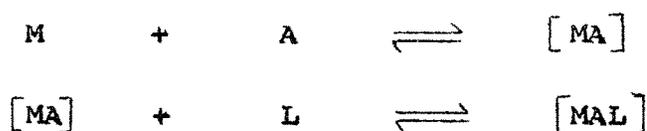


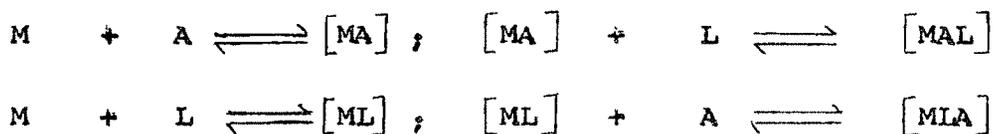
CHAPTER - II

Formation Constants of Ternary Complexes  
Involving 5-nitro-1,10-phenanthroline and  
N-N, N-O<sup>-</sup> or O<sup>-</sup>-O<sup>-</sup> co-ordinating Ligands

The formation of the ternary complexes can take place in two ways. In the first case the two ligands may have different complexing tendencies. The binary complex formed at lower pH between the more complexing ligand and the metal ion is stable upto a higher pH range where the second ligand co-ordinates. The reaction can be shown to takes place in steps.<sup>47</sup>



In the second case, however, the complexing tendencies of the two ligands do not differ very much, and following types of reactions take place, leading to the formation of the mixed ligand complex.<sup>47</sup>



In the first case, in the range of the formation of the mixed ligand complex, the species present in the solution can be considered to be  $[MA]$  and  $[MAL]$ . The formation constant of ternary complex is represented as

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

Formation constants of the ternary complexes of such type, where two ligands co-ordinate in two different pH ranges, and the first ligand is not displaced at higher pH, where the second ligand gets co-ordinated, have been determined by using an extension<sup>of</sup> Irving-Rossotti technique.<sup>48</sup>

In the reaction of the second type the species present in the solution can be  $M^{2+}$ ,  $[MA]$ ,  $[ML]$ ,  $[MA_2]$ ,  $[ML_2]$ ,  $[MAL]$  and also hydroxy species and complexes with protonated ligands. The formation constants in such systems have been determined by pH-metric technique as suggested by Martell and coworkers.<sup>24,25</sup>

The stability constants<sup>49,50</sup> of such ternary complexes are better determined by the help of computer techniques. Sillen developed a widely applicable program called LETAGROP through other programs called KUSKA, PROKAUS, PAIKATB and HALTA. The modified form of KUSKA has been used in Zajicek's iteration technique.<sup>51</sup> Sayce and coworkers<sup>52</sup> used the program SCOUSS (Stability Constant of Unknown Single Species) for studying the complexes of Cu(II) with each of the six possible pairs of the following neutral, monoionic and di-ionic ligands, histamine, ethylenediamine, serine monoanion and salicylate dianion.

Perrin and Sayce and Sayce<sup>53,54</sup> further suggested the computer programs COMICS (Concentration of Metal Ions and Complexing Species), and SCOGS (Stability Constant of Generalized Species) respectively, to work out the equilibrium concentration of all the species in multimetal multiligand systems. Both are essentially pH-meter techniques. Gans and coworkers<sup>55,56</sup> developed a new program, namely MINIQUAD (from the Italian word for least square, *minimi quadrati*), which can deal with potentiometric titration data from systems containing any number of reactant species.

All the formation constants of mixed ligand complexes in the present study were determined by using the computer program SGOGS.<sup>54</sup> This is a powerful physical technique capable of calculating simultaneously or individually, association constants for any of the species found in solution containing upto two metal ions 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 for any species j which can be described by 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 species) zero or negative integer (for a protonated species). The practical overall formation constant  $B_j$  is given by the expression,

$$B_j = \frac{[A]^{A_j} [B]^{B_j} [S]^{S_j} [T]^{T_j} (OH)^{W_j}}{[A]^{A_j} [B]^{B_j} [S]^{S_j} [T]^{T_j} \{OH\}^{W_j}}$$

where square brackets denote concentrations of the species.

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

- (1) No. of jobs to be calculated.
- (2) No. of expts. in the set of expts. under study.

- (3) No. of ligands (two), No. of metals (one) and the No. of complex species formed (including protonated forms of ligand, hydrolysed metal species, etc.).
- (4) Composition of each species has to be described alongwith its approximate formation constant as the logarithm to base 10.
- (5) No. of displaceable protons on ligand (1), and ligand (2).
- (6) Title of the experiment.
- (7) Initial concentrations of the metal, ligands, mineral acid ( $\text{HClO}_4$ ), titrant base and total initial volume. Concentrations are expressed in moles/lit and volumes in ml.
- (8) For each titration-reading bearing values of titre of base, of pH, and of INDEX (a quantity which is zero for all but the last reading of the experiment when INDEX = 1).
- (9) Then return to item 6 to read data for next experiment and repeat until data for all the experiments ; as indicated by item 2, have been read.
- (10) Logarithm to base 10 of the ionic product of water, and the coefficient of hydrogen ion under the conditions of experiment, example at  $30^\circ\text{C}$  and  $I = 0.2$ ).

- (11) The No. of constants to be refined and the No. of calculation cycles to be repeated to get convergency in the formation constant values.
- (12) The particular constant to be varied, given with serial No. as in (4) and, the logarithm increment or decrement to be applied to the formation constant in the numerical differentiation.

The protonation constants for free ligands A and L and the stability constant data for the parent binary complexes of Cu(II) with A and L at 30°C and  $I = 0.2 \text{ mol dm}^{-3} \text{ NaClO}_4$  were held constant in the calculation of ternary system.

The subroutine COGSNR (Concentration of Generalised 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 program is that, after the calculation is over, a systematic output is printed out. This contains the refined values of formation constants alongwith 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 ligand and finally the concentration of each complex species.

Literature Survey and Present Study :

Diamines and amino acids are strongly chelating agents, co-ordinating through two nitrogen atoms, or one nitrogen and one oxygen atom, respectively. Binary system of diamines with Cu(II), Ni(II) have been studied earlier.<sup>57-60</sup> Irving and coworkers<sup>61</sup> studied the influence of ring size on the stabilities of metal chelates of ethylenediamine, 1,2-propylenediamine, 1,3-propylenediamine. Formation constants of Cu(II), Ni(II) or Zn(II) complexes of diamines, having N-substitution have been determined by Irving and coworkers<sup>62</sup> and also by Nasanen and coworkers.<sup>63</sup> A comparative study of the basic strength of N-substituted diamines and their complex forming tendencies shows that the formation constant values are not in keeping with the basic strength. This has been explained to be because of the steric effect produced by the substituted group.<sup>64,65</sup>

The amino acids are of biochemical importance and hence the mixed-ligand complexes containing amino acids have also been investigated in detail.<sup>66-75</sup> Mixed ligand complexes [MAL] where M = Cu(II), Ni(II), Zn(II), A = nitrolotriacetic acid (NTA) and L = amino acids and their esters had been studied earlier.<sup>76-78</sup> Israeli and coworkers<sup>79-81</sup> studied mixed ligand complexes [MAL], where M = Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Pb(II), A = nitrilotriacetic acid (NTA) and L = various  $\alpha$ -amino acids. Various other systems have also been

studied where dyes<sup>82</sup> or Schiff bases<sup>83</sup> are primary ligands and the amino acids or hydroxy acids are the secondary ligands. Martin and coworkers<sup>84-86</sup> studied mixed ligand complexes [MAL], where M = Cu(II), Ni(II), A = glycine,  $\alpha$ -alanine and L = glycylglycine or diglycylglycine. Formation constants of mixed ligand complexes containing a pair of following amino acids ; glycine,  $\alpha$ -alanine, tyrosine, histidine, threonine, have been determined by Martin and coworkers.<sup>87,88</sup> Gergely and coworkers also studied mixed ligand complexes<sup>89,90</sup> containing a pair of amino acids. They further determined the thermodynamic constants by using colorimetric technique.<sup>91</sup>

It was observed that the sizes of the chelate rings affect the formation of mixed ligand complexes involving diamines. Mixed ligand complexes containing two five membered rings are more stable than those with five-six or six-six membered rings.

The investigation of ternary Cu(II) complexes containing 2,2'-dipyridyl and another ligand demonstrates<sup>3,92,93</sup> that the discriminating behaviour of the Cu(II) 2,2'-dipyridyl (1:1) complex and the large stability of the ternary 2,2'-dipyridyl-Cu(II)-O<sup>-</sup>-O<sup>-</sup> complexes is strongly dependent on whether O<sup>-</sup>-O<sup>-</sup> co-ordinating atoms are located on an aliphatic or an aromatic ligand, the stabilization of the ternary complex being more in the latter case.

The extra stabilization has been explained by Sigel<sup>93</sup> in terms of  $\pi$  interaction between the  $\pi$  orbitals of dipyriddy and  $O^-O^-$  aromatic ligand through metal  $d\pi$  orbitals. However, recent studies<sup>94,95</sup> have shown that inter-ligand  $\pi$  interaction is not significant in  $[CuAL]$  and cannot be the contributing factor in stabilizing the mixed ligand complex, to the extent of making  $\Delta \log K$  positive. An alternate explanation in terms of interelectronic repulsion has been extended.

The complexes of the type  $[MAL]$  where  $M = Cu(II)$  or  $Ni(II)$   $A = 2,2'$ -dipyriddy or 1,10-phenanthroline and  $L =$  diamines, amino acids, aliphatic dicarboxylic acids have been studied in aqueous solution<sup>96-98</sup> and also in 50% dioxan-water medium<sup>45</sup> and a nonstatistical stabilization in the order  $O^-O^- > O^-N > N-N$  for  $L$  was observed and explained, as detailed in Chapter I.

In the present chapter ternary complexes where  $A = 5$ -nitro-1,10-phenanthroline ( $A^1$ ) and  $L =$  ethylenediamine ( $L^1$ ), 1,2-propylenediamine ( $L^2$ ), 1,3-propylenediamine ( $L^3$ ),  $N$ -methylethylenediamine ( $L^4$ ),  $N$ -ethylethylenediamine ( $L^5$ ), glycine ( $L^6$ ),  $\alpha$ -alanine ( $L^7$ ),  $\beta$ -alanine ( $L^8$ ), malonate ( $L^9$ ),  $o$ -phenylenediamine ( $L^{10}$ ),  $o$ -aminophenol ( $L^{11}$ ) or catechol ( $L^{12}$ ) have been studied. The values of  $\Delta \log K$  have been compared to see the effect of nitro group over  $A^1$ , and  $Ls$  co-ordinating through  $N-N$ ,  $N-O^-$  and  $O^-O^-$ , on the ternary complex stabilities.

## Experimental

The pH measurement was carried out using a glass calomel electrode and pH-meter combination. All titrations were carried out in aqueous and aqueous-dioxan (1 : 1, v/v) solution. Dioxan was purified by known method.<sup>99</sup> In all the experiments conductivity water was used.

## Ligands and other chemicals

All the ligands used were of A.R. grade. Their standard solutions were prepared by directly dissolving the weighed quantity in known volume of purified dioxan or in aqueous solution. Invariably fresh solutions of ligands were prepared in purified dioxan prior to titration because dioxan on keeping for a longer period develops peroxides.

## Preparation of NaOH

The solution was prepared by dissolving 50 gms. of NaOH (Champal Ltd.) in 500 ml of conductivity water and was kept for two days. The solution was filtered through G<sub>4</sub> sintered glass crucible. The standard solution was prepared by titrating against standard oxalic acid solution. Sodlime guard tube was used to preserve this stock solution which will avoid any contact of CO<sub>2</sub>. This stock solution was then diluted to the required concentration i.e. 0.2M NaOH.

## Sodium Perchlorate

The required quantity of sodium perchlorate (A.R. Reidel) was weighed and dissolved in 500 ml. of conductivity water to prepare 1M solution.

### Perchloric acid solution

The perchloric acid (Riedel) supplied was of 70% concentration. A definite volume of the acid was dissolved in one litre of conductivity water to get a solution of 0.2M strength. The exact concentration was determined by titrating against standard NaOH solution.

### Metal Perchlorate Solution

In order to avoid the complexing tendency of the anion, the perchlorates of the metal ions were used. Copper perchlorate was prepared by dissolving weighed quantity of copper carbonate in known excess of perchloric acid. This is to avoid hydrolysis of Copper(II). From this stock solution, required concentrations of copper perchlorate solutions were prepared by proper dilution. In case of preparation of nickel perchlorate, nickel carbonate was refluxed with perchloric acid, till the excess of metal carbonate was left. The filtrate was a neutral solution of metal perchlorate. The amount of metal ion present in the above perchlorate solution was estimated. From these stock solutions, required concentration of metal perchlorate solutions were prepared by proper dilution.

### Apparata

All glasswares used were of pyrex glass. The microburette was calibrated to 0.01 ml by the method described by Vogel.<sup>100</sup> The measuring flask of various capacities, pipettes etc. were calibrated by using a standard burette.

### pH meter and Accessories

The digital pH-meter ' DIGICHEM 8201 ' supplied by M/s. G.P. Electronics, Baroda was used to measure pH. The accuracy of the pH meter is  $\pm 0.01$

### Details of Irving-Rossoti 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 glass stirrer. Pure nitrogen gas was obtained by passing the nitrogen through alkaline pyrogallol (for absorption of oxygen if any in traces), concentrated  $H_2SO_4$  (for absorption of moisture) and finally through 50% dioxan-water (1 : 1, v/v) medium. Pure nitrogen gas was allowed to pass through the solution by an inlet nozzle fitted at the bottom of the titration vessel.

Protonation and Binary M-L formation constants were determined earlier<sup>48</sup> by Irving-Rossotti method. In cases of Ni(II) complexes all the three species were considered i.e.  $ML$ ,  $ML_2$  and  $ML_3$ .

In 50% dioxan-water medium (1 : 1, v/v) formation of  $[MA]$  species is complete at very low pH, and therefore formation constant of  $[MA]$  could not be determined pH metrically.

Irving and Mellor<sup>101</sup> have suggested solvent extraction method for determination of formation constant

of binary species in aqueous medium. But it is not applicable in the dioxan-water medium because dioxan is miscible with the nonaqueous solvent used for extraction. The formation constant of binary system was therefore determined in indirect way. Using SCOGS computer program, the formation constant of  $[MA_2]$  was first refined by presuming the complete formation of  $[MA]$ . By observing that there is a difference in the values of  $K_{MA_2}^{MA}$  obtained in 50% dioxan-water medium and that reported in aqueous medium, the value of  $K_{MA}^M$  in 50% dioxan-water medium was kept equally less than the reported aqueous values. The value of it is presented in Table 1 .

In order to determine the formation constants of the ternary complexes, following six sets were prepared in every case for titration against NaOH solution.

- (1) 0.02M  $HClO_4$  and 0.18M  $NaClO_4$ .
- (2) 0.02M  $HClO_4$  + 0.002M  $A^1$  and 0.0178M  $NaClO_4$ .
- (3) 0.02M  $HClO_4$  + 0.002MA + 0.002M metal perchlorate and 0.0176M  $NaClO_4$ .
- (4) 0.02M  $HClO_4$  + 0.002ML and 0.0178M  $NaClO_4$ .
- (5) 0.02M  $HClO_4$  + 0.002MA + 0.002ML + 0.002M metal perchlorate and 0.0174M  $NaClO_4$ .
- (6) 0.02M  $HClO_4$  + 0.002M L + 0.002M metal perchlorate + 0.0176M  $NaClO_4$ .

In all the cases ionic strength of 0.2M was maintained at initial stage by the addition of required amount of

sodium perchlorate solution. In all the cases the total volume was so adjusted that the solution was 50% dioxan-water (1 : 1, v/v). The above sets were kept for nearly 20 minutes at room temperature to attain the equilibrium and then all the titrations were carried out in nitrogen atmosphere in order to avoid the aerial oxidation. After addition of each portion of alkali, pH was noted. Corrections for pH in 50% dioxan-water have been made by using the method suggested by Van Uitert and Haas.<sup>102</sup>

In case of  $\text{Cu}^{+2}$  the titration against standard alkali was carried out for solution containing Cu : A : L in 1 : 1 : 1 and 1 : 1 : 2 and in case of  $\text{Ni}^{+2}$  in 1 : 1 : 1 and 1 : 1 : 10 proportions. The formation constants of all the ternary systems were determined below pH 6 in cases of Cu(II) complexes while for Ni(II) complexes it is below pH 7, as hydroxide formation takes place above that pH. In Ni(II) complexes both the formation constants  $K_{\text{NiAL}}^{\text{NiA}}$  and  $K_{\text{NiAL}_2}^{\text{NiAL}}$  were determined.

The formation constants of mixed ligand complexes were subjected to refinement by using the computer program SCOGS.<sup>54</sup> The values of  $K_{\text{CuAL}}^{\text{CuA}}$  were obtained in two ways :

- (1) By considering the reaction of the type  $\text{M} + \text{A} \rightleftharpoons [\text{MA}]$  and  $[\text{MA}] + \text{L} \rightleftharpoons [\text{MAL}]$ . The species present in the solution were considered to be  $\text{LH}_2$ ,  $\text{LH}$ ,  $\text{L}$ ,  $[\text{MA}]$  and  $[\text{MAL}]$ . This gives directly the value of  $\log K_{\text{MAL}}^{\text{MA}}$ .

(2) By considering that the combinations of A and L take place simultaneously i.e.  $M + A + L \rightleftharpoons [MAL]$  and the possible species present in the solution being  $LH_2$ ,  $LH$ ,  $L$ ,  $AH_2$ ,  $AH$ ,  $A$ ,  $M^{2+}$ ,  $[ML]$ ,  $[ML_2]$ ,  $[MA]$ ,  $[MA_2]$  and  $[MAL]$ . In this method the value of  $\log K_{MAL}^M$  is obtained, from which  $\log K_{MAL}^{MA}$  was calculated as follows :

$$\log K_{MAL}^{MA} = \log K_{MAL}^M - \log K_{MA}^M$$

The refined values of  $K_1H$ ,  $K_2H$ ,  $\log K_{ML}^M$ ,  $\log K_{ML_2}^{ML}$ ,  $\log K_{MA_2}^{MA}$  were used.

In case of Ni(II), titrations were carried out in 1 : 1 : 2 and 1 : 1 : 10 ratio because Ni(II) prefers hexaco-ordination. So there is formation of  $[NiAL]$  and  $[NiAL_2]$ . In this case also it is presumed that  $[NiA]$  formation is complete at lower pH and then L combines with  $[NiA]$  forming  $[NiAL]$  and  $[NiAL_2]$ . Therefore, in the first computer method species considered are  $LH_2$ ,  $LH$ ,  $L$ ,  $[NiA]$ ,  $[NiAL]$ ,  $[NiAL_2]$ . But in the second computer method the species considered are  $LH_2$ ,  $LH$ ,  $L$ ,  $AH_2$ ,  $AH$ ,  $A$ , Ni(II),  $[NiA]$ ,  $[NiA_2]$ ,  $[NiL]$ ,  $[NiL_2]$ ,  $[NiL_3]$ ,  $[NiAL]$  and  $[NiAL_2]$ .

Formation constants of the mixed ligands have been presented in Table 1 to 4 for Cu(II) and in Table 5 and 6 for Ni(II) complexes. Values of  $[MA^*L]$  complexes where  $A^* = 1,10$ -phenanthroline have also been represented from literature for comparison.<sup>103</sup>

### Spectral measurement

The spectra were recorded on a Carl Zeiss SPECORD UV/VIS Spectrophotometer with 1 cm. matched quartz cells using water as solvent. Solutions of  $10^{-2}$  mol/lit were used for visible region. Spectra of mixed-ligand complexes were recorded by mixing Cu : A : L in 1 : 1 : 1 ratio. In every case the pH of the solutions were maintained at the value  $\lambda_{\text{max}}$  where the concentration of that particular species was found to be maximum in computer output data and is presented in Table 7.

Table IIA 1

Ternary complex stability constants of Copper(II) in dioxan-water  
 (1 : 1, v/v) medium and 0.2M NaClO<sub>4</sub> at 30°C with standard deviation  
 $\sigma\beta$  in parentheses

Ligands	A <sup>1</sup>	$\Delta \log K$	$\log K_{\text{CuAL}}^{\text{CuA}}$	A*	$\Delta \log K$
L <sup>1</sup>	10.39 ( $\pm$ 0.06)	- 0.20	9.32	9.32	- 1.27
L <sup>2</sup>	9.73 ( $\pm$ 0.03)	- 0.37	9.26	9.26	- 0.84
L <sup>3</sup>	8.76 ( $\pm$ 0.05)	- 1.59	7.95	7.95	- 2.4

\* 1,10-phenanthroline

Table IIA 2

Ternary complex stability constants of Copper(II) in dioxan-water  
(1 : 1, v/v) medium and 0.2M NaClO<sub>4</sub> at 30°C with standard deviation  
 $\sigma\beta$  in parentheses

Ligands	$\log K_{\text{CuA}}^{\text{CuA}}$			
	$A^1$	$\Delta \log K$	$A^*$	
		$\Delta \log K$	$\Delta \log K$	
L <sup>4</sup>	9.7 (+ 0.03)	- 0.43	9.61	- 1.52
L <sup>5</sup>	8.96 (+ 0.05)	- 0.68	7.76	- 1.88
L <sup>6</sup>	8.93 (+ 0.06)	+ 0.20	8.7	- 0.03

\* 1,10-phenanthroline

Table IIA 3

Ternary complex stability constants of Copper(II) in dioxan-water  
 (1 : 1, v/v) medium and 0.2M NaClO<sub>4</sub> at 30°C with standard deviation  
 $\sigma_{\beta}$  in parentheses

Ligand	$\log K_{\text{CuAL}}^{\text{CuA}}$			
	A <sup>1</sup>	$\Delta \log K$	A*	$\Delta \log K$
L <sup>7</sup>	9.23 ( $\pm$ 0.10)	- 0.23	8.98	- 0.48
L <sup>8</sup>	7.28 ( $\pm$ 0.02)	- 0.94	7.22	- 1.0
L <sup>9</sup>	9.54 ( $\pm$ 0.03)	+ 0.86	8.73	+ 0.48

\* 1,10-phenanthroline

Table IIA 4

Ternary complex stability constants of Copper(II) in dioxan-water  
 (1 : 1, v/v) medium and 0.2M NaClO<sub>4</sub> at 30°C with standard deviation  
 $\sigma_{\beta}$  in parentheses

Ligands	log K <sub>CuA</sub> C <sub>CuAL</sub>		
	A <sup>1</sup>	$\Delta \log K$	A*
L <sup>10</sup>	4.38 ( $\pm$ 0.06)	- 0.36	3.83
L <sup>11</sup>	10.34 ( $\pm$ 0.03)	+ 0.63	9.25
L <sup>12</sup>	13.76 ( $\pm$ 0.05)	+ 0.94	13.48

\* 1,10-phenanthroline

Table IIA.5

Ternary complex stability constants of Nickel(II) in dioxan-water (1 : 1, v/v) medium and 0.2M NaClO<sub>4</sub> at 30°C with standard deviation  $\sigma\beta$  in parentheses

Ligands	$\log K_{NiA}^{NiA}$	$\Delta \log K$	$\log K_{NiAL}^{NiAL}$	$A^*$	$\Delta \log K$
L <sup>1</sup>	7.63 ( $\pm$ 0.18)	- 1.20	5.86	7.47	- 1.36
L <sup>2</sup>	7.47 ( $\pm$ 0.12)	- 1.47	4.47	7.22	- 1.72
L <sup>4</sup>	5.95 ( $\pm$ 0.11)	- 1.63	4.82	5.76	- 1.86

\* 1,10-phenanthroline

Table IIA 6

Ternary complex stability constants of Nickel(II) in dioxan-water (1 : 1, v/v) medium and 0.2M NaClO<sub>4</sub> at 30°C with standard deviation  $\sigma$   $\beta$  in parentheses

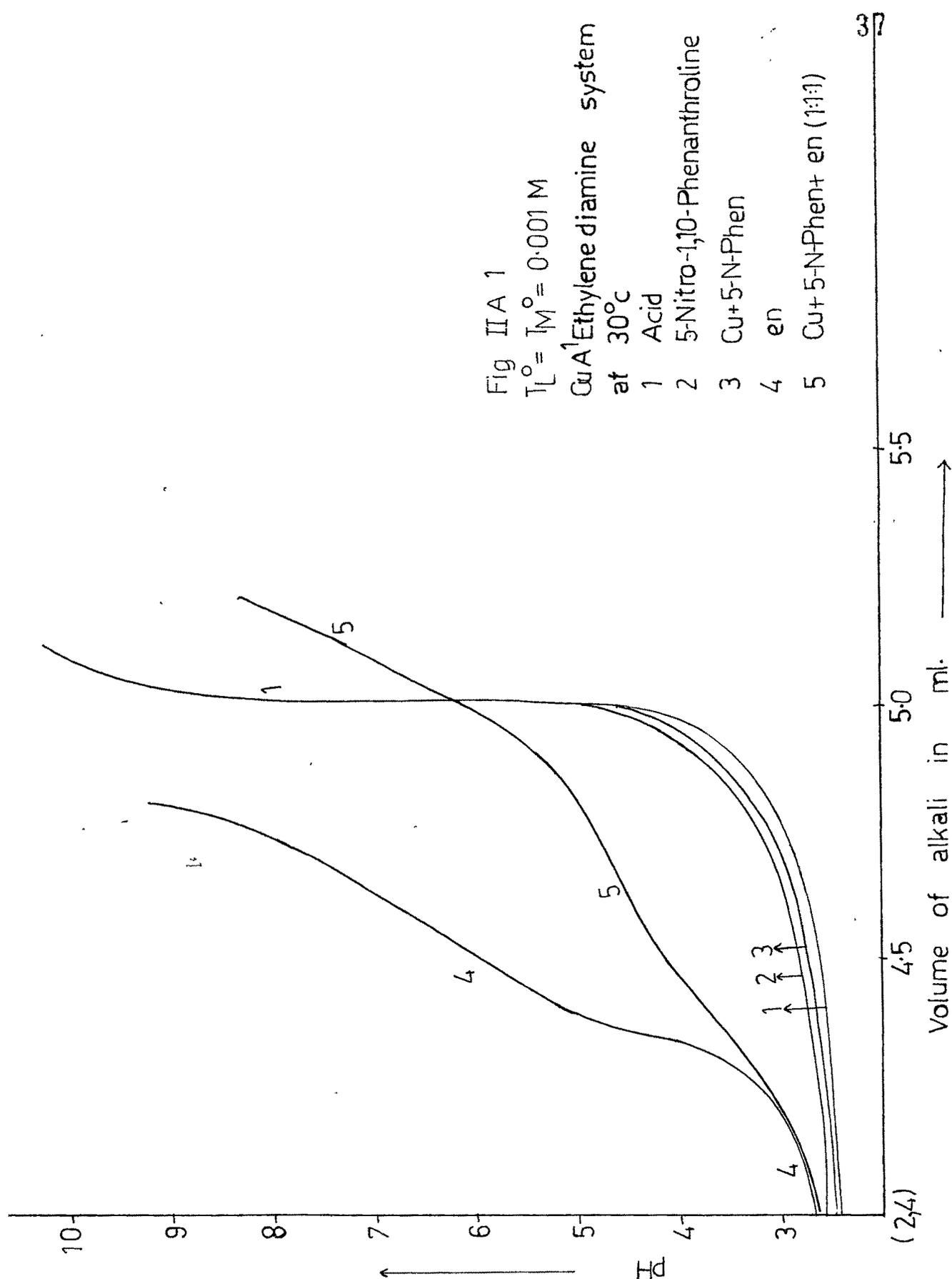
Ligands	$\log K_{\text{NIAL}}^{\text{NIA}}$	$\Delta \log K$	$\log K_{\text{NIAL}_2}^{\text{NIAL}}$	A*	$\Delta \log K$
L <sup>6</sup>	6.22 ( $\pm$ 0.09)	- 1.06	5.11	6.14	- 1.14
L <sup>7</sup>	5.24 ( $\pm$ 0.17)	- 1.04	4.62	5.5	- 0.80
L <sup>8</sup>	5.13 (+ 0.14)	- 0.77	3.23	4.95	- 0.95
L <sup>9</sup>	7.96 (+ 0.17)	+ 0.59	6.94	6.55	- 0.72

\* 1,10-phenanthroline

Table IIA 7

Visible Band Positions ( $\text{cm}^{-1}$ ) of Binary and Ternary  
Complexes in a Dioxan-Water (1 : 1, v/v) Medium

Compound	Calc. average value ( $\text{cm}^{-1}$ )	Obs. value ( $\text{cm}^{-1}$ )	Shift ( $\text{cm}^{-1}$ )
$\text{CuA}^1_2$	-	13,900	-
$\text{CuL}^1_2$	-	17,580	-
$\text{CuL}^6_2$	-	14,500	-
$\text{CuL}^8_2$	-	13,100	-
$\text{CuA}^1\text{L}^1$	15,740	16,900	1160
$\text{CuA}^1\text{L}^6$	14,200	16,390	2190
$\text{CuA}^1\text{L}^8$	13,500	18,120	4620



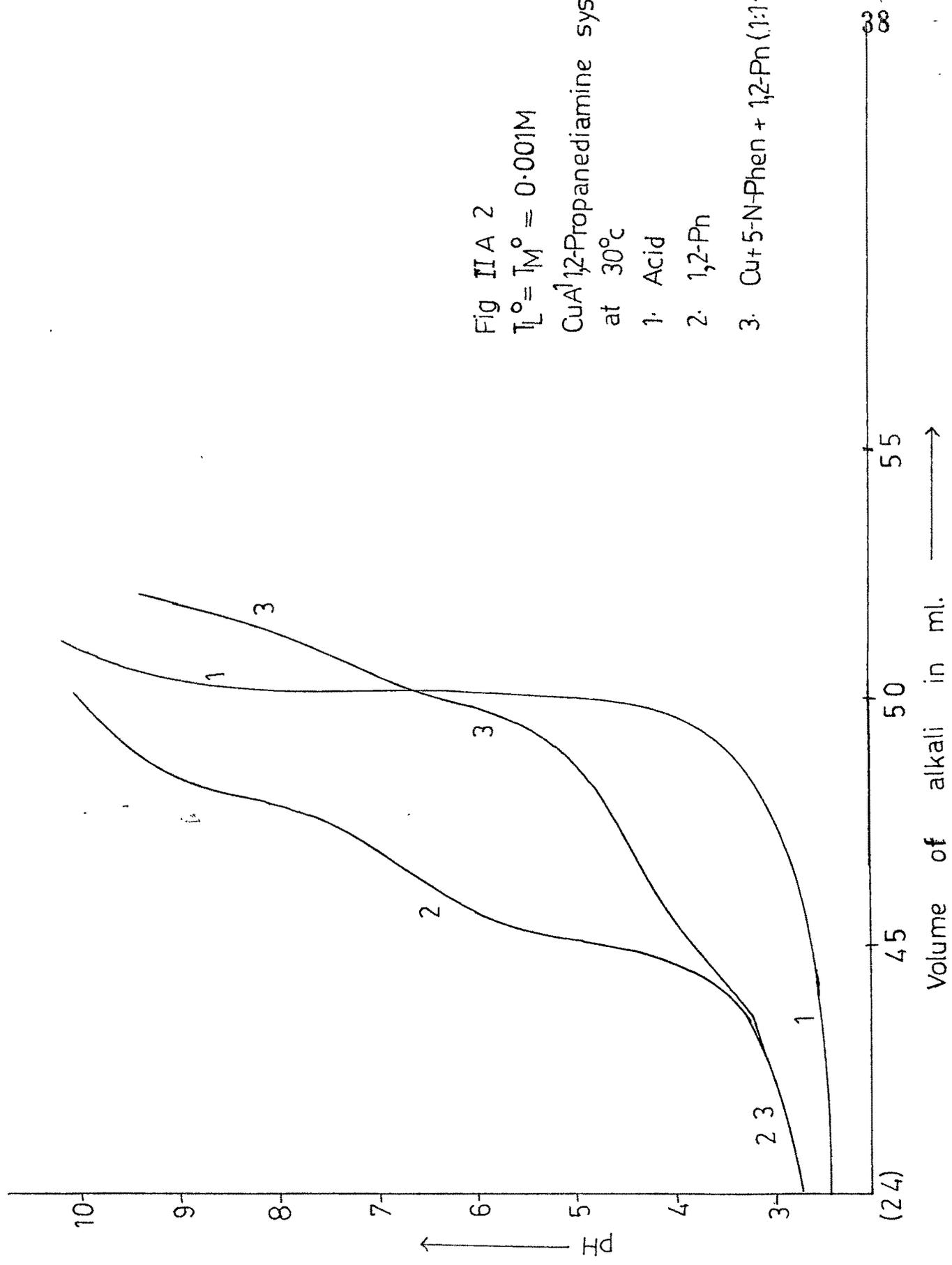


Fig IIA 2  
 $T_L^\circ = T_M^\circ = 0.001M$   
 CuA<sup>12</sup>-Propanediamine system  
 at 30°C  
 1. Acid  
 2. 1,2-Pn  
 3. Cu+5-N-Phen + 1,2-Pn (1:1:1)

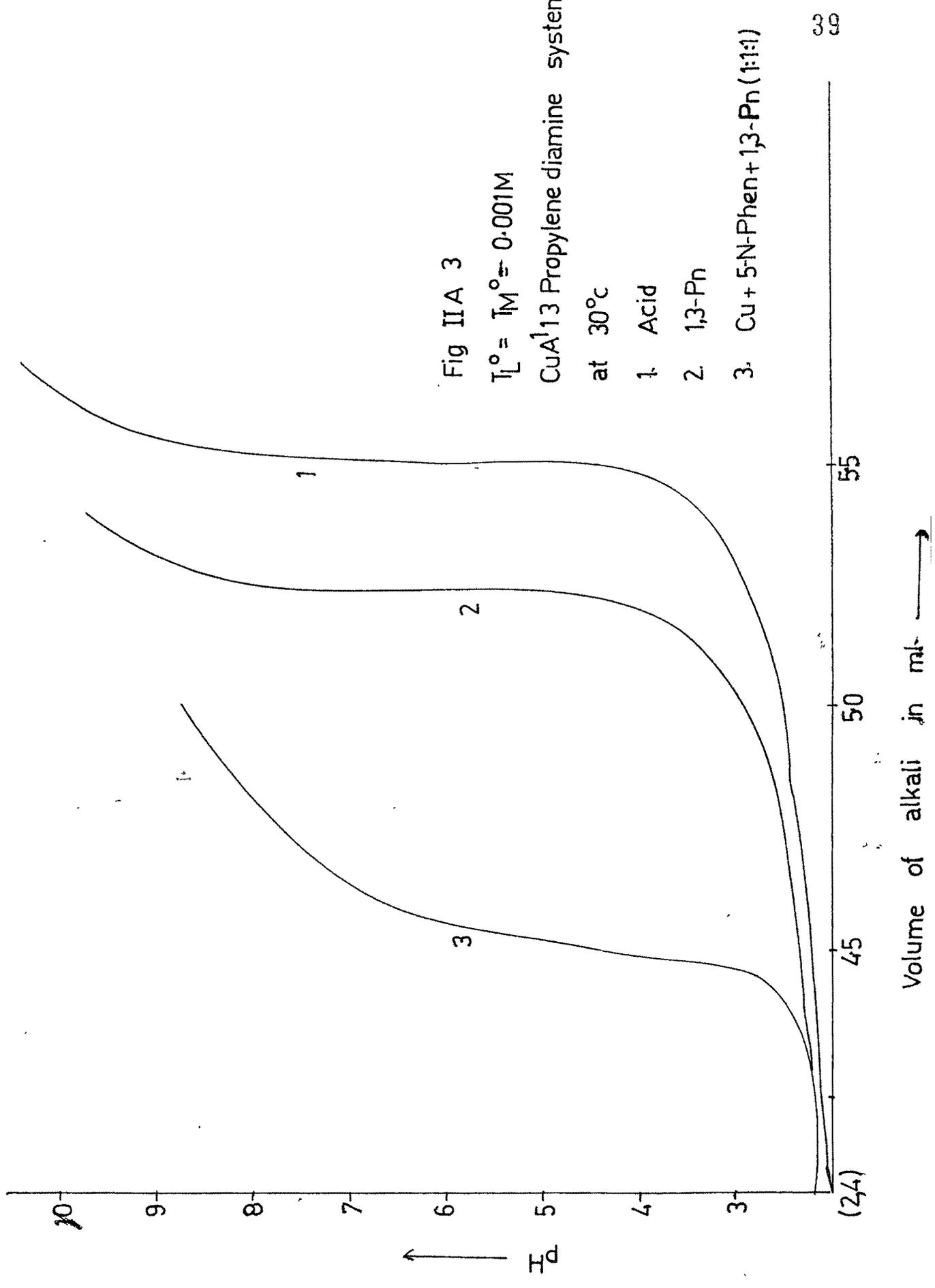


Fig IIA 3

$T_L^0 = T_M^0 = 0.001M$

Cu<sup>13</sup> Propylene diamine system

at 30°C

1. Acid

2. 1,3-Pn

3. Cu + 5-N-Phen + 1,3-Pn (1:1:1)

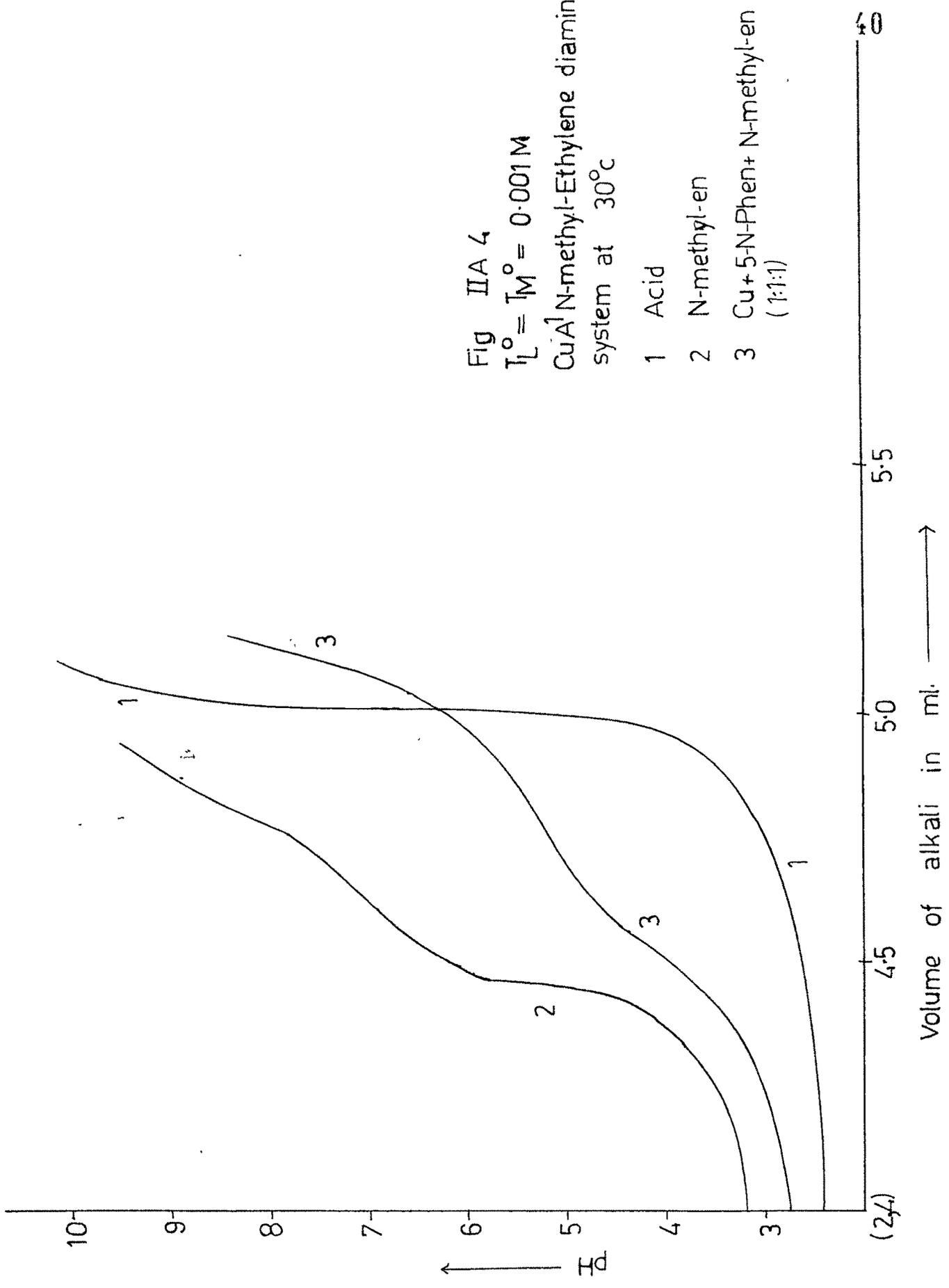
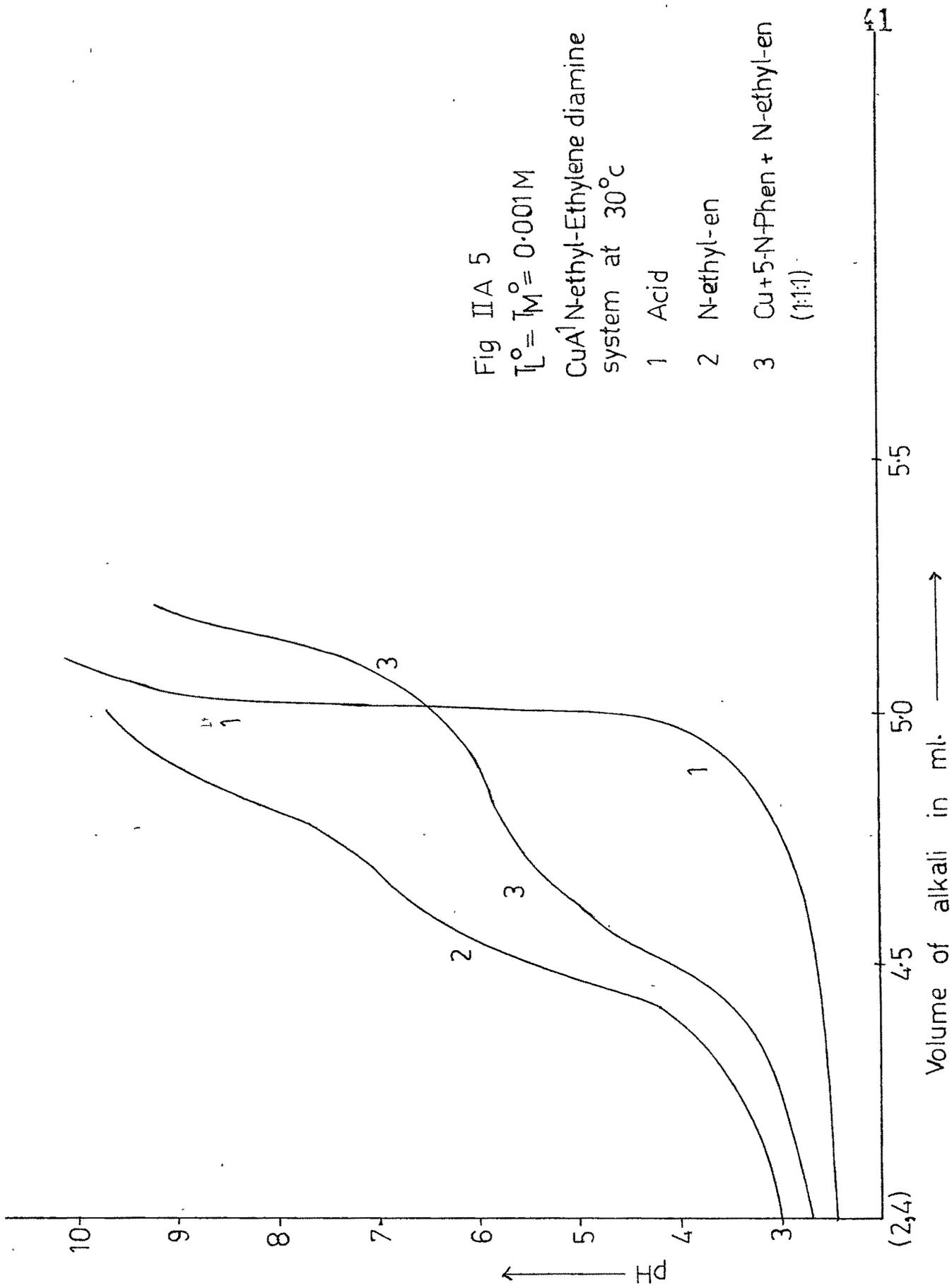


Fig IIA 4  
 $T_L^{\circ} = T_M^{\circ} = 0.001 M$   
 Cu<sup>II</sup> N-methyl-Ethylene diamine  
 system at 30°C

- 1 Acid
- 2 N-methyl-en
- 3 Cu + 5-N-Phen + N-methyl-en (1:1:1)



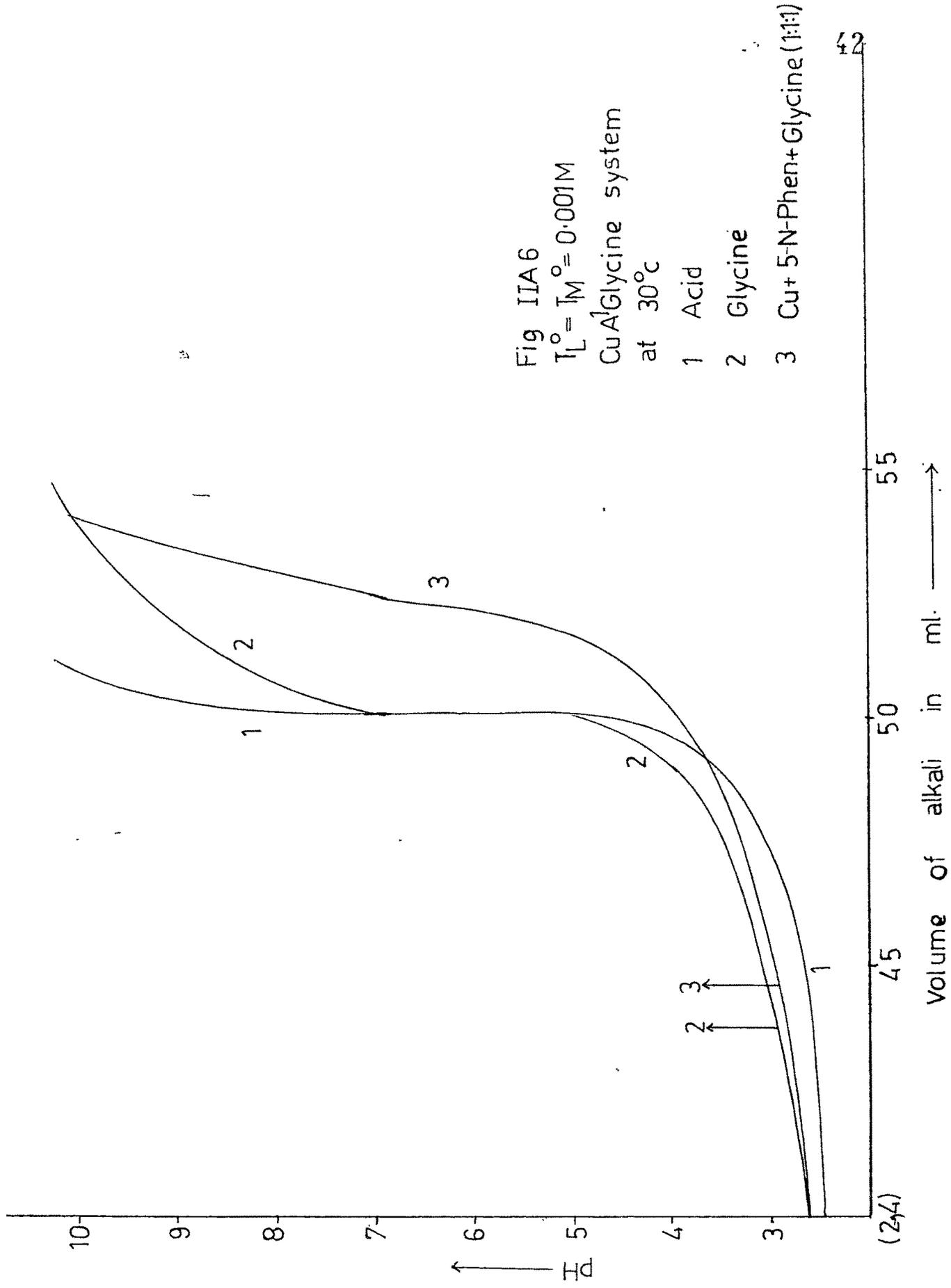


Fig IIA 7

$T_L^0 = T_M^0 = 0.001M$

CuAl<sup>I</sup> α-alanine system

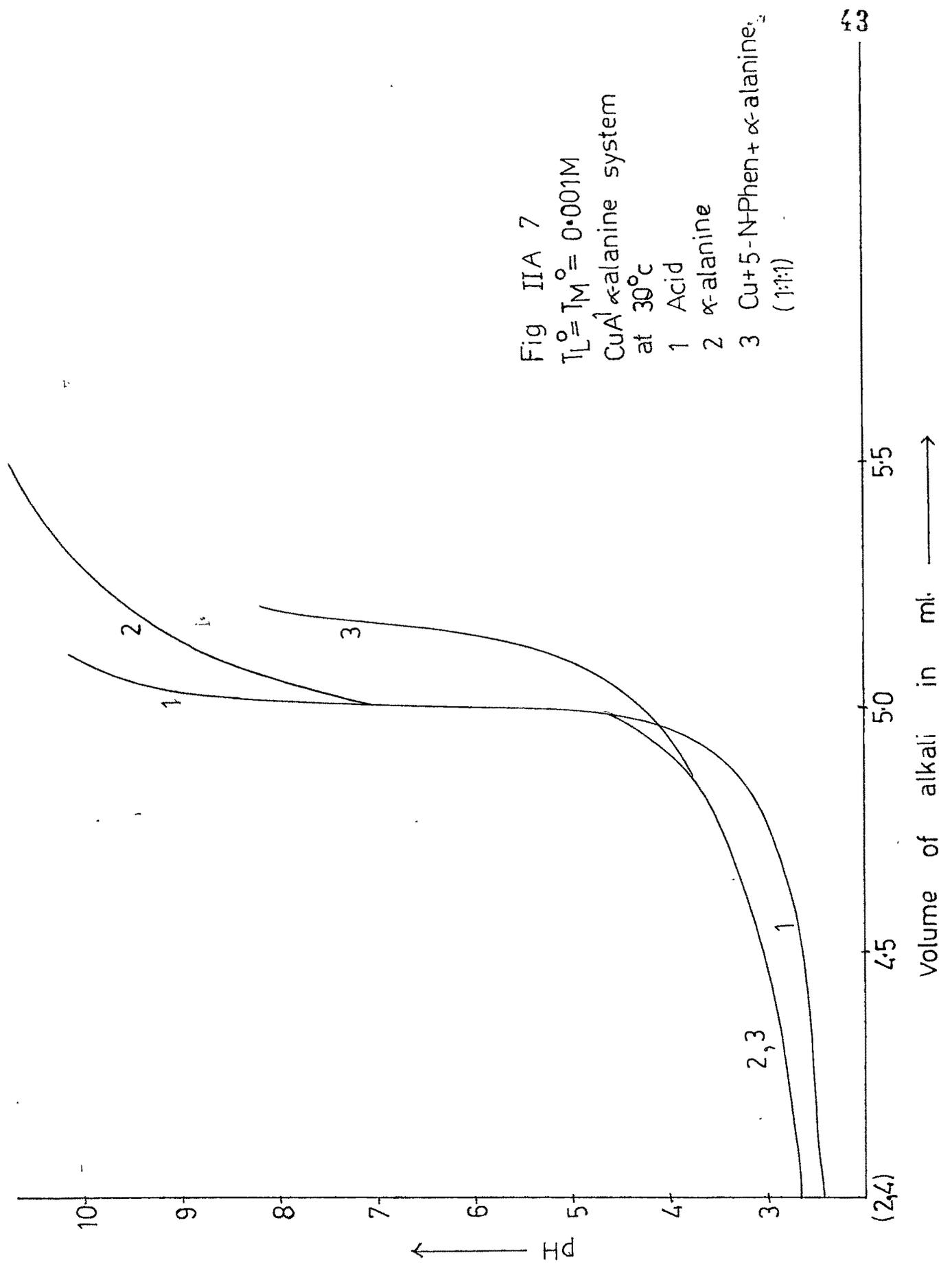
at 30°C

1 Acid

2 α-alanine

3 Cu+5-N-Phen+α-alanine<sub>2</sub>

(1:1:1)



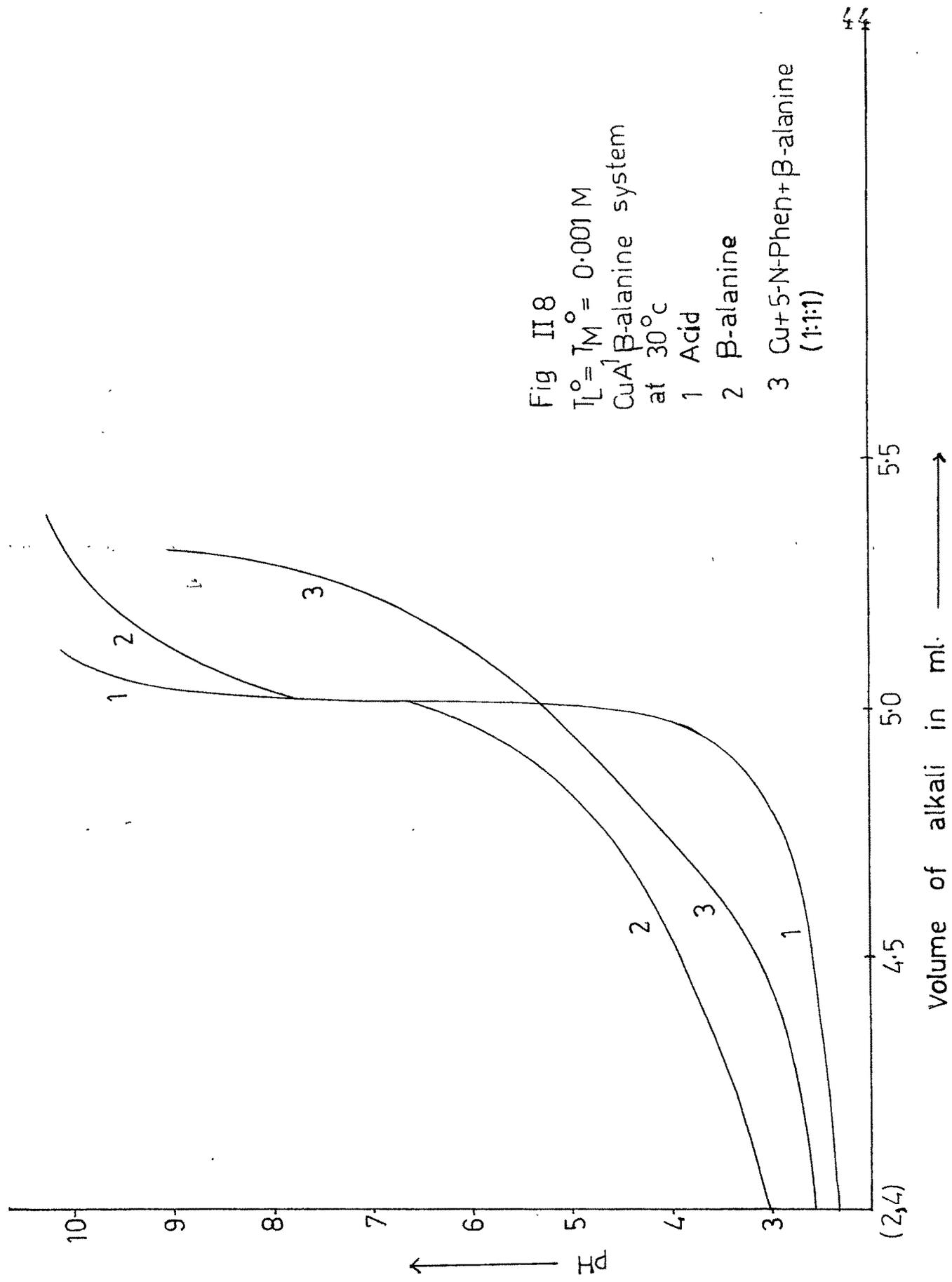


Fig II 8

$T_L^{\circ} = T_M^{\circ} = 0.001 \text{ M}$

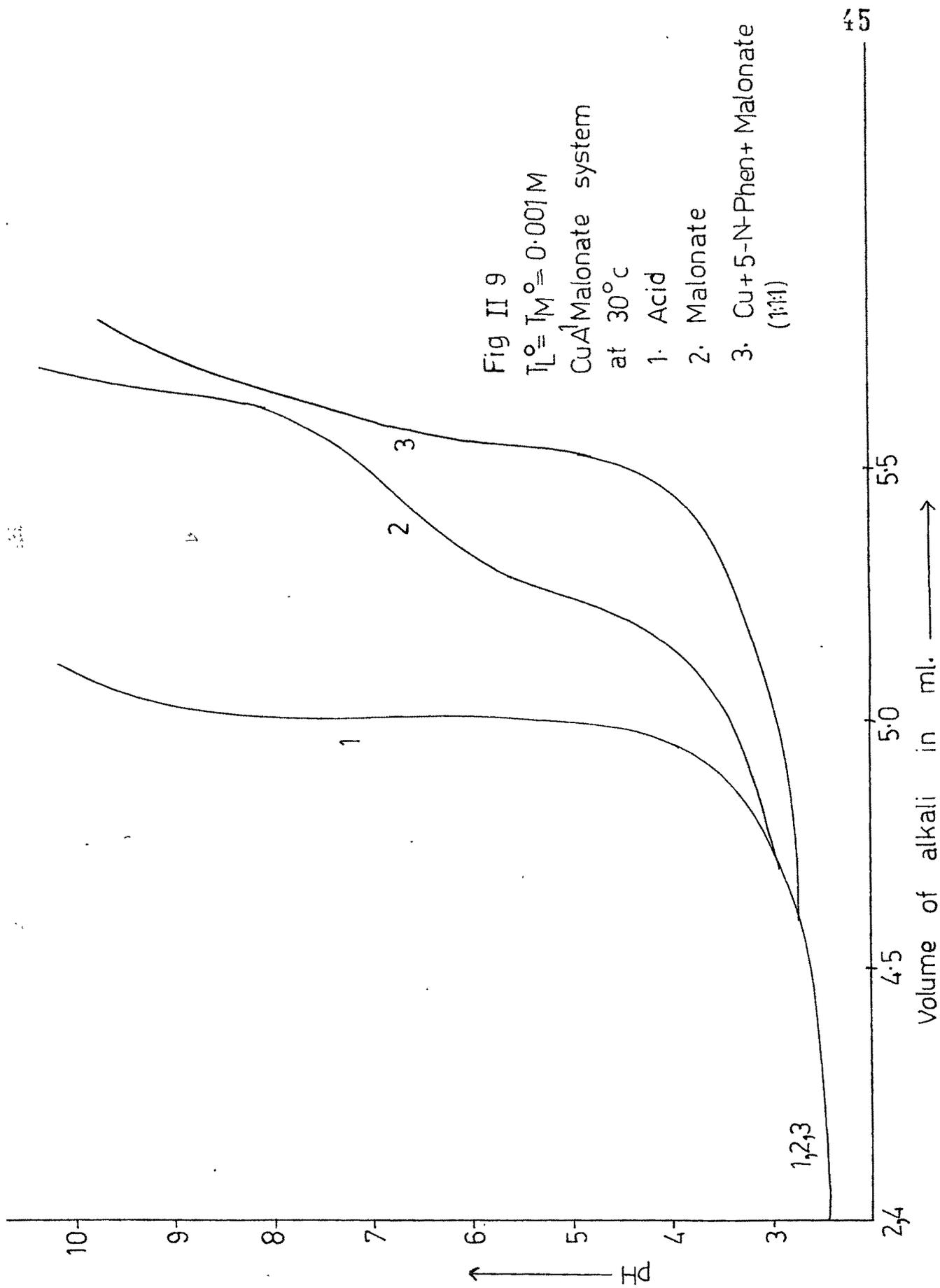
CuA<sup>1</sup> β-alanine system

at 30°C

1 Acid

2 β-alanine

3 Cu+5-N-Phen+β-alanine  
(1:1:1)



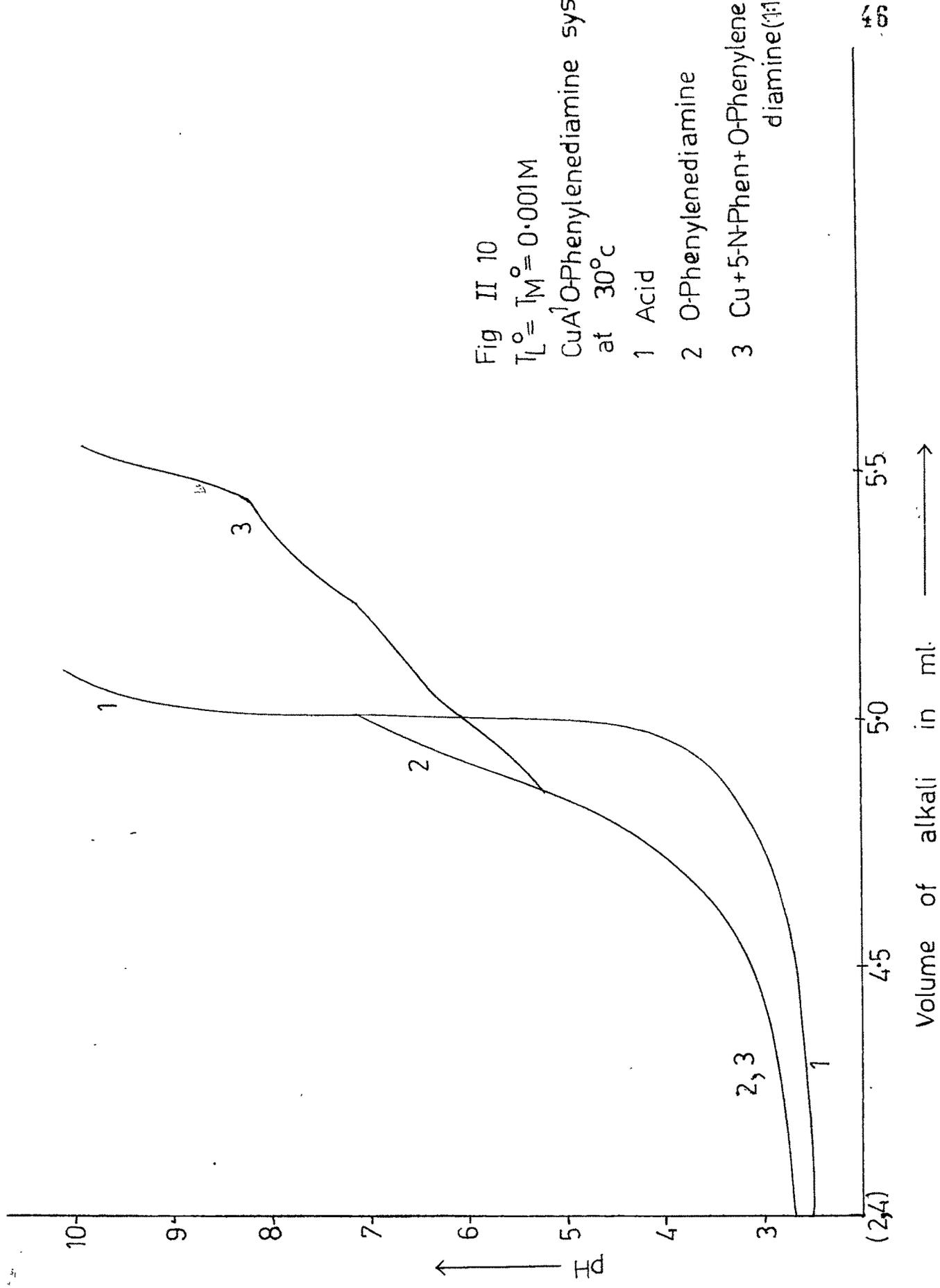
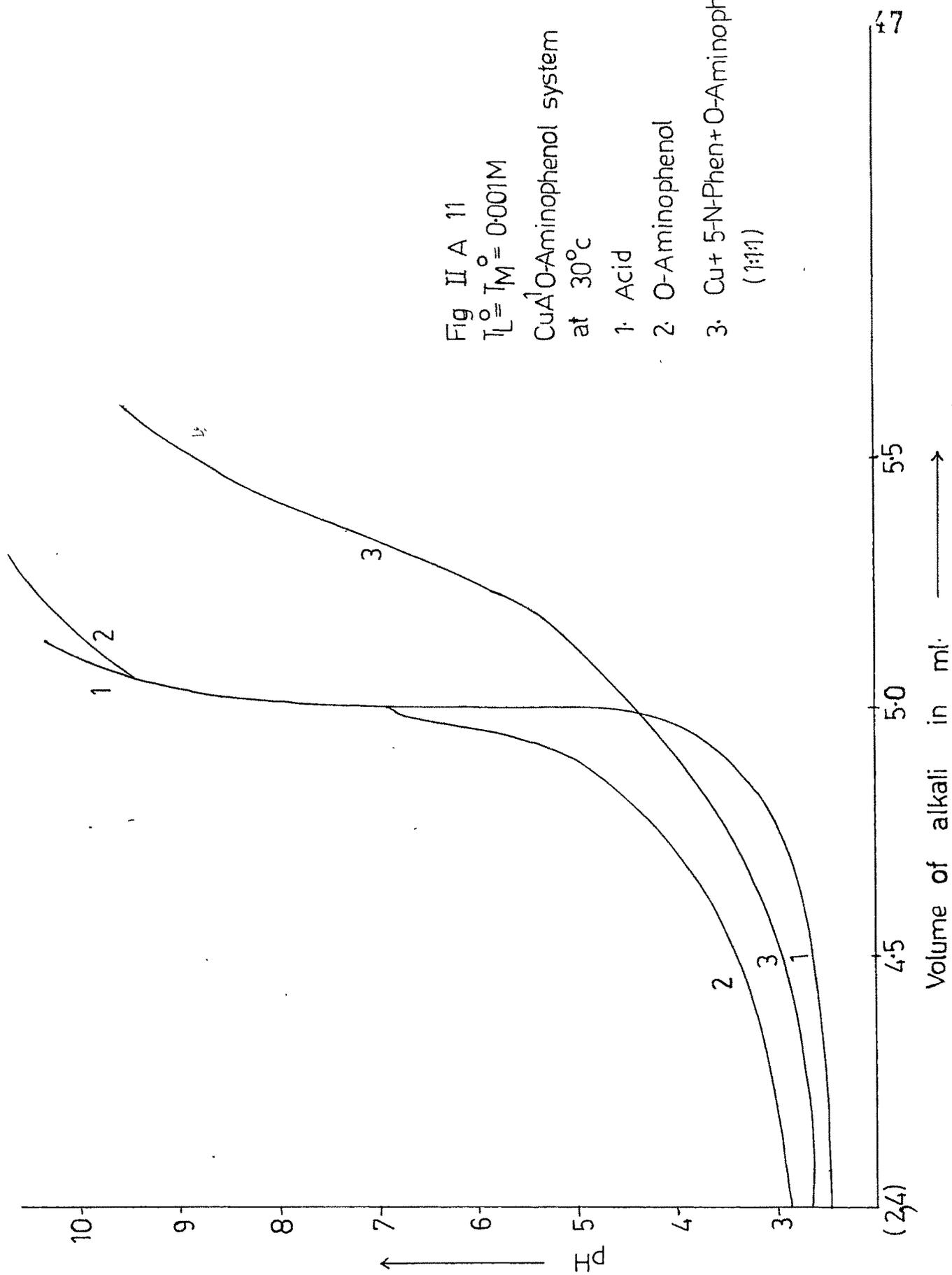


Fig II A 11

$T_L = T_M = 0.001M$

Cu<sup>1+</sup>O-Aminophenol system  
at 30°C

- 1. Acid
- 2. O-Aminophenol
- 3. Cu + 5-N-Phen + O-Aminophenol  
(1:1:1)



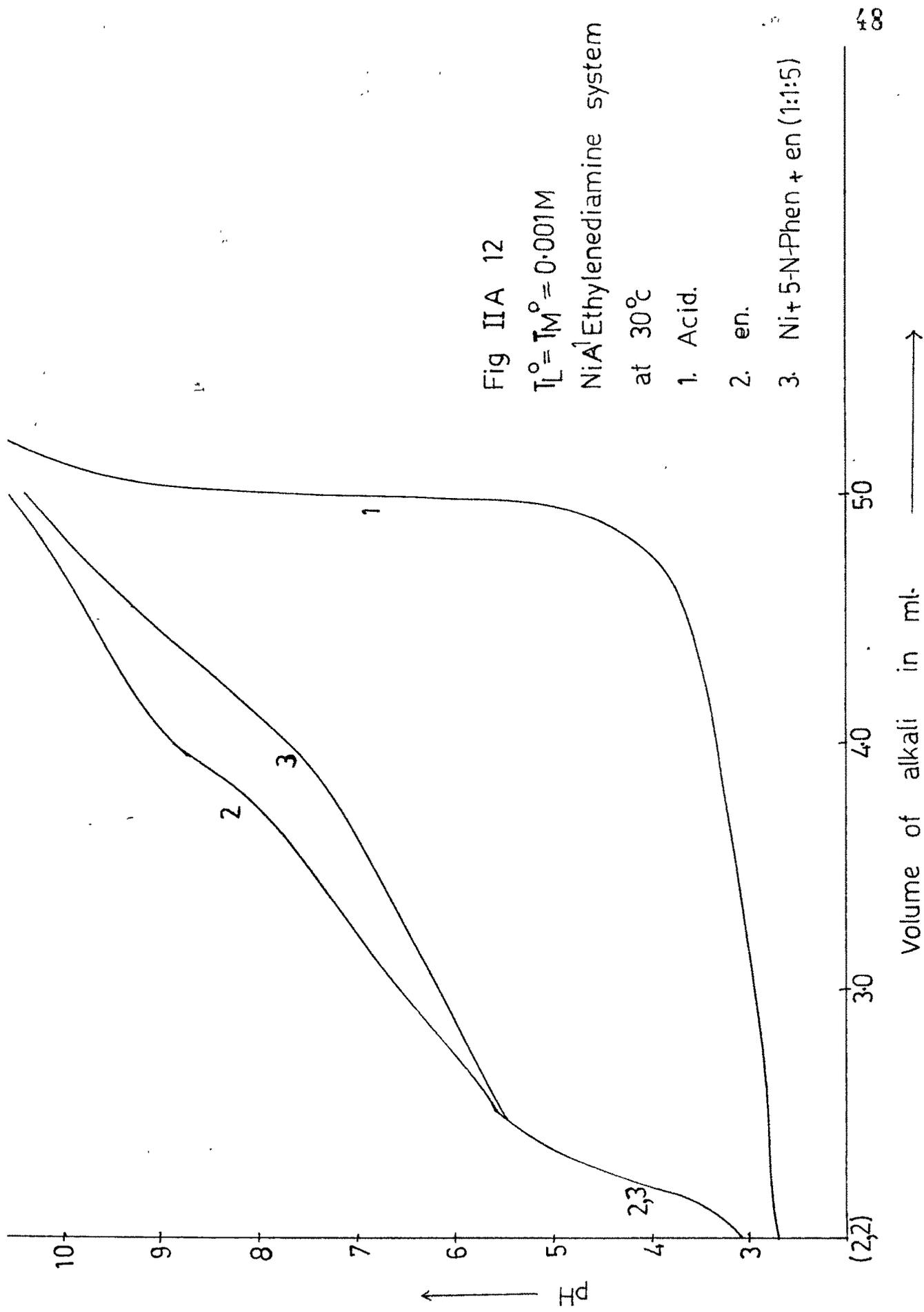


Fig IIA 13  
 $T_M^\circ = 0.001M$   
 Ni<sup>1</sup>1,2-Propylenediamine system  
 at 30°C  
 1. Acid.  
 2. 1,2-Pn.  
 3. Ni + 5 N Phen + 1,2-Pn (1:1:5)

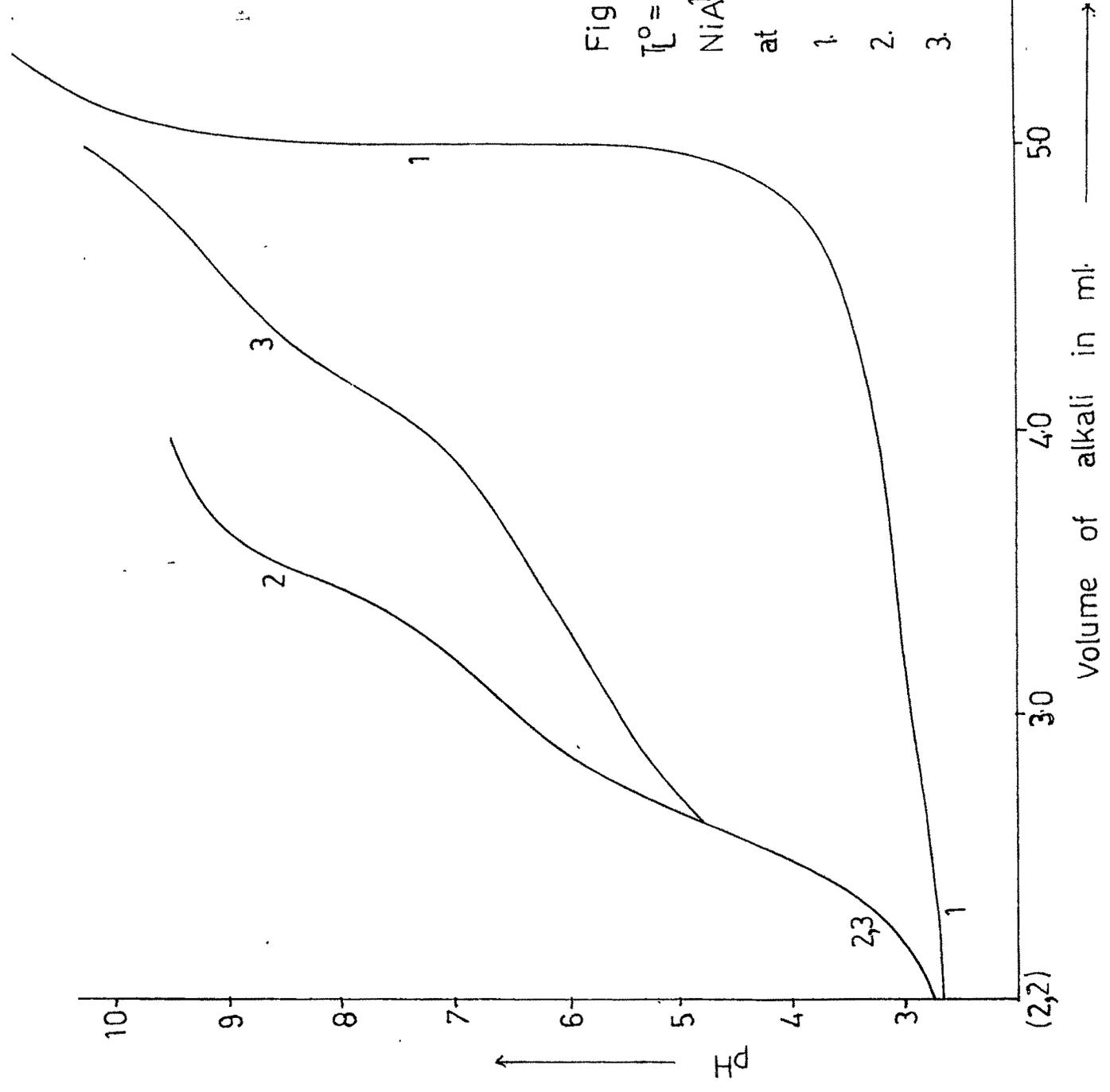
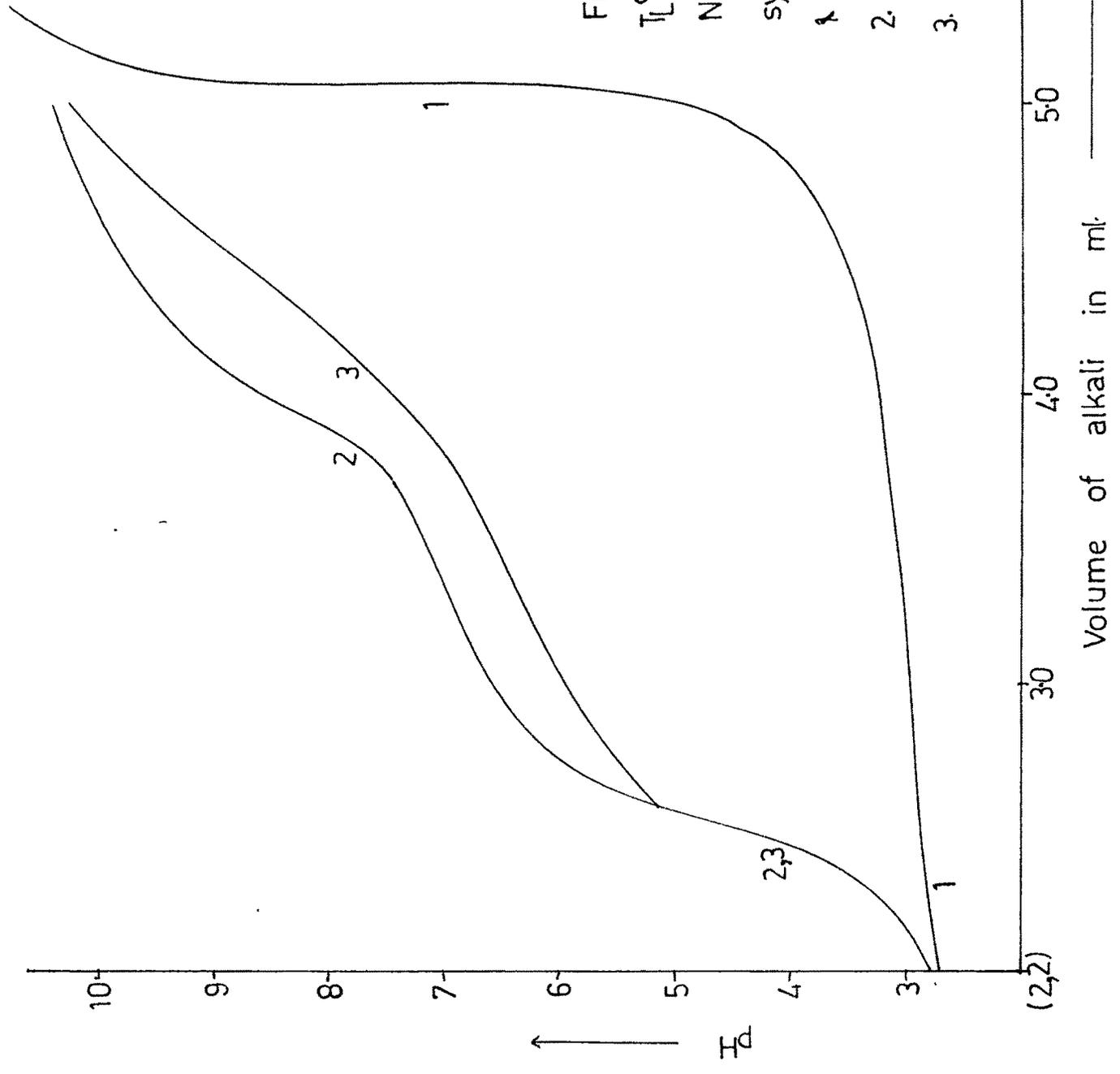


Fig II A 14  
 $T_L^\circ = T_M^\circ = 0.001M$   
 Ni<sup>1</sup>N methyl Ethylenediamine  
 system at 30°C

- 1. Acid.
- 2. N-m-en.
- 3. Ni+5-N-Phen + N-m-en (1:1:5)



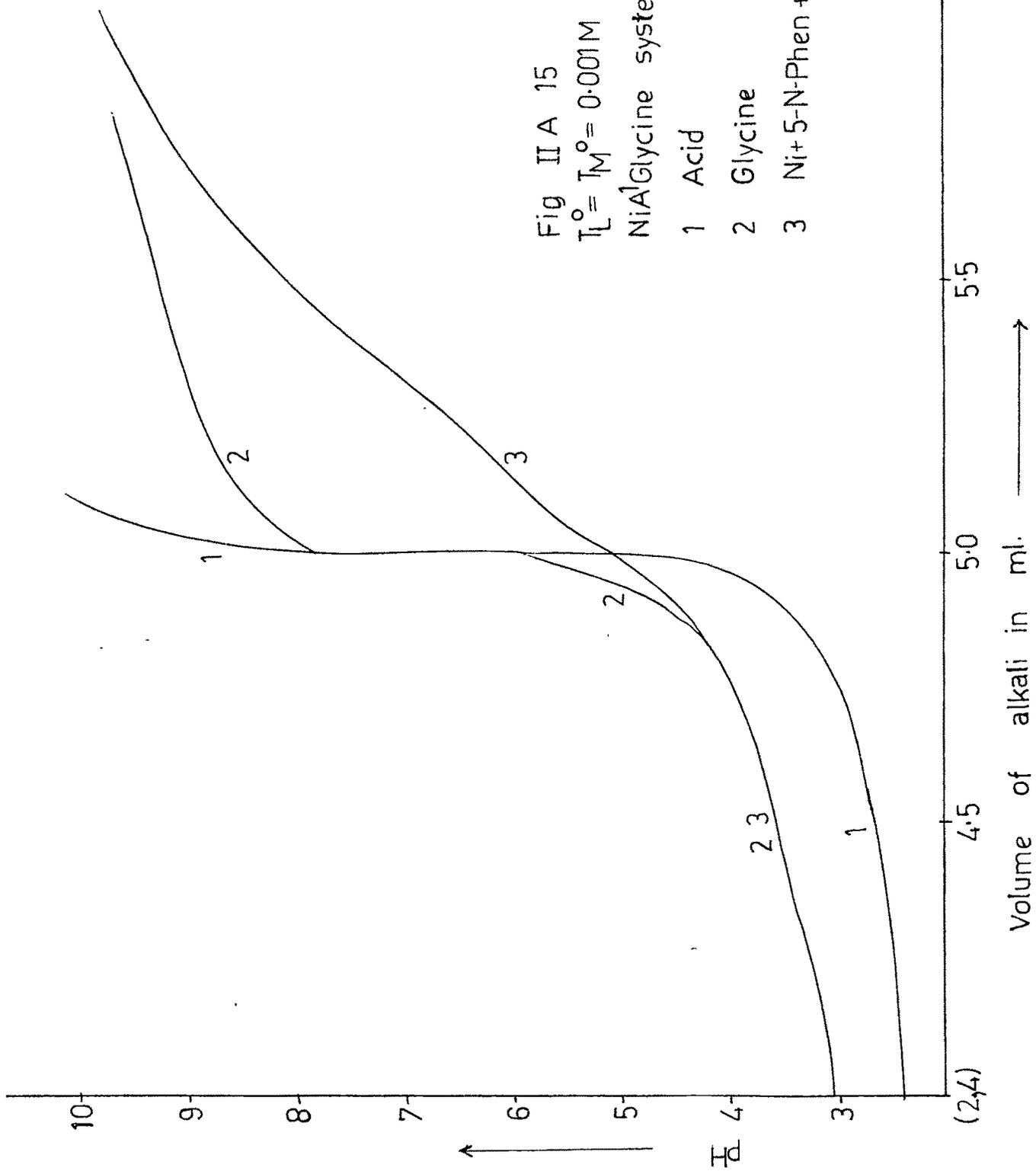


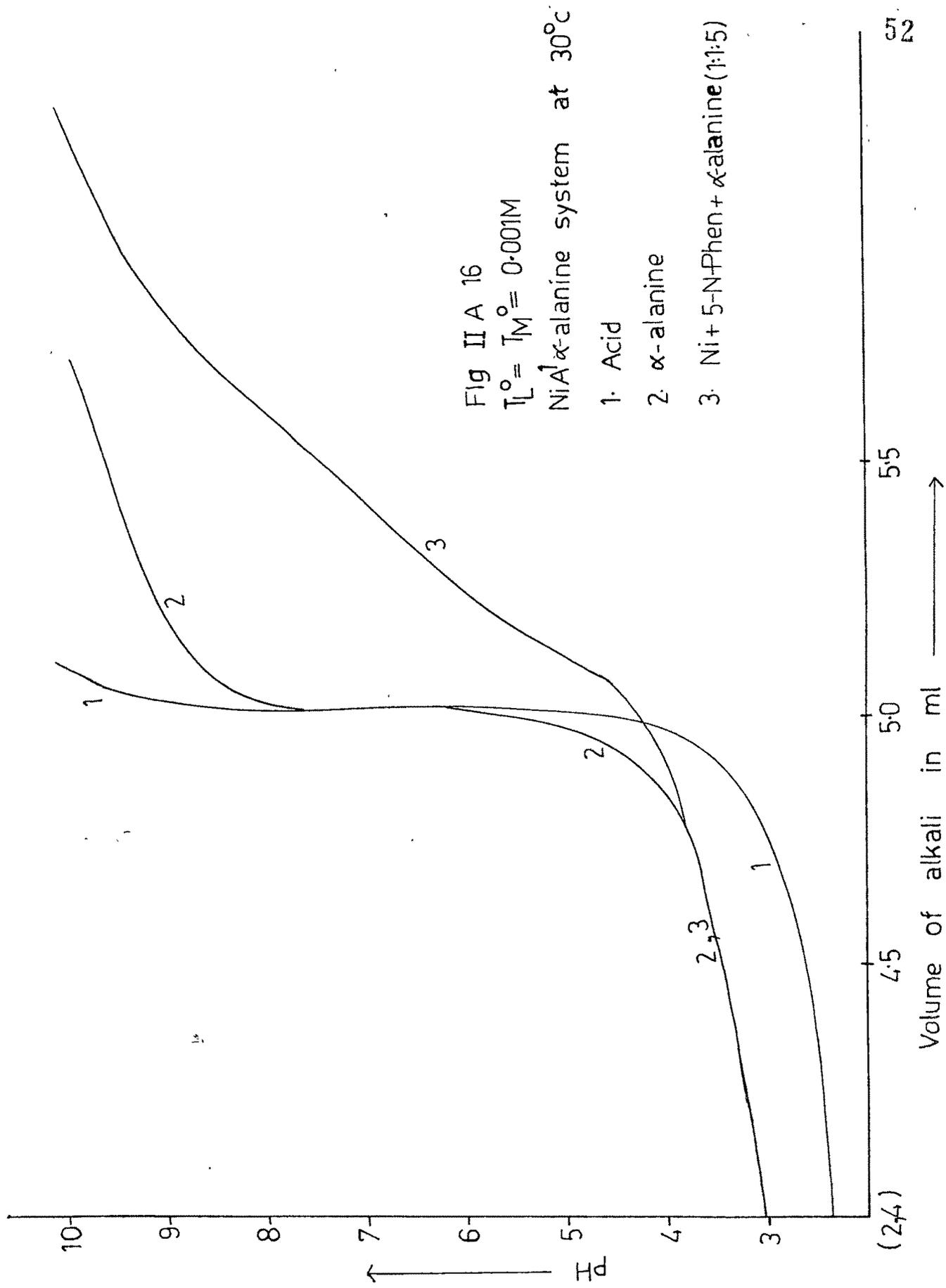
Fig II A 15

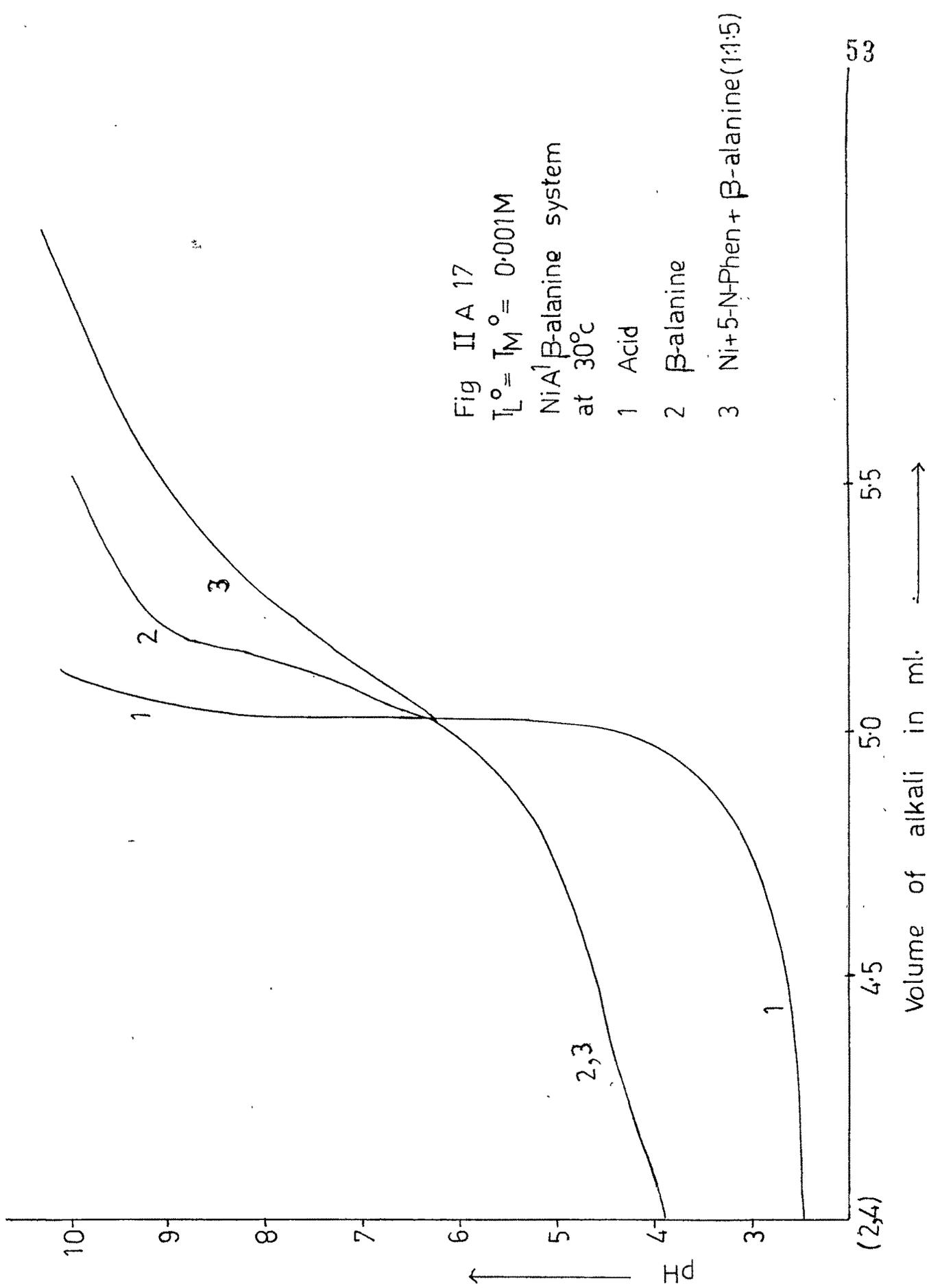
$T_L^0 = T_M^0 = 0.001M$

Ni<sup>2+</sup>Glycine system at 30°C

- 1 Acid
- 2 Glycine
- 3 Ni+5-N-Phen + Glycine (1:1:5)







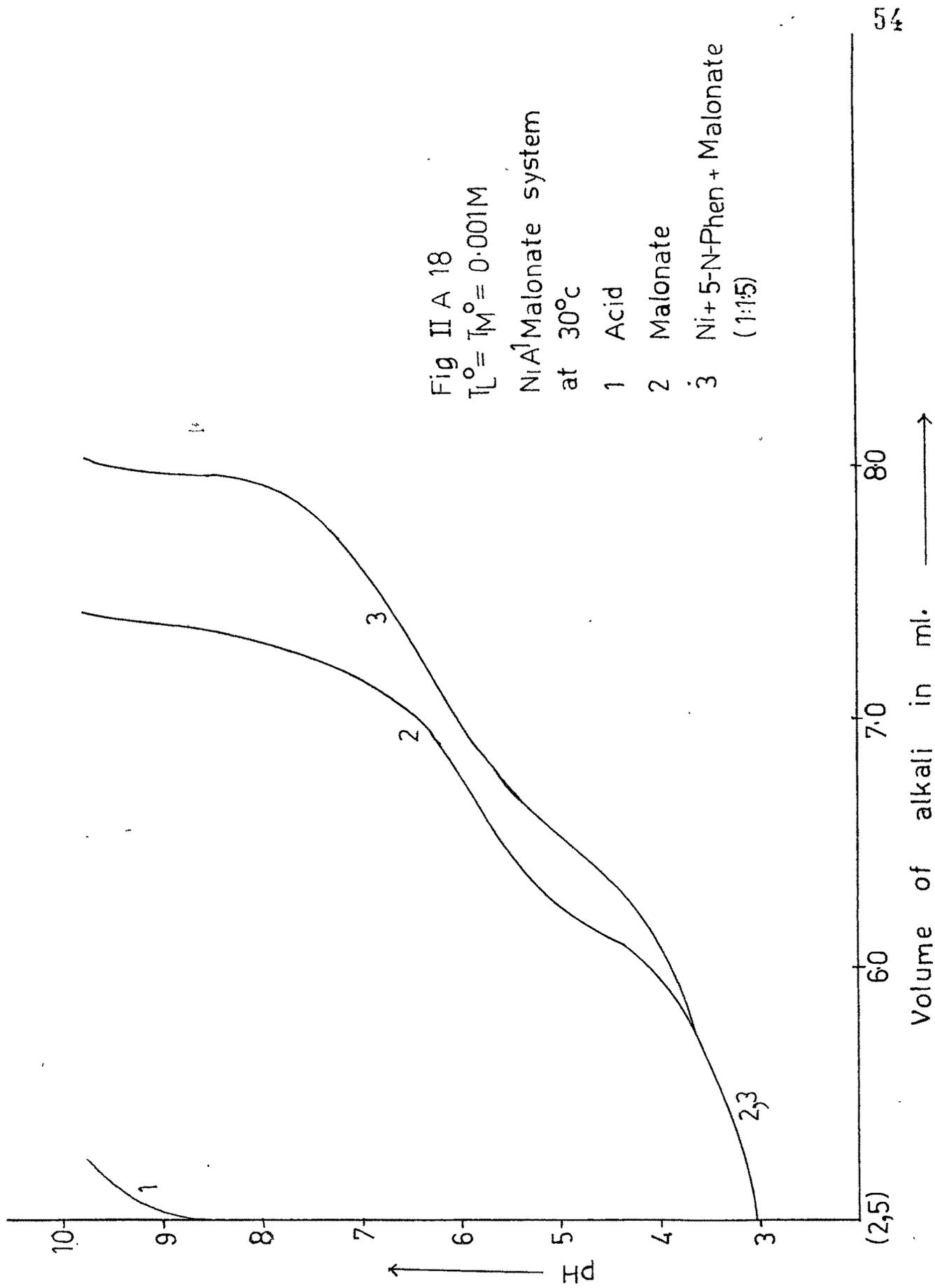
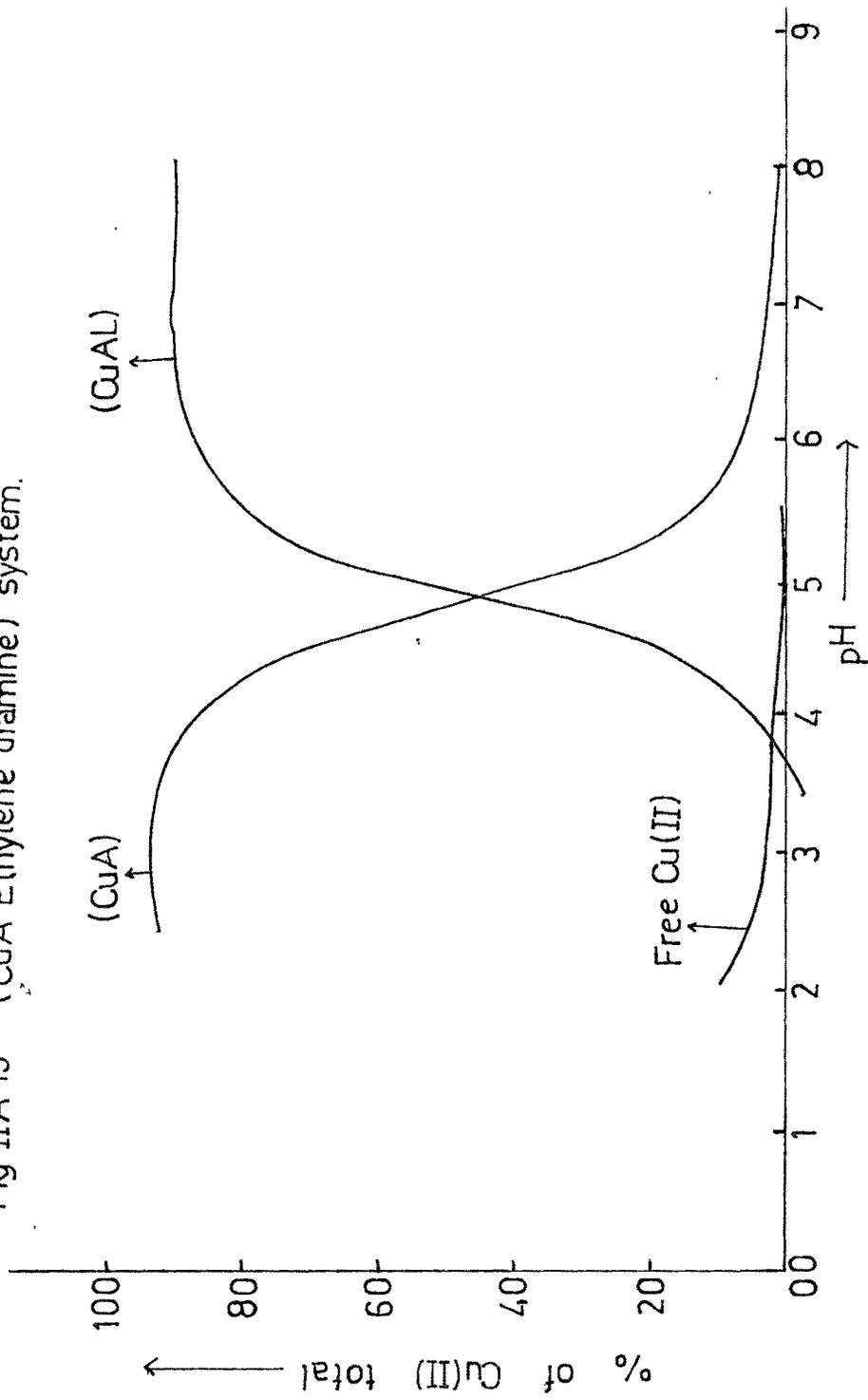
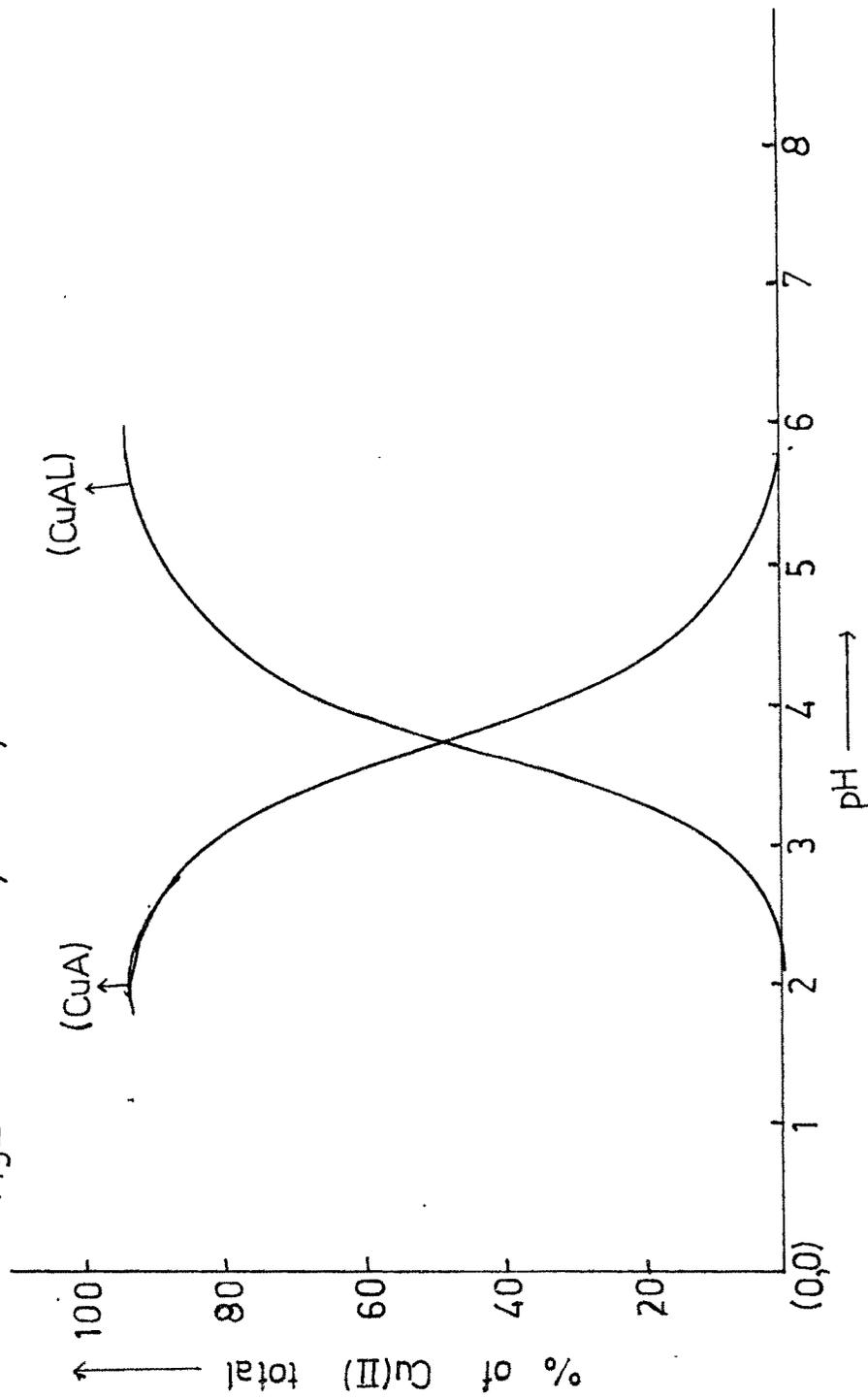


Fig IIA 19 ( $\text{Cu}^{\text{I}}$  Ethylene diamine) system.



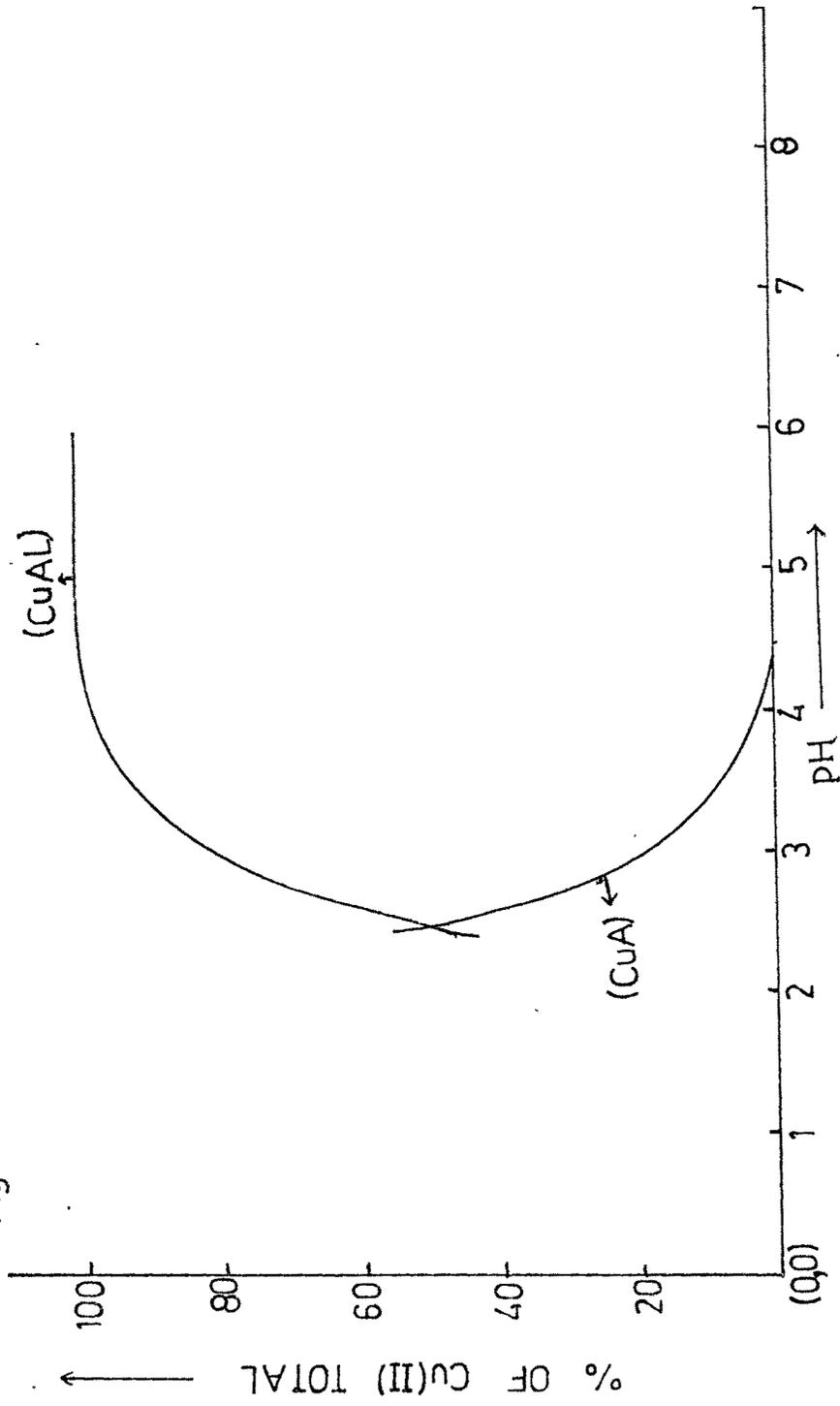
Variation of concentrations of different species with pH

Fig II A 20 (Cu<sup>A</sup>Glycine) system.



Variation of concentrations of different species with pH

Fig IIA ( $\text{Cu}^{\text{I}}$  Malonate) system



Variation of concentration of different species with pH

### Results & Discussion

The calculations of mixed ligand formation constants, using the extension of Irving-Rossotti method<sup>48</sup> were carried out by presuming that [MA] is formed completely and remains stable in the pH range where the co-ordination of secondary ligand takes place. In the first computer method also value of  $\log K_{MAL}^{MA}$  has been calculated by presuming complete formation of [MA].

However, in the second computer method no such presumption has been made for calculation of the mixed ligand formation constant, as the formation of all possible species has been considered. In case of Cu(II) complexes, the values obtained by both the methods are close to each other.

Further, from the plot of the concentrations of the species (fig. 19, 20), it is observed that in the lower pH range (1 to 3) Cu(II) and [CuA] are the major species and in the higher pH range (4 to 7) the species [CuA] and [CuAL] are in copiousness. Formation of [CuA<sub>2</sub>], [CuL<sub>2</sub>] and [Cu L] is very less and could not be plotted in the fig. 19 & 20. This shows that the reaction, forming [MAL], mainly proceeds stepwise.

In the case of [CuAmalonate] system, 99% of the mixed ligand complex is formed. In the case of [CuAminoacids] the maximum percentage of mixed ligand complex is 95% and in the case of [CuAdiamine] the percentage of mixed ligand complex formed is 93%. This

shows that these complexes are similar to  $[\text{CuAL}]$  systems where  $A = 2,2'$ -dipyridyl or 1,10-phenanthroline.<sup>45</sup>

In case of Ni(II), the value of the formation constant  $K_{\text{NiAL}}^{\text{NiA}}$ , obtained by Irving-Rossotti technique, is in agreement with the refined value obtained by using first computer method, presuming the complete formation of  $[\text{NiA}]$  and also the second computer method in which all possible species were considered to be present in the solution.

However, the value of  $K_{\text{NiAL}_2}^{\text{NiA}}$  obtained from the data of titration of  $\text{Ni} : \text{A} : \text{L} = 1 : 1 : 5$  solution, using the extension of Irving-Rossotti method and the first computer method, is not in agreement with the value obtained by the second computer method. This is because  $[\text{NiAL}_2]$  is formed at higher pH and formation of  $[\text{NiL}_2]$  and  $[\text{NiL}_3]$  starts in this range. Hence, the first two methods which do not consider the formation of  $[\text{NiL}_3]$  do not give correct value of  $K_{\text{NiAL}_2}^{\text{NiA}}$ .

The formation constant of the ternary complex  $K_{\text{CuAL}}^{\text{CuA}}$  is more than expected from statistical consideration. The order of stabilization of ternary complexes with L's co-ordinating from different atom is  $\text{O}^- - \text{O}^- > \text{O}^- - \text{N} > \text{N} - \text{N}$ . This can be explained by considering  $\text{Cu} \rightarrow \text{A} \pi$  bond formation as discussed in Chapter I. However, it is observed that stabilization of the ternary complex  $[\text{Cu } 5\text{-nitro-1,10-phenanthroline } \text{L}]$  is more than that of  $[\text{Cu } 1,10\text{-phenanthroline } \text{L}]$ . For L's co-ordinating through  $\text{O}^- - \text{O}^-$ ,  $\Delta \log K$  value is more positive when  $A = 5\text{-nitro-}$

1,10-phenanthroline ( $A^1$ ) than in case where  $A = 1,10$ -phenanthroline ( $A^*$ ). In case where  $L$  is  $O^-N$  co-ordinating,  $\Delta \log K$  is negative when  $A = A^*$  but it is positive when  $A = A^1$ . Similarly, the value of  $\Delta \log K$  is less negative in  $[CuA-N-N]$  complexes where  $A$  is  $A^1$  than where  $A = A^*$ . This can be explained by considering that the nitro group makes 5-nitro-1,10-phenanthroline a stronger  $\pi$  acid than 1,10-phenanthroline. Hence  $Cu \rightarrow 5\text{-nitro-1,10-phenanthroline}$   $\pi$  interaction is more, resulting in greater stabilization of the ternary complexes. As a result of greater back donation from  $M \rightarrow A^1$  in  $[MA^1L]$ , release of repulsion between metal  $d\pi$  electrons and lone pair of electrons over  $O^-$ , as discussed in first chapter, is greater than in case of  $[MA^*L]$ . This explains the more positive  $\Delta \log K$  values of the ternary complexes where  $L = O^-O^-$  and positive  $\Delta \log K$  value in case where  $L = O^-N$ . Positive  $\Delta \log K$  value in the ternary complexes  $[Cu A-O^-N]$  has also been observed in cases where  $A = 2(2'\text{-pyridyl})\text{benzimidazole}$  with greater  $M \rightarrow A$   $\pi$  interaction.<sup>45</sup> This observation was explained by considering that the release of repulsion between metal  $d\pi$  electrons and lone pair of electrons over only one  $O^-$  of amino acid is significant, resulting in positive  $\Delta \log K$ .

The size of the chelate ring ( $L$ ) also affects the stability of the ternary complexes. In case of pairs  $[CuA(en)]$ ,  $[CuA(1,3\text{-pn})]$  and  $[CuA(gly)]$ ,  $[CuA(\beta\text{-ala})]$  the co-ordination sites are of the same kind, but the only difference is the number of members within the second

chelate rings. The values of  $\Delta \log K$  obtained are more positive when  $L = \text{en}$  or glycine than where  $L = 1,3\text{-pn}$  or  $\beta\text{-alanine}$ . This can be explained by considering the fact that the ternary complexes of  $\text{Cu(II)}$  involving five-five membered chelate rings are more stable than those containing five-six membered chelate rings.<sup>30</sup>

In the cases where  $L = L^4$  or  $L^5$ , there is greater lowering in the ternary complex formation constants and  $\Delta \log K$  values are more negative than in case where  $L = L^1$ . This is due to steric hinderance in the ternary complex because of the alkyl groups over the N-atoms in  $L^4$  or  $L^5$ . The value of  $\Delta \log K$  is more negative for  $L^5$  than  $L^4$  because the ethyl group is bulkier and causes more steric hinderance during the formation of the mixed ligand complexes.

The discriminating effect of  $[\text{CuA}]$  is also observed in the set of  $[\text{CuAL}]$  complexes, where  $L =$  aromatic ligands  $L^{10}$ ,  $L^{11}$ ,  $L^{12}$ . It is observed that in the formation of  $[\text{CuAL}^{10}]$  and  $[\text{CuAL}^{11}]$  complexes with N-N and N-O<sup>-</sup> co-ordinating secondary ligands, respectively, the value of  $\Delta \log K$  is negative. The value of  $\Delta \log K$  is more negative in  $[\text{CuAL}^{10}]$  complexes with N-N co-ordination, than  $[\text{CuAL}^{11}]$  with N-O<sup>-</sup> co-ordination. In case of  $[\text{CuAL}^{12}]$  complexes with O<sup>-</sup>-O<sup>-</sup> co-ordination,  $\Delta \log K$  value is positive. Thus in these aromatic ligands the order is same as in cases of N-N, N-O<sup>-</sup> and O<sup>-</sup>-O<sup>-</sup> co-ordinating aliphatic ligand. However,  $\Delta \log K$  values are more positive or less negative in  $[\text{CuAL}]$  complexes, where the co-ordinating atom N-N, N-O<sup>-</sup> or O<sup>-</sup>-O<sup>-</sup> are over

aromatic ring in L, compared to that when they are over aliphatic ligand L.

The additional stabilization in terms of interligand  $\pi$  interaction through metal  $d\pi$  orbital can be ruled out on the basis of spectral studies. The absorption spectrum of free 5-nitro-1,10-phenanthroline exhibits band at 230 nm and 267 nm. The low energy band corresponds to  $\pi \rightarrow \pi^*$  transition. On co-ordination with metal ion, the complex  $[\text{CuA}_2^1]^{2+}$  exhibits bands at 233 nm, 278 nm and 303 nm. The appearance of new band and shift in  $\pi \rightarrow \pi^*$  transition shows that there is interaction between the  $\pi$  orbitals of Cu(II) and those of 5-nitro-1,10-phenanthroline molecule.  $L^1$  exhibits bands at 292.3 and 240.3. However, its complex  $[\text{CuL}_2^1]$  exhibits band at 250.0 and 280.8 nm.  $L^2$  exhibits bands at 239.2 and 292.3 nm, while its complex  $[\text{CuL}_2^2]$  exhibit bands at 250.0 and 280.8 nm.  $L^3$  shows band at 277.7 and its complex  $[\text{CuL}_2^3]$  exhibits bands at 240.9, 281.6 and 298.5 nm. The shift in the position of lowest energy band in each is due to  $L \rightarrow M$  charge transfer interaction. However, in the ternary complex of such ligands,  $[\text{CuA}^1\text{L}]$ , bands corresponding to  $\pi$  transition occur at the same place as in  $[\text{CuA}_2^1]^{2+}$  indicating that  $\pi$ -orbitals of  $[\text{CuA}^1]^{2+}$  are not affected in  $[\text{CuA}^1\text{L}]$ . This shows the absence of interligand  $\pi$ -interaction through metal  $d\pi$  orbitals. Hence, it has been considered by us that in these complexes also stabilization is due to release of electron repulsion in the ternary complex. Since the lone pair of electrons

of  $O^-$  attached to aromatic ring is in the  $p_x$  orbital, the repulsion between metal  $d\pi$  electron and ligand lone pair of electrons is more in the binary complex and the release of repulsion is more in the ternary complex.

The order of stability constants of  $[NiAL]$  complexes is same as that of  $[CuAL]$  complexes.  $[NiA]$  complexes also discriminate the ligand L in the following order of the co-ordinating sites  $O^-O^- > O^-N > N-N$ , though not to the same extent as in case of  $[CuA]$ . This can be explained as in case of Cu(II) complexes, in terms of release of electron repulsion in ternary complex. However, Ni(II) has lesser number of d electrons than Cu(II). It can be expected that the metal d electron and ligand atom electron repulsion in the binary complex is less and hence the release of repulsion in ternary complex is less. Consequently, the stabilization of the ternary complex, compared to the binary complex, is less. However, as in Cu(II) complex, in Ni(II) complexes also the stabilization of the ternary complex  $[Ni \text{ 5-nitro-1,10-phenanthroline } L]$  is more than that of  $[Ni \text{ 1,10-phenanthroline } L]$ .

#### Electronic Spectra of the Complexes

It is normally expected that in the mixed ligand complex  $[MAL]$ , the ligand field created is an average of the ligand fields in the binary complexes  $[MA_2]$  and  $[ML_2]$ . However, in the present complexes the band in the ternary complex is shifted to higher energy region than the calculated average value. The shift is more positive in the order  $O^-O^- > O^-N > N-N$ . Similar observation was

made with A = dipyridyl or 1,10-phenanthroline and was explained by considering that both the ligands A and L create stronger field in the ternary complex  $[\text{CuAL}]$  than in  $[\text{CuA}_2]$  or  $[\text{CuL}_2]$  because of the mutual stabilization of  $\sigma$  and  $\pi$  bonds of L and A, respectively. This further supports the concept of release of electron repulsion in the ternary complex.

It is observed that the shift in the position of the d-d transition band of the ternary complex is more towards higher energy regions in case where  $A = A^1$  than where  $A = A^*$ . This can be expected because the presence of electron withdrawing group in the 5-nitro-1,10-phenanthroline makes it a stronger  $\pi$  acid than 1,10-phenanthroline. Hence, it is obvious that the mutual stabilization of A and L binding will be more in  $[\text{Cu 5-nitro-1,10-phenanthroline}]$  complexes.

The study reveals that in the ternary complexes substitution over the tertiary amine affects the stability of the ternary complex, though the substituting group does not take part in co-ordination.

"Formation constants of ternary complexes involving 5-nitro-1,10-phenanthroline and O<sup>-</sup>-O<sup>-</sup> coordinating ligands".

During the past decade the importance of metal ion in the catalytic activity of phenol oxidases has become evident. Therefore, copper complexes of catechol have been studied extensively.<sup>104-111</sup> The Cu(II) complexes with protocatechuic acid have been studied by spectrophotometric method.<sup>112</sup> The formation constant of Cu(II) and Ni(II) complexes with catechol, pyrogallol, 2,3-dihydroxynaphthalene, protocatechuic acid and gallic acid were determined using Irving-Rossotti titration technique by Bhattacharya and coworkers.<sup>113,114</sup> The stability constants of Cu(II) or Ni(II) and catechol systems have also been determined by absorptiometric method.<sup>115,116</sup>

Catecholamines are also of biochemical importance and their degradation is brought about by the metalloenzymes co-ordinating with two phenolate O<sup>-</sup> of catechol and oxidizing it to a quinone.<sup>117-121</sup> The catecholamines are ambidentate in character and, therefore there are two possibilities for the formation of ternary complexes from O<sup>-</sup>-O<sup>-</sup> or NH<sub>2</sub> co-ordination sites. Depending on the metal ion, the pH and the nature of the second ligand, formation of mixed complexes involving different catechol or amino donor groups of the catechol amines are possible.

Dopamine contains only one chelate forming group pair, amino group being monodentate, while adrenaline contains two separate chelate forming groups within the molecule i.e. ethanol amine like and catechol like.

However, it is observed that both Dopamine and Adrenaline co-ordinate through phenolic hydroxy groups only.<sup>122-125</sup> In case of Cu-adrenaline the occurrence of polymeric species are possible when metal and ligand are in 1 : 1 ratio or possibly in case of metal ion excess.<sup>109,126</sup>

The combined presence of significant quantities of Fe(II), Zn(II), Cu(II), Mg(II) and Ca(II) ions, adenosine triphosphate (ATP) and biogenic amines (like dopamine, noradrenaline and adrenaline) in vesicles of the adrenal medulla and of the terminal varicosities of sympathetic nerves permits the conclusion that the amines may form complexes with the metal ions and with ATP during processes of their storage or their biochemical, physiological or pharmacological action.<sup>127,128</sup>

Rajan and coworkers,<sup>129,130</sup> investigated systems containing ATP and catecholamines with the following metal ions, Fe(II), Zn(II), Cu(II), Mg(II) and Ca(II). They concluded that the metal ion ATP complexes are formed at lower pH (3.0 - 6.4) and mixed ligand complex (1 : 1 : 1) are formed above pH 6.5. The complexes of [CuATP catecholamine] have been studied by Muro and coworkers<sup>131</sup> and Seifter and coworkers<sup>132</sup> also. It has been concluded that adrenaline participates in O<sup>-</sup>-O<sup>-</sup> co-ordination and the phosphate group of ATP are bound to the metal ion forming strong bonds. A weak bonding between the ligands was interpreted as an interaction between the adenine ring of ATP and the catechol ring of ATP and the catechol ring of adrenaline.

It has been observed<sup>91,92,133,134</sup> that  $\Delta \log K$  in  $[M.bipy.O^-O^-]$  is less negative or more positive when  $O^-O^-$  is over an aromatic ring as in catecholates than on an aliphatic compound such as malonate. Griesser and Sigel have put forth two explanations for  $[M.bipy.Cat]$  systems. Firstly, as a result of back donation of electrons from the metal d orbitals to 2,2'-bipyridyl, the metal ion becomes a hard acid. This in turn favours co-ordination of metal ion with oxygen containing ligands rather than with nitrogen containing ligands. Secondly, the  $\pi$  systems of the oxygen containing secondary ligand may have some effect in increasing the  $\log K_{MAL}^{MA}$  values. There may be an interaction between metal d $\pi$  orbitals with  $\pi$ -orbitals over 2,2'-bipyridyl molecule and the delocalized  $\pi$  electron cloud over the catecholate ion, resulting in a higher value of  $\log K_{MAL}^{MA}$ . The aliphatic diamines and  $O^-O^-$  co-ordinating ligands like malonate do not have such extensive  $\pi$  electron clouds and hence  $\pi$  electron delocalization in the complex molecules is restricted. The existence of  $\pi$  interaction has been supported by result of ESR spectral studies carried out by Sigel and coworkers.<sup>126</sup> However, Sigel believes that it is not very reliable and our study<sup>45</sup> of UV spectra of  $[CuAL]$ , where L = orthophenylenediamine, orthoaminophenol and catechol, shows absence of an interligand  $\pi$  interaction through metal atom orbital in complexes having aromatic ring in the secondary ligands. Study of complexes  $[CuAL]$  where A = 2,2'-dipyridyl, 1,10-phenanthroline, 2(2'-pyridyl)imidazoline, 2(2'-pyridyl)benzimidazole and L = catechol derivatives has been worked out earlier.<sup>135</sup>

In order to further study the effect of substitution on A and L on the ternary complex stability, in the present chapter [Cu 5-nitro-1,10-phenanthroline L] complexes have been studied, where L = dianion of catechol (L<sup>12</sup>), tiron (L<sup>13</sup>), pyrogallol (L<sup>14</sup>), protocatechuic acid (L<sup>15</sup>), catecholaldehyde (L<sup>16</sup>), 2,3-dihydroxynaphthalene (L<sup>17</sup>), 1,8-dihydroxynaphthalene (L<sup>18</sup>), dopamine (L<sup>19</sup>) or Adrenaline (L<sup>20</sup>), in 50% dioxan-water (1 : 1, v/v) medium at initially constant ionic strength 0.2M NaClO<sub>4</sub> and at 30°C.

## Experimental

Standardization of all the required solutions of copper perchlorate, sodium hydroxide, perchloric acid were done in the same way as detailed in Section A of this chapter. The ligands ( $L^{12}$  to  $L^{20}$ ) were also of A.R. grade (EDH, Merck pure).

The mixed ligand formation constants have been presented in Table 1 and 2. These tables also include  $\Delta \log K$  values and the standard deviation ( $\sigma\beta$ ) in formation constants, obtained by computer method.

The titration data are given in the form of figure 1 to 9. In every case, the concentration of various reagents taken have also been shown in the figures. The secondary ligand solutions of the required concentrations were freshly prepared prior to titration to avoid oxidation.

As discussed in previous section of thesis the computer method was used in two ways :

- (i) By considering the reaction to take place in steps and the species present in the solution being  $LH_2$ ,  $LH$ ,  $L$ ,  $[MA]$  and  $[MAL]$ .
- (ii) By considering all the possible species present in the solution  $LH_2$ ,  $LH$ ,  $L$ ,  $AH_2$ ,  $AH$ ,  $A$ ,  $M(II)$ ,  $[ML]$ ,  $[ML_2]$ ,  $[MA]$ ,  $[MA_2]$  and  $[MAL]$ .

The computer calculations were repeated using the titration data of the  $M : A : L$  taken in the ratios  $1 : 1 : 1$ ,  $1 : 1 : 2$  and  $1 : 1 : 10$ . The  $\log K_{MAL}^{MA}$  values obtained in different computer runs are very close to each other. The refined values of mixed ligand formation constants obtained by computer technique have been presented in Table 1 and 2.

Table IIB 1

Ternary complex stability constants of Copper(II) in dioxan-water  
(1 : 1, v/v) medium and 0.2M NaClO<sub>4</sub> at 30°C with standard deviation

$\sigma$   $\beta$  in parentheses

Ligand	$\log K_{\text{CuAL}}^{\text{CUA}}$			
	$A^1$	$\Delta \log K$	$A^*$	$\Delta \log K$
L <sup>12</sup>	13.76 (+ 0.1)	+ 0.96	13.47	+ 0.67
L <sup>13</sup>	14.56 (+ 0.07)	+ 0.15	14.25	- 0.15
L <sup>14</sup>	15.51 (+ 0.1)	+ 0.10	14.78	- 0.52
L <sup>15</sup>	16.05 (+ 0.07)	+ 0.49	15.36	- 0.32

\* 1,10-phenanthroline

Table IIB 2

Ternary complex stability constants of Copper(II) in dioxan-water  
(1 : 1, v/v) medium and 0.2M NaClO<sub>4</sub> at 30°C with standard deviation

$\sigma$   $\beta$  in parentheses

Ligands	$\log K_{CuA}^{CuA}$			
	$A^1$	$\Delta \log K$	$A^*$	$\Delta \log K$
L <sup>16</sup>	14.39 (+ 0.09)	+ 0.54	13.7	- 0.15
L <sup>17</sup>	15.35 (+ 0.09)	+ 0.80	14.74	+ 0.19
L <sup>18</sup>	10.66 (+ 0.1)	+ 0.09	9.41	- 1.16
L <sup>19</sup>	14.28 (+ 0.05)	+ 0.28	13.46	- 0.54
L <sup>20</sup>	15.67 (+ 0.1)	+ 1.01	15.15	+ 0.40

\* 1,10-phenanthroline

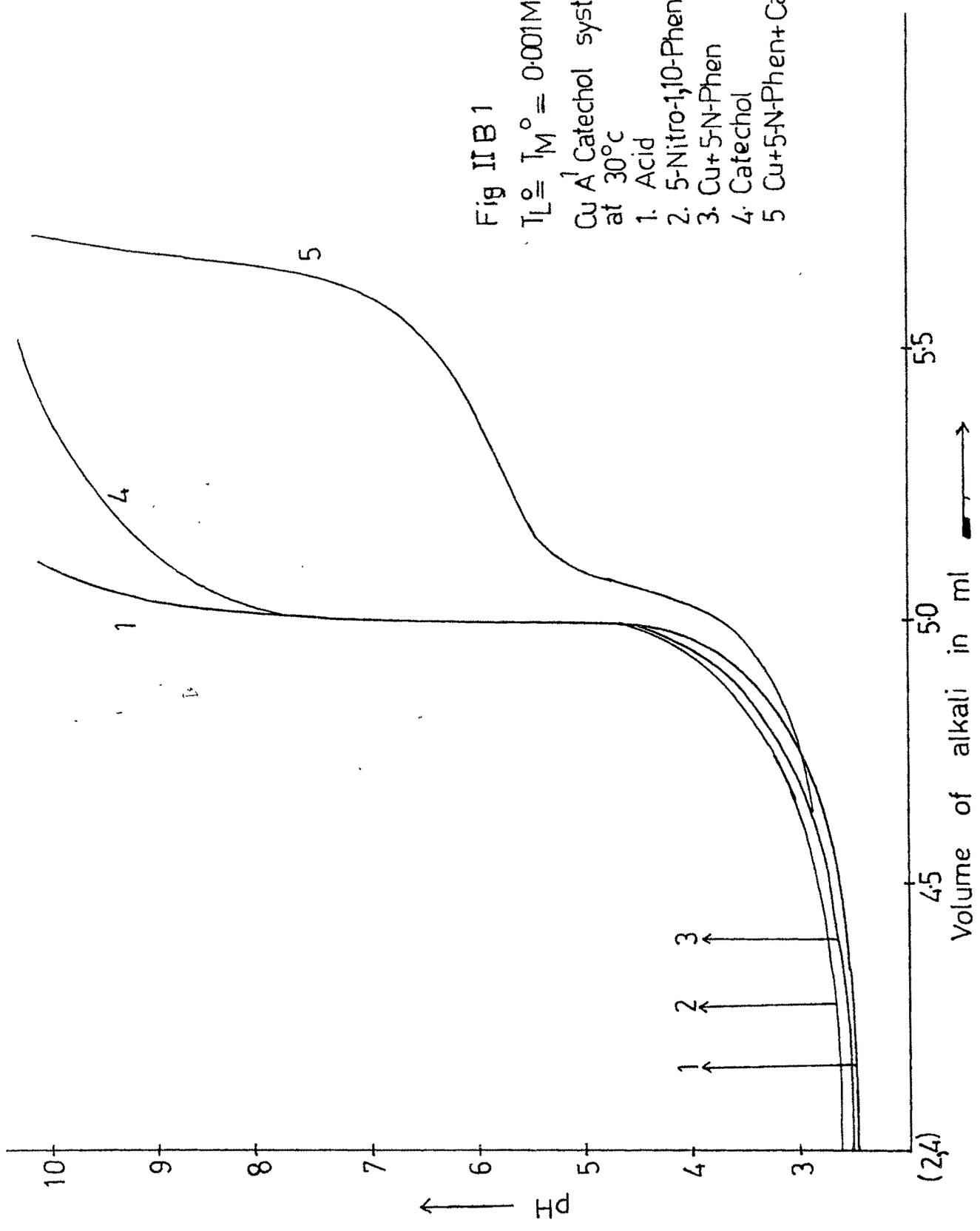


Fig IIB1

$T_L \cong T_M \cong 0.001M$

Cu A<sup>1</sup> Catechol system at 30°C

- 1. Acid
- 2. 5-Nitro-1,10-Phen
- 3. Cu+5-N-Phen
- 4. Catechol
- 5. Cu+5-N-Phen+Catechol (1:1:1)

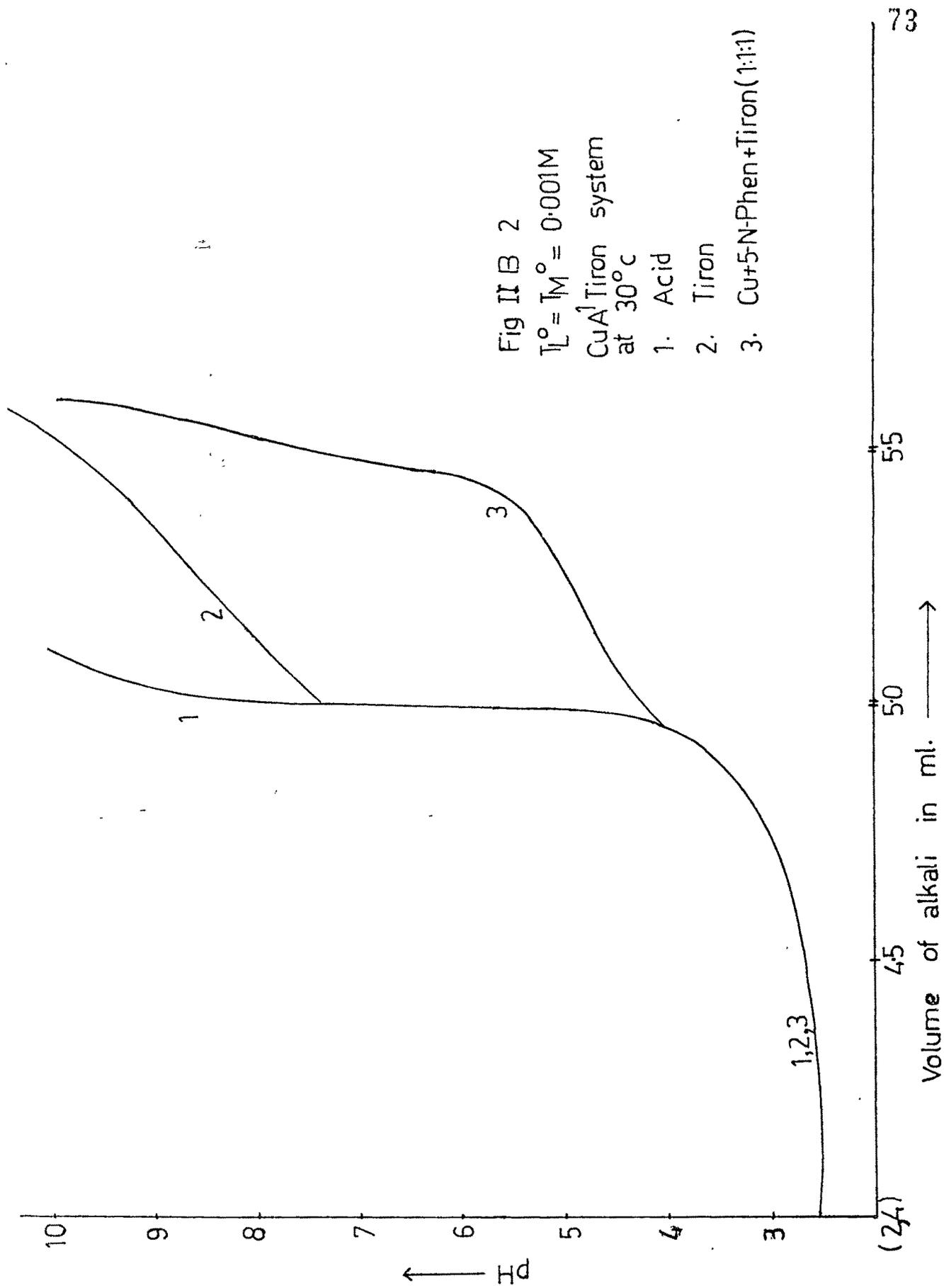
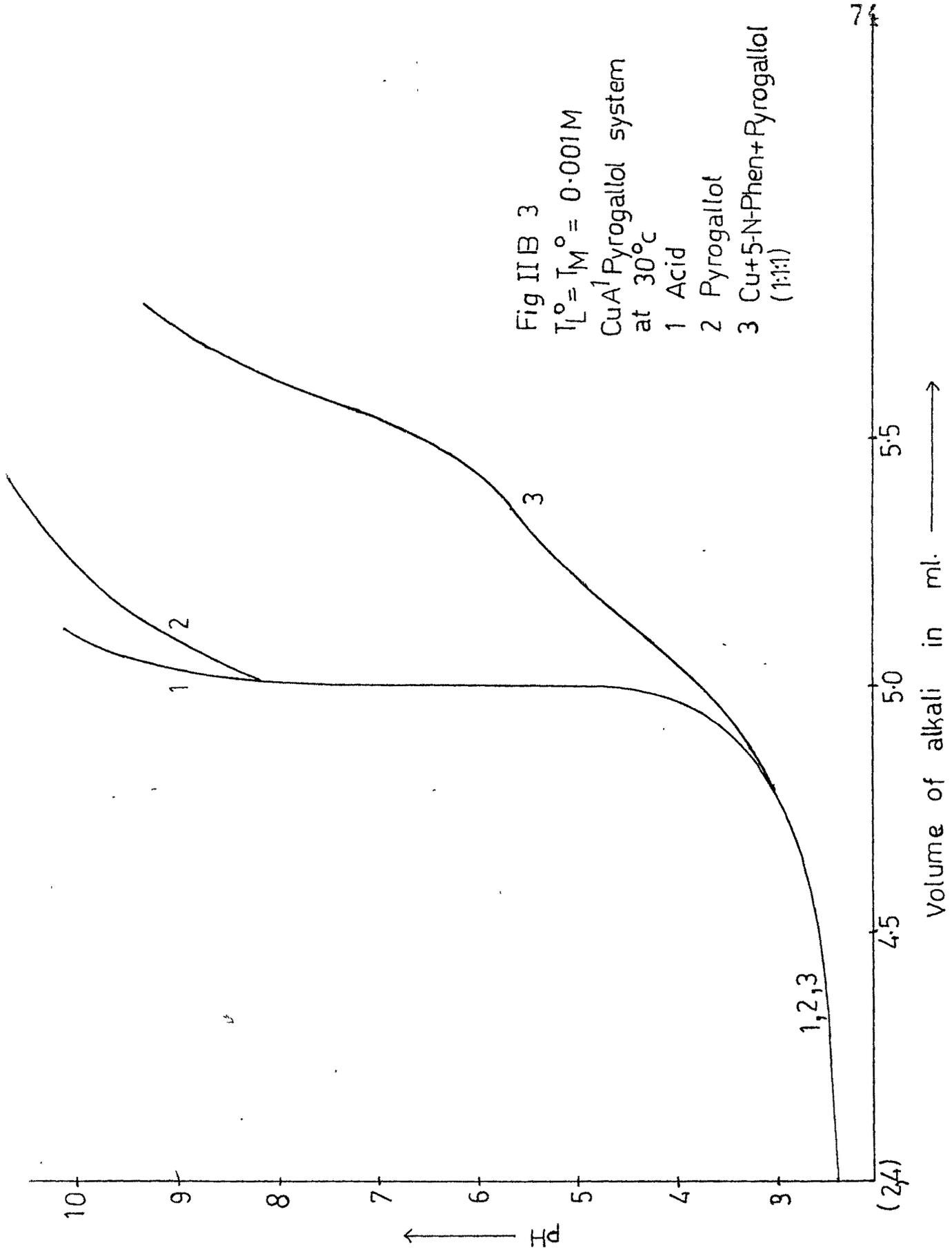


Fig IIB 3

$T_L^{\circ} = T_M^{\circ} = 0.001M$

CuA<sup>1</sup> Pyrogallol system  
at 30°C

- 1 Acid
- 2 Pyrogallol
- 3 Cu+5-N-Phen+Pyrogallol  
(1:1:1)



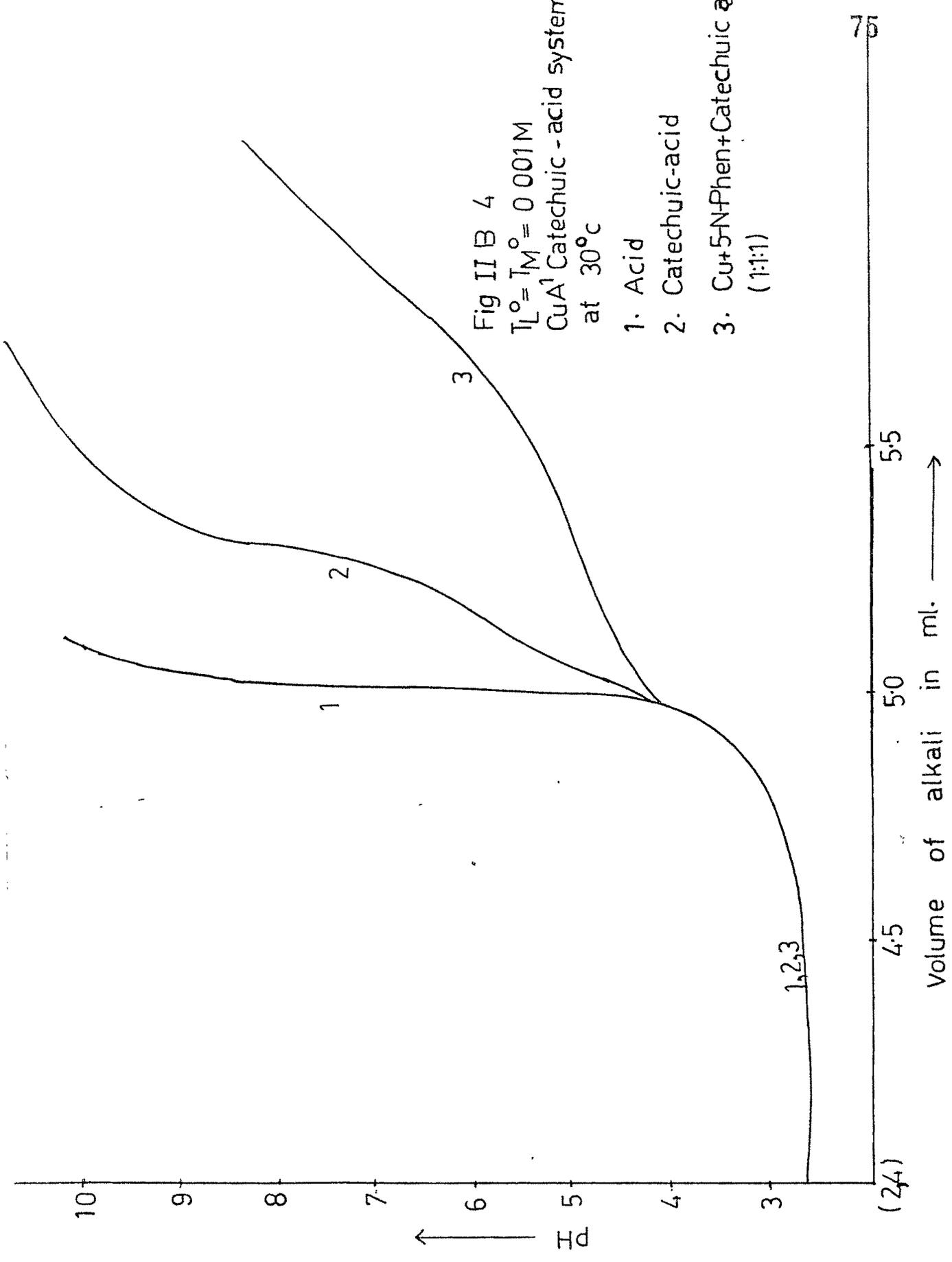


Fig II B 4

$T_L^0 = T_M^0 = 0.001M$

CuA<sup>1</sup> Catechuic - acid system  
at 30°C

- 1. Acid
- 2. Catechuic-acid
- 3. Cu+5N-Phen+Catechuic acid (1:1:1)

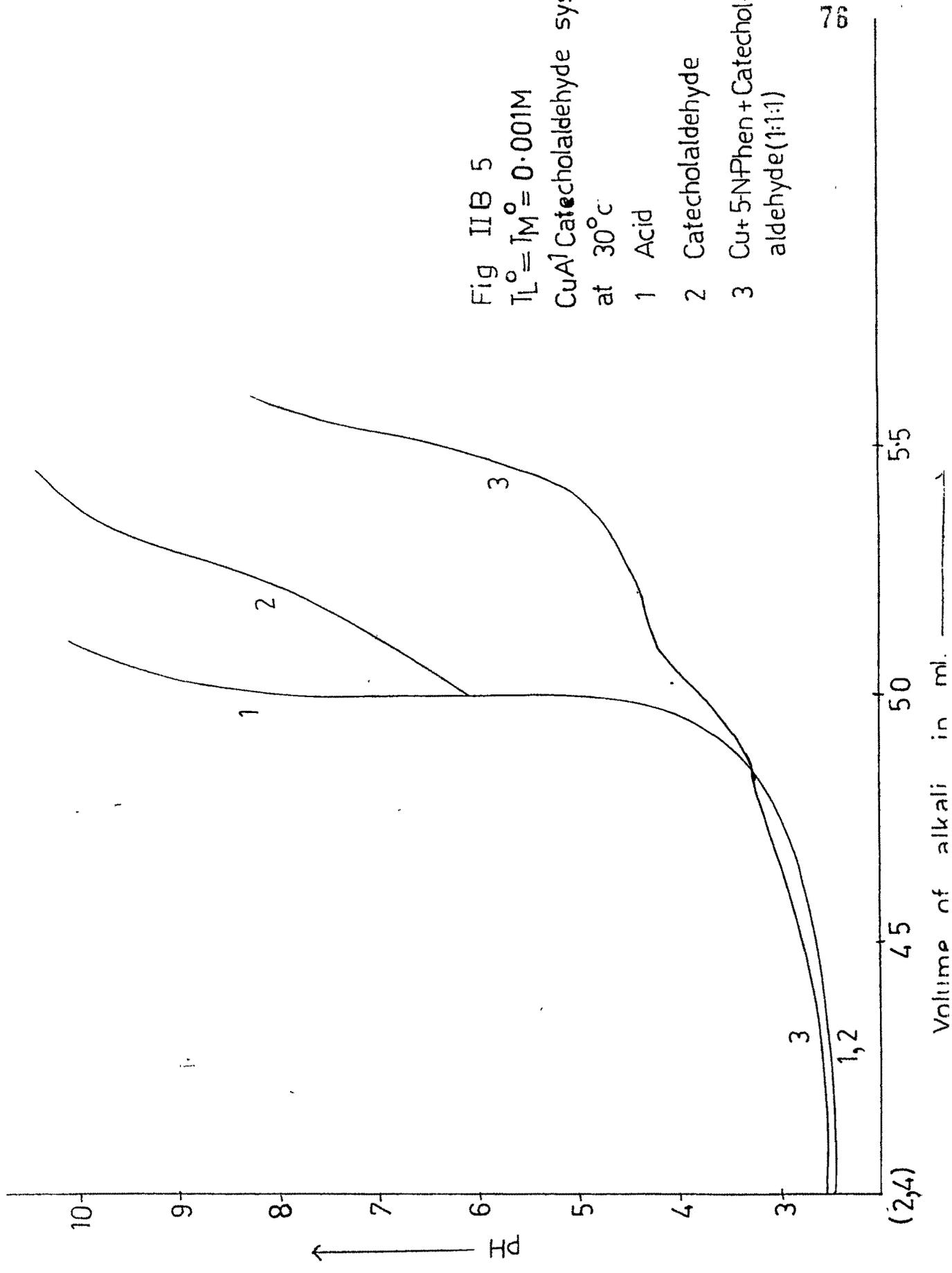


Fig IIB 5  
 $T_L^\circ = T_M^\circ = 0.001M$   
 Cu(II) Catecholaldehyde system  
 at 30°C

- 1 Acid
- 2 Catecholaldehyde
- 3 Cu+5-NPhen+Catecholaldehyde (1:1:1)

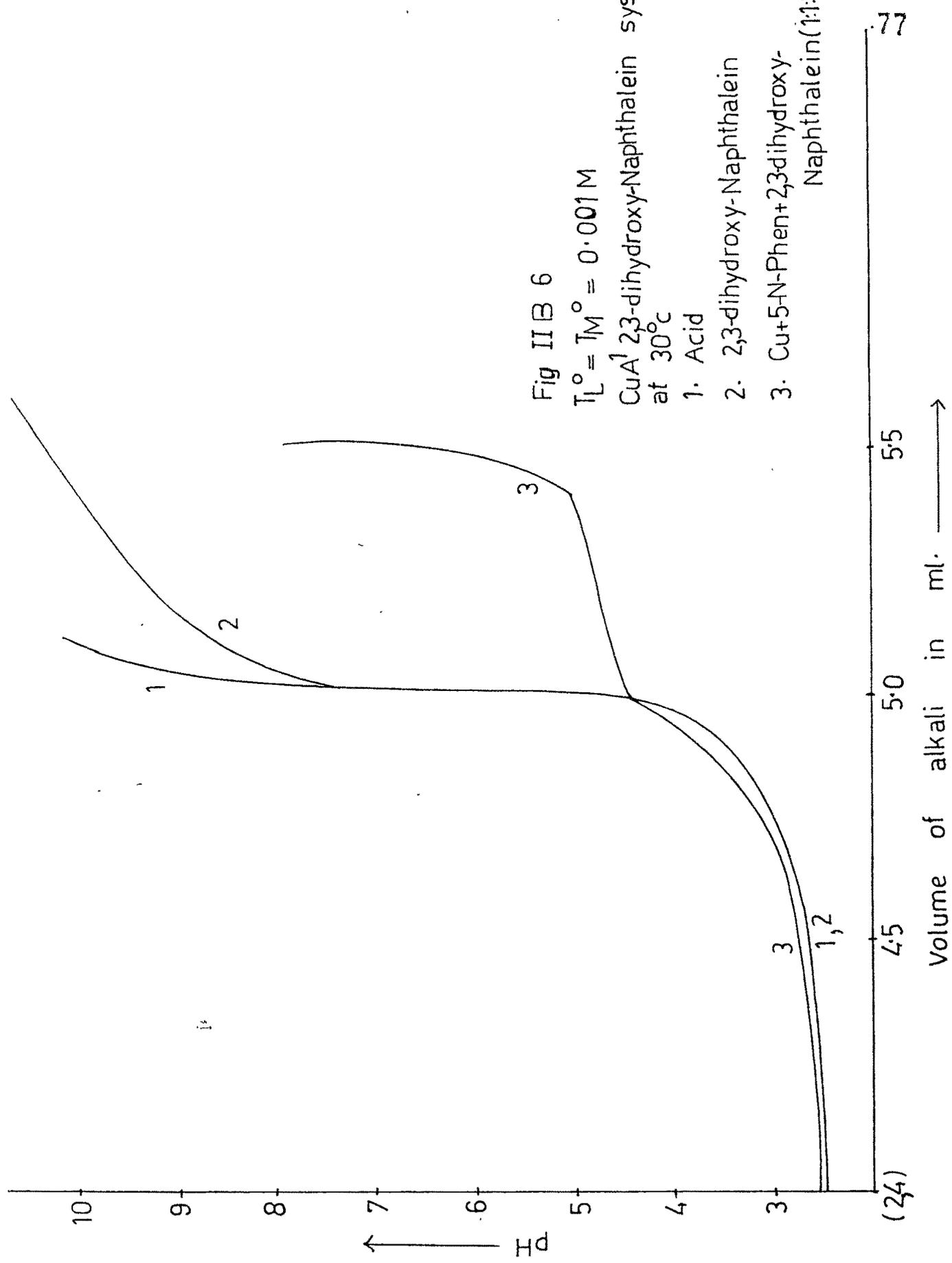


Fig II B 6

$T_L^\circ = T_M^\circ = 0.001 M$

CuA<sup>1</sup> 2,3-dihydroxy-Naphthalein system  
at 30°C

1. Acid
2. 2,3-dihydroxy-Naphthalein
3. Cu+5-N-Phen+2,3-dihydroxy-Naphthalein(1:1:1)

(24)

77

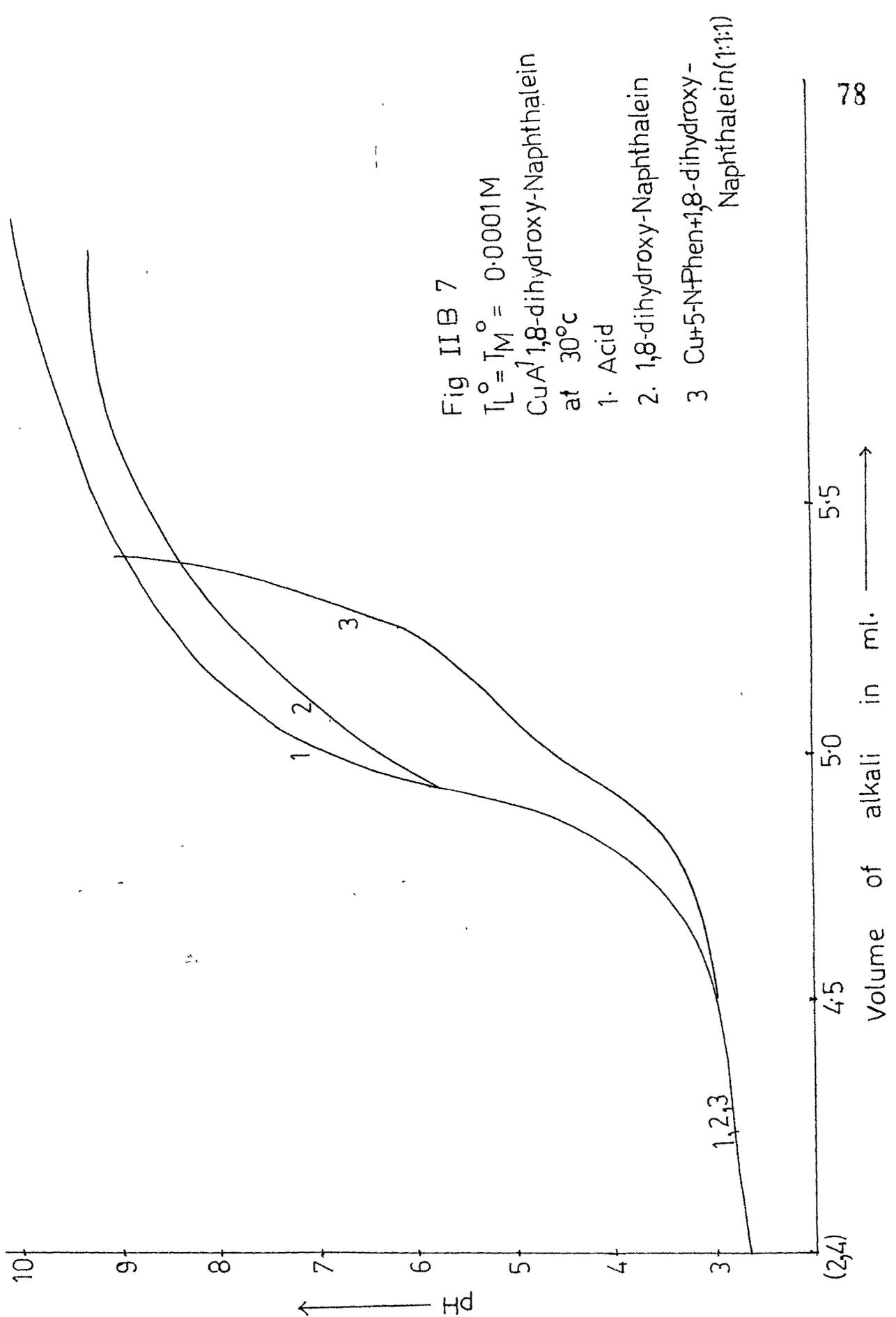
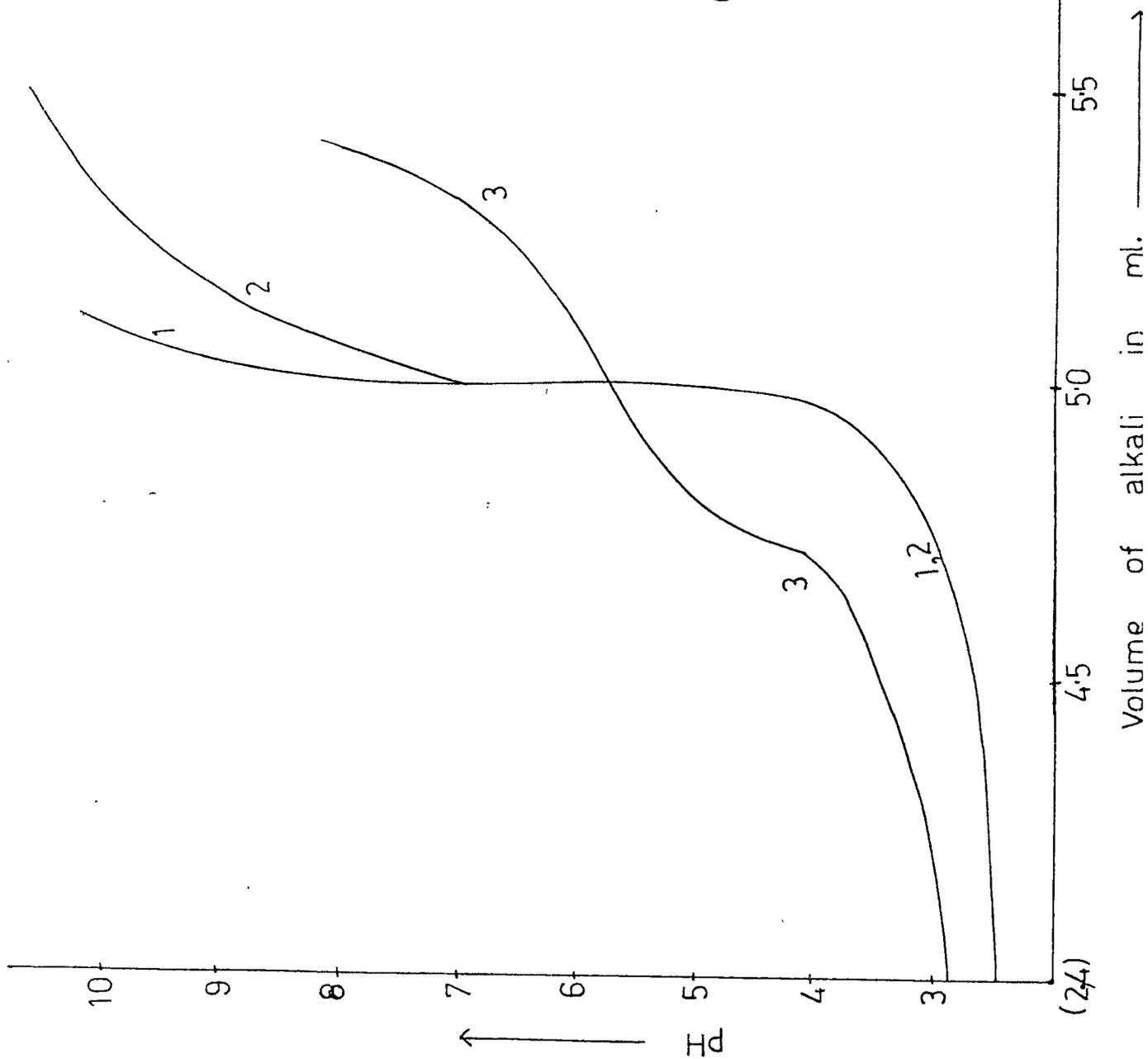


Fig IIB 7

$T_L^{\circ} = T_M^{\circ} = 0.0001M$

$CuA^{1,8}$ -dihydroxy-Naphthalein  
at  $30^{\circ}C$

- 1. Acid
- 2. 1,8-dihydroxy-Naphthalein
- 3.  $Cu+5-NPhen+1,8$ -dihydroxy-Naphthalein(1:1:1)



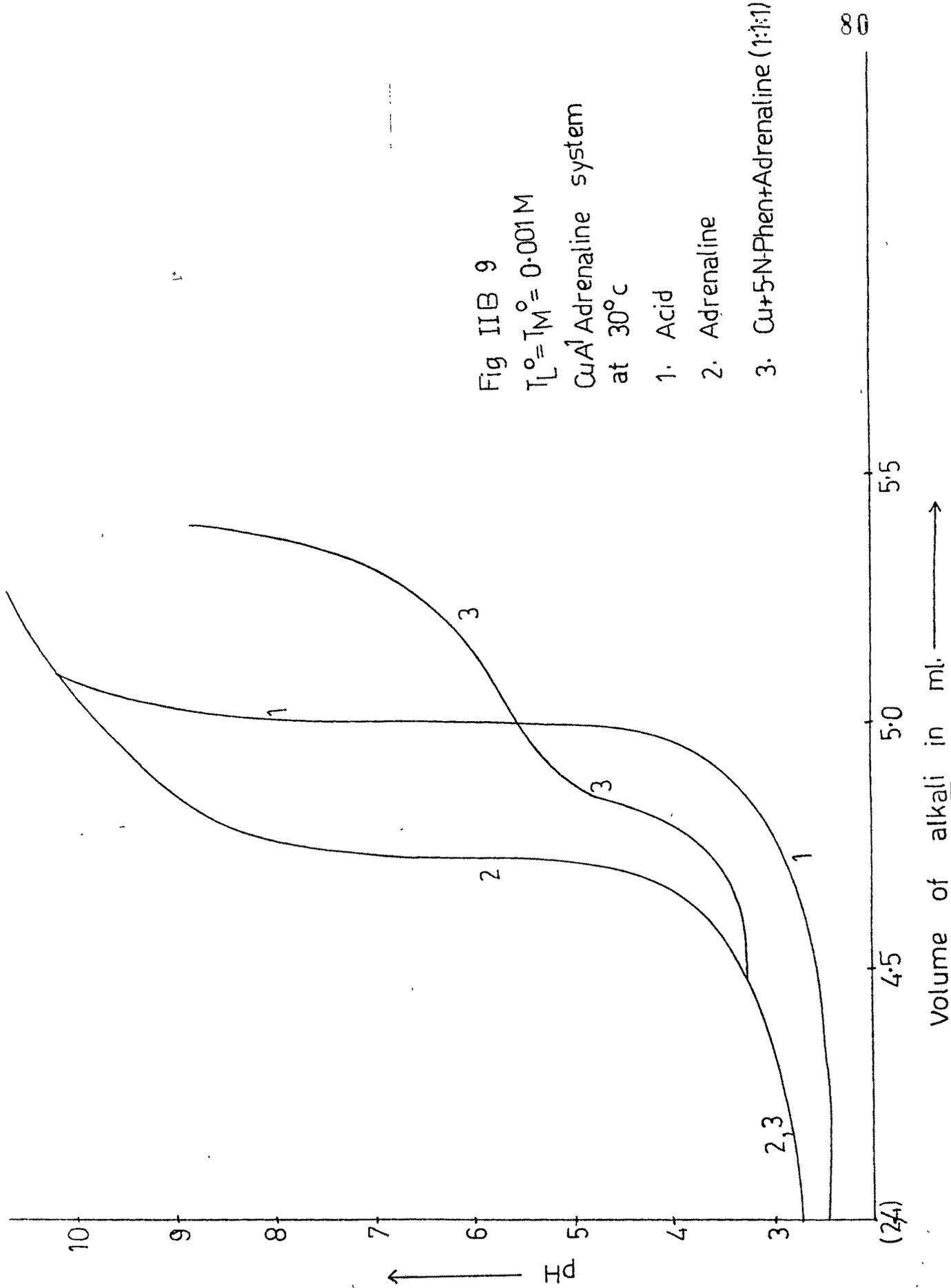


Fig IIB 9

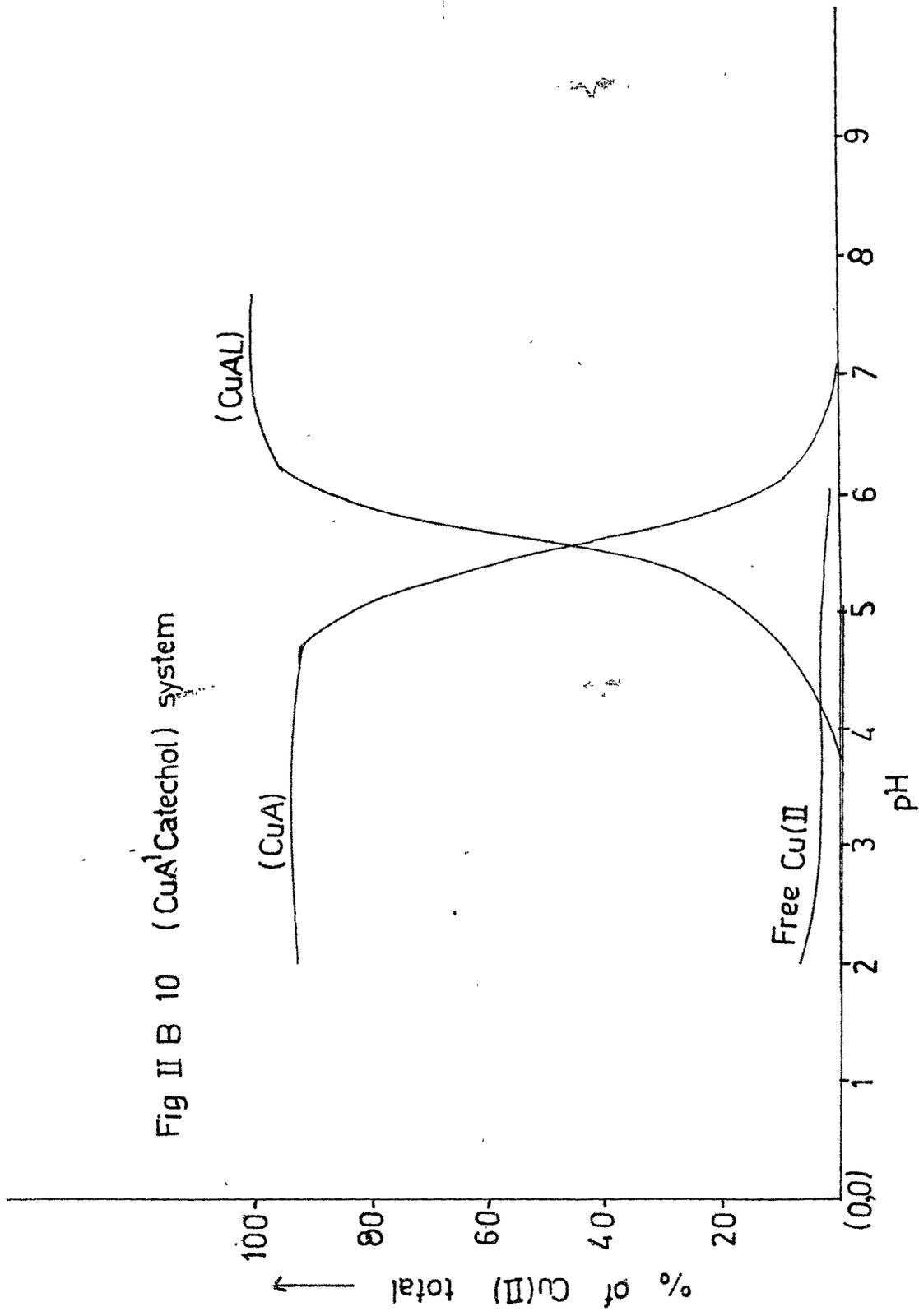
$T_L^{\circ} = T_M^{\circ} = 0.001M$

$Cu^{2+}$  Adrenaline system  
at  $30^{\circ}C$

1. Acid

2. Adrenaline

3. Cu+5-N-Phen+Adrenaline (1:1:1)



Variation of concentrations of different species with pH.

### Results & Discussions

From the plot of concentrations of the species (fig. 10) it is observed that in the lower pH range (1 to 3) Cu(II) and  $[CuA]$  are the major species and in the higher range (pH 4 to 7) the species  $[CuA]$  and  $[CuAL]$  are in copiousness. Formation of  $[CuA_2]$ ,  $[CuL_2]$  and  $[CuL]$  is very less and could not be plotted in the fig. 10. In case of all the complexes, upto 98% of mixed ligand complex is formed and the sums of the percentages of  $[CuA]^{2+}$  and  $[CuAL]$  over the pH range 3.0 to 7.0 total to almost 100%.

It is observed that the stabilization of the ternary complexes  $[Cu \text{ 5-nitro-1,10-phenanthroline}]$  is more than that of  $[Cu \text{ 1,10-phenanthroline L}]$ . This can be explained by considering that the electron withdrawing nitro group makes 5-nitro-1,10-phenanthroline a stronger  $\pi$  acid than 1,10-phenanthroline and hence  $\pi$  interaction is more, resulting in greater stabilization of ternary complexes.

The more positive  $\Delta \log K$  values observed in case of  $[CuAL]$ , where L = catechol, catecholaldehyde, 2,3-dihydroxynaphthalene, dopamine, adrenaline, than in case of  $[CuA \text{ malonate}]$  can be explained in terms of greater release of electron repulsion in the ternary complex involving aromatic  $O^- - O^-$  rather than aliphatic  $O^- - O^-$  as explained in chapter I. Moreover, malonate forms a six membered ring while catecholate forms a five membered ring. The ternary complex involving

five-five membered chelate rings are more stable than those containing five-six membered chelate rings.

In the case of [CuA Tiron], [CuA pyrogallol], [CuA protocatechuic acid], [CuA catecholaldehyde] complexes the values of  $\Delta \log K$  are less positive than in case of [CuA catecholate]. The substituted groups on the ring like sulfonates, carboxylates or aldehyde, being electron withdrawing groups deplete the electron density on the ring. Thus the negative charge over  $O^-$  is reduced in these ligands than in case of unsubstituted catecholate. This makes the value of  $\Delta \log K$  less positive.

The values of  $\Delta \log K$  of mixed ligand complexes of [CuAL<sup>12</sup>] and [CuAL<sup>17</sup>] should be same. But 2,3-dihydroxy naphthalene (L<sup>17</sup>) complexes have less positive  $\Delta \log K$  values than catecholate (L<sup>12</sup>) complexes. This may be because of the fact that in case of L<sup>17</sup>, the electron density, due to the lone pair of electrons over the two  $O^-$  on the ring, gets delocalized over the second ring also, resulting in the depletion of effective electron density over the  $O^-$  of L<sup>17</sup> than in case of L<sup>12</sup>.

The size of the chelate ring also affects the stability of the ternary complexes. It has been observed normally that the ternary complexes of Cu(II) containing two five membered chelate rings are more stable than those containing either one five and one six membered ring or two six membered chelate rings. The order of stabilization of chelate rings of ternary complexes of Cu(II) are five-five membered > five-six membered > six-six membered.

In case of  $[\text{CuAL}^{18}]$  complexes in spite of  $\text{O}^-$  co-ordination of  $\text{L}^{18}$ ,  $\Delta \log K$  is found to be more negative than  $[\text{CuAL}^{17}]$ . This may be because  $\text{L}^{18}$  forms six membered ring. A five-six membered ternary complex becomes less stable. The additional effect could be that in case of  $\text{L}^{18}$  the two  $\text{O}^-$  are on different benzene rings. This reduces the negative charge on two  $\text{O}^-$ , resulting in negative  $\Delta \log K$  value.

In case of  $[\text{CuAL}]$  where  $\text{L} = \text{Dopamine (L}^{19})$  or Adrenaline ( $\text{L}^{20}$ ) also, co-ordination is not from amino group but from the phenolate  $\text{O}^-$ . This can be confirmed by observing the visible spectra. A high intensity absorption at  $\sim 470 \text{ nm}$  is seen in all these complexes, which is characteristic of  $\text{L} \rightarrow \text{M}$  charge transfer in catecholate complexes.<sup>136,137</sup> This shows that the co-ordination in  $\text{L}^{19}$  and  $\text{L}^{20}$  is from catecholate end and amino group is not involved in co-ordination. The proton association constant of the amine in catecholamines is higher and proton does not dissociate till pH 7.5. Hence in the pH range (pH 3.0 to 6.0) where  $\text{L}$  co-ordinates with  $[\text{CuA}]^{2+}$ , it can be considered that the secondary ligands combine in monoprotonated form, the amine proton remaining undissociated. Therefore, in case of catecholamines, the protonated amino group withdraws the electron density from the ring, thereby destabilizing the ternary complexes. Hence, the value of  $\Delta \log K$  is less positive in  $[\text{CuAL}^{19}\text{H}]$  than in case of  $[\text{CuAL}^{12}]$ . In the complexes  $[\text{CuAL}^{20}\text{H}]$ , electron releasing methyl group is present. This reduces the

electron withdrawing effect of  $\text{NH}_3^+$  group, hence  $\Delta \log K$  value is more positive than  $[\text{CuAL}^{19}]$  and is nearly same as in catechol complexes.