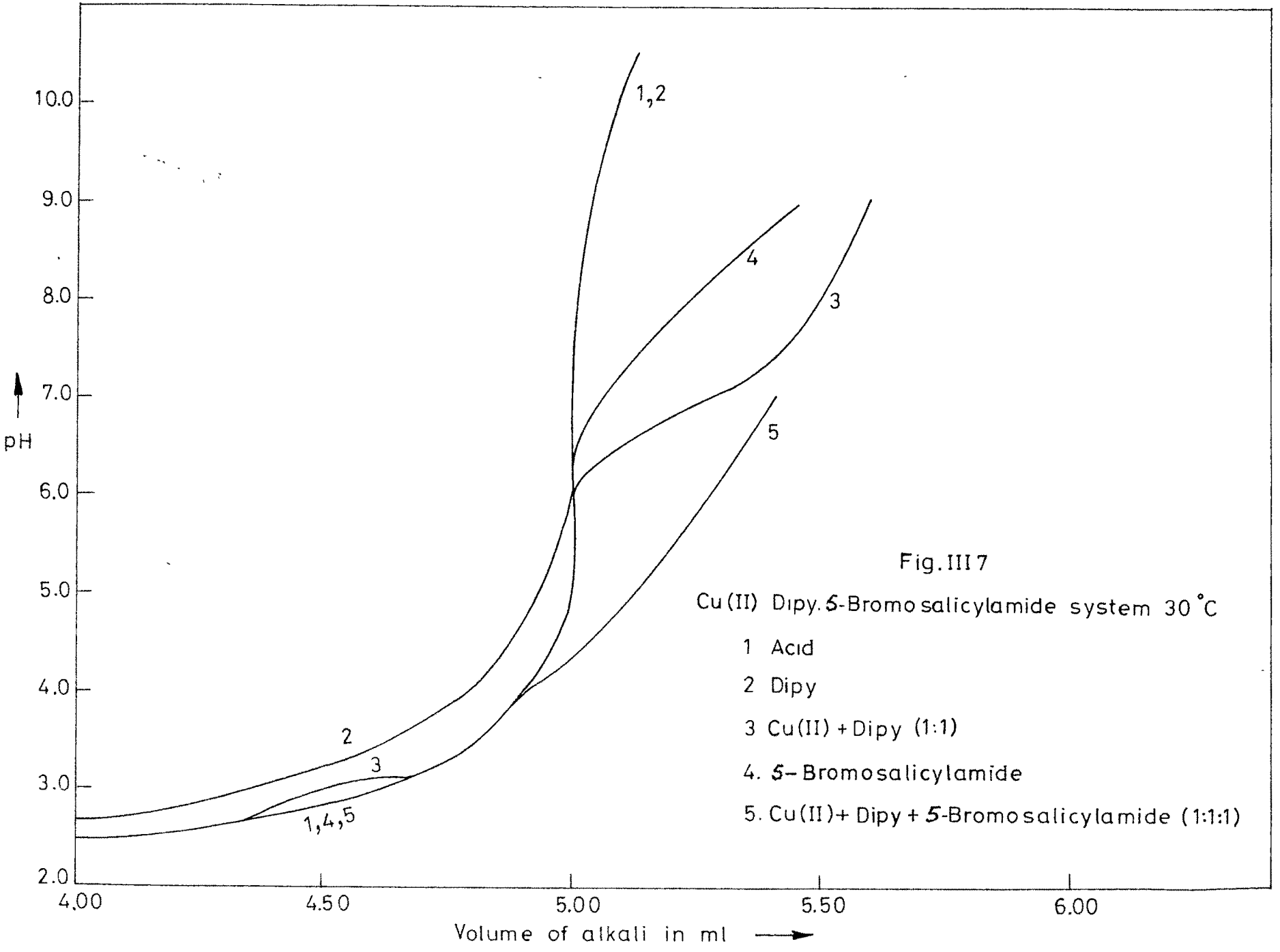


Fig. III 7

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

1 Acid

2 Dipy

3 Cu(II) + Dipy (1:1)

4. 5- Bromosalicylamide

5. Cu(II) + Dipy + 5-Bromosalicylamide (1:1:1)

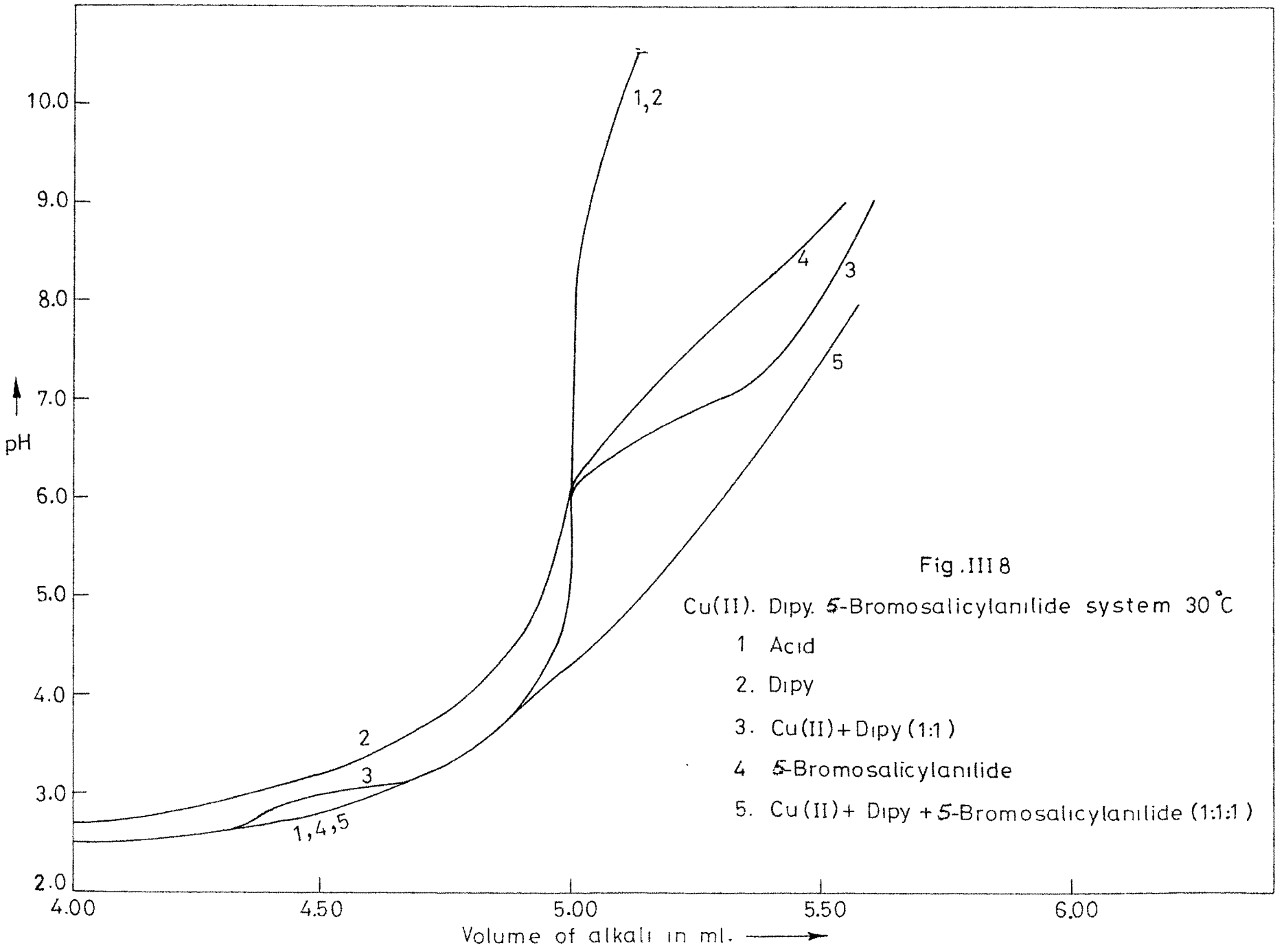


Fig. III 8

Cu(II). Dipy. 5-Bromosalicylanilide system 30 °C

1 Acid

2. Dipy

3. Cu(II)+Dipy (1:1)

4 5-Bromosalicylanilide

5. Cu(II)+ Dipy +5-Bromosalicylanilide (1:1:1)

Table III 6

$N = 0.2M \quad V^o = 50\ ml \quad T_A^o = 0.001M$

$E^o = 0.02M \quad I = 0.2M \quad T_M^o = 0.001M \quad t = 30\ ^oC$

Acid		A^2		Cu(II) + A^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	1.95	1.00	1.90
2.00	2.00	2.00	2.05	2.00	2.00
3.00	2.20	3.00	2.25	3.00	2.20
4.00	2.50	4.00	2.65	4.00	2.50
4.50	2.80	4.30	2.85	4.50	2.80
4.60	2.95	4.50	3.05	4.60	2.95
4.70	3.20	4.60	3.30	4.70	3.20
4.80	3.50	4.70	3.75	4.80	3.70
4.85	3.70	4.80	4.25	4.90	4.05
4.90	3.95	4.90	5.00	4.95	4.90
4.94	4.25	4.95	5.55	5.00	6.10
4.96	4.50	4.98	6.10	5.01	6.25
4.98	4.75	5.00	7.50	5.03	6.35
5.00	7.25	5.01	8.50	5.05	6.50
5.01	8.50	5.04	9.25	5.10	6.85
5.04	9.25	5.07	9.75	5.20	7.85 ppt
5.07	9.75	5.10	10.30	5.30	9.20
5.10	10.30				

Table III 7

$N = 0.2M$ $V^{o} = 50$ ml $T_A^{o} = 0.001M$ $T_L^{o} = 0.001M$

$E^{o} = 0.02M$ $I = 0.2M$ $T_M^{o} = 0.001M$ $t = 30\ ^{o}C$

L^1		$Cu(II) + A^2 + L^1$		L^2		$Cu(II) + A^2 + L^2$	
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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.95
4.95	4.40	4.95	4.40	4.95	4.40	4.95	4.40
5.00	7.60	5.00	4.85	5.00	7.80	5.00	4.65
5.02	8.50	5.05	5.10	5.02	8.50	5.05	5.00
5.05	9.00	5.10	5.45	5.05	9.00	5.10	5.50
5.10	9.50	5.15	5.95	5.10	9.55	5.15	6.00
5.20	10.40	5.20	6.60	5.20	10.65	5.20	6.70
		5.30	8.30			5.30	8.50

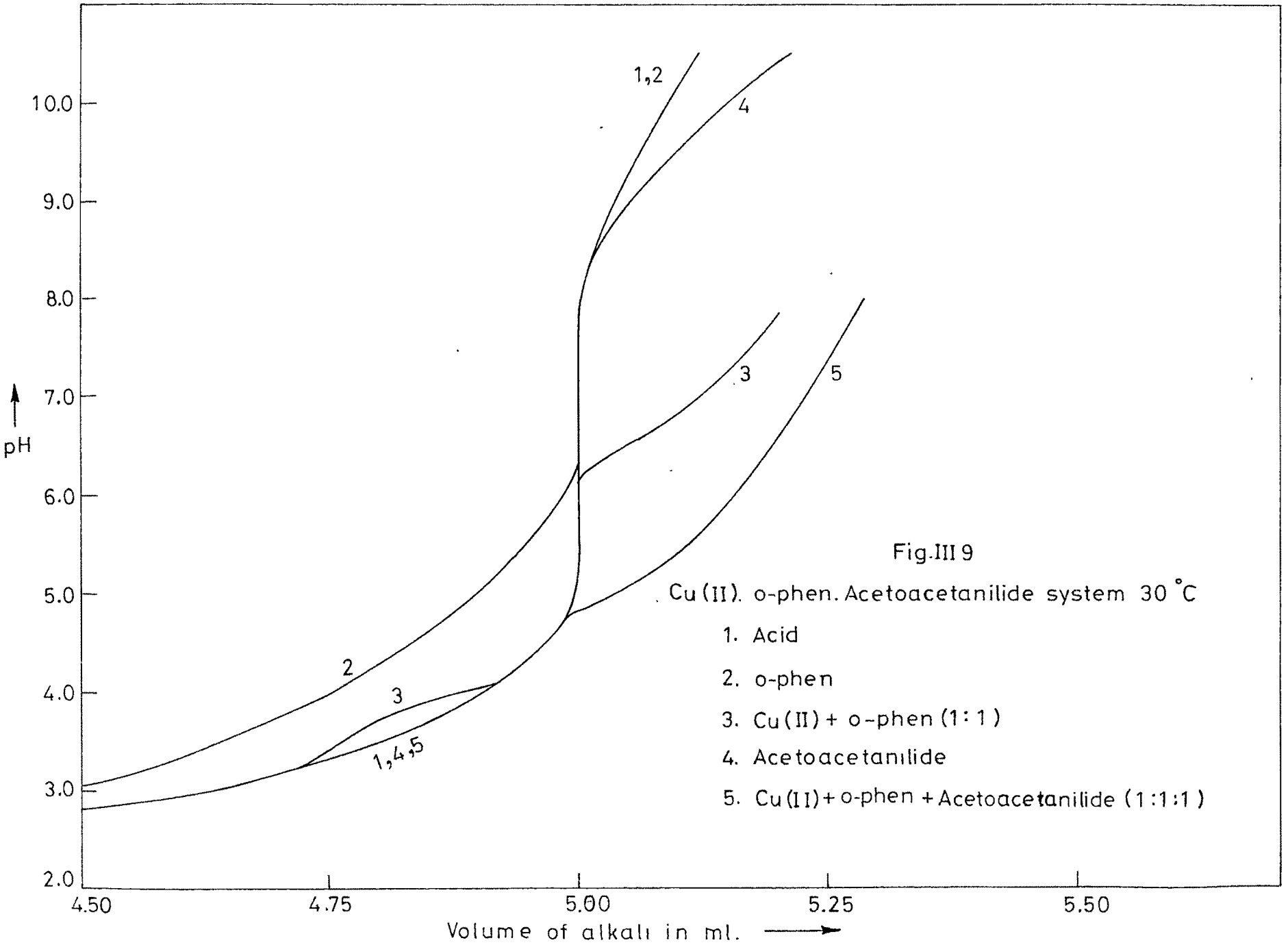


Fig.III 9

Cu (II). o-phen. Acetoacetanilide system 30 °C

1. Acid
2. o-phen
3. Cu (II) + o-phen (1 : 1)
4. Acetoacetanilide
5. Cu (II) + o-phen + Acetoacetanilide (1 : 1 : 1)

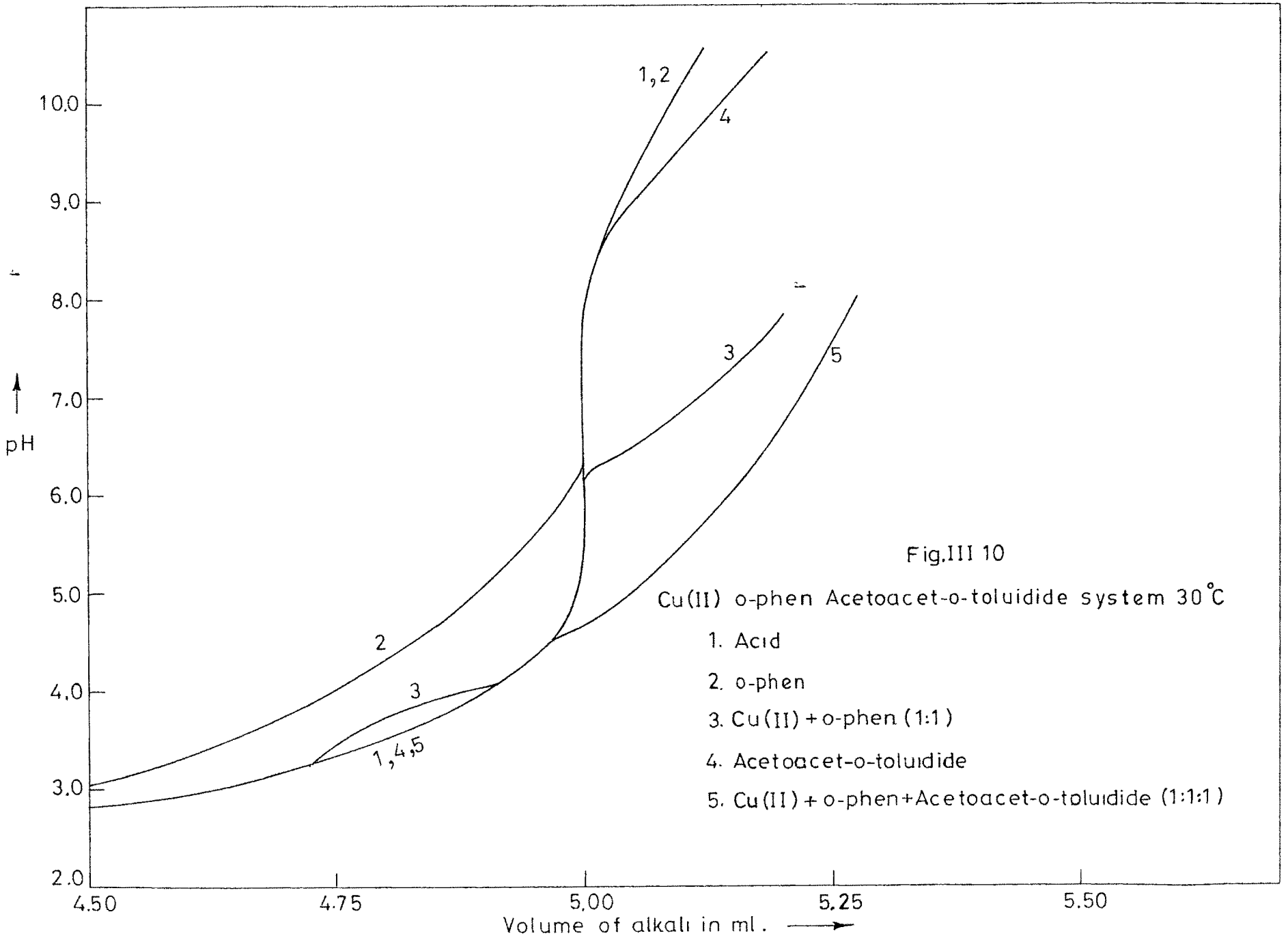


Fig.III 10

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

1. Acid
2. o-phen
3. Cu(II) + o-phen (1:1)
4. Acetoacet-o-toluidide
5. Cu(II) + o-phen + Acetoacet-o-toluidide (1:1:1)

Table III 8

$N = 0.2M$ $V^o = 50$ ml $T_A^o = 0.001M$ $T_L^o = 0.001M$

$E^o = 0.02M$ $I = 0.2M$ $T_M^o = 0.001M$ $t = 30\ ^oC$

L^3		$Cu(II) + A^2 + L^3$		L^4		$Cu(II) + A^2 + L^4$	
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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.95
4.95	4.40	4.95	4.40	4.95	4.40	4.95	4.15
5.00	7.90	5.00	4.85	5.00	7.50	5.00	4.25
5.02	8.40	5.05	5.00	5.02	8.40	5.05	4.50
5.05	8.85	5.10	5.30	5.05	8.85	5.10	4.90
5.10	9.55	5.15	5.75	5.10	9.45	5.15	5.45
5.20	10.70	5.20	6.40	5.20	10.30	5.20	6.20
		5.30	8.60			5.30	9.10

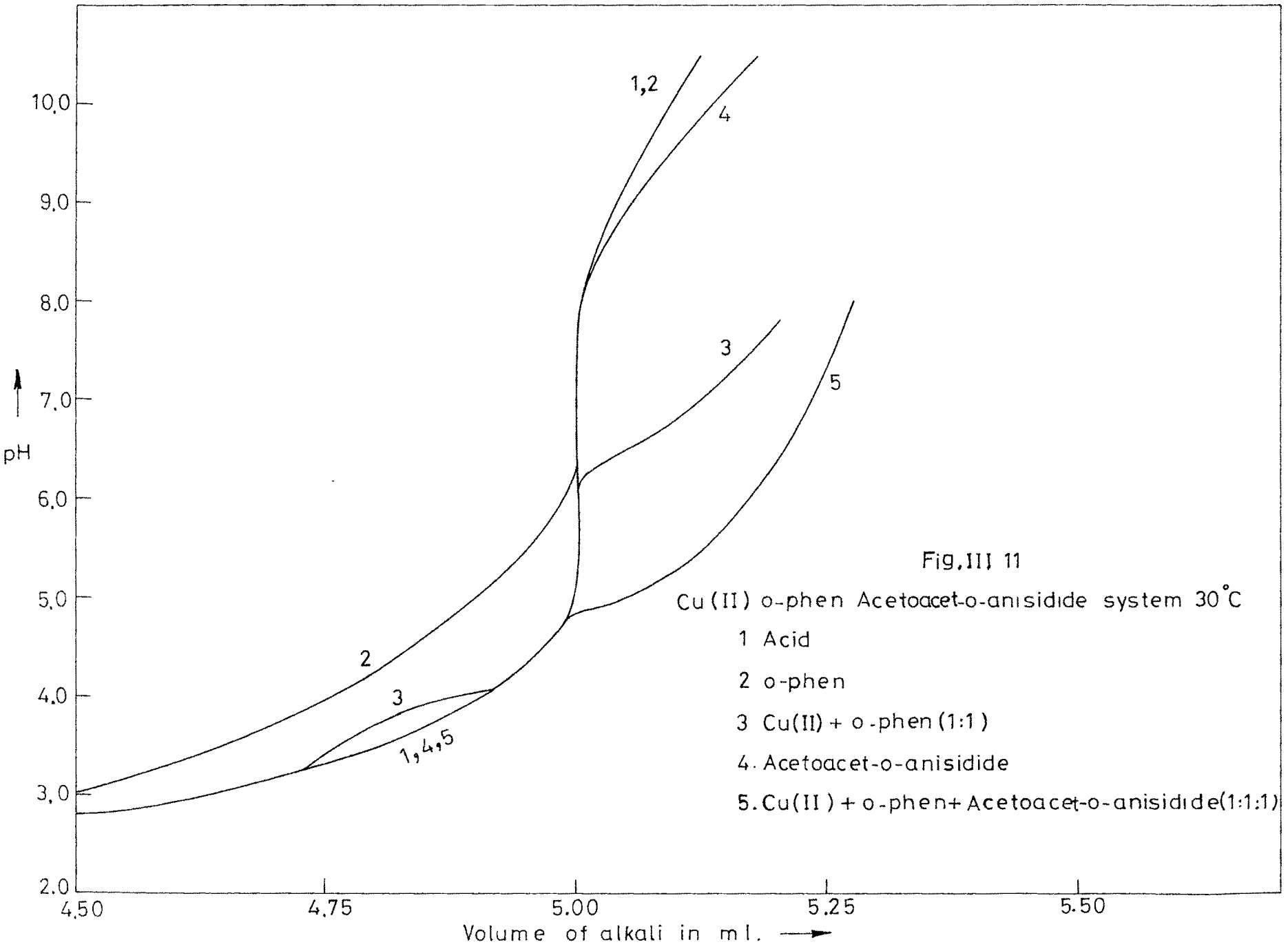


Fig. III 11

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

1 Acid

2 o-phen

3 Cu(II) + o-phen (1:1)

4. Acetoacet-o-anisidide

5. Cu(II) + o-phen + Acetoacet-o-anisidide (1:1:1)

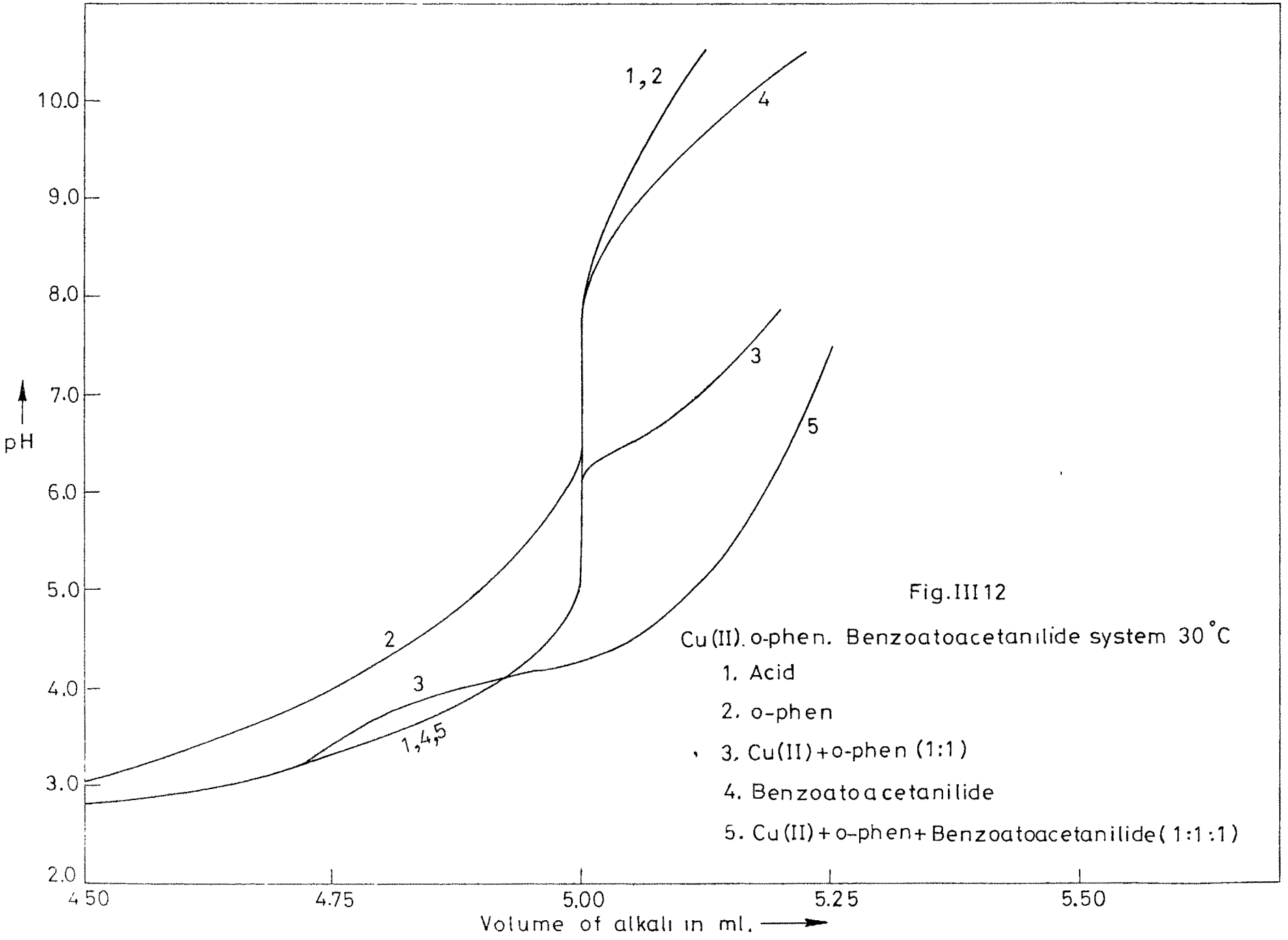


Fig. III 12

Cu(II). o-phen. Benzoatoacetanilide system 30 °C

1. Acid
2. o-phen
3. Cu(II) + o-phen (1:1)
4. Benzoatoacetanilide
5. Cu(II) + o-phen + Benzoatoacetanilide (1:1:1)

Table III 9

$N = 0.2M$ $V^o = 50$ ml $T_A^o = 0.001M$ $T_L^o = 0.001M$

$E^o = 0.02M$ $I = 0.2M$ $T_M^o = 0.001M$ $t = 30\ ^oC$

L^5		$Cu(II) + A^2 + L^5$		L^6		$Cu(II) + A^2 + L^6$	
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	o.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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.95
4.95	4.40	4.95	4.40	4.95	4.40	4.95	4.40
5.00	7.50	5.00	4.80	5.00	6.75	5.00	5.10
5.02	8.25	5.05	5.25	5.02	7.35	5.05	5.50
5.05	8.50	5.10	5.70	5.05	7.70	5.10	6.00
5.10	8.90	5.15	6.30	5.10	8.20	5.15	6.50
5.20	9.50	5.20	6.95	5.20	9.10	5.20	7.15
5.30	9.90	5.30	8.40			5.30	8.75

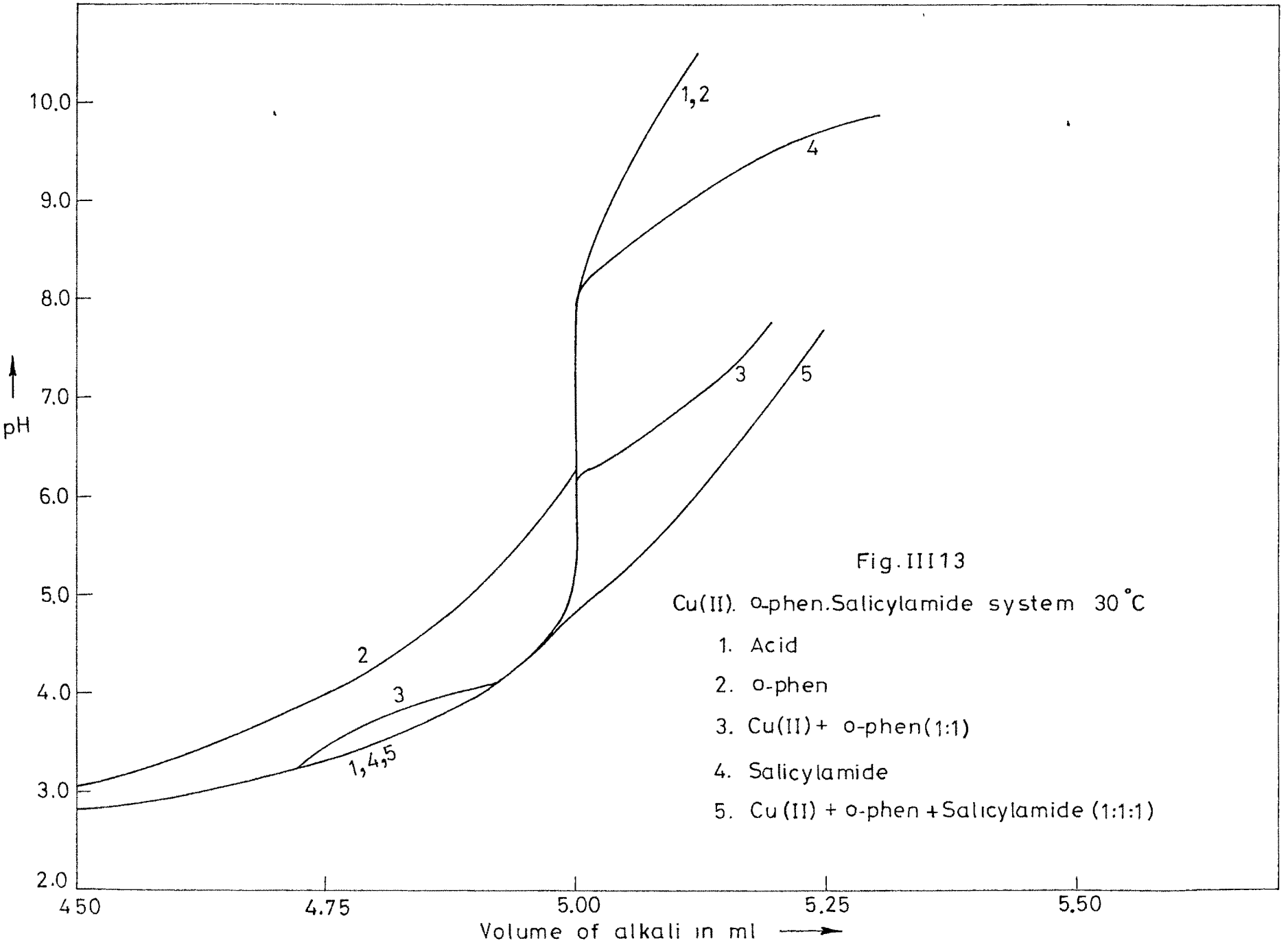


Fig. III 13

Cu(II). o-phen. Salicylamide system 30 °C

1. Acid
2. o-phen
3. Cu(II) + o-phen (1:1)
4. Salicylamide
5. Cu (II) + o-phen + Salicylamide (1:1:1)

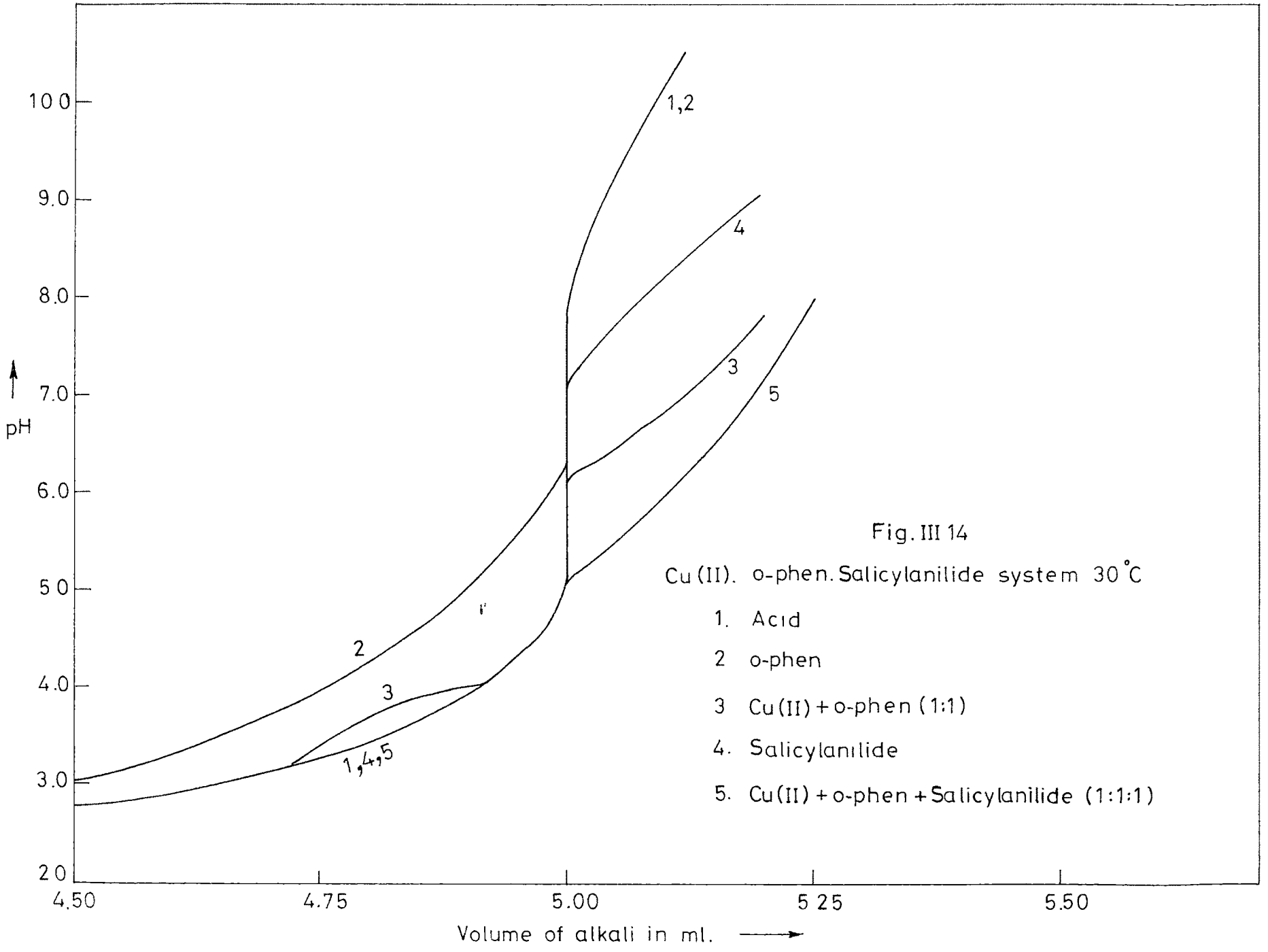


Fig. III 14

Cu (II). o-phen. Salicylanilide system 30 °C

1. Acid
2. o-phen
3. Cu(II) + o-phen (1:1)
4. Salicylanilide
5. Cu(II) + o-phen + Salicylanilide (1:1:1)

Table III 10

$N = 0.2M$ $V^o = 50$ ml $T_A^o = 0.001M$ $T_L^o = 0.001M$

$E^o = 0.02M$ $I = 0.2M$ $T_M^o = 0.001M$ $t = 30\ ^oC$

L^7		$Cu(II) + A^2 + L^7$		L^8		$Cu(II) + A^2 + L^8$	
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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.95
4.95	4.40	4.95	4.40	4.95	4.40	4.95	4.40
5.00	6.00	5.00	4.65	5.00	6.20	5.00	4.70
5.02	7.00	5.05	5.20	5.02	6.55	5.05	5.20
5.05	7.40	5.10	5.90	5.05	6.90	5.10	5.80
5.10	7.95	5.15	6.60	5.10	7.45	5.15	6.50
5.20	8.85	5.20	7.40	5.20	8.40	5.20	7.30
5.30	9.50	5.30	9.00	5.30	9.60	5.30	8.90

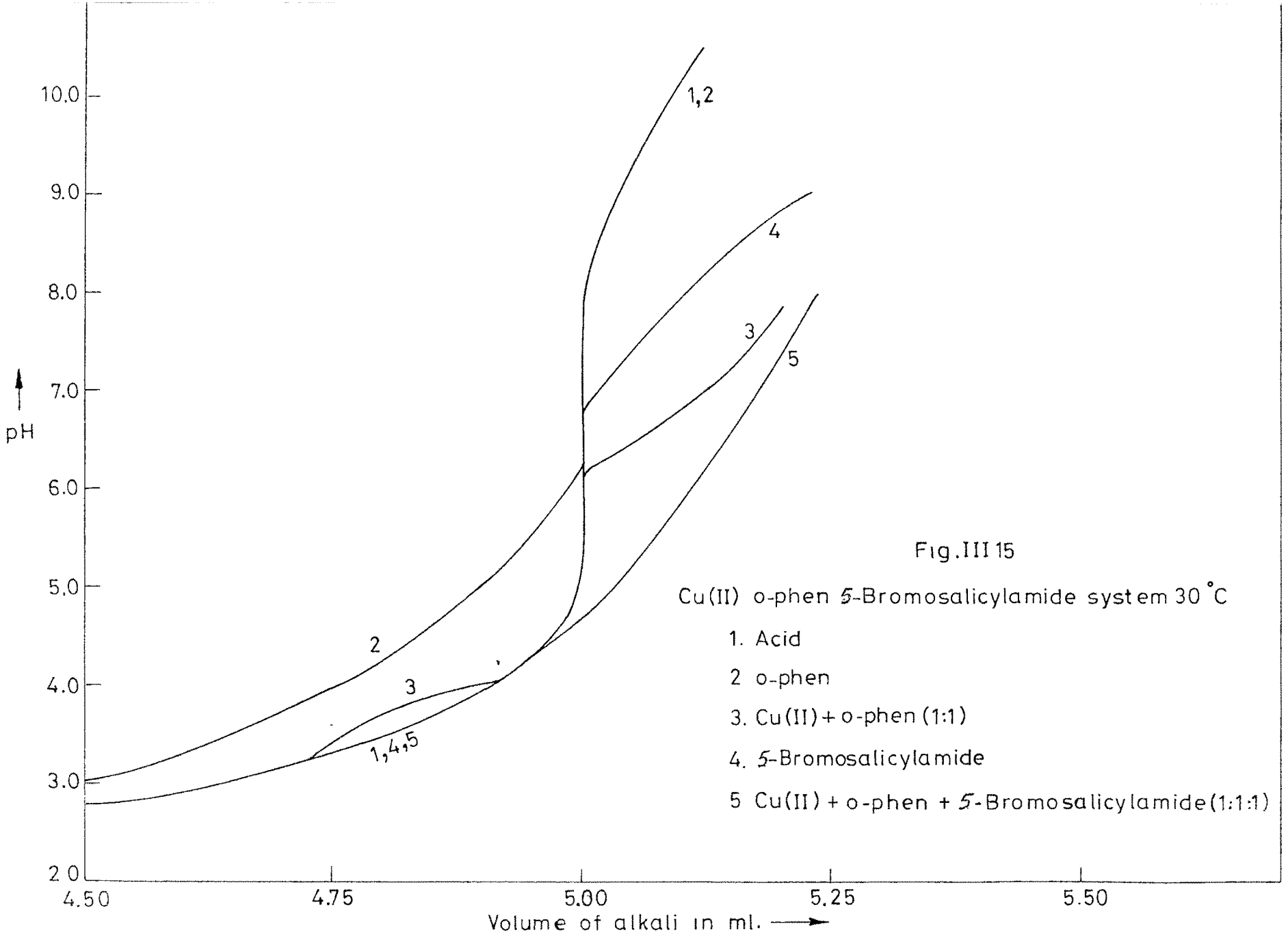


Fig. III 15

Cu(II) o-phen 5-Bromosalicylamide system 30 °C

1. Acid
2. o-phen
3. Cu(II) + o-phen (1:1)
4. 5-Bromosalicylamide
5. Cu(II) + o-phen + 5-Bromosalicylamide (1:1:1)

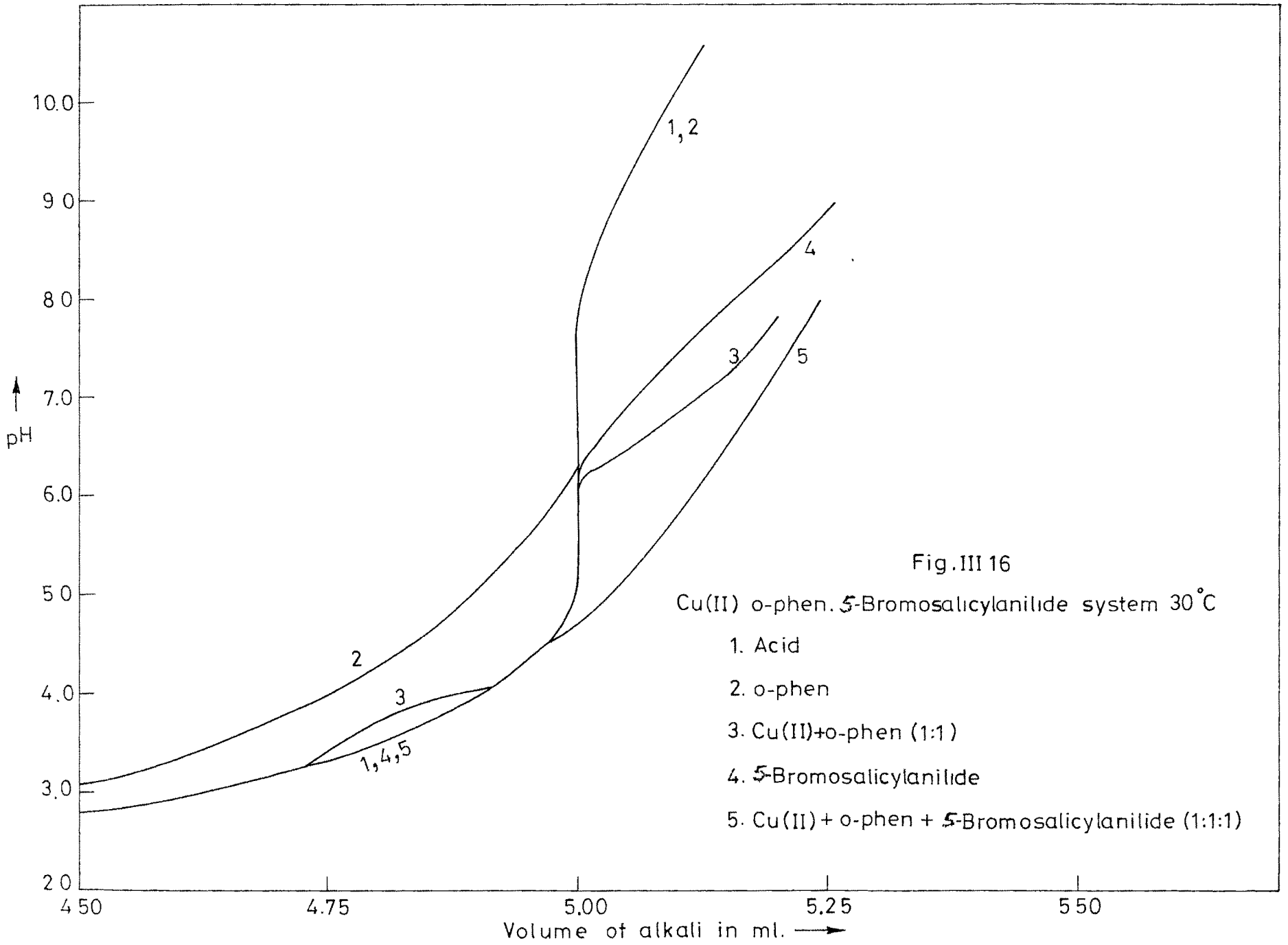


Fig. III 16

Cu(II) o-phen. 5-Bromosalicylanilide system 30°C

1. Acid
2. o-phen
3. Cu(II)+o-phen (1:1)
4. 5-Bromosalicylanilide
5. Cu(II) + o-phen + 5-Bromosalicylanilide (1:1:1)

Table III 11

N = 0.2M V^{o} = 50 ml T_{A}^{o} = 0.002M

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

Acid		A^{3}		Cu(II) + A^{3}	
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	2.10	2.00	2.00
3.00	2.20	3.00	2.30	3.00	2.20
4.00	2.50	4.00	2.70	4.00	2.50
4.50	2.80	4.30	2.95	4.50	2.80
4.60	2.95	4.50	3.30	4.60	3.10
4.70	3.20	4.60	3.55	4.70	3.35
4.80	3.50	4.70	3.85	4.80	3.60
4.85	3.70	4.80	4.20	4.90	3.95
4.90	3.95	4.90	4.70	4.95	4.40
4.94	4.25	4.95	5.15	5.00	5.90
4.96	4.50	5.00	7.25	5.02	6.00
4.98	4.75	5.01	8.50	5.05	6.10
5.00	7.25	5.04	9.25	5.10	6.25
5.01	8.50	5.07	9.75	5.20	6.50
5.04	9.25	5.10	10.30	5.30	6.70
5.07	9.75			5.40	6.95
5.10	10.30			5.50	7.50

Table III 12

$N = 0.2M$ $V^o = 50$ ml $T_A^o = 0.002M$ $T_L^o = 0.002M$

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

L^1		$Cu(II) + A^3 + L^1$		L^2		$Cu(II) + A^3 + L^2$	
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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.85
4.95	4.40	4.95	4.30	4.95	4.40	4.95	4.00
5.00	7.50	5.00	4.40	5.00	7.60	5.00	4.20
5.02	8.50	5.05	4.60	5.02	8.60	5.05	4.40
5.05	8.75	5.10	4.75	5.05	8.85	5.10	4.60
5.10	9.20	5.20	5.25	5.10	9.25	5.20	5.05
5.20	10.00	5.30	5.65	5.20	10.00	5.30	5.65
5.30	10.60	5.40	6.10	5.30	10.65	5.40	6.20
		5.50	6.45			5.50	6.65
		5.70	7.10			5.70	7.35
		5.90	7.70			5.90	7.90

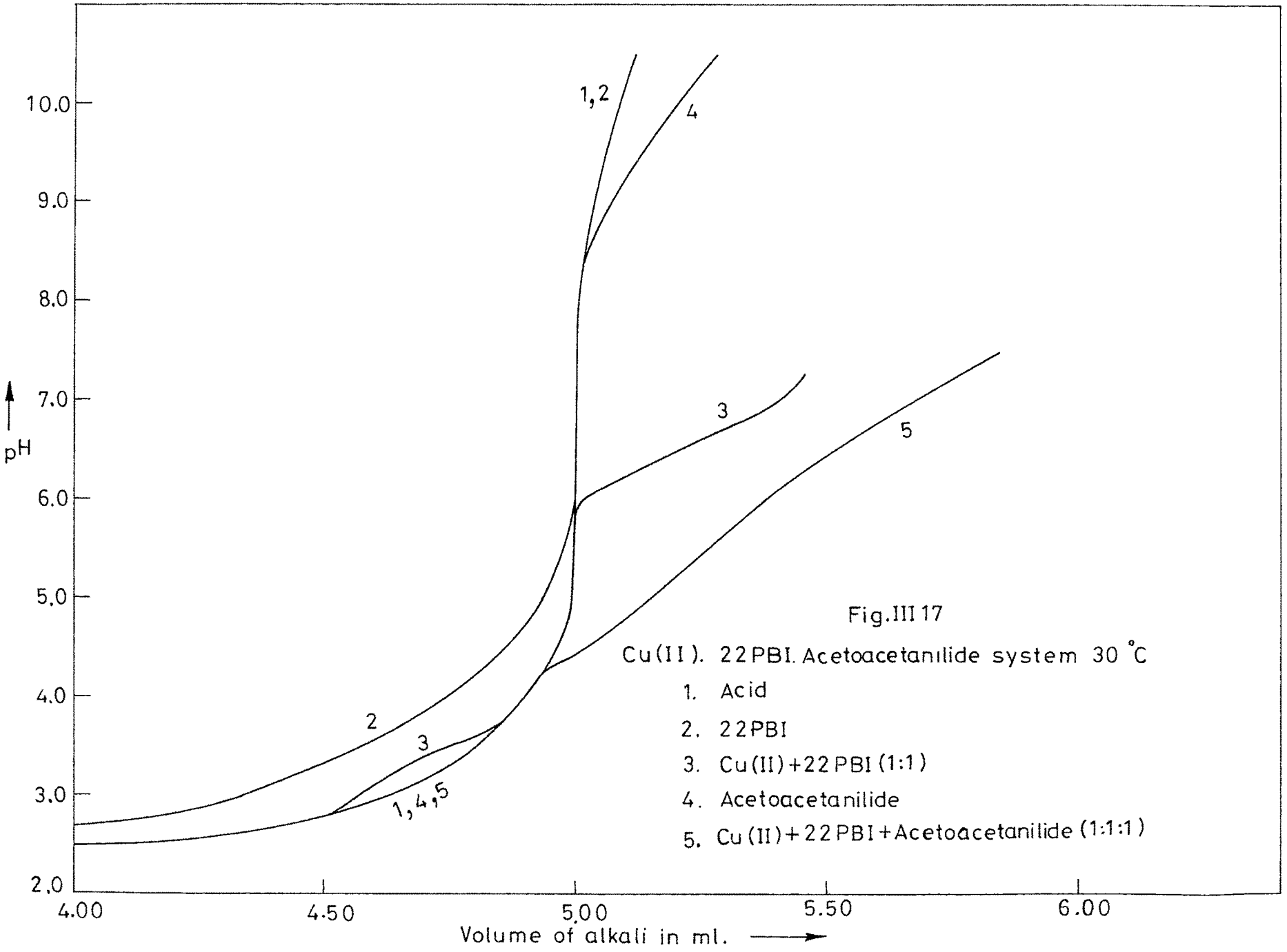


Fig.III 17

Cu(II). 22PBI. Acetoacetanilide system 30 °C

1. Acid
2. 22PBI
3. Cu(II)+22PBI (1:1)
4. Acetoacetanilide
5. Cu(II)+22PBI+Acetoacetanilide (1:1:1)

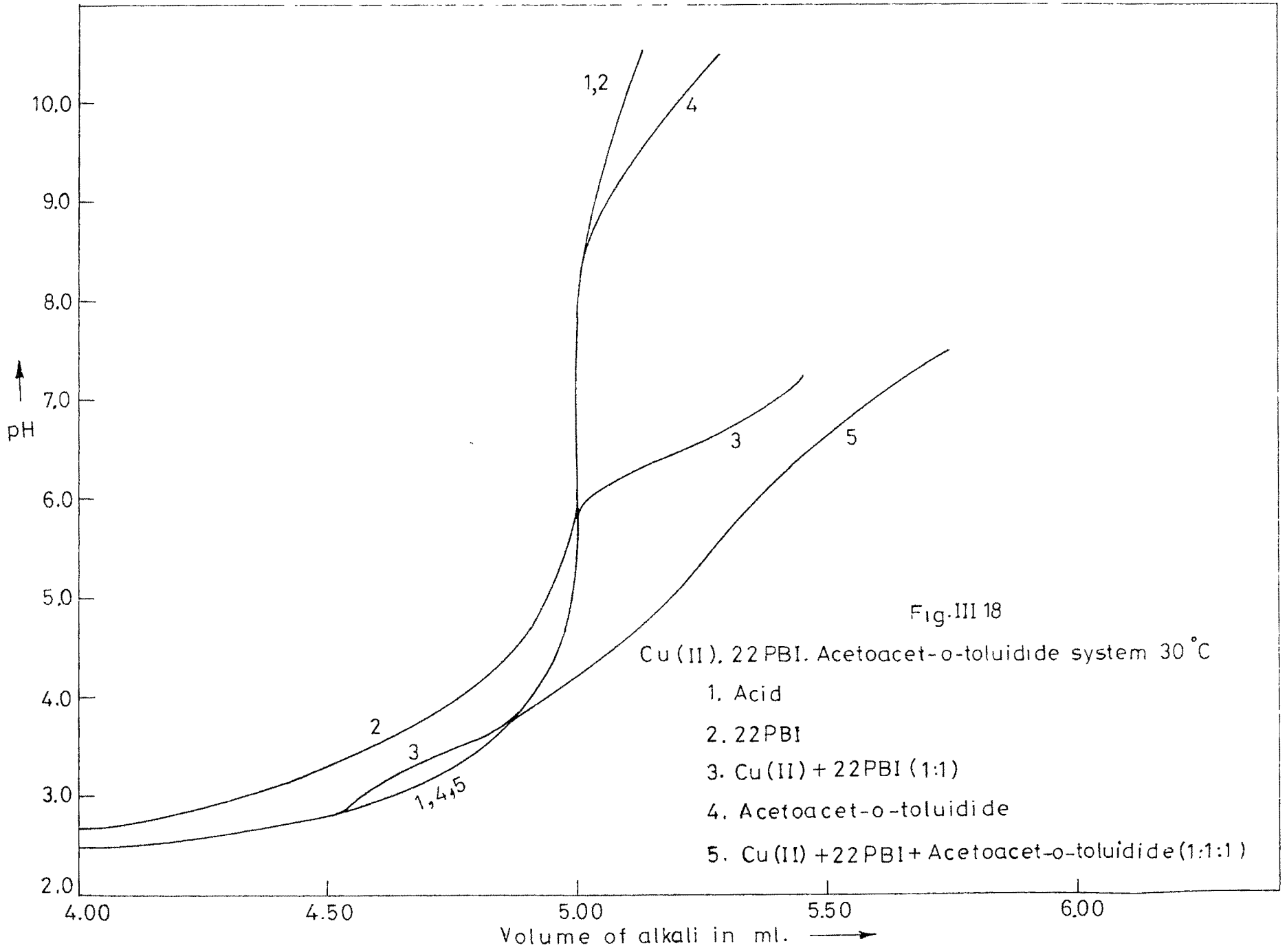


Fig. III 18

Cu (II), 22 PBI. Acetoacet-o-toluidide system 30 °C

1. Acid
2. 22PBI
3. Cu (II) + 22PBI (1:1)
4. Acetoacet-o-toluidide
5. Cu (II) + 22PBI + Acetoacet-o-toluidide (1:1:1)

Table III 13

N = 0.2M V^{o} = 50 ml T_A^o = 0.002M T_L^o = 0.002M

E^{o} = 0.02M I = 0.2M T_M^o = 0.002M t = 30 °C

L^3		Cu(II) + A^3 + L^3		L^4		Cu(II) + A^3 + 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
4.70	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	3.50
4.90	3.95	4.90	3.90	4.90	3.95	4.90	3.85
4.95	4.40	4.95	4.05	4.95	4.40	4.95	3.90
5.00	7.70	5.00	4.25	5.00	7.25	5.00	4.00
5.02	8.25	5.05	4.45	5.02	8.25	5.05	4.10
5.05	8.65	5.10	4.65	5.05	8.60	5.10	4.20
5.10	9.25	5.20	5.10	5.10	9.05	5.20	4.55
5.20	10.20	5.30	5.60	5.20	9.75	5.30	5.05
5.30	10.80	5.40	6.15	5.30	10.20	5.40	5.90
		5.50	6.80	5.40	10.60	5.50	7.10
		5.70	8.10			5.70	8.50

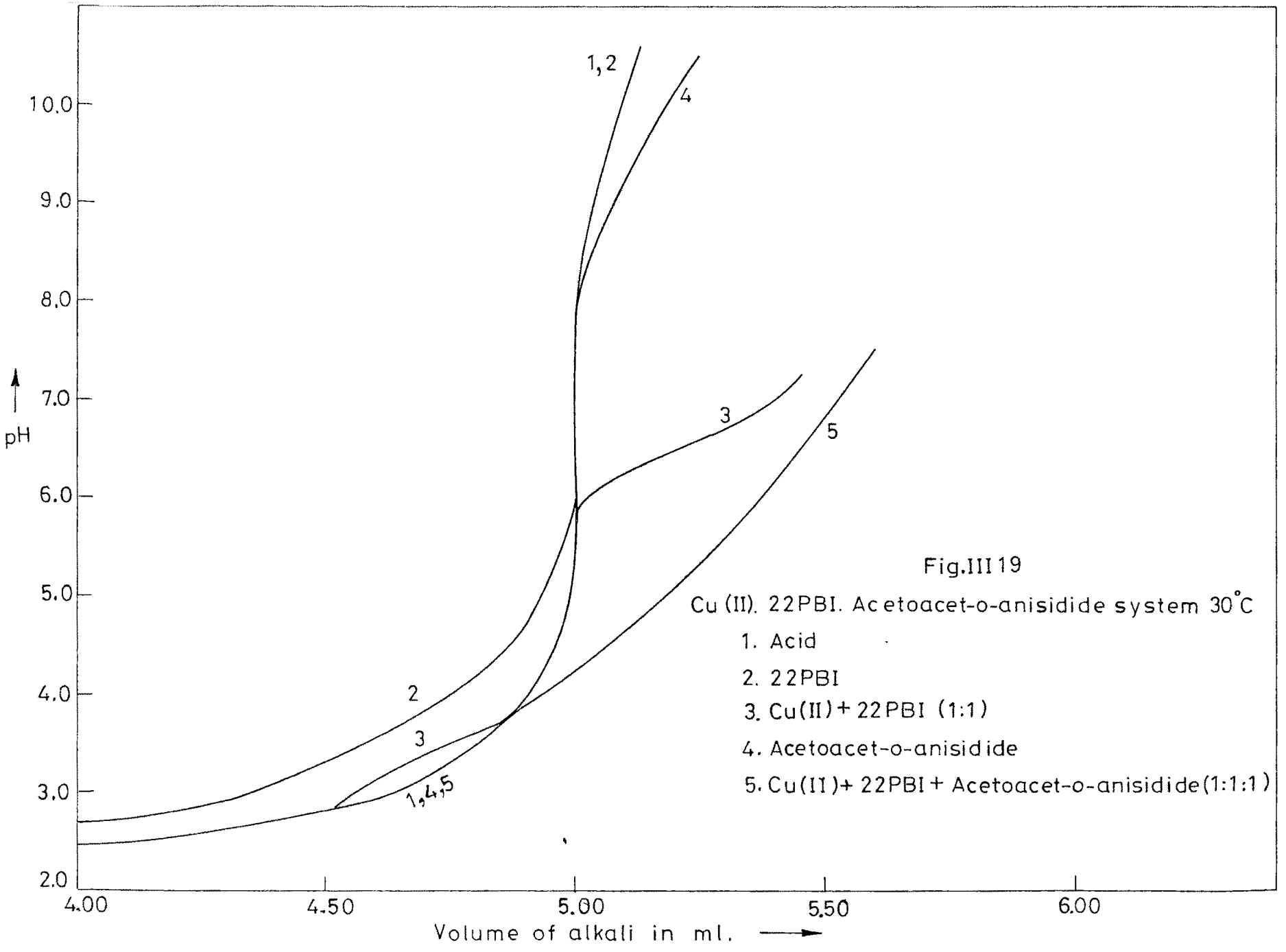


Fig.III 19

Cu (II). 22PBI. Acetoacet-o-anisidide system 30°C

1. Acid
2. 22PBI
3. Cu(II) + 22PBI (1:1)
4. Acetoacet-o-anisidide
5. Cu(II) + 22PBI + Acetoacet-o-anisidide (1:1:1)

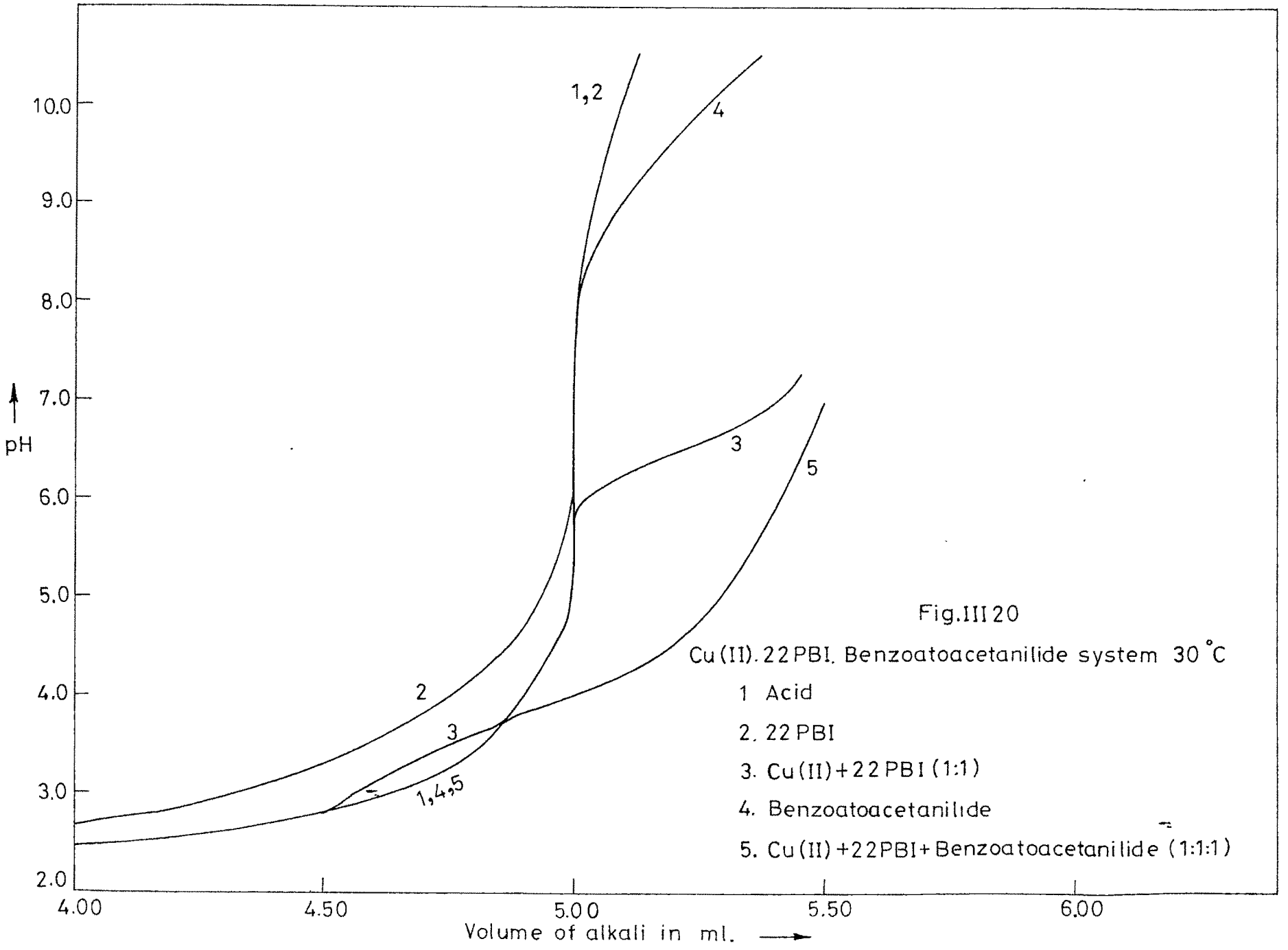


Fig.III 20

Cu(II). 22PBI. Benzoatoacetanilide system 30 °C

1 Acid

2. 22 PBI

3. Cu(II)+22 PBI (1:1)

4. Benzoatoacetanilide

5. Cu(II)+22PBI+Benzoatoacetanilide (1:1:1)

Table III 14

$N = 0.2M \quad V^{o} = 50\ ml \quad T_{A}^{o} = 0.001M$

$E^{o} = 0.02M \quad I = 0.2M \quad T_{M}^{o} = 0.001M \quad t = 30\ ^{o}C$

Acid		A^{3}		$Cu(II) + A^{3}$	
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	2.30	3.00	2.20
4.00	2.50	4.00	2.80	4.00	2.50
4.50	2.80	4.50	3.05	4.50	2.80
4.60	2.95	4.60	3.25	4.60	2.95
4.70	3.20	4.70	3.50	4.70	3.25
4.80	3.50	4.80	3.85	4.80	3.50
4.85	3.70	4.90	4.40	4.90	3.95
4.90	3.95	4.95	4.85	4.95	4.40
4.94	4.25	5.00	6.25	5.00	5.85
4.96	4.50	5.01	8.25	5.02	6.00
4.98	4.75	5.04	9.10	5.05	6.25
5.00	7.25	5.07	9.75	5.10	6.50
5.01	8.50	5.10	10.20	5.20	7.10
5.04	9.25			5.30	8.00
5.07	9.75				
5.10	10.30				

Table III 15

N = 0.2M V^{o} = 50 ml T_A^o = 0.001M T_L^o = 0.001M

E^{o} = 0.02M I = 0.2M T_M^o = 0.001M t = 30 °C

L^5		$Cu(II) + A^3 + L^5$		L^6		$Cu(II) + A^3 + L^6$	
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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.95
4.95	4.40	4.95	4.40	4.95	4.40	4.95	4.40
5.00	7.50	5.00	4.70	5.00	6.75	5.00	4.90
5.02	8.25	5.05	5.10	5.02	7.35	5.05	5.30
5.05	8.50	5.10	5.60	5.05	7.70	7.10	5.80
5.10	8.90	5.15	6.10	5.10	8.20	5.15	6.25
5.20	9.50	5.20	6.60	5.20	9.10	5.20	6.75
5.30	9.90	5.30	8.00			5.30	7.90

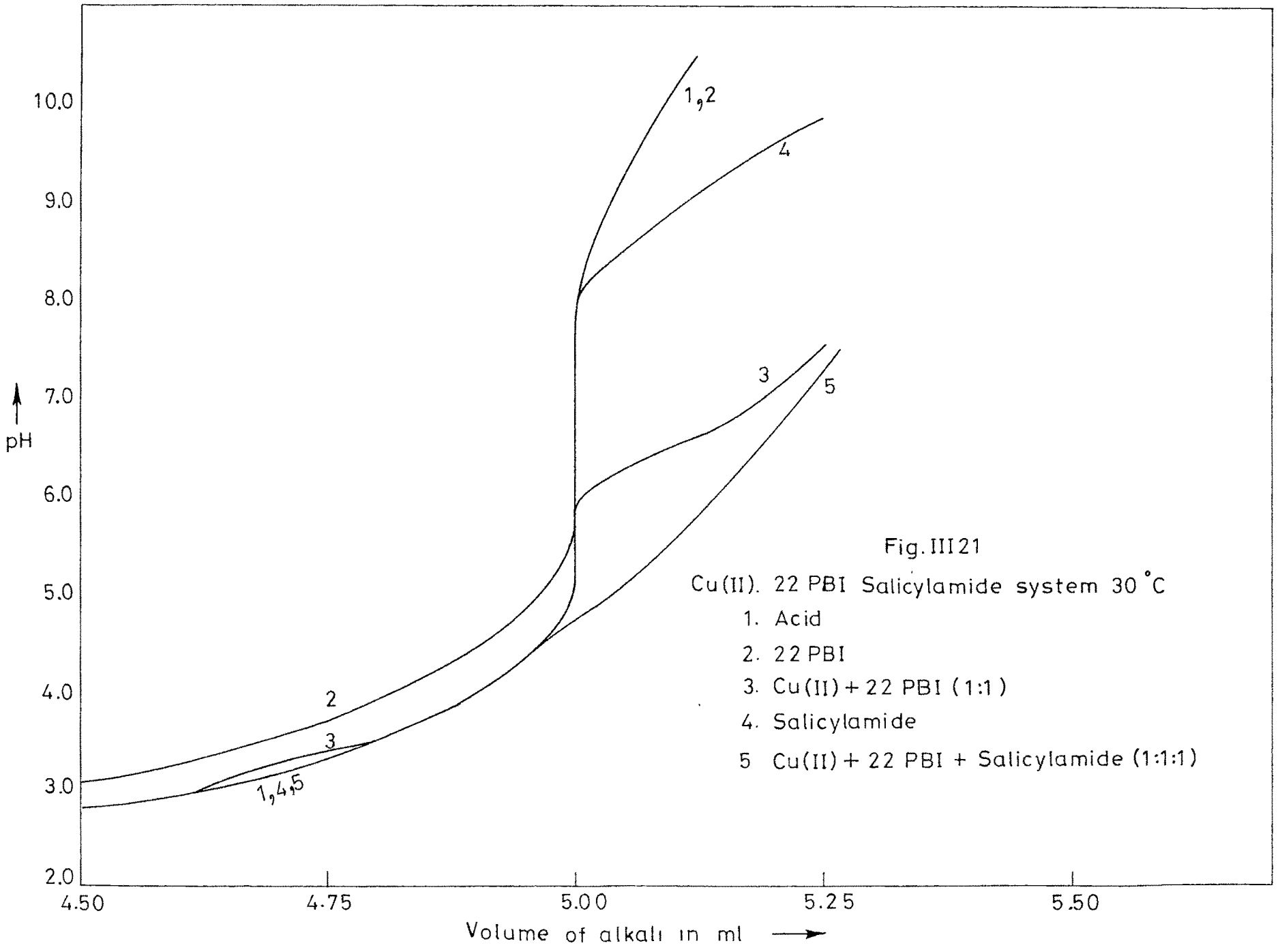


Fig. III 21

Cu(II). 22 PBI Salicylamide system 30 °C

1. Acid
2. 22 PBI
3. Cu(II) + 22 PBI (1:1)
4. Salicylamide
5. Cu(II) + 22 PBI + Salicylamide (1:1:1)

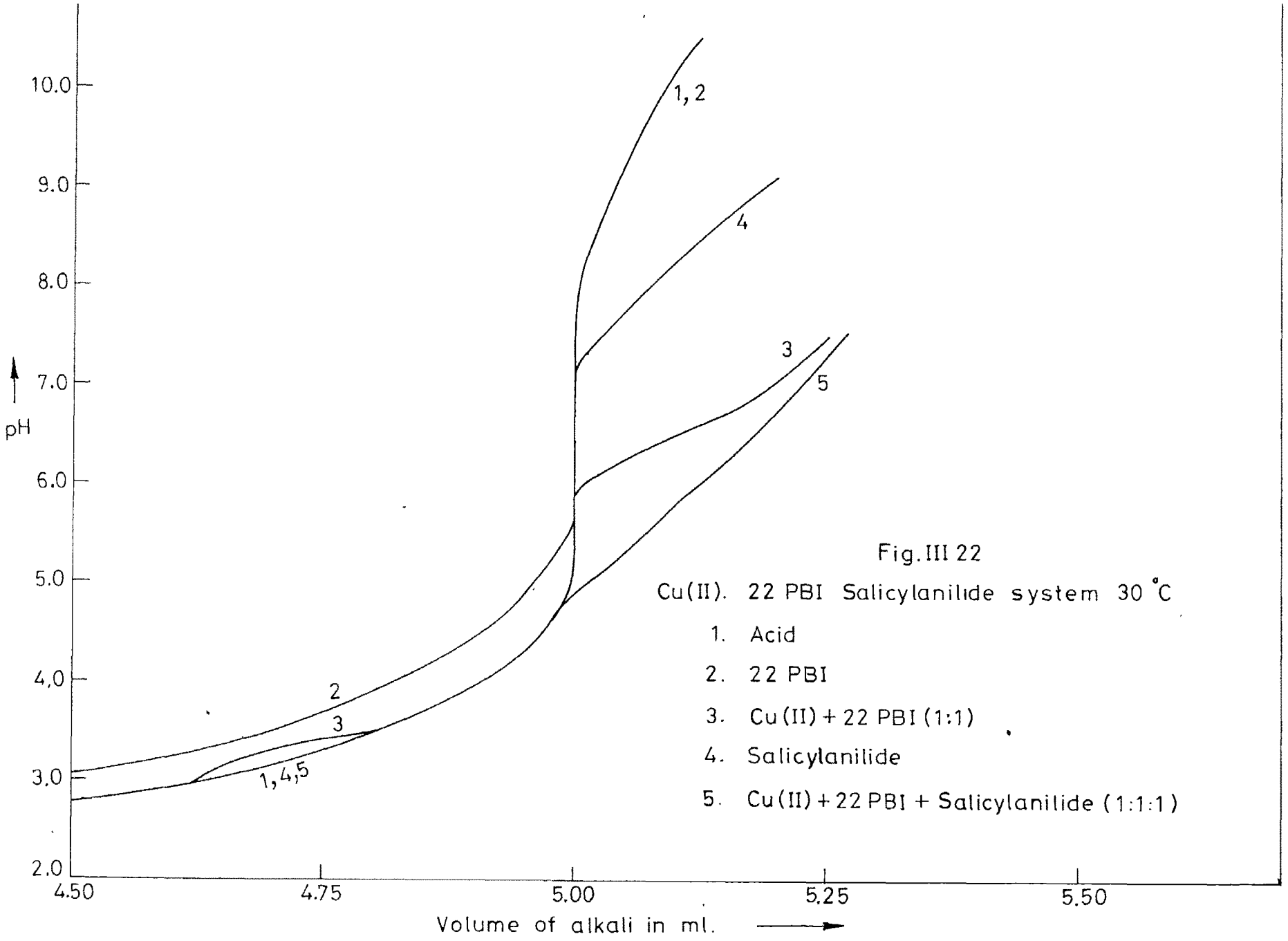


Fig. III 22

Cu(II). 22 PBI Salicylanilide system 30 °C

1. Acid
2. 22 PBI
3. Cu(II) + 22 PBI (1:1)
4. Salicylanilide
5. Cu(II) + 22 PBI + Salicylanilide (1:1:1)

Table III 16

$N = 0.2M$ $V^o = 50$ ml $T_A^o = 0.001M$ $T_L^o = 0.001M$

$E^o = 0.02M$ $I = 0.2M$ $T_M^o = 0.001M$ $t = 30\ ^oC$

L^7		$Cu(II) + A^3 + L^7$		L^8		$Cu(II) + A^3 + L^8$	
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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.95
4.95	4.40	4.95	4.40	4.95	4.40	4.95	4.40
5.00	6.00	5.00	4.60	5.00	6.20	5.00	4.60
5.02	7.00	5.05	5.00	5.02	6.55	5.05	4.95
5.05	7.40	5.10	5.50	5.05	6.90	5.10	5.35
5.10	7.95	5.15	5.95	5.10	7.45	5.15	5.85
5.20	8.85	5.20	6.50	5.20	8.40	5.20	6.45
5.30	9.50	5.30	7.50	5.30	8.60	5.30	7.70

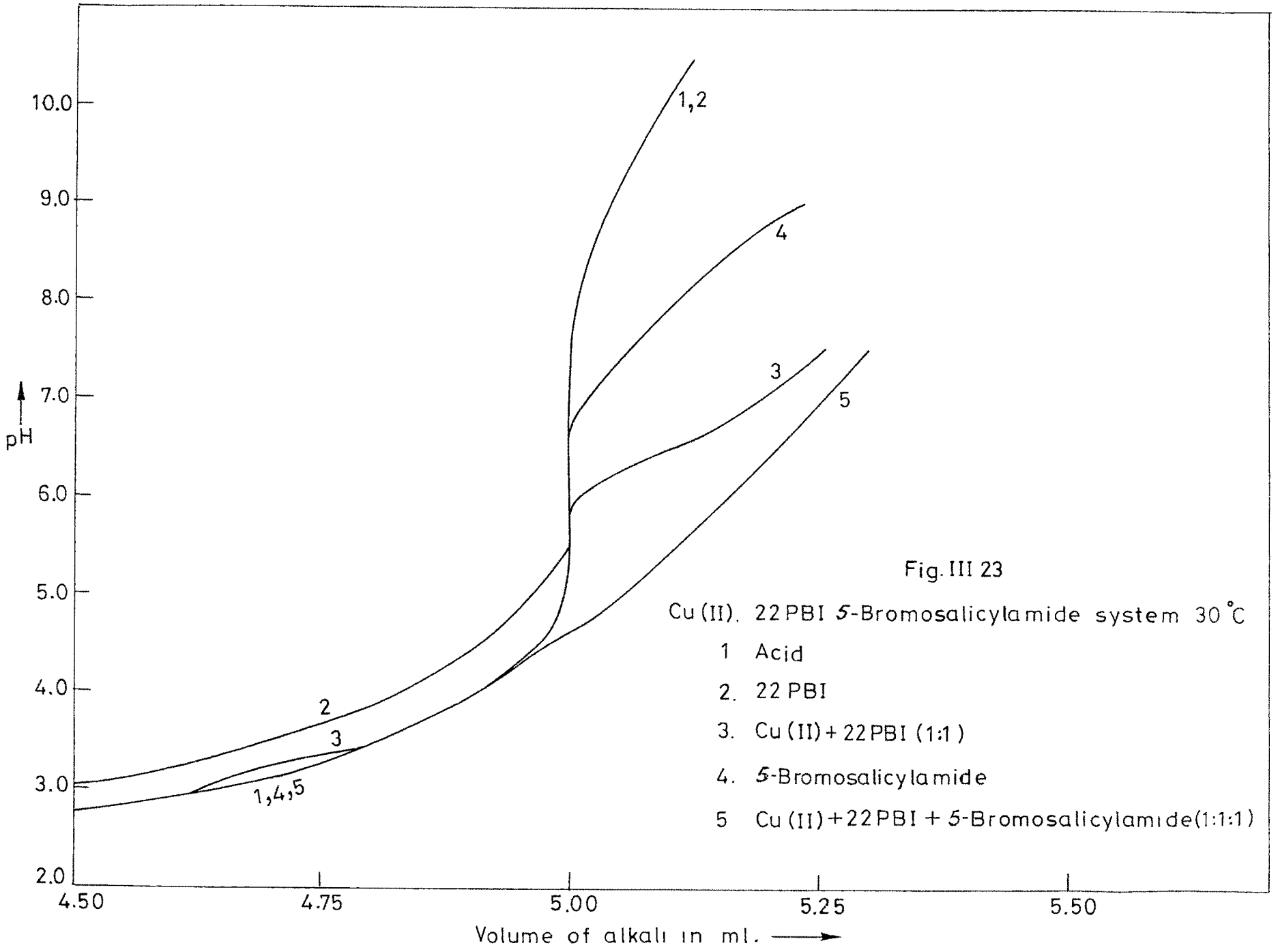


Fig. III 23

Cu (II). 22 PBI 5-Bromosalicylamide system 30 °C

1 Acid

2. 22 PBI

3. Cu (II) + 22 PBI (1:1)

4. 5-Bromosalicylamide

5 Cu (II) + 22 PBI + 5-Bromosalicylamide (1:1:1)

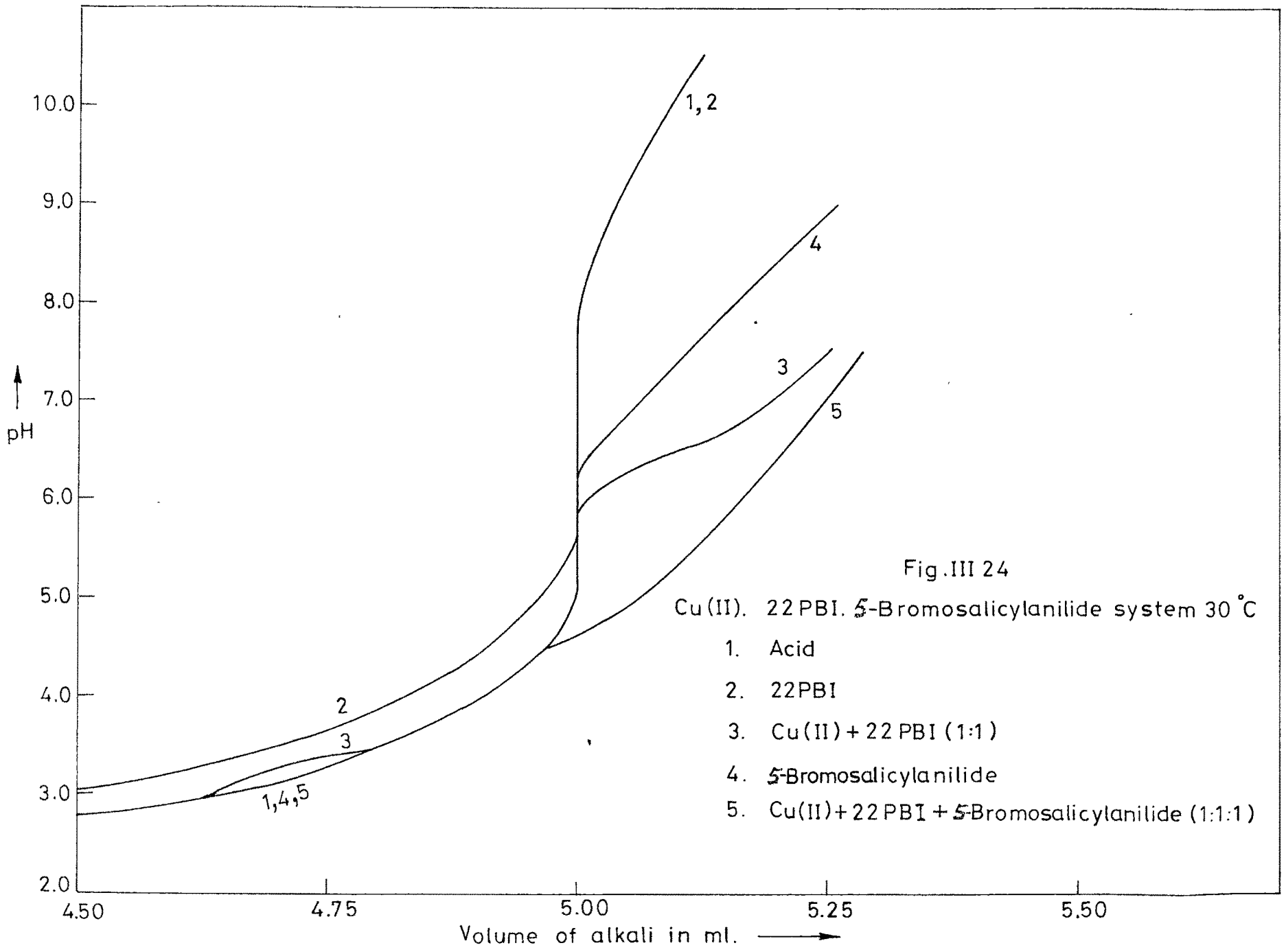


Fig. III 24

Cu(II). 22 PBI. 5-Bromosalicylanilide system 30 °C

1. Acid
2. 22PBI
3. Cu(II) + 22 PBI (1:1)
4. 5-Bromosalicylanilide
5. Cu(II) + 22 PBI + 5-Bromosalicylanilide (1:1:1)

Table III 17

$N = 0.2M \quad V^{o} = 50\ ml \quad T_{A}^{o} = 0.001M$

$E^{o} = 0.02M \quad I = 0.2M \quad T_{M}^{o} = 0.001M \quad t = 30\ ^{o}C$

Acid		A^{4}		Cu(II) + A^{4}	
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	2.00	1.00	1.90
2.00	2.00	2.00	2.20	2.00	2.00
3.00	2.20	3.00	2.40	3.00	2.20
4.00	2.50	4.00	2.70	4.00	2.50
4.50	2.80	4.20	2.90	4.50	2.80
4.60	2.95	4.40	3.00	4.60	2.95
4.70	3.20	4.50	3.15	4.70	3.20
4.80	3.50	4.60	3.55	4.80	3.75
4.85	3.70	4.65	3.95	4.90	4.24
4.90	3.95	4.70	4.60	4.95	4.50
4.94	4.25	4.75	7.00	5.00	6.15
4.96	4.50	4.80	7.95	5.01	6.30
4.98	4.75	4.85	8.40	5.03	6.40
5.00	7.25	4.90	8.80	5.05	6.50
5.01	8.50	4.95	9.20	5.10	6.80
5.04	9.25	5.00	9.55	5.20	7.55
5.07	9.75	5.05	9.80	5.30	8.60
5.10	10.20	5.10	10.20		

Table III 18

$N = 0.2M$ $V^o = 50$ ml $T_A^o = 0.001M$ $T_L^o = 0.001M$

$E^o = 0.02M$ $I = 0.2M$ $T_M^o = 0.001M$ $t = 30\ ^oC$

L^1		$Cu(II) + A^4 + L^1$		L^2		$Cu(II) + A^4 + L^2$	
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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.95
4.95	4.40	4.95	4.40	4.95	4.40	4.95	4.40
5.00	7.60	5.00	5.00	5.00	7.80	5.00	5.10
5.02	8.50	5.05	5.50	5.02	8.50	5.05	5.60
5.05	9.00	5.15	5.95	5.05	9.00	5.10	6.05
5.10	9.50	5.20	6.50	5.10	9.55	5.15	6.45
5.20	10.40	5.30	7.70	5.20	10.65	5.20	6.80
		5.40	9.20			5.30	8.00

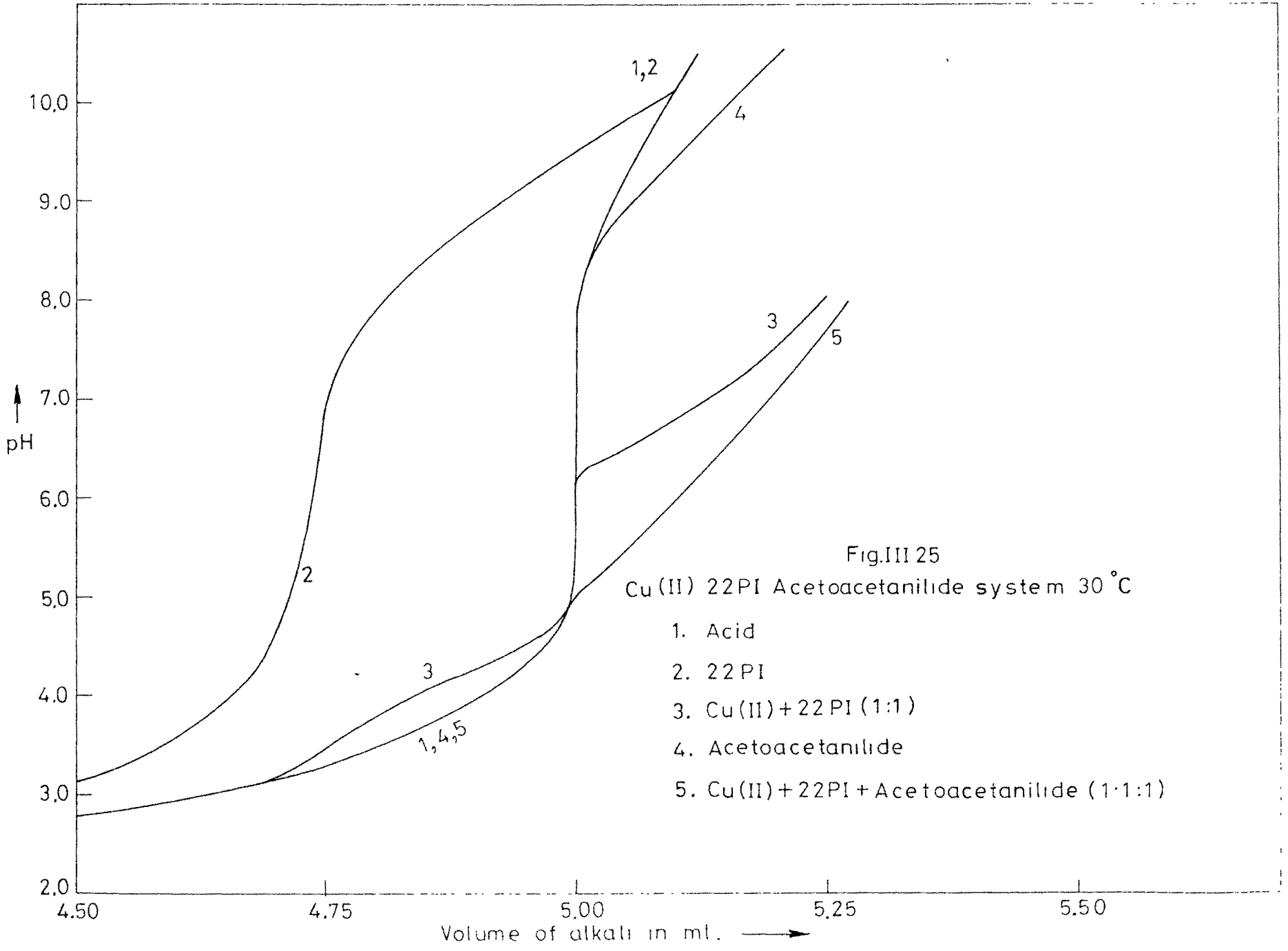


Fig.III 25

Cu(II) 22PI Acetoacetanilide system 30 °C

1. Acid
2. 22PI
3. Cu(II)+22PI (1:1)
4. Acetoacetanilide
5. Cu(II)+22PI+Acetoacetanilide (1:1:1)

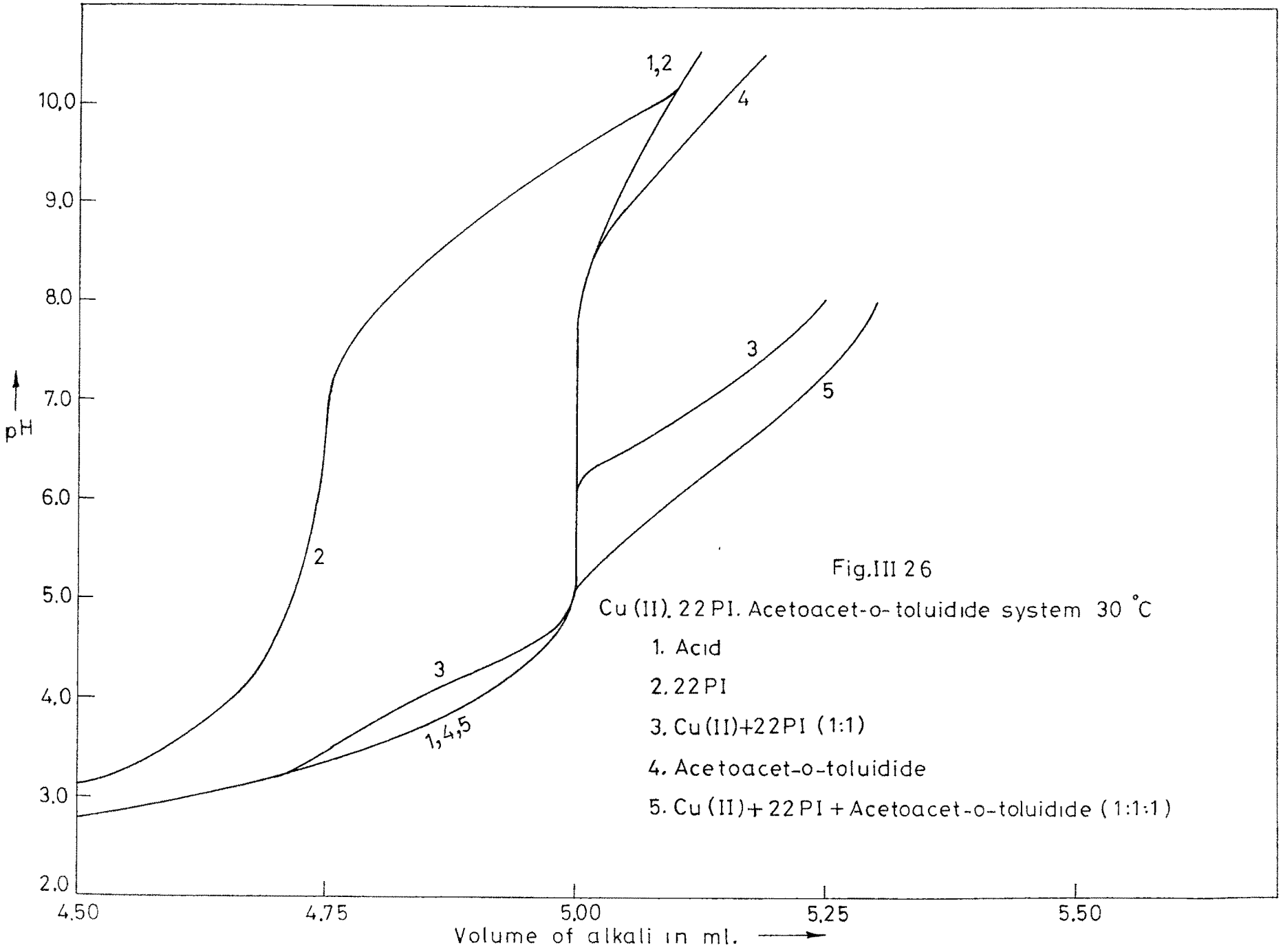


Fig.III 26

Cu (II). 22 PI. Acetoacet-o-toluidide system 30 °C

1. Acid
2. 22 PI
3. Cu (II)+22 PI (1:1)
4. Acetoacet-o-toluidide
5. Cu (II)+ 22 PI + Acetoacet-o-toluidide (1:1:1)

Table III 19

$N = 0.2M$ $V^o = 50$ ml $T_A^o = 0.001M$ $T_L^o = 0.001M$

$E^o = 0.02M$ $I = 0.2M$ $T_M^o = 0.001M$ $t = 30\ ^oC$

L^3		$Cu(II) + A^4 + L^3$		L^4		$Cu(II) + A^4 + L^4$	
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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.95
4.95	4.40	4.95	4.40	4.95	4.40	4.95	4.40
5.00	7.90	5.00	5.20	5.00	7.50	5.00	4.70
5.02	8.40	5.05	5.60	5.02	8.40	5.05	4.95
5.05	8.85	5.10	6.00	5.05	8.85	5.10	5.30
5.10	9.55	5.15	6.50	5.10	9.45	5.15	5.75
5.20	10.70	5.20	7.00	5.20	10.30	5.20	6.30
		5.30	8.25			5.30	8.20

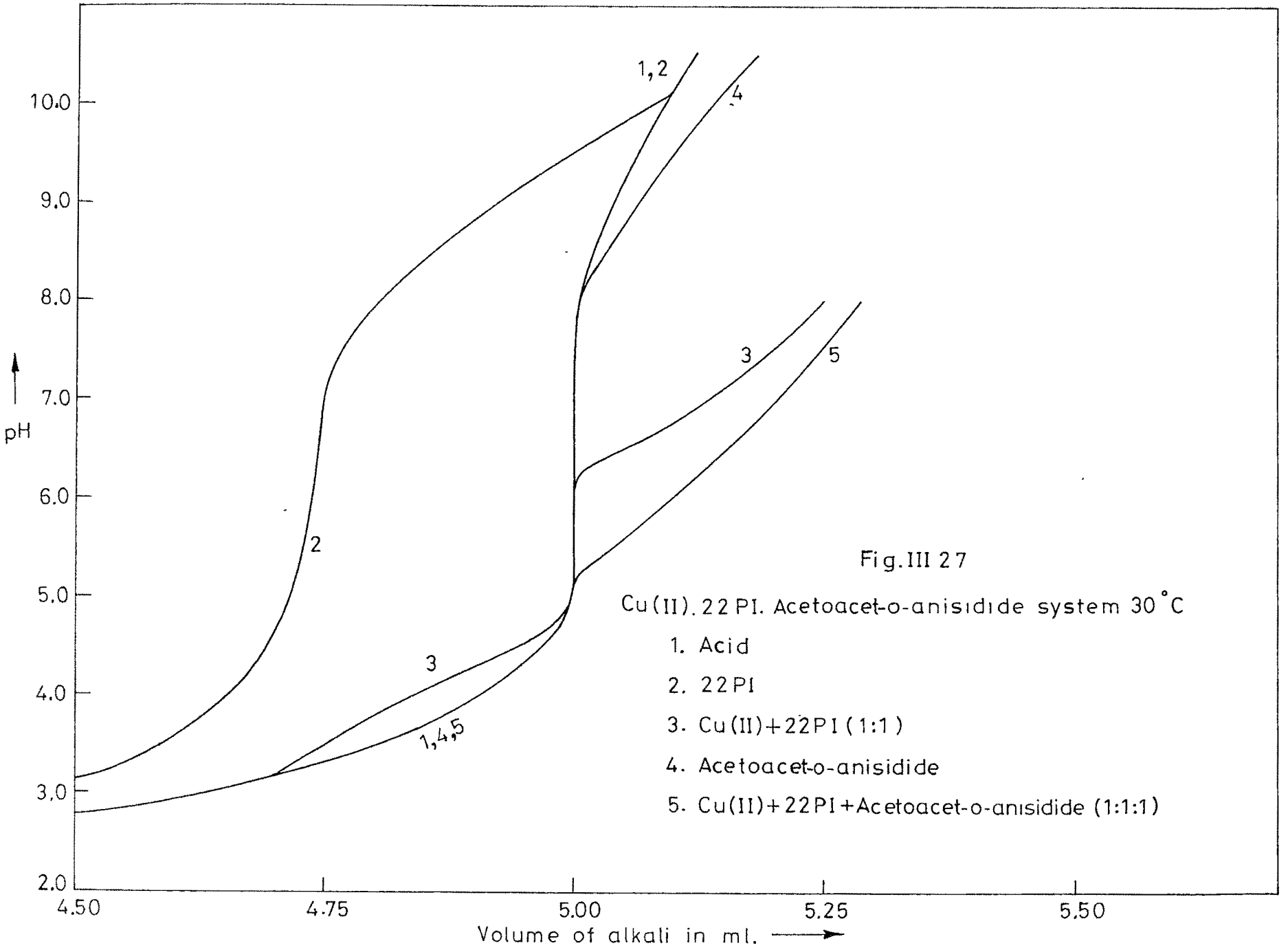


Fig. III 27

Cu(II). 22 PI. Acetoacet-o-anisidide system 30 °C

1. Acid
2. 22PI
3. Cu(II)+22PI (1:1)
4. Acetoacet-o-anisidide
5. Cu(II)+22PI+Acetoacet-o-anisidide (1:1:1)

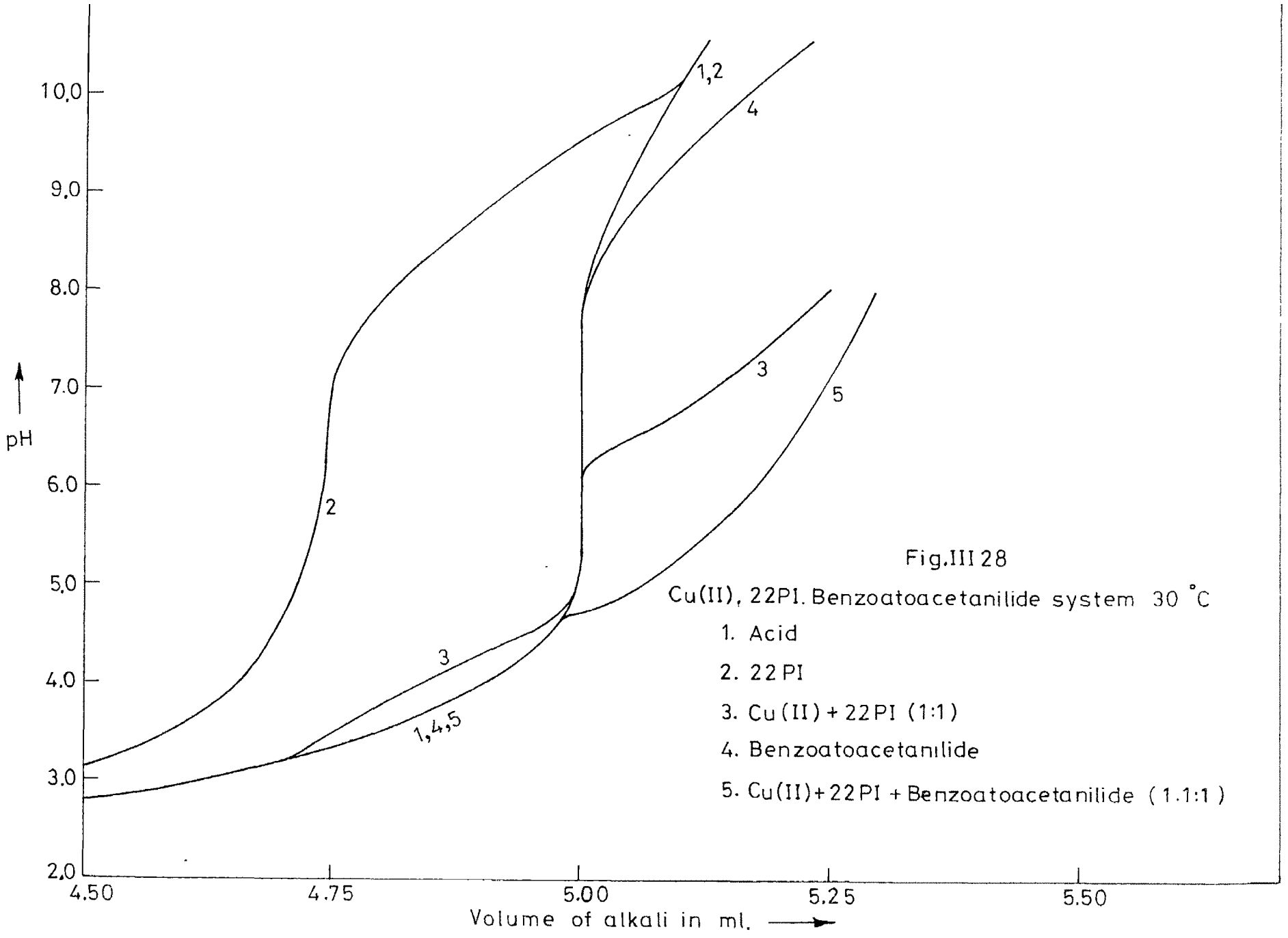


Fig.III 28

Cu(II), 22PI. Benzoatoacetanilide system 30 °C

1. Acid
2. 22 PI
3. Cu (II) + 22PI (1:1)
4. Benzoatoacetanilide
5. Cu(II)+22PI + Benzoatoacetanilide (1.1:1)

Table III 20

$N = 0.2M$ $V^o = 50$ ml $T_A^o = 0.001M$ $T_L^o = 0.001M$

$E^o = 0.02M$ $I = 0.2M$ $T_M^o = 0.001M$ $t = 30\ ^oC$

L^5 $Cu(II) + A^4 + L^5$ L^6 $Cu(II) + A^4 + L^6$

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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.95
4.95	4.40	4.95	4.40	4.95	4.40	4.95	4.40
5.00	7.50	5.00	5.15	5.00	6.75	5.00	5.25
5.02	8.25	5.05	5.80	5.02	7.35	5.05	5.90
5.05	8.50	5.10	6.40	5.05	7.70	5.10	6.70
5.10	8.90	5.15	6.90	5.10	8.20	5.15	7.75
5.20	9.50	5.20	7.50	5.20	9.10	5.20	9.00
5.30	9.90	5.25	8.40				

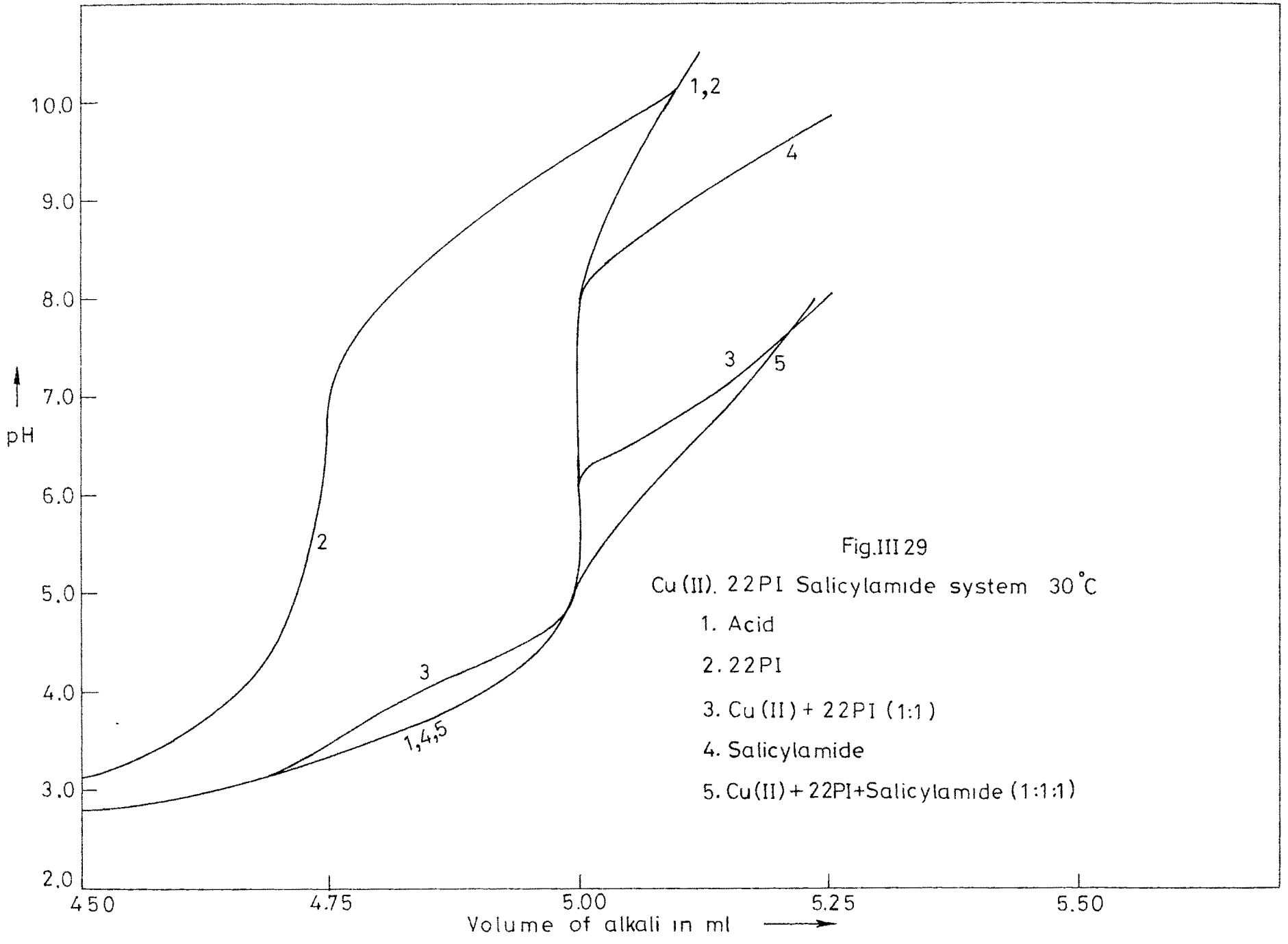


Fig.III 29

Cu (II). 22PI Salicylamide system 30 °C

1. Acid
2. 22PI
3. Cu (II) + 22PI (1:1)
4. Salicylamide
5. Cu(II) + 22PI+Salicylamide (1:1:1)

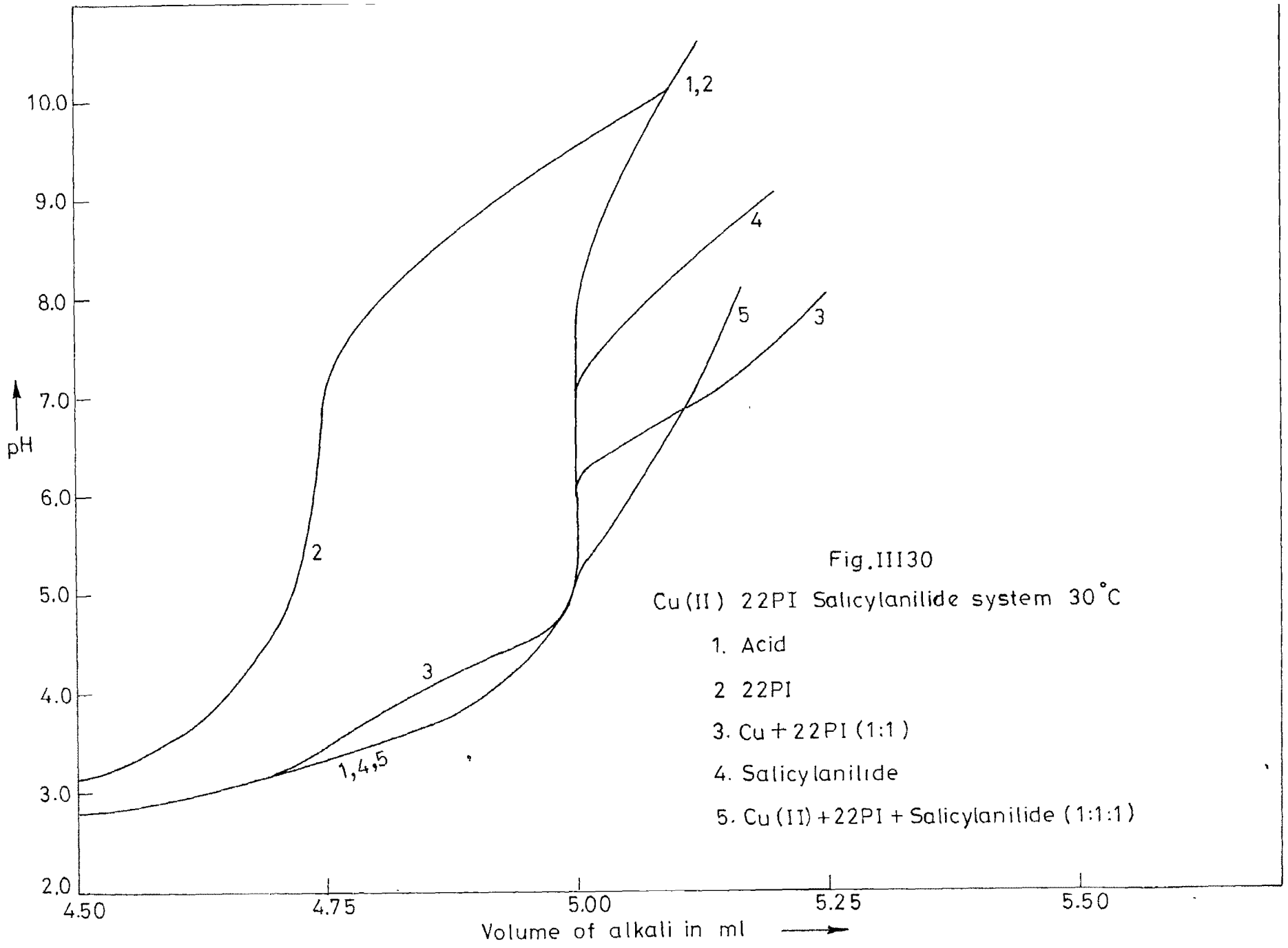


Fig. III30

Cu(II) 22PI Salicylanilide system 30°C

1. Acid
2. 22PI
3. Cu + 22PI (1:1)
4. Salicylanilide
5. Cu (II) + 22PI + Salicylanilide (1:1:1)

Table III 21

$N = 0.2M$ $V^o = 50$ ml $T_A^o = 0.001M$ $T_L^o = 0.001M$

$E^o = 0.02M$ $I = 0.2M$ $T_M^o = 0.001M$ $t = 30\ ^oC$

L^7		$Cu(II) + A^4 + L^7$		L^8		$Cu(II) + A^4 + L^8$	
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
4.70	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	3.50
4.90	3.95	4.90	3.95	4.90	3.95	4.90	3.95
4.95	4.40	4.95	4.40	4.95	4.40	4.95	4.40
5.00	6.00	5.00	5.30	5.00	6.20	5.00	5.50
5.02	7.00	5.05	5.80	5.02	6.55	5.05	6.00
5.05	7.40	5.10	6.40	5.05	6.90	5.10	6.55
5.10	7.95	5.15	7.20	5.10	7.45	5.15	7.20
5.20	8.85	5.20	8.50	5.20	8.40	5.20	8.00
5.30	9.50			5.30	9.60		

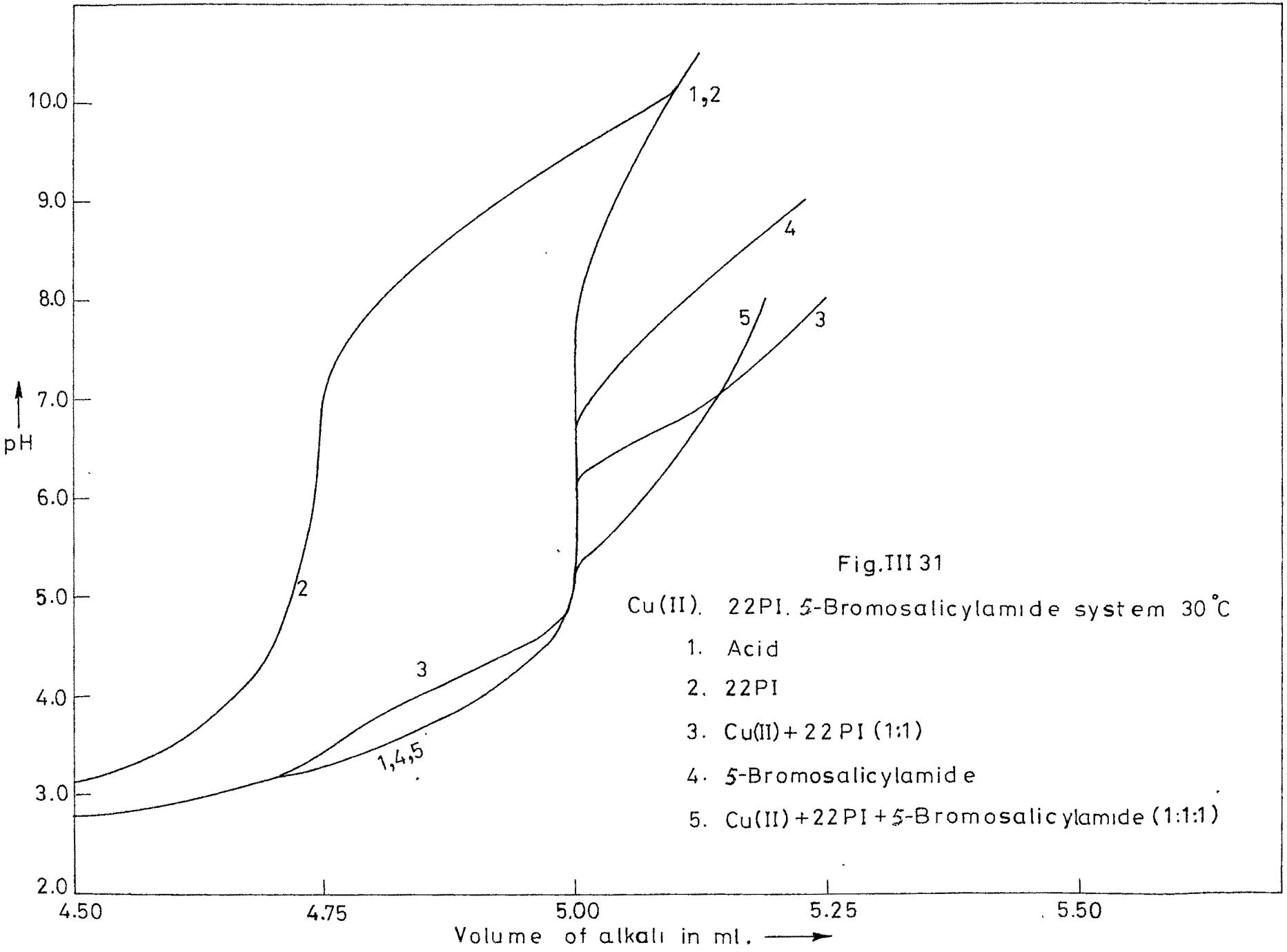


Fig.III 31

Cu(II). 22PI. 5-Bromosalicylamide system 30 °C

1. Acid
2. 22PI
3. Cu(II) + 22 PI (1:1)
4. 5-Bromosalicylamide
5. Cu(II) + 22PI + 5-Bromosalicylamide (1:1:1)

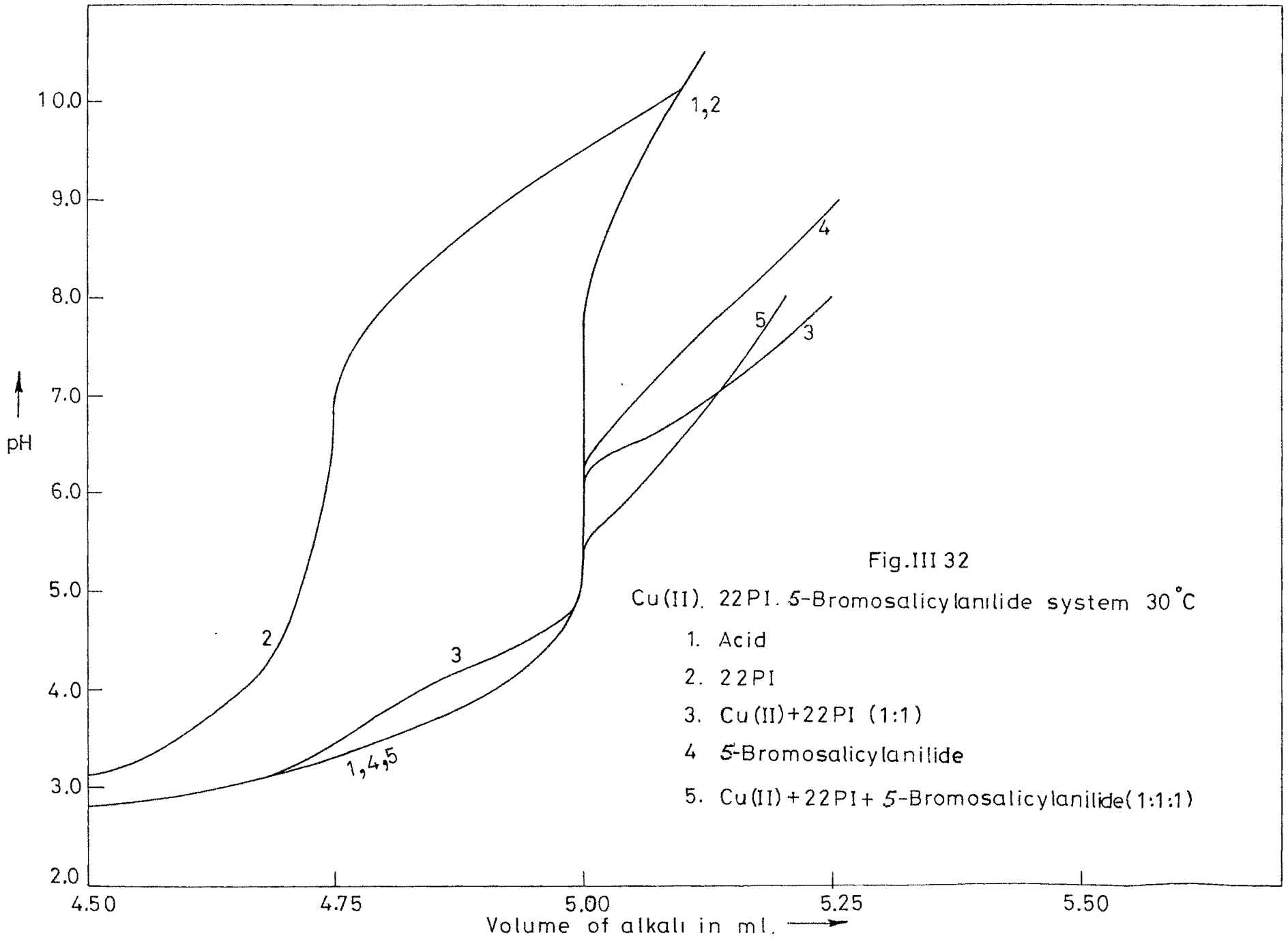


Fig.III 32

Cu(II). 22PI. 5-Bromosalicylanilide system 30 °C

1. Acid
2. 22PI
3. Cu(II)+22PI (1:1)
4. 5-Bromosalicylanilide
5. Cu(II)+22PI+ 5-Bromosalicylanilide(1:1:1)

Table III 22

B, $\bar{n}_H$, $\bar{n}$, log $\left[(1 - \bar{n})/\bar{n}\right]$ pL and pL - log $\left[(1 - \bar{n})/\bar{n}\right]$ data for Cu(II) + 2,2'-dipyridyl + Acetoacetanilide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
4.40	1.000	4.950	5.090	0.280	0.410	10.084	9.674
4.50	1.000	4.960	5.120	0.320	0.327	10.009	9.682
4.60	1.000	4.970	5.150	0.360	0.250	9.935	9.685
4.70	1.000	4.980	5.180	0.400	0.976	9.864	9.688
4.80	1.000	4.990	5.210	0.440	0.105	9.794	9.689
4.90	1.000	4.995	5.235	0.480	0.035	9.276	9.691
5.00	1.000	4.995	5.260	0.530	$\bar{1}$.948	9.670	9.722
5.10	1.000	5.000	5.280	0.560	$\bar{1}$.895	9.599	9.704
5.20	1.000	5.000	5.310	0.620	$\bar{1}$.787	9.563	9.776
5.30	1.000	5.000	5.330	0.660	$\bar{1}$.712	9.511	9.799

Average value of log K^{CuA}_{CuAL} = 9.71

Table III 23

B, $\bar{n}_H$, $\bar{n}$, log $\left[(1 - \bar{n})/\bar{n}\right]$ pL and pL - log $\left[(1 - \bar{n})/\bar{n}\right]$ data for Cu(II) + 2,2'-dipyridyl + Acetoacet-o-toluidide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
4.50	1.000	4.960	5.120	0.320	0.327	9.709	9.382
4.60	1.000	4.970	5.150	0.360	0.250	9.635	9.385
4.70	1.000	4.980	5.170	0.380	0.213	9.549	9.336
4.80	1.000	4.990	5.195	0.410	0.158	9.471	9.313
4.90	1.000	4.995	5.220	0.450	0.087	9.402	9.315
5.00	1.000	4.995	5.240	0.490	0.018	9.335	9.317
5.10	1.000	5.000	5.260	0.520	$\bar{1}$.965	9.261	9.296
5.20	1.000	5.000	5.270	0.540	$\bar{1}$.930	9.180	9.250
5.30	1.000	5.000	5.300	0.600	$\bar{1}$.824	9.141	9.317
5.40	1.000	5.000	5.320	0.640	$\bar{1}$.750	9.087	9.337

Average value of log K^{CuA}_{CuAL} = 9.33

Table III 24

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and $pL - \log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2,2'-dipyridyl + Acetoacet-o-anisidide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
4.00	1.000	4.900	5.045	0.290	0.389	10.290	9.901
4.10	1.000	4.915	5.085	0.340	0.288	10.222	9.934
4.20	1.000	4.930	5.120	0.380	0.213	10.149	9.936
4.30	1.000	4.940	5.150	0.420	0.140	10.078	9.938
4.40	1.000	4.950	5.180	0.460	0.070	10.009	9.939
4.50	1.000	4.960	5.210	0.500	0.000	9.943	9.943
4.60	1.000	4.970	5.240	0.540	$\bar{1}$.930	9.879	9.949
4.70	1.000	4.980	5.260	0.560	$\bar{1}$.895	9.799	9.904
4.80	1.000	4.990	5.290	0.600	$\bar{1}$.824	9.741	9.917
4.90	1.000	4.995	5.310	0.630	$\bar{1}$.769	9.675	9.906
5.00	1.000	4.995	5.330	0.670	$\bar{1}$.692	9.624	9.932
5.10	1.000	5.000	5.350	0.700	$\bar{1}$.632	9.566	9.934
5.20	1.000	5.000	5.370	0.740	$\bar{1}$.546	9.528	9.982

Average value of log K^{CuA}_{CuAL} = 9.93

Table III 25

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and $pL - \log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2,2'-dipyridyl + Salicylamide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
5.10	1.000	5.000	5.130	0.260	0.500	7.030	6.530
5.20	1.000	5.000	5.150	0.300	0.368	6.947	6.579
5.30	1.000	5.000	5.170	0.340	0.288	6.872	6.584
5.40	1.000	5.000	5.190	0.380	0.213	6.800	6.587
5.50	1.000	5.000	5.210	0.420	0.140	6.729	6.589
5.60	1.000	5.000	5.230	0.460	0.070	6.660	6.590
5.70	1.000	5.000	5.250	0.500	0.000	6.593	6.593
5.80	1.000	5.000	5.270	0.540	$\bar{1}$.930	6.520	6.590

Average value of log K^{CuA}_{CuAL} = 6.58

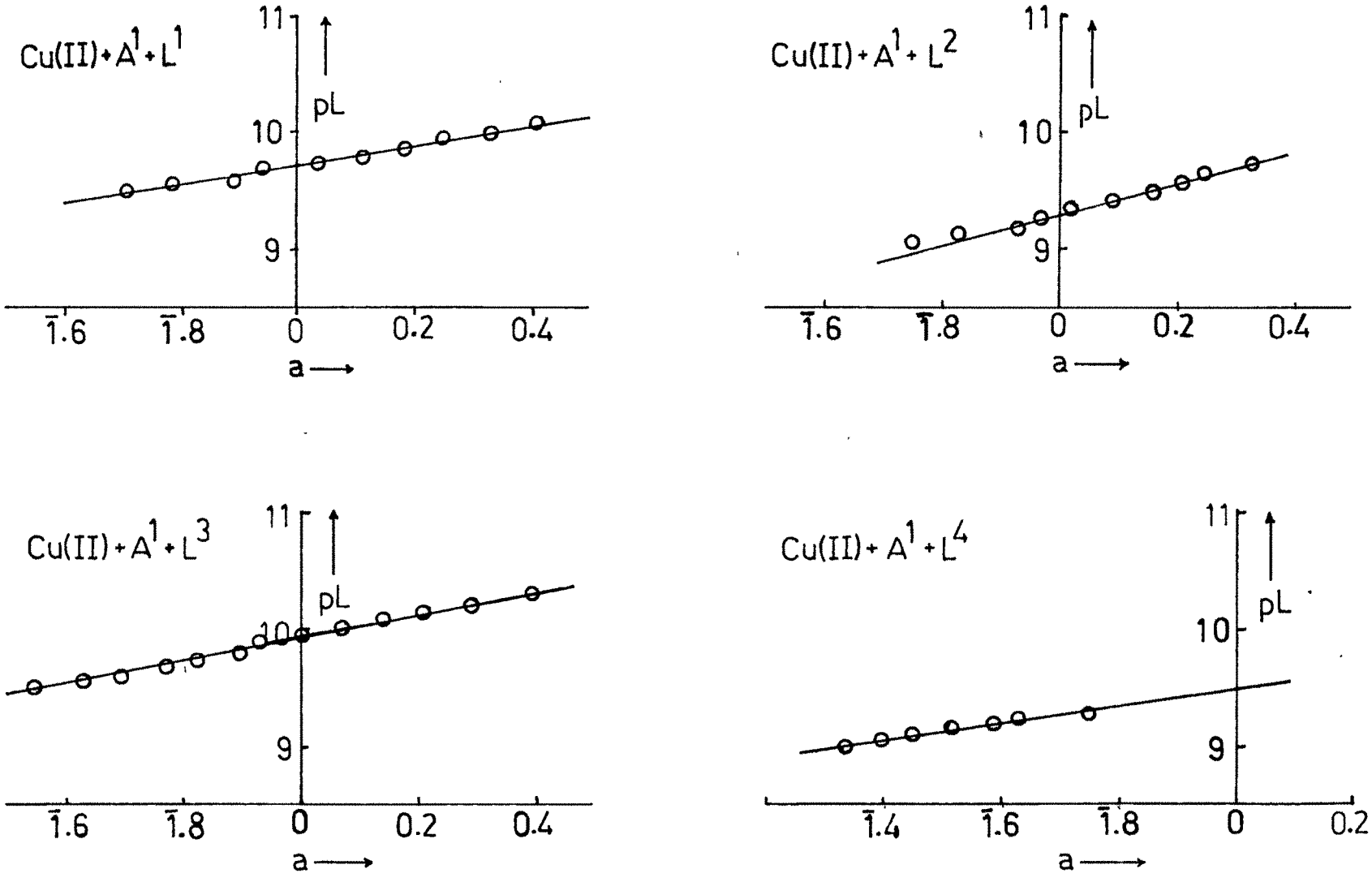

Cu(II)+A¹+L¹
11
10
9
pL
1̄.6
1̄.8
0
0.2
0.4
a
Cu(II)+A¹+L²
11
10
9
pL
1̄.6
1̄.8
0
0.2
0.4
a
Cu(II)+A¹+L³
11
10
9
pL
1̄.6
1̄.8
0
0.2
0.4
a
Cu(II)+A¹+L⁴
11
10
9
pL
1̄.4
1̄.6
1̄.8
0
0.2
a

FIG. III 33

Table III 26

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and pL - $\log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2,2'-dipyridyl + Benzoatoacetanilide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
4.30	1.000	4.940	5.260	0.640	$\bar{1}$.750	9.286	9.536
4.40	1.000	4.950	5.300	0.700	$\bar{1}$.632	9.266	9.634
4.50	1.000	4.960	5.320	0.720	$\bar{1}$.590	9.196	9.606
4.60	1.000	4.970	5.345	0.750	$\bar{1}$.523	9.145	9.622
4.70	1.000	4.980	5.370	0.780	$\bar{1}$.450	9.101	9.651
4.80	1.000	4.990	5.390	0.800	$\bar{1}$.398	9.042	9.644
4.90	1.000	4.995	5.405	0.820	$\bar{1}$.342	8.988	9.646

Average value of $\log K^{CuA}_{CuAL}$ = 9.62

Table III 27

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$ pL and pL - $\log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2,2'-dipyridyl + Salicylanilide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
5.40	1.000	5.000	5.140	0.280	0.410	6.034	5.624
5.50	1.000	5.000	5.160	0.320	0.328	5.959	5.631
5.60	1.000	5.000	5.175	0.350	0.269	5.879	5.610
5.70	1.000	5.000	5.190	0.380	0.213	5.800	5.587
5.80	1.000	5.000	5.210	0.420	0.140	5.729	5.589
5.90	1.000	5.000	5.220	0.440	0.105	5.644	5.539
6.00	1.000	5.000	5.240	0.480	0.034	5.576	5.542
6.10	1.000	5.000	5.255	0.510	$\bar{1}$.983	5.502	5.519

Average value of $\log K^{CuA}_{CuAL}$ = 5.58

Table III 28

B, $\bar{n}_H$, $\bar{n}$, log $\left[(1 - \bar{n})/\bar{n}\right]$ pL and pL - log $\left[(1 - \bar{n})/\bar{n}\right]$ data for Cu(II) + 2,2'-dipyridyl + 5-Bromosalicylamide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
5.20	1.000	5.000	5.160	0.320	0.327	5.909	5.582
5.30	1.000	5.000	5.175	0.350	0.269	5.829	5.560
5.40	1.000	5.000	5.190	0.380	0.213	5.750	5.537
5.50	1.000	5.000	5.205	0.410	0.158	5.671	5.513
5.60	1.000	5.000	5.220	0.440	0.104	5.594	5.490
5.70	1.000	5.000	5.235	0.470	0.052	5.518	5.466
5.80	1.000	5.000	5.250	0.500	0.000	5.443	5.443
5.90	1.000	5.000	5.260	0.520	$\bar{1}$.965	5.361	5.396
6.00	1.000	5.000	5.275	0.550	$\bar{1}$.913	5.266	5.353
6.10	1.000	5.000	5.290	0.580	$\bar{1}$.860	5.219	5.359

Average value of log K^{CuA}_{CuAL} = 5.47

Table III 29

B, $\bar{n}_H$, $\bar{n}$, log $\left[(1 - \bar{n})/\bar{n}\right]$ pL and pL - log $\left[(1 - \bar{n})/\bar{n}\right]$ data for Cu(II) + 2,2'-dipyridyl + 5-Bromosalicylanilide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
5.30	1.000	5.000	5.190	0.380	0.213	5.240	5.027
5.40	1.000	5.000	5.210	0.420	0.140	5.169	5.029
5.50	1.000	5.000	5.225	0.450	0.087	5.092	5.005
5.60	1.000	5.000	5.240	0.480	0.034	5.016	4.982
5.70	1.000	5.000	5.255	0.510	$\bar{1}$.983	4.943	4.960
5.80	1.000	5.000	5.270	0.540	$\bar{1}$.930	4.870	4.940
5.90	1.000	5.000	5.290	0.580	$\bar{1}$.860	4.809	4.950
6.00	1.000	5.000	5.300	0.600	$\bar{1}$.824	4.730	4.907
6.10	1.000	5.000	5.320	0.640	$\bar{1}$.750	4.676	4.927

Average value of log K^{CuA}_{CuAL} = 4.97

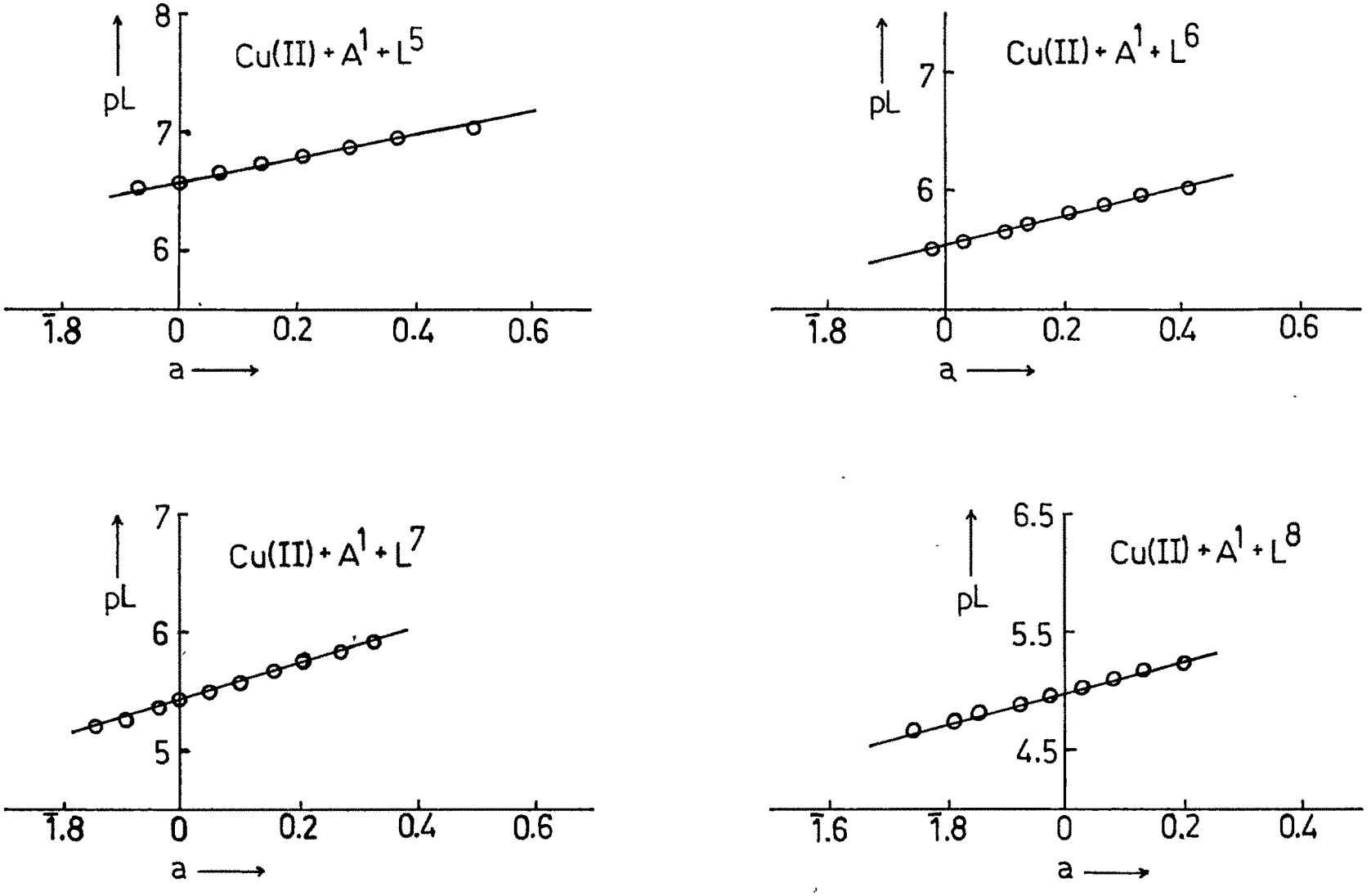

Cu(II) + A1 + L5
pL
8
7
6
1̄.8
0
0.2
0.4
0.6
a
Cu(II) + A1 + L6
pL
7
6
1̄.8
0
0.2
0.4
0.6
a
Cu(II) + A1 + L7
pL
7
6
5
1̄.8
0
0.2
0.4
0.6
a
Cu(II) + A1 + L8
pL
6.5
5.5
4.5
1̄.6
1̄.8
0
0.2
0.4
a

FIG. III 34

Table III 30

B, $\bar{n}_H$, $\bar{n}$, log $[(1 - \bar{n})/\bar{n}]$, pL and pL - log $[(1 - \bar{n})/\bar{n}]$ data for Cu(II) + 1,10-phenanthroline + Acetoacetanilide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
5.30	1.000	5.000	5.085	0.340	0.288	9.523	9.235
5.40	1.000	5.000	5.095	0.380	0.213	9.450	9.237
5.50	1.000	5.000	5.105	0.420	0.140	9.379	9.239
5.60	1.000	5.000	5.115	0.460	0.070	9.310	9.240
5.70	1.000	5.000	5.125	0.500	0.000	9.243	9.243
5.80	1.000	5.000	5.135	0.540	$\bar{1}$.930	9.170	9.240
5.90	1.000	5.000	5.145	0.580	$\bar{1}$.860	9.119	9.259
6.00	1.000	5.000	5.155	0.620	$\bar{1}$.787	9.063	9.276
6.10	1.000	5.000	5.160	0.640	$\bar{1}$.756	8.986	9.230
6.20	1.000	5.000	5.170	0.680	$\bar{1}$.673	8.938	9.265

Average value of log K^{CuA}_{CuAL} = 9.25

Table III 31

B, $\bar{n}_H$, $\bar{n}$, log $[(1 - \bar{n})/\bar{n}]$ pL and pL - log $[(1 - \bar{n})/\bar{n}]$ data for Cu(II) + 1,10-phenanthroline + Acetoacet-o-anisidide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
5.30	1.000	5.000	5.105	0.420	0.140	9.380	9.240
5.40	1.000	5.000	5.115	0.460	0.070	9.310	9.240
5.50	1.000	5.000	5.125	0.500	0.000	9.243	9.243
5.60	1.000	5.000	5.135	0.540	$\bar{1}$.930	9.180	9.250
5.70	1.000	5.000	5.145	0.580	$\bar{1}$.860	9.119	9.259
5.80	1.000	5.000	5.155	0.620	$\bar{1}$.787	9.063	9.276
5.90	1.000	5.000	5.165	0.660	$\bar{1}$.712	9.011	9.299
6.00	1.000	5.000	5.175	0.700	$\bar{1}$.632	8.966	9.334

Average value of log K^{CuA}_{CuAL} = 9.27

Table III 32

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and $pL - \log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 1,10-phenanthroline + Acetoacet-o-toluidide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
5.20	1.000	5.000	5.070	0.280	0.410	9.285	8.875
5.30	1.000	5.000	5.080	0.320	0.327	9.210	8.883
5.40	1.000	5.000	5.090	0.360	0.250	9.123	8.873
5.50	1.000	5.000	5.100	0.400	0.176	9.064	8.888
5.60	1.000	5.000	5.110	0.440	0.105	8.994	8.889
5.70	1.000	5.000	5.120	0.480	0.034	8.926	8.892
5.80	1.000	5.000	5.130	0.520	$\bar{1}$.965	8.861	8.896
5.90	1.000	5.000	5.140	0.560	$\bar{1}$.895	8.799	8.904
6.00	1.000	5.000	5.150	0.600	$\bar{1}$.824	8.741	8.917
6.10	1.000	5.000	5.155	0.620	$\bar{1}$.788	8.663	8.875
6.20	1.000	5.000	5.165	0.660	$\bar{1}$.712	8.611	8.899
6.30	1.000	5.000	5.170	0.680	$\bar{1}$.673	8.538	8.865

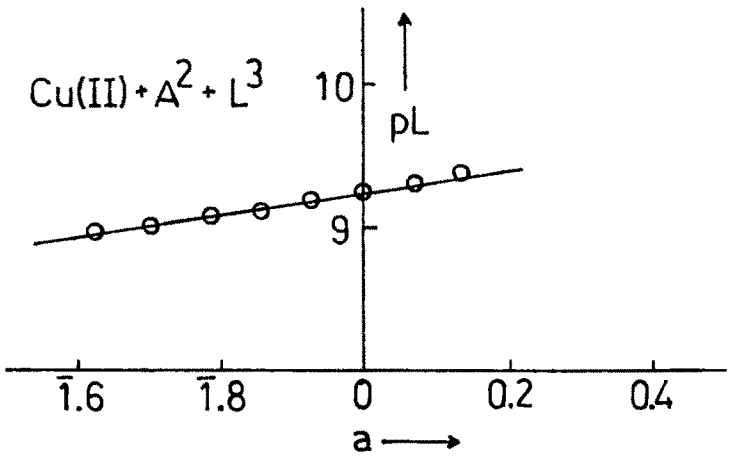
Average value of $\log K^{CuA}_{CuAL}$ = 8.89

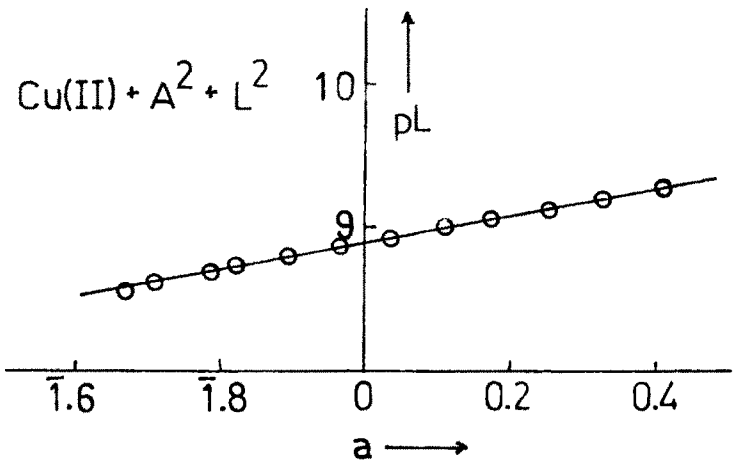
Table III 33

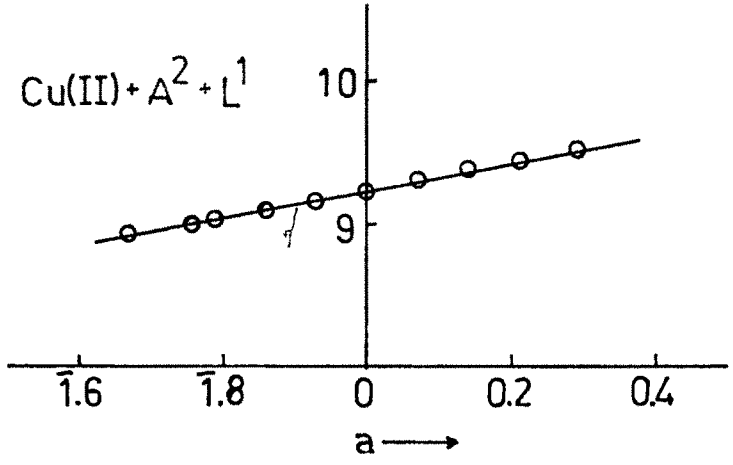
B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and $pL - \log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 1,10-phenanthroline + Salicylamide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
5.40	1.000	5.000	5.070	0.280	0.410	7.035	6.625
5.50	1.000	5.000	5.080	0.320	0.328	6.954	6.626
5.60	1.000	5.000	5.090	0.360	0.250	6.886	6.636
5.70	1.000	5.000	5.100	0.400	0.176	6.814	6.638
5.80	1.000	5.000	5.110	0.440	0.105	6.744	6.639
5.90	1.000	5.000	5.115	0.460	0.070	6.660	6.590
6.00	1.000	5.000	5.125	0.500	0.000	6.593	6.593
6.10	1.000	5.000	5.135	0.540	$\bar{1}$.930	6.530	6.600
6.20	1.000	5.000	5.140	0.560	$\bar{1}$.895	6.449	6.554

Average value of $\log K^{CuA}_{CuAL}$ = 6.61


Cu(II) + A² + L³
10
pL
9
1̄.6
1̄.8
0
0.2
0.4
a


Cu(II) + A² + L²
10
pL
9
1̄.6
1̄.8
0
0.2
0.4
a


Cu(II) + A² + L¹
10
9
1̄.6
1̄.8
0
0.2
0.4
a

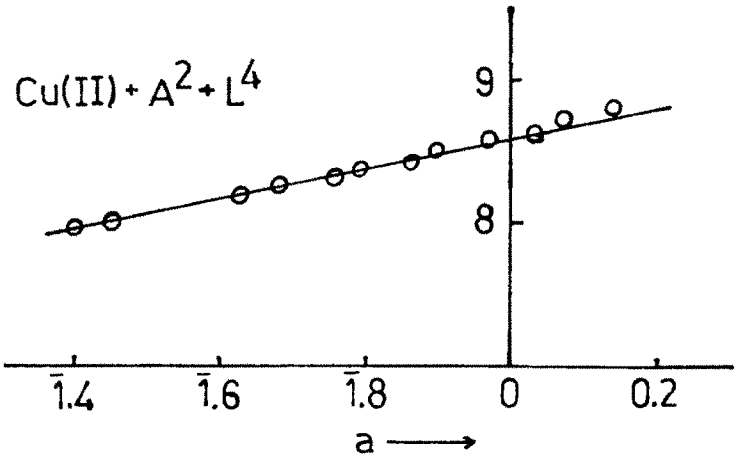

Cu(II) + A² + L⁴
9
8
1̄.4
1̄.6
1̄.8
0
0.2
a

FIG. III 35

Table III 34

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and $pL - \log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 1,10-phenanthroline + Benzoatoacetanilide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
4.90	1.000	4.995	5.100	0.420	0.140	8.779	8.639
5.00	1.000	4.995	5.110	0.460	0.070	8.710	8.640
5.10	1.000	5.000	5.120	0.480	0.034	8.626	8.592
5.20	1.000	5.000	5.130	0.520	$\bar{1}$.965	8.561	8.596
5.30	1.000	5.000	5.140	0.560	$\bar{1}$.895	8.499	8.604
5.40	1.000	5.000	5.145	0.580	$\bar{1}$.860	8.419	8.559
5.50	1.000	5.000	5.155	0.620	$\bar{1}$.787	8.363	8.576
5.60	1.000	5.000	5.160	0.640	$\bar{1}$.756	8.286	8.536
5.70	1.000	5.000	5.170	0.680	$\bar{1}$.673	8.238	8.565
5.80	1.000	5.000	5.175	0.700	$\bar{1}$.632	8.166	8.534
6.10	1.000	5.000	5.195	0.780	$\bar{1}$.450	8.001	8.551
6.20	1.000	5.000	5.200	0.800	$\bar{1}$.398	7.942	8.554

Average value of $\log K^{CuA}_{CuAL}$ = 8.58

Table III 35

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$ pL and $pL - \log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 1,10-phenanthroline + Salicylanilide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
5.50	1.000	5.000	5.050	0.200	0.602	6.189	5.587
5.60	1.000	5.000	5.060	0.240	0.500	6.111	5.611
5.70	1.000	5.000	5.070	0.280	0.410	6.035	5.625
5.80	1.000	5.000	5.080	0.320	0.328	5.960	5.632
5.90	1.000	5.000	5.090	0.360	0.250	5.886	5.636
6.00	1.000	5.000	5.100	0.400	0.176	5.814	5.638
6.10	1.000	5.000	5.115	0.460	0.070	5.760	5.690
6.20	1.000	5.000	5.125	0.500	0.000	5.693	5.693

Average value of $\log K^{CuA}_{CuAL}$ = 5.64

Table III 36

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and $pL - \log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 1,10-phenanthroline + 5-Bromosalicylamide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
5.30	1.000	5.000	5.055	0.220	0.550	6.050	5.500
5.40	1.000	5.000	5.065	0.260	0.454	5.973	5.519
5.50	1.000	5.000	5.070	0.280	0.400	5.885	5.485
5.60	1.000	5.000	5.080	0.320	0.327	5.810	5.483
5.70	1.000	5.000	5.085	0.340	0.288	5.723	5.435
5.80	1.000	5.000	5.090	0.360	0.250	5.636	5.386
5.90	1.000	5.000	5.100	0.400	0.176	5.564	5.388

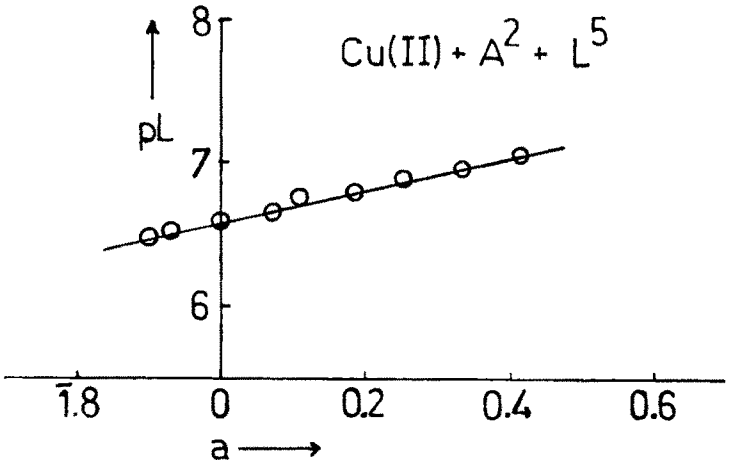
Average value of $\log K^{CuA}_{CuAL} = 5.46$

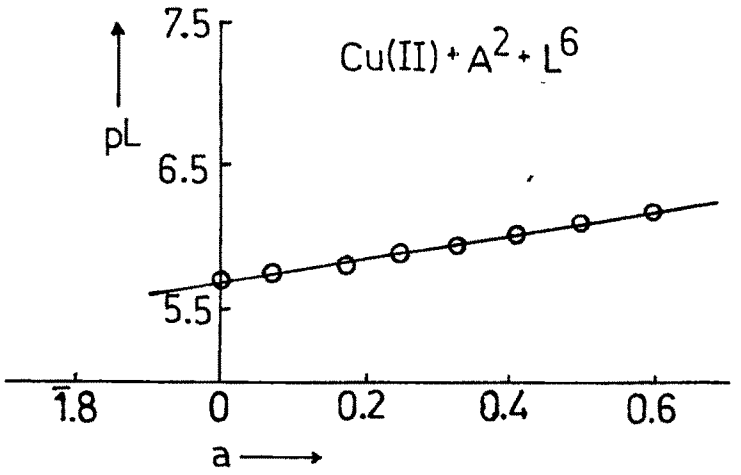
Table III 37

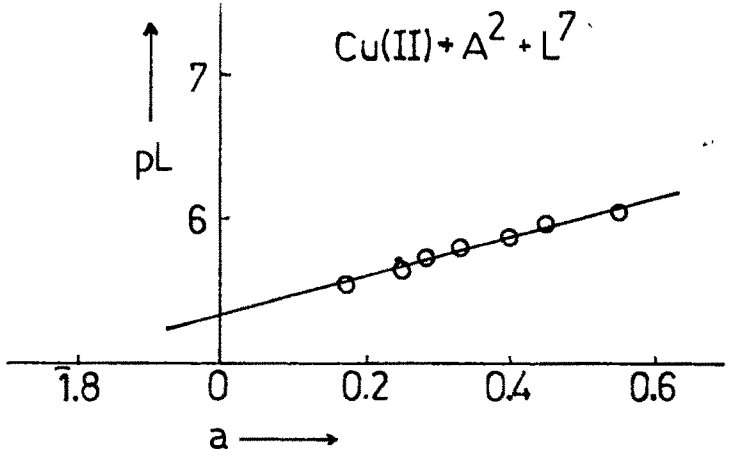
B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and $pL - \log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 1,10-phenanthroline + 5-Bromosalicylanilide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
5.40	1.000	5.000	5.070	0.280	0.410	5.375	4.965
5.50	1.000	5.000	5.075	0.300	0.368	5.287	4.919
5.60	1.000	5.000	5.085	0.340	0.288	5.213	4.925
5.70	1.000	5.000	5.090	0.360	0.250	5.126	4.876
5.80	1.000	5.000	5.100	0.400	0.176	5.054	4.884
5.90	1.000	5.000	5.105	0.420	0.140	4.969	4.799
6.00	1.000	5.000	5.110	0.440	0.105	4.884	4.779
6.10	1.000	5.000	5.120	0.480	0.034	4.816	4.782

Average value of $\log K^{CuA}_{CuAL} = 4.87$


Cu(II) + A2 + L5
pL
8
7
6
1̄.8
0
0.2
0.4
0.6
a


Cu(II) + A2 + L6
pL
7.5
6.5
5.5
1̄.8
0
0.2
0.4
0.6
a


Cu(II) + A2 + L7
pL
7
6
1̄.8
0
0.2
0.4
0.6
a

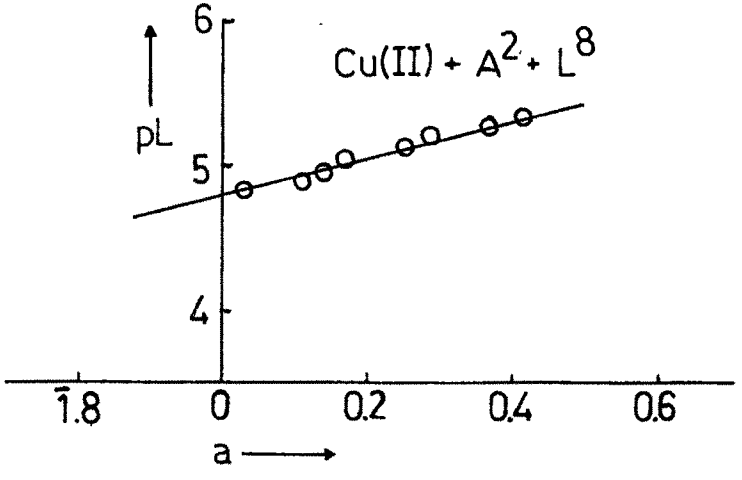

Cu(II) + A2 + L8
pL
6
5
4
1̄.8
0
0.2
0.4
0.6
a

FIG III 36

Table III 38

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and pL - $\log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2-22'-pyridyl)benzimidazole + Acetoacetanilide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
5.00	1.000	4.995	5.155	0.320	0.327	9.509	9.182
5.10	1.000	5.000	5.170	0.350	0.269	9.429	9.160
5.20	1.000	5.000	5.195	0.390	0.194	9.357	9.163
5.30	1.000	5.000	5.215	0.430	0.123	9.286	9.163
5.40	1.000	5.000	5.235	0.470	0.052	9.218	9.166
5.50	1.000	5.000	5.260	0.520	$\bar{1}$.965	9.161	9.196
5.60	1.000	5.000	5.285	0.570	$\bar{1}$.878	9.109	9.231
5.70	1.000	5.000	5.310	0.620	$\bar{1}$.788	9.063	9.275

Average value of $\log K^{CuA}_{CuAL}$ = 9.19

Table III 39

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and pL - $\log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)benzimidazole + Acetoacet-o-toluidide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
4.80	1.000	4.990	5.140	0.300	0.368	9.396	9.028
4.90	1.000	4.995	5.165	0.340	0.288	9.322	9.034
5.00	1.000	4.995	5.185	0.380	0.213	9.250	9.037
5.10	1.000	5.000	5.205	0.410	0.158	9.171	9.013
5.20	1.000	5.000	5.225	0.450	0.087	9.102	9.015
5.30	1.000	5.000	5.245	0.490	0.017	9.035	9.018
5.40	1.000	5.000	5.260	0.520	$\bar{1}$.965	8.961	8.996
5.50	1.000	5.000	5.280	0.560	$\bar{1}$.895	8.899	9.004
5.60	1.000	5.000	5.295	0.590	$\bar{1}$.842	8.830	8.988
5.70	1.000	5.000	5.310	0.620	$\bar{1}$.788	8.763	8.975

Average value of $\log K^{CuA}_{CuAL}$ = 9.01

Table III 40

B, $\bar{n}_H$, $\bar{n}$, log $[(1 - \bar{n})/\bar{n}]$, pL and pL - log $[(1 - \bar{n})/\bar{n}]$ data for Cu(II) + 2-(2'-pyridyl)benzimidazole + Acetoacet-o-anisidide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
4.70	1.000	4.980	5.110	0.260	0.454	9.572	9.118
4.80	1.000	4.990	5.140	0.300	0.368	9.496	9.128
4.90	1.000	4.995	5.165	0.340	0.288	9.422	9.134
5.00	1.000	4.995	5.180	0.370	0.231	9.342	9.111
5.10	1.000	5.000	5.200	0.400	0.176	9.264	9.088
5.20	1.000	5.000	5.220	0.440	0.105	9.194	9.089
5.30	1.000	5.000	5.240	0.480	0.034	9.126	9.092
5.40	1.000	5.000	5.260	0.520	$\bar{1}$.965	9.061	9.096
5.50	1.000	5.000	5.275	0.550	$\bar{1}$.913	8.989	9.076
5.60	1.000	5.000	5.295	0.590	$\bar{1}$.842	8.930	9.088
5.70	1.000	5.000	5.320	0.640	$\bar{1}$.750	8.887	9.137

Average value of log K^{CuA}_{CuAL} = 9.11

Table III 41

B, $\bar{n}_H$, $\bar{n}$, log $[(1 - \bar{n})/\bar{n}]$ pL and pL - log $[(1 - \bar{n})/\bar{n}]$ data for Cu(II) + 2-(2'-pyridyl)benzimidazole + Salicylamide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
5.10	1.000	5.000	5.050	0.200	0.550	7.300	6.750
5.20	1.000	5.000	5.060	0.240	0.500	7.211	6.711
5.30	1.000	5.000	5.070	0.280	0.410	7.135	6.725
5.40	1.000	5.000	5.080	0.320	0.328	7.060	6.732
5.50	1.000	5.000	5.090	0.360	0.250	6.986	6.736
5.60	1.000	5.000	5.100	0.400	0.176	6.914	6.738
5.70	1.000	5.000	5.110	0.440	0.105	6.844	6.739
5.80	1.000	5.000	5.120	0.480	0.034	6.776	6.742

Average value of log K^{CuA}_{CuAL} = 6.74

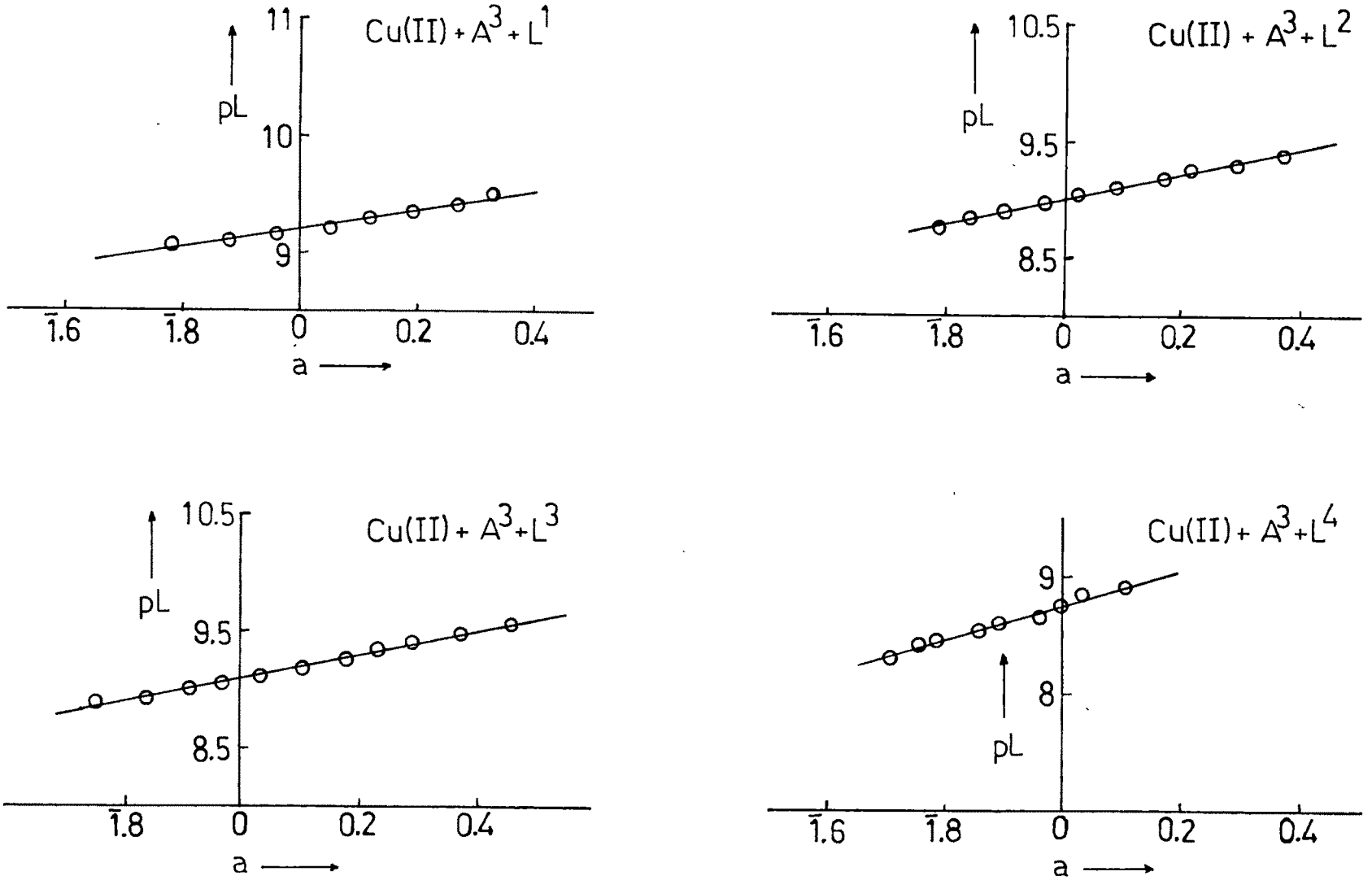

Cu(II) + A3 + L1
11
10
9
pL
1.6
1.8
0
0.2
0.4
a
Cu(II) + A3 + L2
10.5
9.5
8.5
pL
1.6
1.8
0
0.2
0.4
a
Cu(II) + A3 + L3
10.5
9.5
8.5
pL
1.8
0
0.2
0.4
a
Cu(II) + A3 + L4
9
8
pL
1.6
1.8
0
0.2
0.4
a

FIG III 37

Table III 42

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and $pL - \log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)benzimidazole + Benzoatoacetanilide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
4.50	1.000	4.960	5.180	0.440	0.105	8.894	8.789
4.60	1.000	4.970	5.210	0.480	0.034	8.826	8.792
4.70	1.000	4.980	5.230	0.500	0.000	8.743	8.743
4.80	1.000	4.990	5.250	0.520	$\bar{1}$.965	8.661	8.696
4.90	1.000	4.995	5.275	0.560	$\bar{1}$.895	8.599	8.704
5.00	1.000	5.000	5.290	0.580	$\bar{1}$.860	8.519	8.659
5.10	1.000	5.000	5.310	0.620	$\bar{1}$.787	8.463	8.676
5.20	1.000	5.000	5.320	0.640	$\bar{1}$.756	8.387	8.631
5.30	1.000	5.000	5.330	0.660	$\bar{1}$.712	8.311	8.599

Average value of $\log K^{CuA}_{CuAL}$ = 8.70

Table III 43

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and $pL - \log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)benzimidazole + Salicylanilide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
5.30	1.000	5.000	5.050	0.200	0.550	6.389	5.839
5.40	1.000	5.000	5.060	0.240	0.500	6.311	5.811
5.50	1.000	5.000	5.070	0.280	0.410	6.235	5.825
5.60	1.000	5.000	5.080	0.320	0.328	6.160	5.832
5.70	1.000	5.000	5.090	0.360	0.250	6.086	5.836
5.80	1.000	5.000	5.100	0.400	0.176	6.014	5.838
5.90	1.000	5.000	5.110	0.440	0.105	5.944	5.839

Average value of $\log K^{CuA}_{CuAL}$ = 5.83

Table III 44

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and pL - $\log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)benzimidazole + 5-Bromosalicylamide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
5.00	1.000	4.995	5.050	0.220	0.550	6.350	5.800
5.10	1.000	5.000	5.060	0.240	0.500	6.261	5.761
5.20	1.000	5.000	5.070	0.280	0.410	6.185	5.775
5.30	1.000	5.000	5.080	0.320	0.328	6.110	5.782
5.40	1.000	5.000	5.090	0.360	0.250	6.036	5.786
5.50	1.000	5.000	5.105	0.420	0.140	5.979	5.839
5.60	1.000	5.000	5.115	0.460	0.070	5.910	5.840
5.70	1.000	5.000	5.125	0.500	0.000	5.843	5.843

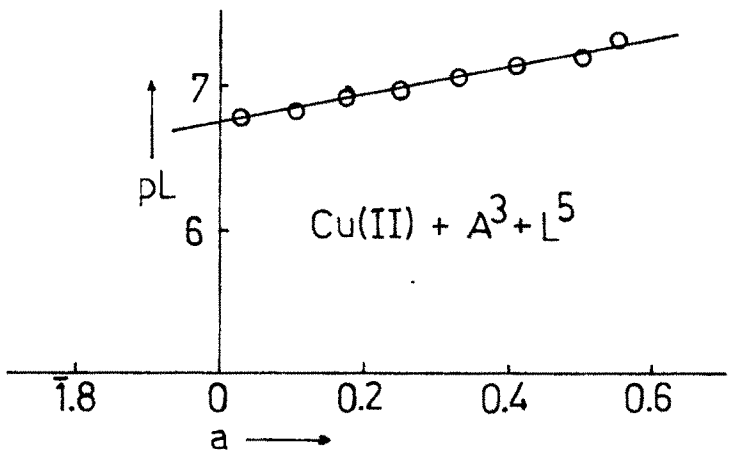
Average value of $\log K^{CuA}_{CuAL}$ = 5.80

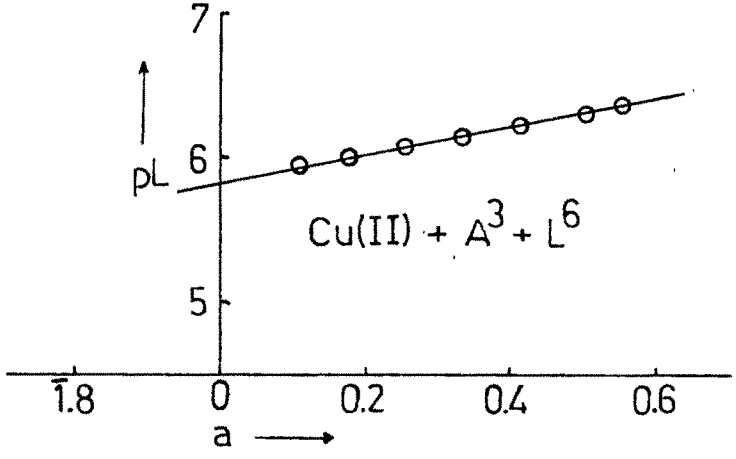
Table III 45

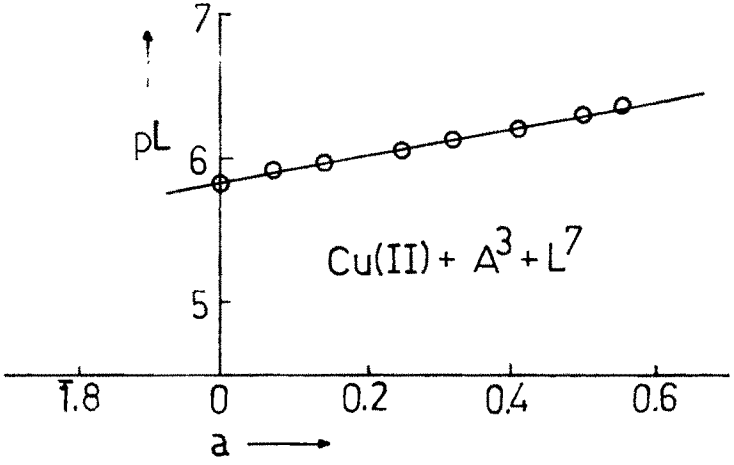
B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and pL - $\log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)benzimidazole + 5-Bromosalicylanilide system.

B	$\bar{n}_H$	V"	V"'	$\bar{n}$	a	pL	b
5.00	1.000	4.995	5.055	0.240	0.500	5.751	5.251
5.10	1.000	5.000	5.070	0.280	0.410	5.675	5.265
5.20	1.000	5.000	5.080	0.320	0.328	5.600	5.272
5.30	1.000	5.000	5.090	0.360	0.250	5.526	5.276
5.40	1.000	5.000	5.105	0.420	0.140	5.469	5.329
5.50	1.000	5.000	5.115	0.460	0.070	5.400	5.330
5.60	1.000	5.000	5.125	0.500	0.000	5.333	5.333
5.70	1.000	5.000	5.135	0.540	$\bar{1}$.930	5.270	5.340

Average value of $\log K^{CuA}_{CuAL}$ = 5.30


7
pL
6
Cu(II) + A3 + L5
1.8
0
0.2
0.4
0.6
a


7
pL
6
5
Cu(II) + A3 + L6
1.8
0
0.2
0.4
0.6
a


7
pL
6
5
Cu(II) + A3 + L7
1.8
0
0.2
0.4
0.6
a

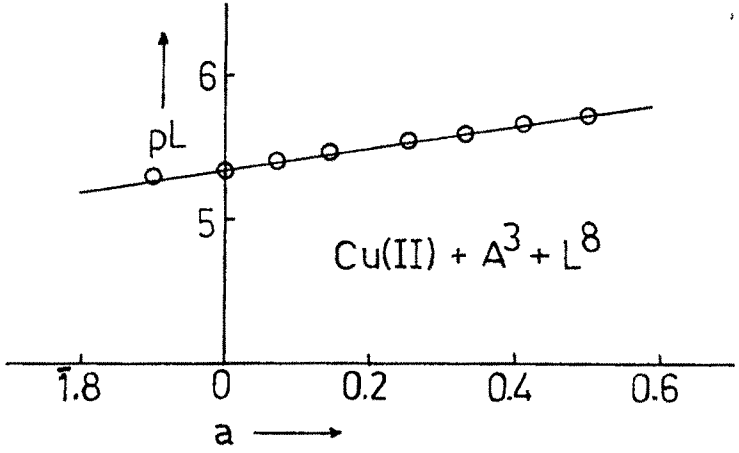

6
pL
5
Cu(II) + A3 + L8
1.8
0
0.2
0.4
0.6
a

FIG III 38

Table III 46

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and $pL - \log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)imidazoline + Acetoacetanilide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
5.50	1.000	5.000	5.050	0.200	0.602	9.239	8.637
5.60	1.000	5.000	5.060	0.240	0.501	9.161	8.660
5.70	1.000	5.000	5.070	0.280	0.410	9.085	8.675
5.80	1.000	5.000	5.080	0.320	0.327	9.010	8.683
5.90	1.000	5.000	5.090	0.360	0.250	8.936	8.686
6.00	1.000	5.000	5.100	0.400	0.176	8.864	8.688
6.10	1.000	5.000	5.110	0.440	0.105	8.794	8.689
6.20	1.000	5.000	5.120	0.480	0.036	8.726	8.690
6.30	1.000	5.000	5.130	0.520	$\bar{1}$.965	8.661	8.696
6.40	1.000	5.000	5.140	0.560	$\bar{1}$.895	8.599	8.704

Average value of $\log K^{CuA}_{CuAL}$ = 8.68

Table III 47

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and $pL - \log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)imidazoline + Acetoacet-o-toluidide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
5.60	1.000	5.000	5.050	0.200	0.602	8.839	8.237
5.70	1.000	5.000	5.060	0.240	0.501	8.761	8.260
5.80	1.000	5.000	5.070	0.280	0.410	8.685	8.275
5.90	1.000	5.000	5.080	0.320	0.327	8.610	8.283
6.00	1.000	5.000	5.095	0.380	0.213	8.550	8.347
6.10	1.000	5.000	5.105	0.420	0.140	8.479	8.339
6.20	1.000	5.000	5.115	0.460	0.070	8.410	8.340
6.30	1.000	5.000	5.130	0.520	$\bar{1}$.965	8.361	8.396
6.40	1.000	5.000	5.145	0.580	$\bar{1}$.860	8.319	8.456

Average value of $\log K^{CuA}_{CuAL}$ = 8.33

Table III 48

B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and pL - $\log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)imidazoline + Acetoacet-o-anisidide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
5.60	1.000	5.000	5.050	0.200	0.602	8.939	8.337
5.70	1.000	5.000	5.060	0.240	0.501	8.861	8.360
5.80	1.000	5.000	5.075	0.300	0.368	8.797	8.429
5.90	1.000	5.000	5.085	0.340	0.288	8.723	8.435
6.00	1.000	5.000	5.100	0.400	0.176	8.664	8.488
6.10	1.000	5.000	5.110	0.440	0.105	8.594	8.489
6.20	1.000	5.000	5.120	0.480	0.036	8.526	8.490
6.30	1.000	5.000	5.130	0.520	$\bar{1}$.965	8.461	8.496
6.40	1.000	5.000	5.140	0.560	$\bar{1}$.895	8.399	8.504

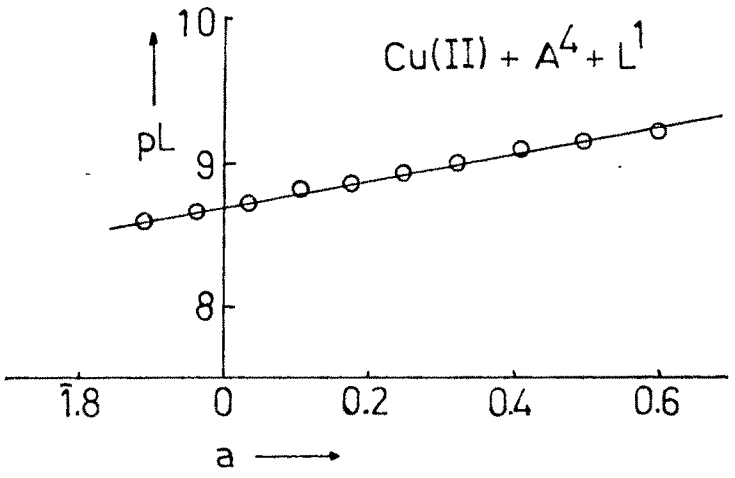
Average value of $\log K^{CuA}_{CuAL}$ = 8.45

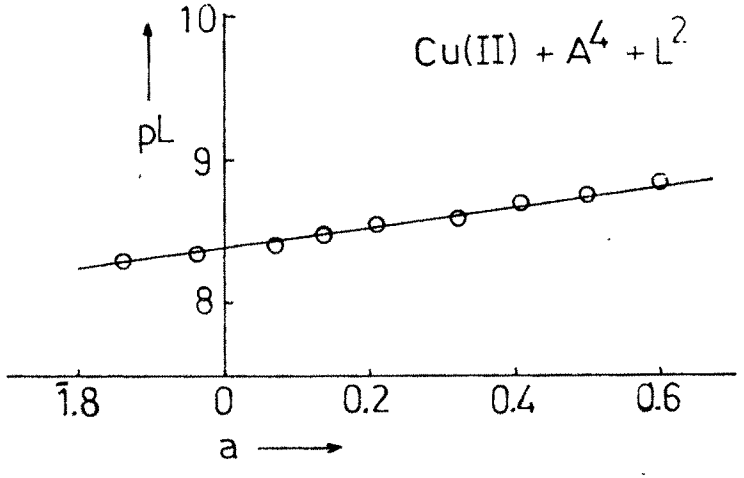
Table III 49

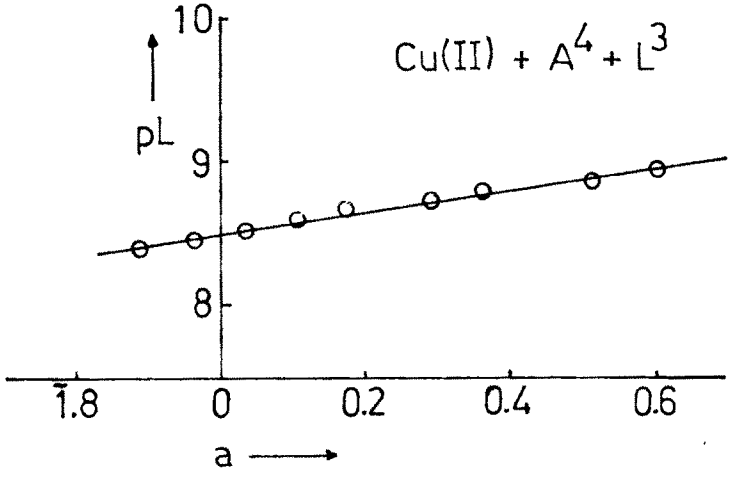
B, $\bar{n}_H$, $\bar{n}$, $\log\left[(1-\bar{n})/\bar{n}\right]$, pL and pL - $\log\left[(1-\bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)imidazoline + Benzoatoacetanilide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
5.10	1.000	5.000	5.075	0.300	0.368	8.497	8.129
5.20	1.000	5.000	5.090	0.360	0.250	8.436	8.186
5.30	1.000	5.000	5.100	0.400	0.176	8.364	8.188
5.40	1.000	5.000	5.110	0.440	0.105	8.294	8.189
5.50	1.000	5.000	5.120	0.480	0.036	8.226	8.190
5.60	1.000	5.000	5.135	0.540	$\bar{1}$.930	8.180	8.250
5.70	1.000	5.000	5.145	0.580	$\bar{1}$.860	8.119	8.259
5.80	1.000	5.000	5.155	0.620	$\bar{1}$.787	8.063	8.276
5.90	1.000	5.000	5.165	0.660	$\bar{1}$.712	8.011	8.299

Average value of $\log K^{CuA}_{CuAL}$ = 8.22


Cu(II) + A4 + L1
pL
10
9
8
1̄.8
0
0.2
0.4
0.6
a


Cu(II) + A4 + L2
pL
10
9
8
1̄.8
0
0.2
0.4
0.6
a


Cu(II) + A4 + L3
pL
10
9
8
1̄.8
0
0.2
0.4
0.6
a

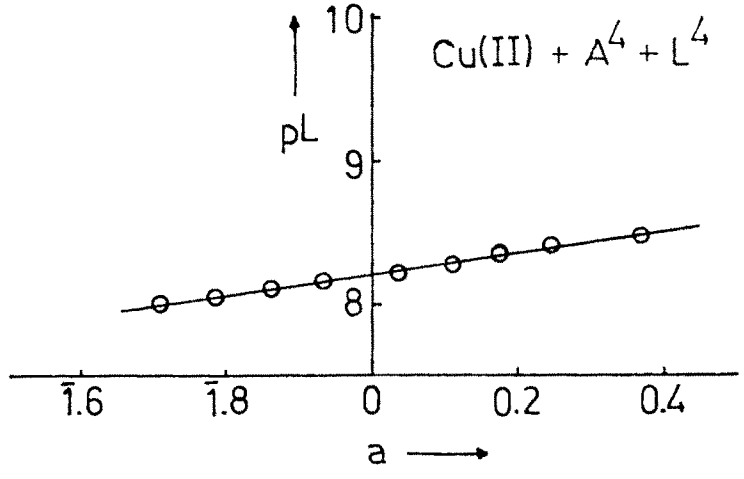

Cu(II) + A4 + L4
pL
10
9
8
1̄.6
1̄.8
0
0.2
0.4
a

FIG III 39

Table III 50

B, $\bar{n}_H$, $\bar{n}$, log $\left[(1 - \bar{n})/\bar{n}\right]$, pL and pL - log $\left[(1 - \bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)imidazoline + Salicylamide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
5.70	1.000	5.000	5.040	0.160	0.720	6.667	5.947
5.80	1.000	5.000	5.050	0.200	0.602	6.599	5.997
5.90	1.000	5.000	5.060	0.240	0.501	6.521	6.020
6.00	1.000	5.000	5.065	0.260	0.454	6.433	5.979
6.10	1.000	5.000	5.075	0.300	0.368	6.348	5.980
6.20	1.000	5.000	5.085	0.340	0.288	6.273	5.985
6.30	1.000	5.000	5.095	0.380	0.213	6.200	5.987
6.40	1.000	5.000	5.100	0.400	0.176	6.114	5.938

Average value of $\log K^{CuA}_{CuAL}$ = 5.98

Table III 51

B, $\bar{n}_H$, $\bar{n}$, log $\left[(1 - \bar{n})/\bar{n}\right]$, pL and pL - log $\left[(1 - \bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)imidazoline + Salicylanilide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
5.70	1.000	5.000	5.035	0.140	0.788	5.957	5.159
5.80	1.000	5.000	5.045	0.180	0.659	5.899	5.240
5.90	1.000	5.000	5.050	0.200	0.602	5.789	5.187
6.00	1.000	5.000	5.055	0.220	0.550	5.700	5.150
6.10	1.000	5.000	5.060	0.240	0.501	5.611	5.110
6.20	1.000	5.000	5.070	0.280	0.410	5.535	5.125
6.30	1.000	5.000	5.075	0.300	0.368	5.457	5.089
6.40	1.000	5.000	5.080	0.320	0.327	5.360	5.033

Average value of $\log K^{CuA}_{CuAL}$ = 5.14

Table III 52

B, $\bar{n}_H$, $\bar{n}$, log $\left[(1 - \bar{n})/\bar{n}\right]$, pL and pL - log $\left[(1 - \bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)imidazoline + 5-Bromosalicylamide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
5.70	1.000	5.000	5.040	0.160	0.720	5.617	4.897
5.80	1.000	5.000	5.050	0.200	0.602	5.539	4.937
5.90	1.000	5.000	5.055	0.220	0.550	5.450	4.900
6.00	1.000	5.000	5.065	0.260	0.454	5.373	4.919
6.10	1.000	5.000	5.075	0.300	0.368	5.297	4.929
6.20	1.000	5.000	5.085	0.340	0.288	5.223	4.935
6.30	1.000	5.000	5.090	0.360	0.250	5.136	4.886
6.40	1.000	5.000	5.100	0.400	0.176	5.064	4.888

Average value of $\log K^{CuA}_{CuAL}$ = 4.91

Table III 53

B, $\bar{n}_H$, $\bar{n}$, log $\left[(1 - \bar{n})/\bar{n}\right]$, pL and pL - log $\left[(1 - \bar{n})/\bar{n}\right]$ data for Cu(II) + 2-(2'-pyridyl)imidazoline + 5-Bromosalicylanilide system.

B	$\bar{n}_H$	V''	V'''	$\bar{n}$	a	pL	b
5.90	1.000	5.000	5.040	0.160	0.720	4.807	4.087
6.00	1.000	5.000	5.050	0.200	0.602	4.729	4.127
6.10	1.000	5.000	5.060	0.240	0.501	4.651	4.150
6.20	1.000	5.000	5.070	0.280	0.410	4.575	4.165
6.30	1.000	5.000	5.075	0.300	0.365	4.487	4.122
6.40	0.980	5.005	5.085	0.320	0.327	4.400	4.073

Average value of $\log K^{CuA}_{CuAL}$ = 4.12

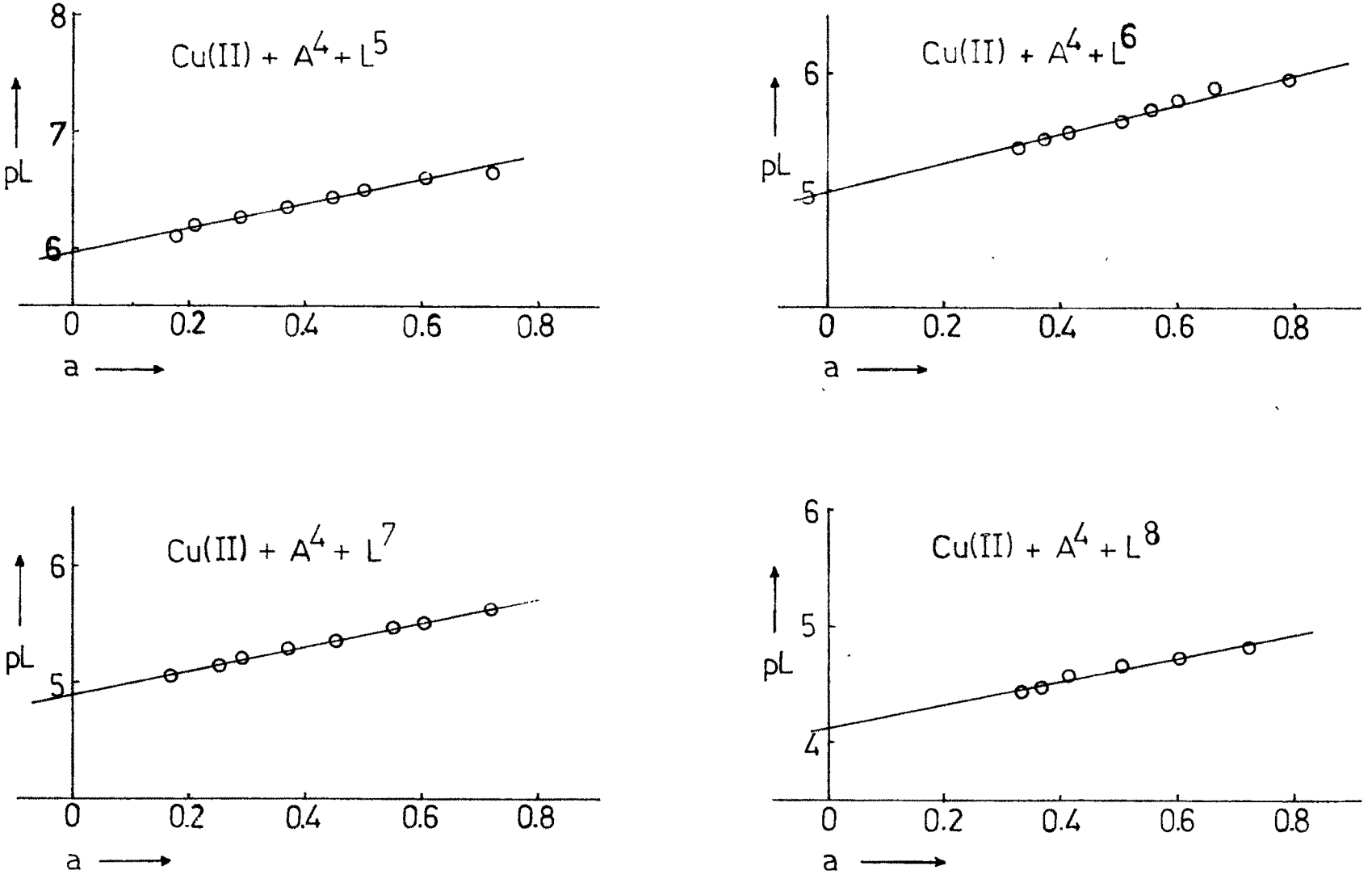


FIG. III 40

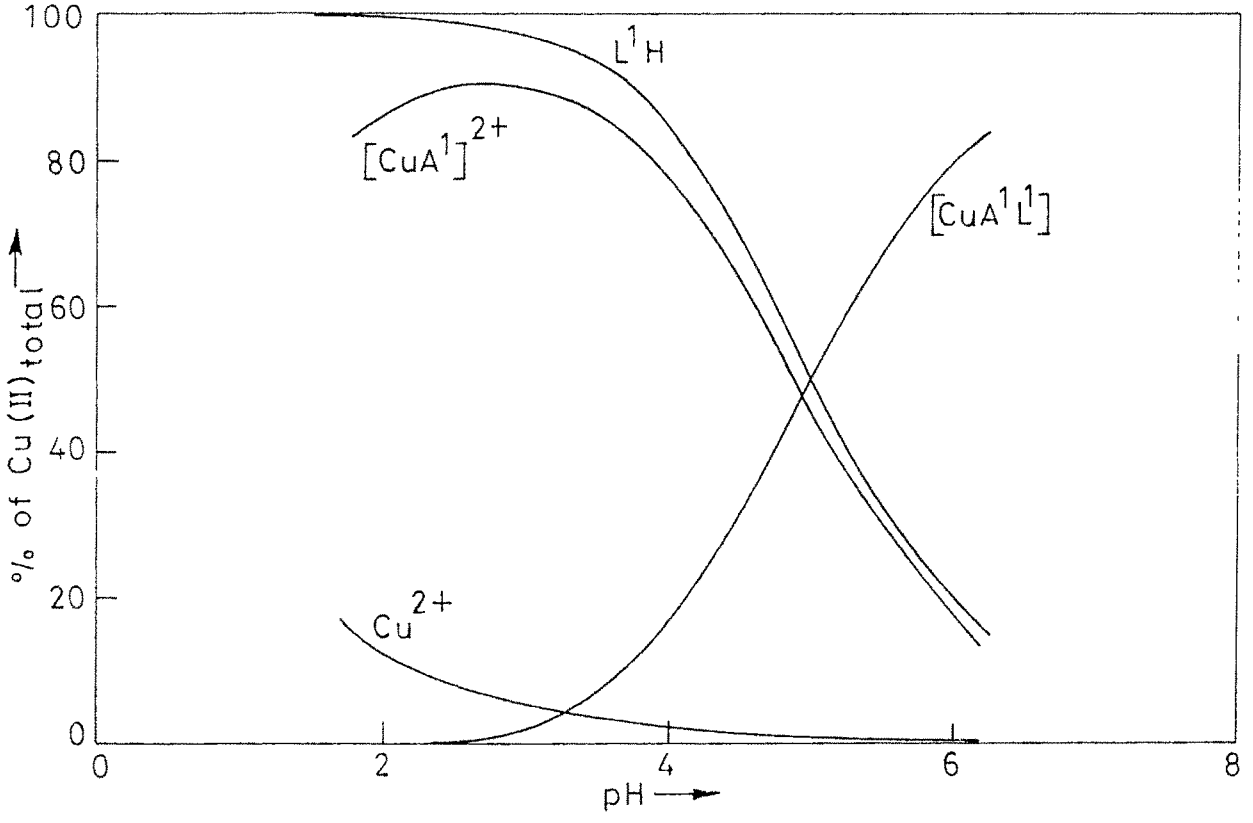


FIG.III 41 Variation of concentration of different species with pH. $Cu(II)+A^1+L^1$ system

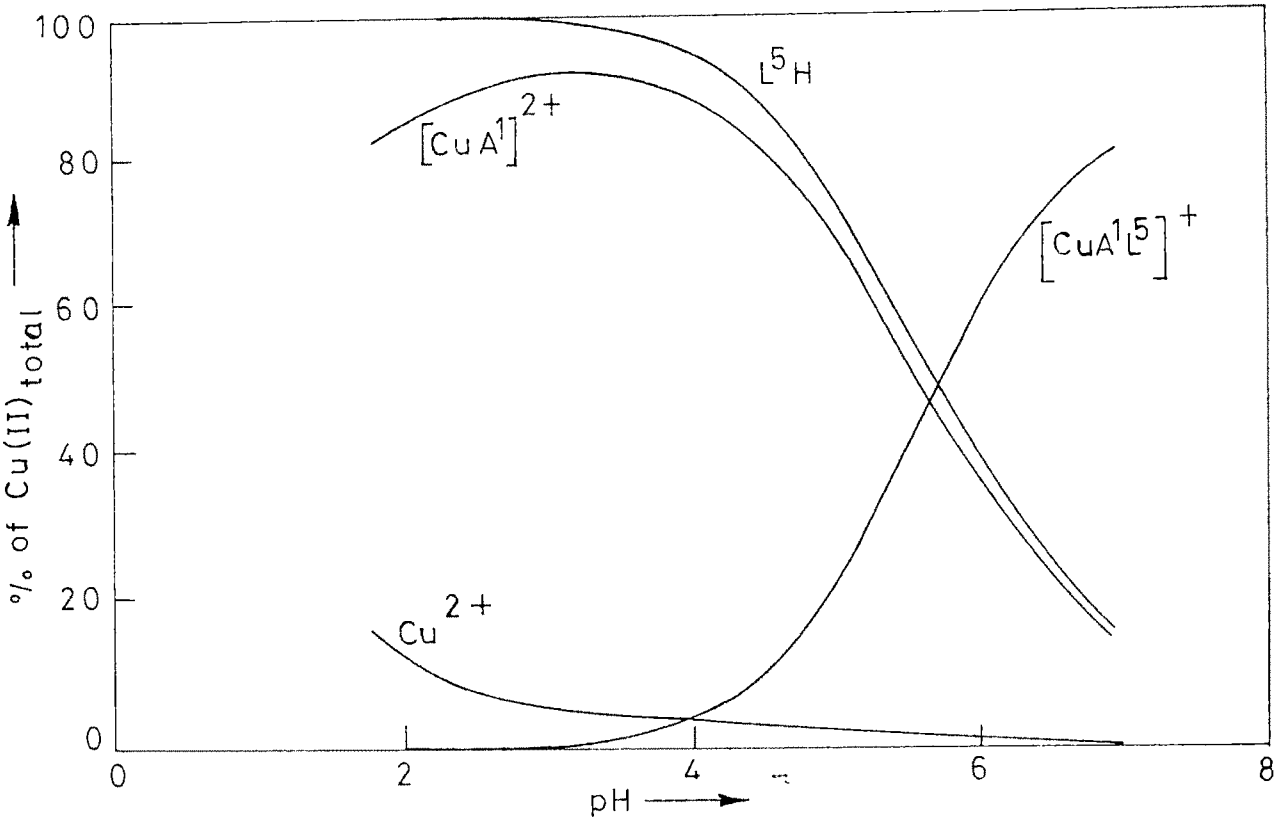


Fig. III 42 Variation of concentration of different species with pH.
$Cu(II) + A^1 + L^5$ system

Table III 54 : Ternary system stability constants of Copper(II) in dioxan-water (1 : 1 v/v) medium and 0.2M $NaClO_4$ at 30°C.

L	$\log K^{CuA}_{CuAL}$							
	A^1				A^2			
	m_1	m_2	$m_3(\sigma\beta)$	$\Delta \log K$	m_1	m_2	$m_3(\sigma\beta)$	$\Delta \log K$
L^1	9.71	9.62	9.66(0.16)	+ 0.80	9.25	9.23	9.31(0.01)	+ 0.45
L^2	9.33	9.34	9.37(0.03)	+ 0.80	8.89	8.90	8.96(0.00)	+ 0.39
L^3	9.93	9.88	9.91(0.06)	+ 0.81	9.27	9.16	9.26(0.02)	+ 0.16
L^4	9.62	9.30	9.33(0.07)	+ 1.18	8.58	8.60	8.67(0.01)	+ 0.52
L^5	6.58	6.59	6.61(0.01)	+ 0.82	6.61	6.59	6.67(0.01)	+ 0.88
L^6	5.58	5.59	5.62(0.01)	+ 0.67	5.64	5.66	5.73(0.01)	+ 0.78
L^7	5.47	5.08	5.10(0.03)	+ 0.23	5.46	5.34	5.40(0.03)	+ 0.53
L^8	4.97	4.95	4.97(0.01)	+ 0.49	4.87	4.79	4.84(0.03)	+ 0.36

Table III 55 : Ternary system stability constants of Copper(II) in dioxan-water (1 : 1 v/v) medium and 0.2M $NaClO_4$ at 30°C.

L	log K^{CuA}_{CuAL}					
	A^3			A^4		
	m_1	m_2 ($\sigma\beta$)	Δlog K	m_1	m_2 ($\sigma\beta$)	Δlog K
L^1	9.19	9.26(0.05)	+ 0.40	8.68	8.71(0.02)	- 0.15
L^2	9.01	9.02(0.02)	+ 0.45	8.33	8.43(0.05)	- 0.14
L^3	9.11	9.13(0.02)	+ 0.03	8.45	8.49(0.02)	- 0.61
L^4	8.70	8.65(0.01)	+ 0.50	8.22	8.27(0.02)	+ 0.12
L^5	6.74	6.74(0.01)	+ 0.95	5.98	5.95(0.01)	+ 0.21
L^6	5.83	5.85(0.02)	+ 0.90	5.14	5.00(0.04)	+ 0.05
L^7	5.80	5.85(0.02)	+ 0.98	4.91	4.83(0.03)	- 0.04
L^8	5.30	5.31(0.02)	+ 0.83	4.12	3.95(0.03)	- 0.53

RESULTS AND DISCUSSION

The calculation of mixed-ligand formation constant using the extension of Irving-Rossotti method is based on the presumption that $[CuA]^{+}$ is formed completely and remains stable in the pH range where the coordination of secondary ligand takes place. The observed trends of the titration curves (e.g. Figure III 1) support this presumption. In Figure III 1, curve (3), (i.e. Cu(II) + dipyridyl) diverges from the curve (2), (dipyridyl), at lower pH indicating that the $[Cu.dipy]^{2+}$ is formed by the dissociation of the protons attached with the tertiary nitrogens of dipyridyl molecule. Till then it is above the curve (1), (perchloric acid), because of the protons attached to free dipyridyl molecules. It almost merges with the acid curve (1) at pH = 3.0 showing that the formation of $[Cu.dipy]^{2+}$ is almost complete at that pH. Curve (3) again diverges from curve (1) at higher pH (6.10) indicating that the formation of hydroxo complex $[Cu(dipy)(OH)_n]$ starts at higher pH. The mixed-ligand curve (5) remains merged with curve (4) at lower pH showing that complexation of the second ligand does not take place at low pH. Curve (5) diverges from curve (4) above pH 3.50 i.e. the second ligand starts coordinating in the pH range where $[Cu.dipy]^{2+}$ formation is complete and the formation of the hydroxo-complex does not start. Thus, the horizontal distance between curve (5) and curve (4) is due to the protons liberated from the secondary ligand on coordinating with $[CuA]^{2+}$.

The above observation is true in cases of complexes involving other primary ligands i.e., 1,10-phenanthroline, 2-(2'-pyridyl)benzimidazole and 2-(2'-pyridyl)imidazoline.

In the first computer method (Method II) also value of K^{CuA}_{CuAL} is calculated by presuming complete formation of $[CuA]^{2+}$.

However, in Method III no such presumption is made for the calculation of the mixed-ligand formation constants as the formation of all possible species in the solution is considered.

It is interesting to observe that in case of ternary complexes $[CuAL]^{+}$, where L = L^1 to L^8, the values of the formation constants obtained by the use of the extension of Irving-Rossotti titration technique[26] presuming the formation of the complex in steps CuA + L $\rightleftharpoons$ CuAL, and the values obtained by using the two computer methods are nearly equal. This supports the presumption that $[CuA]^{2+}$ formation is almost complete in the lower pH range and L^- combines with $[CuA]^{2+}$ forming $[CuAL]^{+}$ is valid. This is further confirmed by observing the plot of the concentration of various species (as percentage of total Cu^{2+} present) against pH (Figures III 41 and III 42). It is clearly seen that in the lower pH range (pH 1 to 3) Cu^{2+} and $[CuA]^{2+}$ are the major species and in the higher pH range (pH 3 to 7) the major species are $[CuA]^{+2}$ and $[CuAL]^{+}$ totalling to almost 100%.

The replacement of $[CuA]^{2+}$ by $[CuAL]^{+}$ in these systems is strikingly obvious from the symmetrical rise and fall in the concentrations of the species $[CuAL]^{+}$ and $[CuA]^{2+}$, respectively, as the pH increases. The concentrations of other species $[CuA_2]^{2+}$, $[CuL]^{+}$ and $[CuL_2]$ are negligible. Thus, this study validates the use of the extension of Irving-Rossotti titration technique for the determination of the formation constant values of the mixed-ligand complexes containing dipyridyl or similar diamines and secondary ligands coordinating through two oxygen atoms.

A detailed study[48,49] of mixed-ligand complexes of the type $[Cu.A.\ \beta\text{-diketonate}]^{+}$, where A = 2,2'-dipyridyl or 1,10-phenanthroline as primary ligands has shown that the value of $\Delta \log K$ is almost zero. However, in the present mixed-ligand complexes $[CuAL]^{+}$, where L = L^1 to L^4, the Δ log K values are positive. Thus, though β-ketoanilides form less stable binary complexes $[CuL]$ than β-diketones, the stabilities of their ternary complexes are greater. The stabilization of the ternary complexes of β-diketones has been attributed to the pseudoaromatic characters and π bonding in the chelate ring. However, as discussed in Chapter II, π bonding in the β-ketoanilides complexes is less. The reason for the greater stability of the ternary complexes involving β-ketoanilides should, therefore, be sought elsewhere.

A probable explanation is as follows :

β-ketoanilides have an anilide group with an additional lone pair of electrons over the anilide nitrogen. Because of this increased π electron density in the chelate ring there is repulsion between the metal $d\pi$ electrons and the ligand electrons. This repulsion is more in the binary complex. In $[CuAL]^+$, however, the $d\pi$ electron density on the Cu(II) is reduced due to the delocalization of metal $d\pi$ electrons over the tertiary amine π orbitals. Therefore, the tendency of L^- to bind with $[CuA]^{2+}$ increases resulting in higher value of the formation constant K^{CuA}_{CuAL}. The effect is more pronounced with the increase in the electron density in the π orbitals of β-ketoanilide, leading to a positive value of $\Delta \log K$.

In all the mixed-ligand complexes $[CuAL]^+$, where $L = L^1$ to L^8, it is observed that $\Delta \log K$ is positive, except when $A = A^4$. This is because the extent of stabilization of the mixed-ligand complex should depend on the extent of π delocalization in $[CuA]^{2+}$. In the case of A^4, where there is coordination from one pyridine nitrogen and one imidazoline nitrogen, π interaction is possible only with the pyridine ring as imidazoline is a saturated ring with no delocalized π electron cloud. Due to this A^4 is less π interacting than A^1, A^2 or A^3 and the ternary complexes containing A^4 are less stable than other ternary complexes, resulting in negative $\Delta \log K$ value.

In order to see the effect of the presence of aromatic ring in the secondary ligand and the substitution over the aromatic ring, on the mixed-ligand complex formation constant values, the studies of the complexes $[CuAL]^+$ where L = salicylamide derivatives (L^5 to L^8) were carried out. In all these complexes also Δ log K values are found to be positive. The explanation in terms of electron repulsion being more in binary complexes and a lowering of repulsion in ternary complexes is applicable in these cases also. The increased electron density over the ligand, L^-, coordinating through two oxygen atoms and with a lone pair of electrons over amide/anilide nitrogen atoms, will make the binary complex less stable whereas the ternary complex will be more stabilized.

$[CuAL^6]^+$ complexes have less positive Δ log K than $[CuAL^5]^+$ complexes. This may be because of the delocalization of the anilide nitrogen lone pair of electrons over the aromatic ring to which it is attached. However, the difference of 0.1 log unit is too small to be interpreted in detail. In cases of bromoderivatives the effect is more. The Δ log K values of L^7 and L^8 complexes are less positive than those of L^5 and L^6 complexes, respectively. The substituted bromine atom withdraws electrons from the phenyl ring and hence the negative charge over O^- is less in these ligands than in the case of unsubstituted ligands. The Δ log K value is, therefore, less positive. The substitution of an electron withdrawing group, therefore, lowers the

stability of such ternary complexes. This observation is interesting because it shows the effect of groups not directly linked to the metal ion on the stability of the ternary complexes. This effect is similar to the role of a substituent group, not directly linked to the metal ion, in increasing the efficiency of metalloenzymes.

The order of formation constants of mixed-ligand complexes of the different tertiary diamines with the series of secondary ligands (L^5 to L^8) is as follows :

$$\left[CuA^3L\right]^+ > \left[CuA^1L\right]^+ \approx \left[CuA^2L\right]^+ > \left[CuA^4L\right]^+ .$$

The order is different from that in the case of the β-ketoanilide (L^1 to L^4) complexes. However, the order is same as in the mixed-ligand complexes $\left[CuAL\right]$, where L = σ bonding ligands like malonic acid, amino acids and primary amines.[102] In addition to the dependance on the extent of Cu → A π interaction, the enhanced stability of mixed-ligand complexes should also depend on the nature of interaction between metal ion and the secondary ligand. Therefore, the variation in the order of formation constants for the two sets of secondary ligands (L^1 to L^4 and L^5 to L^8) may be due to the extent of σ and π interaction with the secondary ligand. When Cu → L π interactions is greater, the order is reversed. 2-(2'-pyridyl)benzimidazole with maximum Cu → A π bonding reduces Cu → L π interaction in the ternary complexes and hence stabilization of $\left[CuA^3L^{1-4}\right]$ complexes is

less than that of $[CuA^1L^{1-4}]$ complexes.

However, in all these ligands the major effect is the presence of the extra lone pair of electrons over the nitfogen atom of the amide/anilide group. This point is further confirmed by UV and visible spectral studies of the mixed-ligand complexes as detailed in the next chapter which shows that in the ternary complex $[CuAL]^+$ the π bonding in $[CuA]^{2+}$ does not affect the extent of π bonding in $[CuL]^+$. Hence, the greater stability of the ternary complex is mainly due to the reduction of the Copper $d\pi$ electrons and ligand electrons repulsion in the mixed-ligand complex rather than the cooperative effect of the inter-ligand π interaction through the Copper $d\pi$ orbitals.