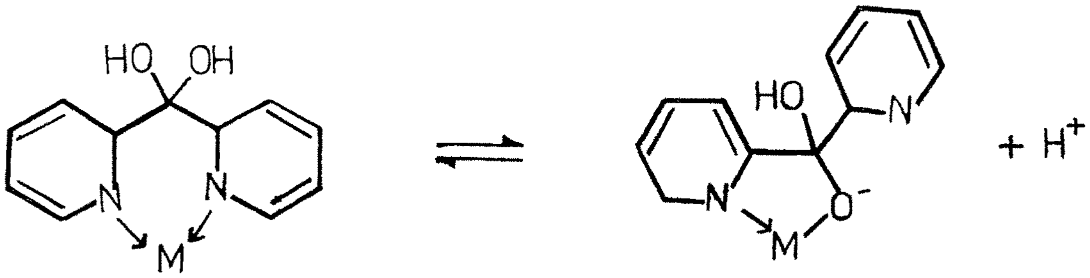
CHAPTER - III

Formation Constants of Ternary Complexes Involving dpk or dpa and N-N, N-O^- or O^--O^- co-ordinating Ligands

As discussed in the first chapter[15,46] it is observed that the formation constants of the ternary complexes increase with increasing π acidity of the N-heteroaromatic base. In a detailed solution study of the formation constants of mixed ligand complexes of the type [M.A.Catecholate], where M = Co(II), Ni(II), Cu(II) or Zn(II) and A=2,2'-dipyridylketone (dpk), 2,2'-dipyridylmethane (dpm) or 2,2'-dipyridylamine (dpa),[15,46] it has been shown that the Δ log K values decrease in the following order dpk > dpm > dpa. This has been explained to be due to the positive or negative inductive effect of the additional groups on the tertiary amines. The carbonyl group in dpk is expected to reduce the electron density on the ring due to its electron withdrawing effect. Contrary to this, the amino group in dpa increases the electron density on the ring due to the interaction of nitrogen lone-pair with the π system of aromatic moiety. Similarly, in case of dpm the methyl group, being electron releasing, increases the electron density on the ring but not to the extent as the amino group. As a pyridyl moiety with a lower electron density can act as a better acceptor of π back bonding electrons from d π orbitals of the metal ions, π acceptor ability decreases in the order dpk > dpm > dpa, same as the order of stabilization of ternary complexes with these tertiary amines.

It was observed by Sigel[33] that the stability of [CudpkCat] is not as much as expected. This was explained to be due to the diol form of dpk in aqueous solution of the complex. It has been further indicated by Sigel that an equilibrium of following type may exist at higher pH. Equation - 1.



The metal ion co-ordinated gem-diol form of bis(2-pyridyl)ketone rearranges under deprotonation of the diol moiety to an N-O^- co-ordination.

In order to further study the nature of the ternary complexes with substituted dipyridyl and the structural changes in co-ordinated dpk in relation to the second co-ordinated ligand, in the present chapter, the study of the ternary complexes [CuAL] where A = 2,2'-dipyridylketone (dpk) (A^2) 2,2'-dipyridylamine (dpa) (A^3) and L = ethylenediamine (L^1), 1,2-propanediamine (L^2), 1,3-propylenediamine (L^3), N-methylethylenediamine (L^4), N-ethyl ethylenediamine (L^5), glycine (L^6), α-alanine (L^7), β-alanine (L^8), malonate (L^9), o-phenylenediamine (L^{10}), o-aminophenol (L^{11}), Catechol (L^{12}), tiron (L^{13}), pyrogallol (L^{14}), protocatechuic acid (L^{15}), catecholaldehyde (L^{16}), 2,3-dihydroxynaphthalene (L^{17}), 1,8-dihydroxynaphthalene (L^{18}), dopamine (L^{19}) or adrenaline (L^{20}) have been carried out in 50% dioxan-water (1 : 1, v/v) medium at initially constant ionic strength 0.2M $NaClO_4$ at 30°C. The formation constants were also determined in aqueous and aqueous-dioxan solution 1:1:1 and 1:1:3 ratio.

Experimental

Standardization of all the required solutions of metal perchlorate, sodium hydroxide and perchloric acid were carried out in the same way as detailed in chapter II. The primary ligands A^2 and A^3 were of A.R. grade (Sigma pure). The secondary ligands were also of A.R. grade (BDH, Merck pure). The caliberations of microburettes, pipettes etc. and pH meter were done in the same way as described in chapter II.

The titration data for aqueous, 25% and 50% dioxan-water are presented in figures III 55 to III 67 where the concentrations of various reagents taken have also been shown.

Titration curves for [Cudpk] 1 : 1 ratio, [Cudpk L] 1 : 1 : 1 and [Cudpa L] 1 : 1 : 1 against sodium hydroxide are presented in fig. 68. The concentrations of reagents are also shown in the figure. The titrations were carried out for all [Cudpk L] systems but only two of the sample curves have been presented.

The values of K_1H of primary ligand A and log K^{M}_{MA} and log K^{MA}_{MAL} have been refined in aqueous and aqueous-dioxan solvents (1 : 1, 3 : 1, v/v). The values were subjected to refinement by using the computer program SCOGS. The values of log K^{M}_{MA} and log $K^{MA}_{MA_2}$ were determined in 25% dioxan-water medium in the same way as determined in 50% dioxan-water medium, described in chapter II.

The mixed ligand formation constants were determined in aqueous and different percentages of aqueous-dioxan medium using SCOGS method considering stepwise and simultaneous formation of the ternary complex as discussed in chapter II. The values of the formation constants have been presented in Table III 9 and 10. These tables also include Δ log K values and standard deviation ($\sigma\beta$) in formation constant.

Spectral Measurements

The spectra were recorded on a Carl Zeiss SPECORD UV/VIS Spectrophotometer with 1 cm. matched quartz cells using aqueous, 25% or 50% dioxan-water as solvent. Solutions of concentrations 10^{-4} and 10^{-3} mol/lt. were used for UV and Visible regions, respectively. Spectra of complexes $[\mathrm{Cudpk}]$ and $[\mathrm{Cu(dpk)_2}]$ obtained by mixing copper perchlorate and dpk in 1 : 1 and 1 : 2 have been recorded. The spectra were recorded at different pH range to see the conversion of keto to gem-diol form in case of dpk.

Table III 1

Ternary complex stability constants of Copper(II) in dioxan-water (1 : 1, v/v) medium and 0.2M $NaClO_4$ at 30°C with standard deviation 3 in parentheses

Ligand	$\log K^{Cu}_{CuAL}$					
	A^2	log K	A^3	log K	A^*	log K
L^1	10.60 ($\pm$ 0.08)	+ 0.02	9.86 ($\pm$ 0.04)	- 0.73	9.51	- 1.08
L^2	9.71 ($\pm$ 0.01)	- 0.39	9.00 ($\pm$ 0.04)	- 1.1	9.1	- 1.00
L^3	9.67 ($\pm$ 0.1)	- 0.68	7.99 ($\pm$ 0.09)	- 2.36	7.82	- 2.53

* 2,2'-dipyridyl

Table III 2

Ternary complex stability constants of Copper(II) in dioxan-water (1 : 1, v/v) medium and 0.2M $NaClO_4$ at 30°C with standard deviation 3 in parentheses

Ligands	$\log K^{Cu}_{CuAL}$					
	A^1	log K	A^2	log K	A^{3*}	log K
L^4	9.61 (± 0.1)	- 0.52	8.78 (± 0.07)	- 1.35	8.57	- 1.56
L^5	9.42 (± 0.01)	- 0.79	8.05 (± 0.1)	- 1.64	7.73	1.91
L^6	9.5 (± 0.04)	+ 0.82	8.52 (± 0.067)	- 0.21	8.29	- 0.44

* 2,2'-dipyridyl

Table III 3

Ternary complex stability constants of Copper(II) in dioxan-water (1 : 1, v/v) medium and 0.2M $NaClO_4$ at 30°C with standard deviation 3 in parantheses

Ligands	$\log K^{Cu}_{CuAL}$					
	A^1	log K	A^2	log K	A^{3*}	log K
L^7	9.58 (± 0.09)	+ 0.53	8.38 (± 0.08)	- 0.67	8.55	- 0.50
L^8	7.89 (± 0.06)	- 0.32	6.76 (± 0.07)	- 1.46	7.15	- 0.83
L^9	9.2 (± 0.09)	+ 0.95	8.81 (± 0.1)	+ 0.56	8.73	+ 0.48

* 2,2'-Dipyridyl

Table III 4

Ternary complex stability constants of Copper(II) in dioxan-water (1 : 1, v/v) medium and 0.2M $NaClO_4$ at 30°C with standard deviation 3 in parentheses

Ligands	$\log K^{CuA}_{CuAL}$					
	A^2	log K	A^3	log K	A^*	log K
L^{10}	4.42 (± 0.08)	- 0.32	3.62 (± 0.03)	- 1.12	3.85	- 0.75
L^{11}	10.41 (± 0.08)	+ 0.70	9.02 (± 0.02)	- 0.69	9.76	+ 0.05
L^{12}	14.65 (+ 0.03)	+ 1.85	13.58 (+ 0.06)	+ 0.75	13.6	+ 0.80

* 2,2'-dipyridyl

Table III 5

Ternary complex stability constants of Copper(II) in dioxan-water (1 : 1, v/v) medium and 0.2M $NaClO_4$ at $30^{\circ}C$ with standard deviation 3 in parentheses

Ligands	$\log K^{CuA}_{CuAL}$					
	A^2	log K	A^3	log K	A^*	log K
L^{13}	15.06 (± 0.05)	+ 0.65	14.35 (± 0.09)	- 0.06	14.39	- 0.02
L^{14}	15.66 (± 0.25)	+ 0.25	15.39 (± 0.03)	- 0.02	15.04	- 0.37
L^{15}	15.9 (± 0.07)	+ 0.34	14.88 (± 0.1)	- 0.68	15.04	- 0.52
L^{16}	14.35 (± 0.09)	+ 0.50	13.79 (± 0.1)	- 0.06	14.13	+ 0.28

* 2,2'-dipyridyl

Table III 6

Ternary complex stability constants of Copper(II) in dioxan-water (1 : 1, v/v) and 0.2M $NaClO_4$ at 30°C with standard deviation 3 in parentheses

Ligands	$\log K^{CuA}_{CuAL}$					
	A^2	log K	A^3	log K	A^*	log K
L^{17}	15.15 (± 0.1)	+ 0.60	14.8 (± 0.09)	+ 0.25	14.92	+ 0.37
L^{18}	10.18 (± 0.1)	- 0.39	9.54 (± 0.08)	- 1.03	9.05	- 1.53
L^{19}	14.78 (± 0.07)	+ 0.78	13.85 (± 0.1)	- 0.15	13.94	- 0.06
L^{20}	16.11 (± 0.1)	+ 1.45	14.66 (± 0.05)	+ 0.82	15.27	+ 0.61

* 2,2'-dipyridyl

Table III 7

Ternary complex stability constants of Copper(II) in aqueous and dioxan-water (1 :9, 1 : 3, 1 : 1, v/v) medium and 0.2M $NaClO_4$ at 30°C, with standard deviation 3 in parentheses

	$\log K^{Cudpk}_{CudpkL}$				$\log K^{Cudpa}_{CudpaL}$	
	Aqueous	10%	25%	50%	25%	50%
L^1	9.03 (± 0.08)	9.06 (± 0.06)	9.66 (± 0.10)	10.62 (± 0.04)	9.26 (± 0.08)	9.86 (± 0.01)
log K	- 1.4	- 0.63	- 0.56	+ 0.02	- 0.83	- 0.73
L^7	8.54 (± 0.05)	8.6 (± 0.05)	8.92 (± 0.03)	9.5 (± 0.08)	8.3 (± 0.06)	8.51 (± 0.05)
log K	+ 0.27	+ 0.33	+ 0.42	+ 0.82	- 0.3	- 0.22
L^9		6.13 (± 0.02)	6.51 (± 0.06)	9.20 (± 0.09)	6.8 (± 0.07)	8.81 (± 0.03)
log K		- 0.83	+ 0.34	+ 0.95	+ 0.63	+ 0.56

Table III 8

Stability constant of ternary complexes of CudpkL at different percentages of dioxan-water medium

Different Percentages of dioxan	$CuAL^1$	log K	$CuAL^8$	log K
Aqueous	14.78 (± 0.06)	+ 0.82	10.91 (± 0.05)	+ 0.05
25%	14.14 (± 0.10)	+ 1.34	11.53 (± 0.04)	+ 0.53
50%	14.65 (± 0.07)	+ 1.85	14.78 (± 0.12)	+ 0.78

Table III 9

Ternary complex stability constants of Nickel(II) in dioxan-water (1 : 1, v/v) medium and 0.2M $NaClO_4$ at 30°C with standard deviation 3 in parentheses

Ligands	$\log K^{NiA}_{NiAL}$					
	A^2	log K	A^3	log K	A^*	log K
L^1	7.29 (± 0.12)	- 1.54	7.13 (± 0.08)	- 1.70	7.34	- 1.23
L^2	7.78 (± 0.14)	- 1.16	6.79 (± 0.10)	- 2.15	7.23	- 1.72
L^3	9.67 (± 0.1)	- 0.68	7.99 (± 0.09)	- 2.36	7.82	- 2.53

* 2,2'-dipyridyl

Table III 10

Ternary complex stability constants of Nickel(II) in dioxan-water (1 : 1, v/v) medium and 0.2M $NaClO_4$ at 30°C with standard deviation 3 in parentheses

Ligands	$\log K^{NiA}_{NiAL}$					
	A^2	log K	A^3	log K	A^*	log K
L^6	6.17 (± 0.08)	- 1.11	5.78 (± 0.08)	- 1.49	5.86	- 1.24
L^7	5.5 (± 0.11)	- 0.78	5.08 (± 0.09)	- 1.20	5.62	- 0.33
L^8	5.41 (± 0.16)	- 0.49	4.72 (± 0.13)	- 1.18	4.73	- 0.65
L^9	7.88 (+ 0.10)	+ 0.61	6.38 (+ 0.19)	- 0.89	6.64	- 0.63

* 2,2'-dipyridyl

Table III 11

Ternary complex stability constants of Nickel(II) in dioxan-water (1 : 1, v/v) medium and 0.2M $NaClO_4$ at 30°C with standard deviation $\sigma \beta$ in parentheses

Ligands	$\log K^{NiA^2}_{NiA^2L}$	$\Delta \log K$	$\log K^{NiA^2L}_{NiA^2L_2}$	$\log K^{NiA^3}_{NiA^3L}$	$\Delta \log K$	$\log K^{NiA^3L}_{NiA^3L_2}$	A^*	$\Delta \log K$
L^1	7.29 (± 0.12)	- 1.54	6.51	7.13 (± 0.08)	- 1.70	5.45	7.34	- 1.23
L^2	7.78 (± 0.14)	- 1.16	5.96	6.79 (± 0.1)	- 2.15	4.85	7.23	- 1.72
L^4	5.77 (± 0.14)	- 1.81	4.63	5.2 (± 0.12)	- 2.38	4.18	5.72	- 1.86
L^6	6.17 (+ 0.08)	- 1.11	5.75	5.79 (+ 0.08)	- 1.49	4.96	5.86	- 1.24

* 2,2'-dipyridyl

Table III 12

Ternary complex stability constants of Nickel(II) in dioxan-water (1 : 1, v/v) medium and 0.2M $NaClO_4$ at 30°C with standard deviation $\sigma\beta$ in parentheses

Ligands	$\log K^{NiA^2}_{NiA^2L}$	$\Delta \log K$	$\log K^{NiA^2L}_{NiA^2L_2}$	$\log K^{NiA^3}_{NiA^3L}$	$\Delta \log K$	$\log K^{NiA^3L}_{NiA^3L_2}$	A^*	$\Delta \log K$
L^7	5.5 (± 0.11)	- 0.78	4.72	5.08 (± 0.09)	- 1.20	3.48	5.62	- 0.33
L^8	5.41 (± 0.16)	- 0.49	5.01	4.72 (± 0.13)	- 1.18	3.00	4.73	- 0.65
L^9	7.88 (± 0.10)	+ 0.61	5.62	6.38 (± 0.10)	- 0.89	3.35	6.64	- 0.63

* 2,2'-dipyridyl

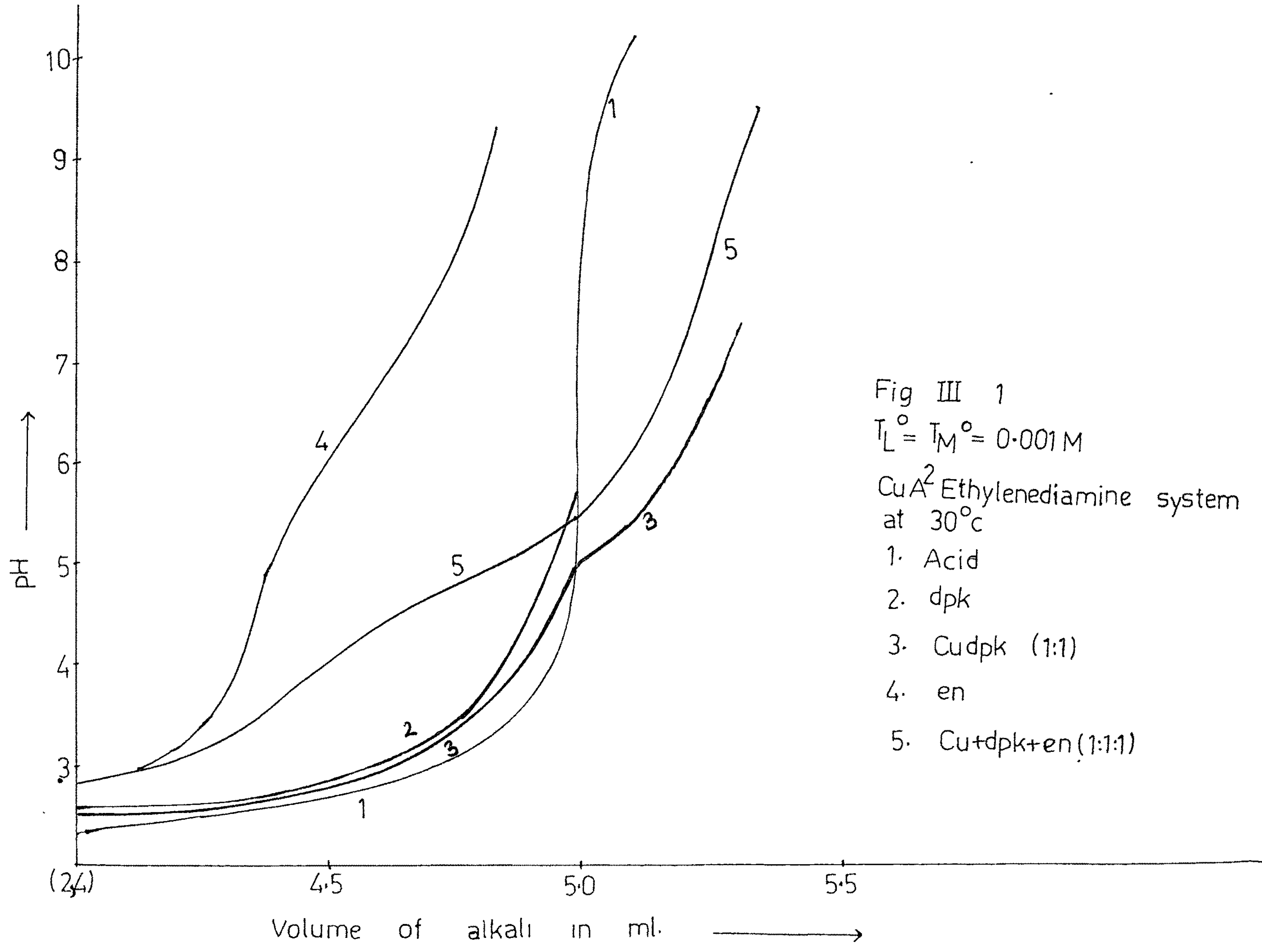


Fig III 1

$T_L^o = T_M^o = 0.001$ M

CuA^2 Ethylenediamine system at 30°c

1. Acid
2. dpk
3. Cudpk (1:1)
4. en
5. Cu+dpk+en (1:1:1)

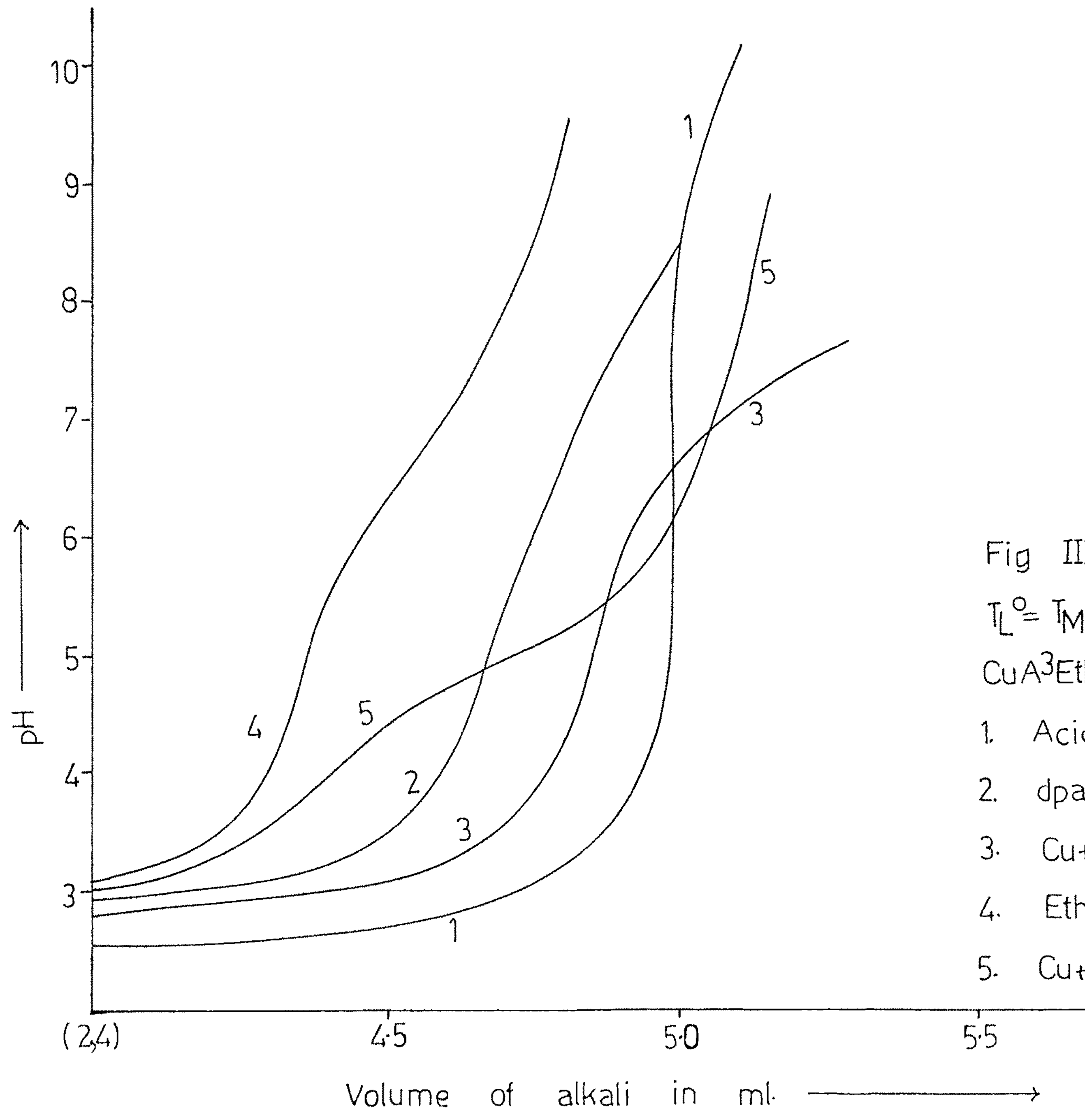


Fig III 2

$T_L^o = T_M^o = 0{\cdot}001\,M$

CuA^3Ethylene-diamine system at 30°c

1. Acid.
2. dpa
3. Cu+dpa (1:1)
4. Ethylene-diamine
5. Cu+dpa+Ethylene-diamine(1·1:1)

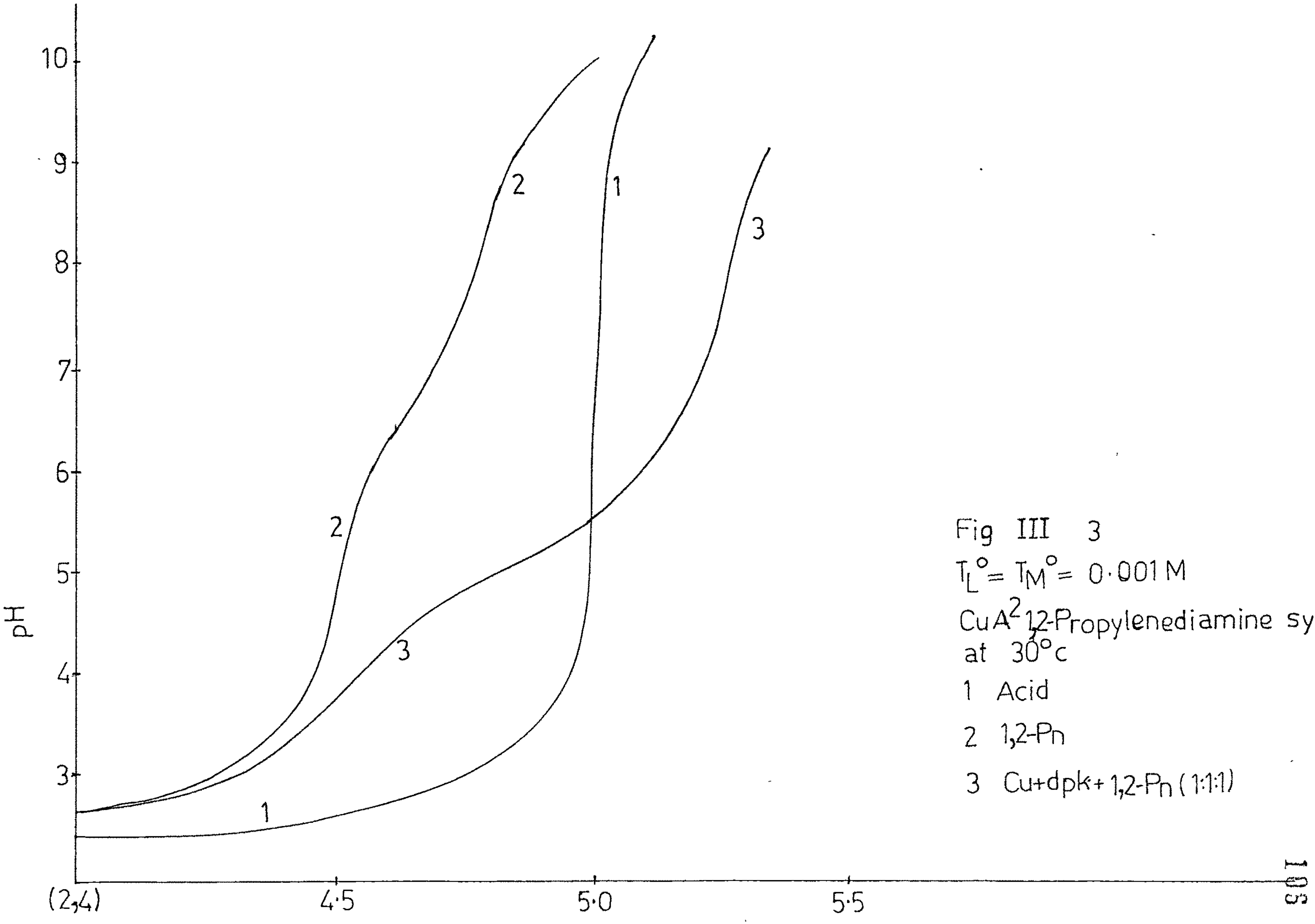


Fig III 3
$T_L^\circ = T_M^\circ = 0{\cdot}001\,M$
CuA^2 1,2-Propylenediamine system
at 30°c
1 Acid
2 1,2-Pn
3 Cu+dpk+1,2-Pn (1:1:1)

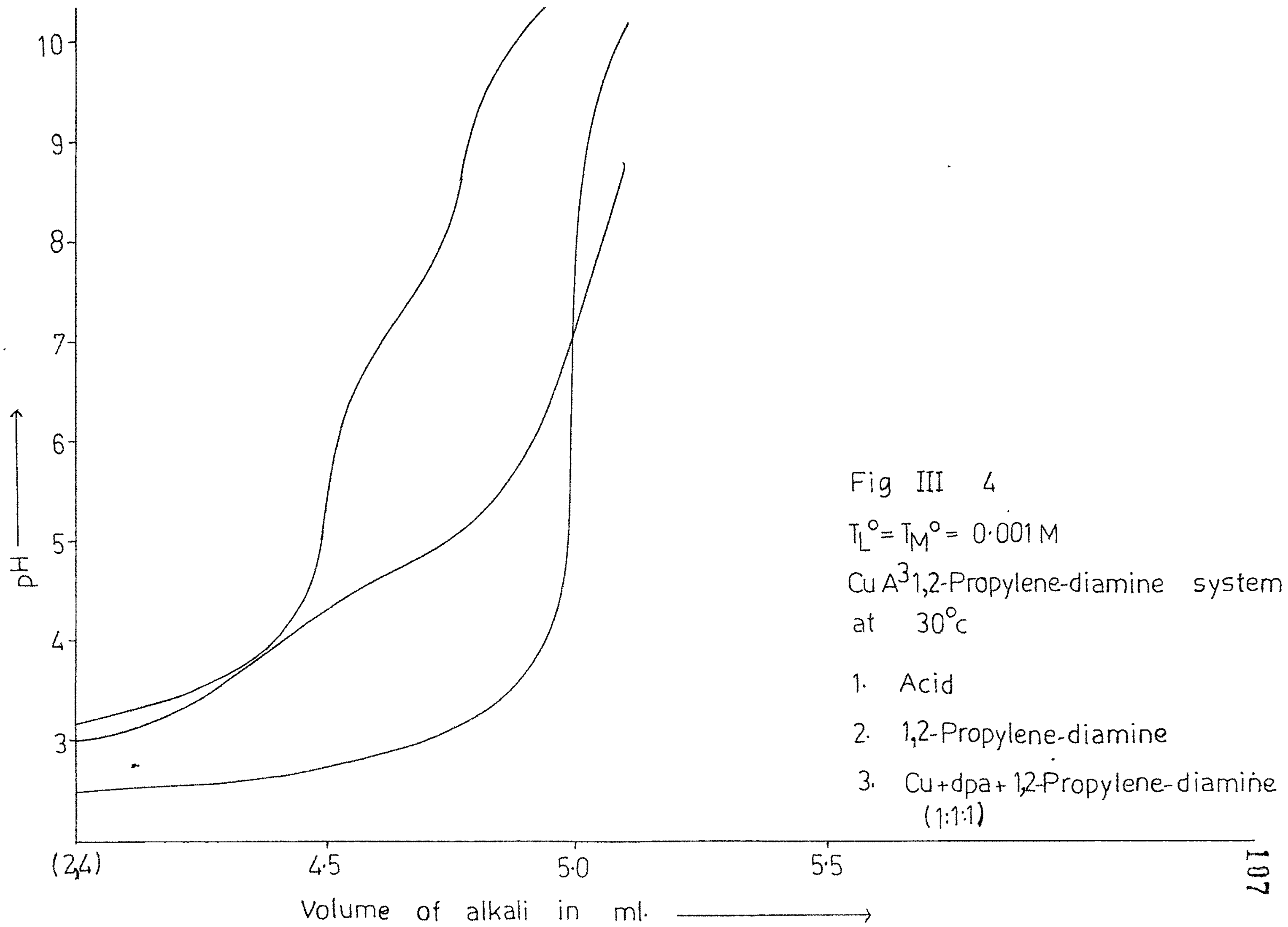


Fig III 4

$T_L^\circ = T_M^\circ = 0{\cdot}001\,M$

Cu A^3 1,2-Propylene-diamine system at 30°c

1. Acid
2. 1,2-Propylene-diamine
3. Cu+dpa+1,2-Propylene-diamine (1:1:1)

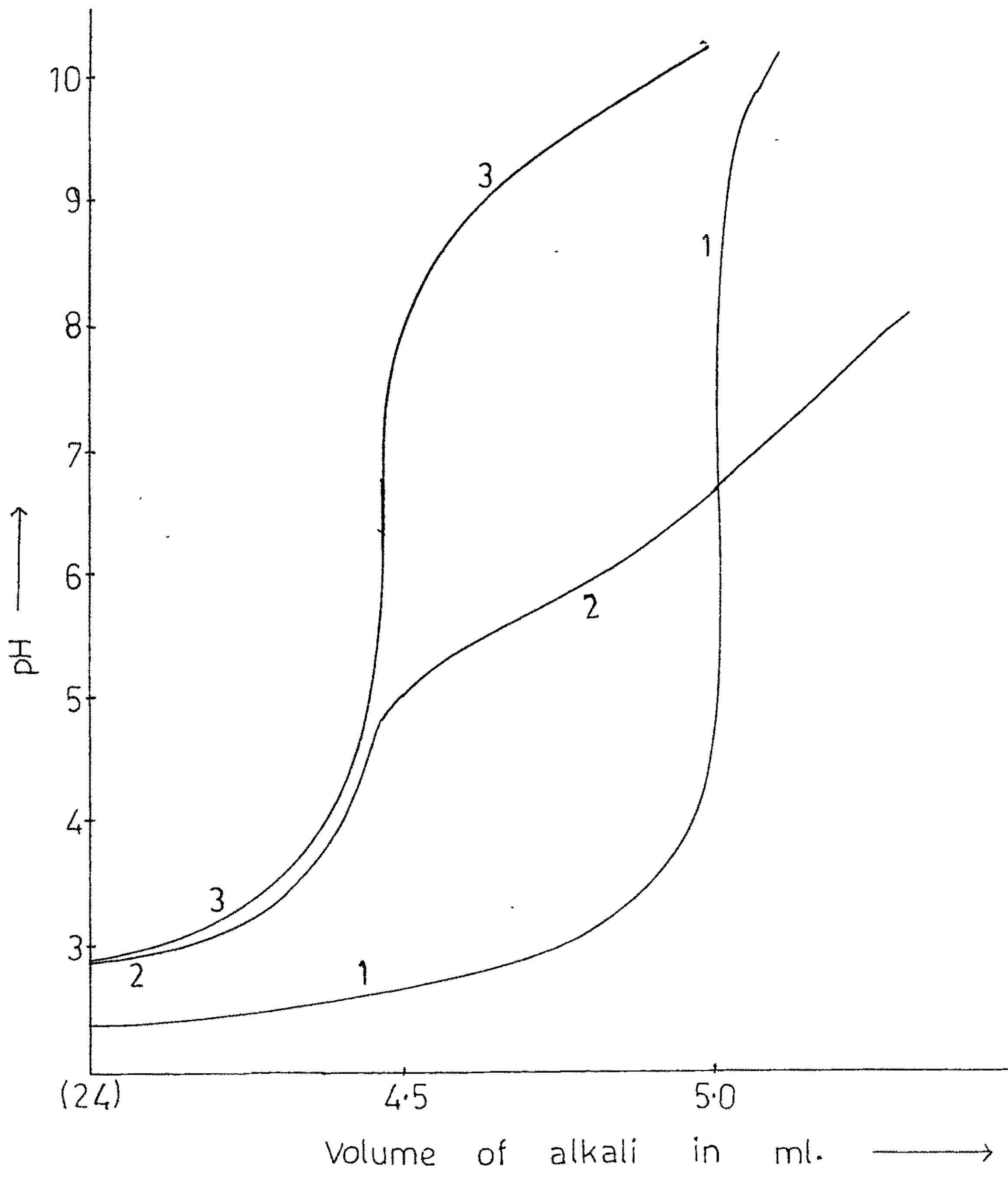


Fig III 5

$T_L^o = T_M^o = 0{\cdot}001M$

CuA^2 1,3-Propylenediamine system at 30°c

1· Acid

2· 1,3-Pn

3· Cu+dpk+1,3-Pn (1:1:1)

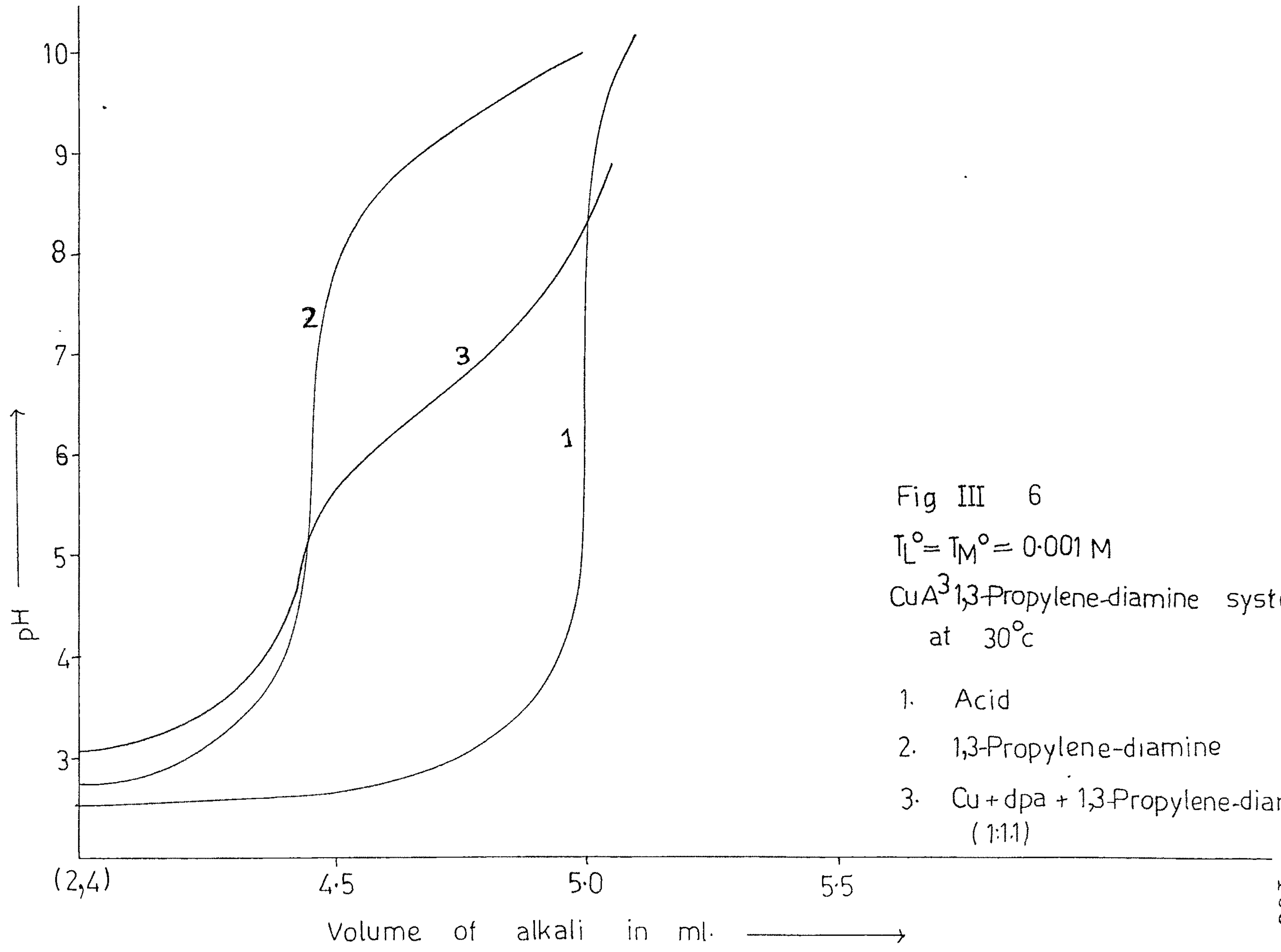


Fig III 6

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001$ M

CuA^3 1,3-Propylene-diamine system at 30°c

1. Acid
2. 1,3-Propylene-diamine
3. Cu + dpa + 1,3-Propylene-diamine (1:1:1)

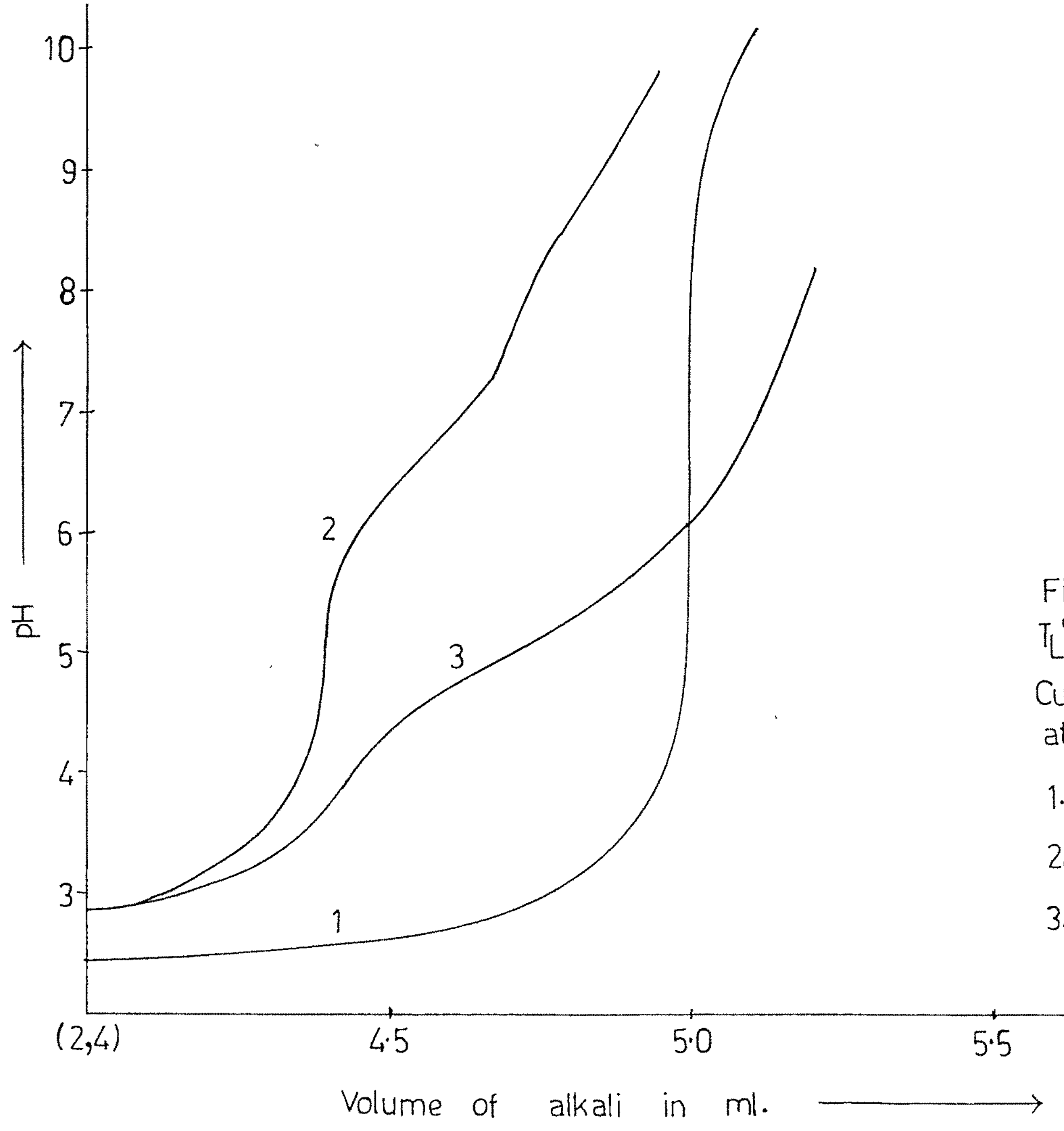


Fig III 7
$T_L^\circ = T_M^\circ = 0{\cdot}001$M
CuA^{2}N methyl Ethylenediamine system
at 30°c

1. Acid
2. N-m-en
3. Cu+ dpk + N-m-en (1:1:1)

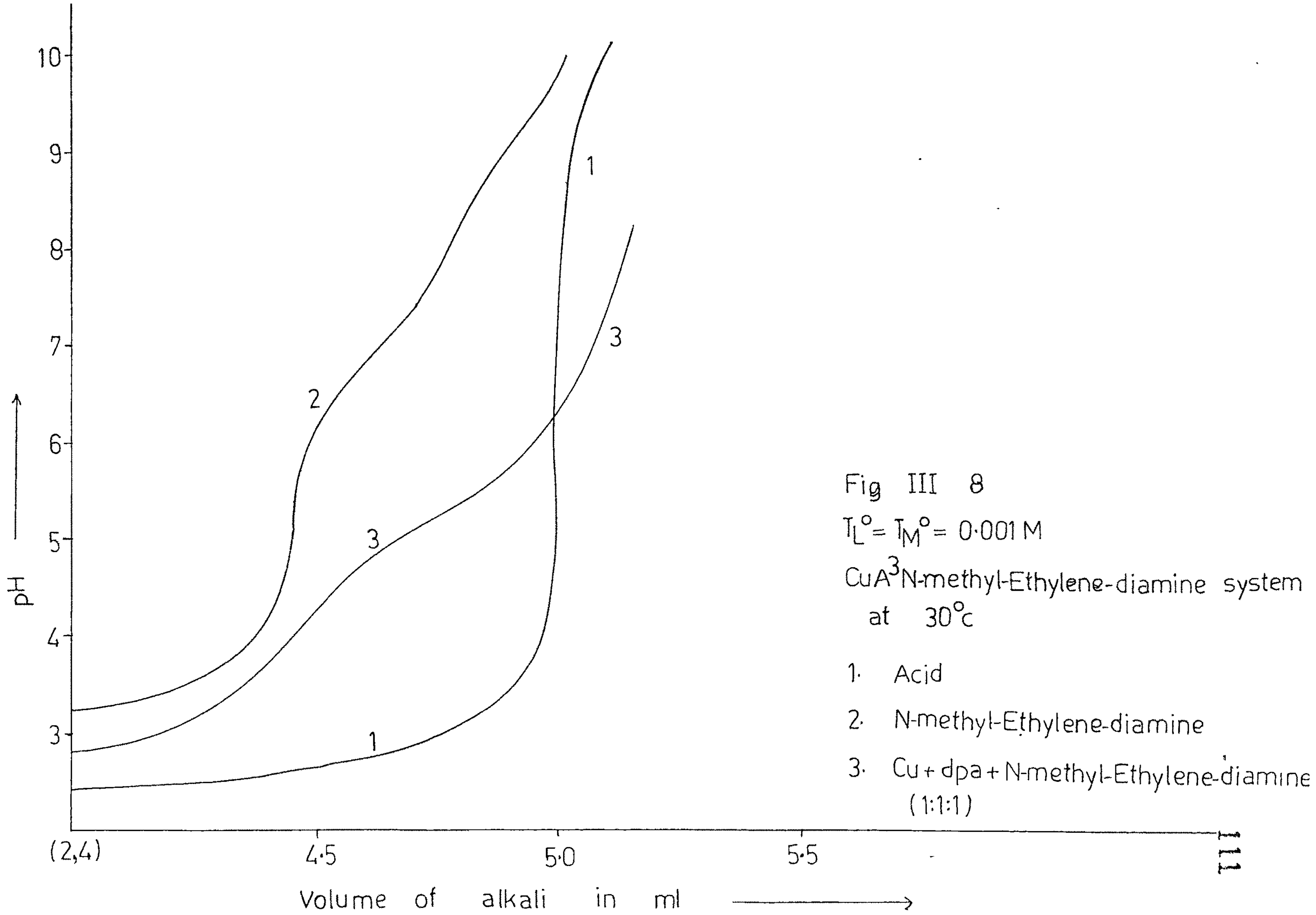


Fig III 8

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001\ M$

CuA^{3}N-methyl-Ethylene-diamine system at 30°c

1. Acid
2. N-methyl-Ethylene-diamine
3. Cu + dpa + N-methyl-Ethylene-diamine (1:1:1)

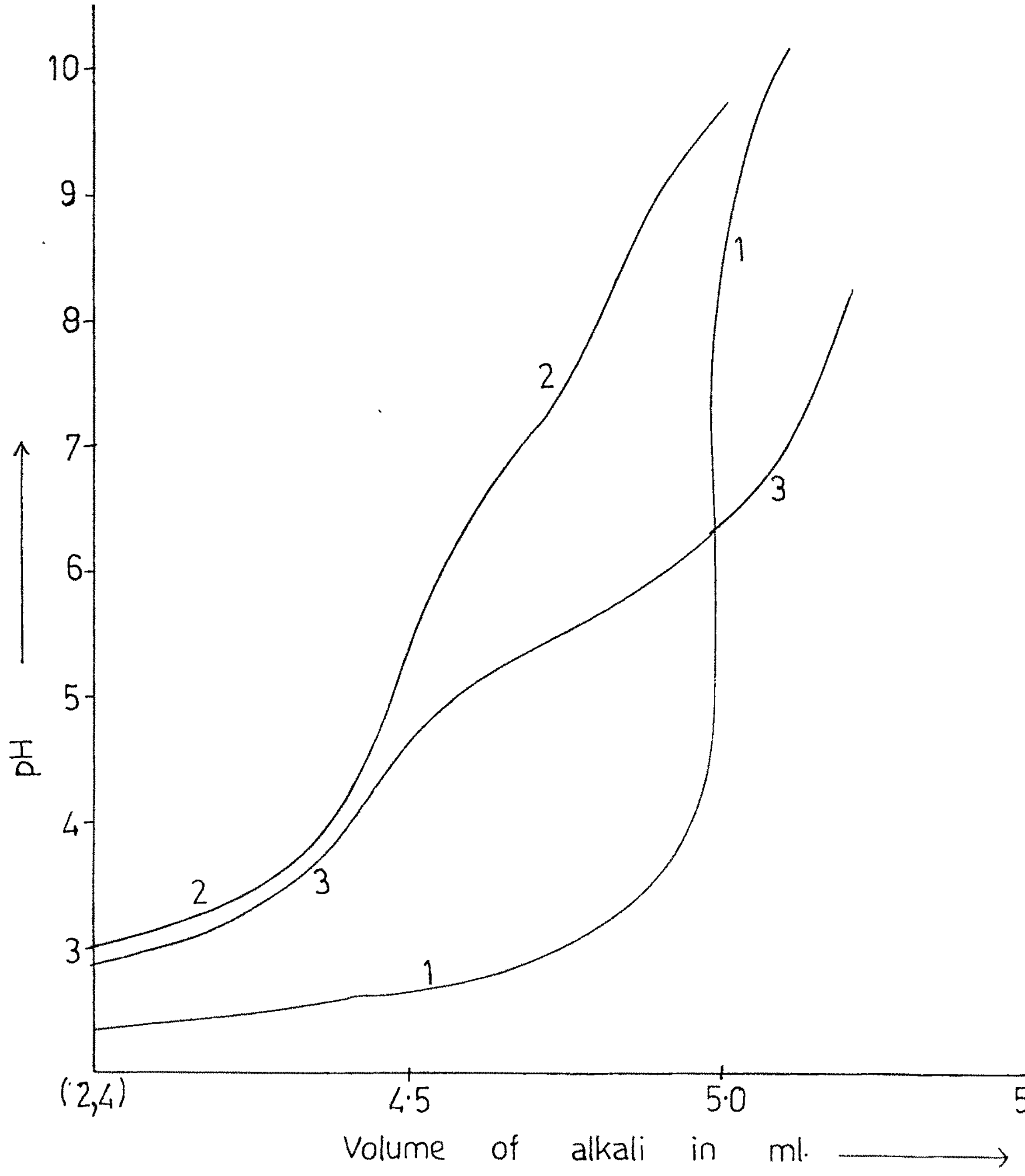


Fig III 9

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001\,M$

CuA^{2}N-ethyl-ethylenediamine system at 30°c

1 Acid

2 N-e-en

3 Cu+ dpk+ N-e-en (1:1:1)

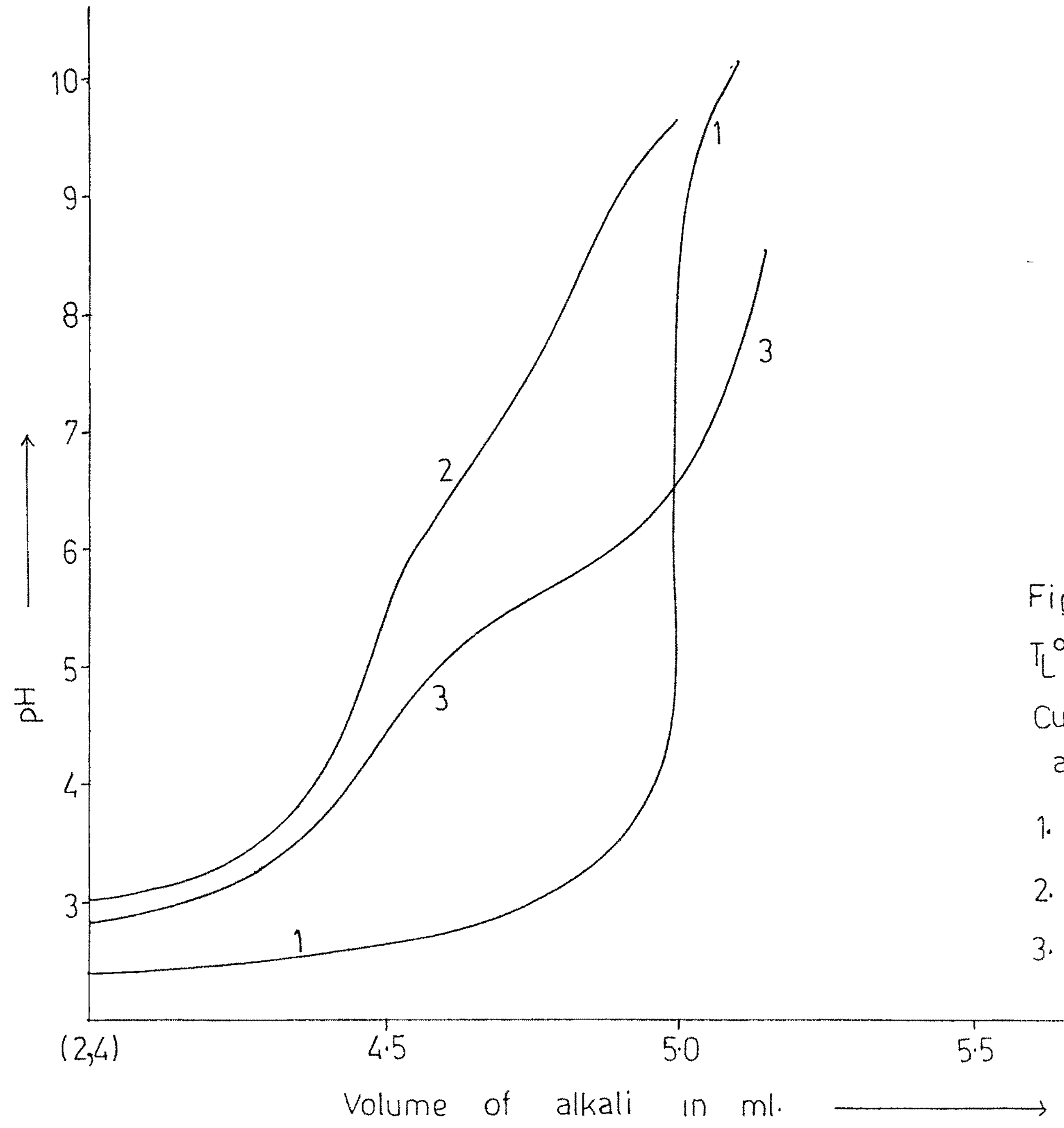


Fig III 10

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001$ M

CuA^{3}N-ethyl-Ethylene-diamine system
at 30°c

1. Acid.

2. N-ethyl-Ethylene-diamine.

3. Cu + dpa + N-ethyl-Ethylene-diamine
(1:1:1).

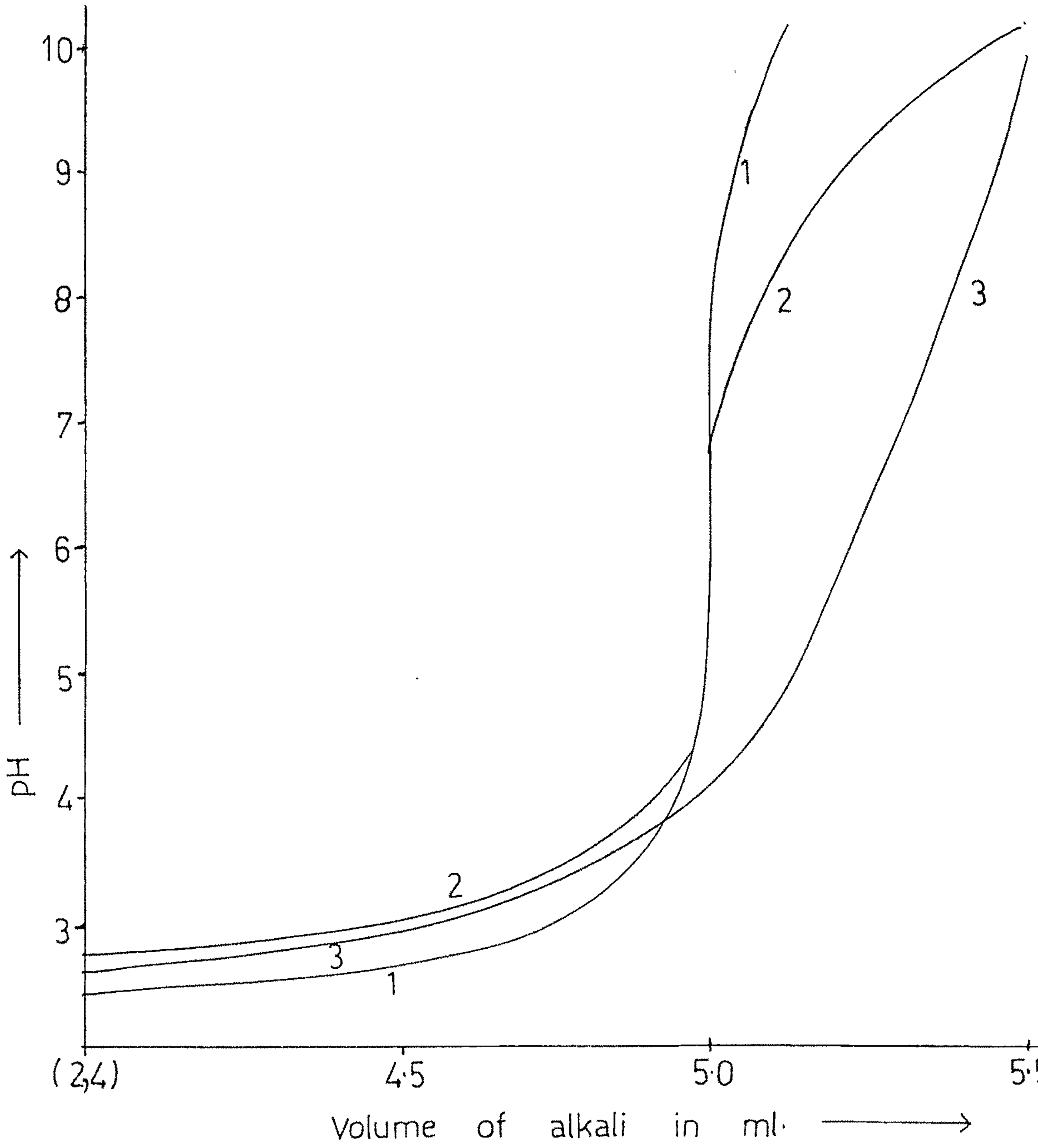


Fig III 11

$T_L^o = T_M^o = 0{\cdot}001M$

CuA^{2}Glycine system at 30°c

1. Acid

2. Glycine

3. Cu+ dpk+ Glycine (1:1:1)

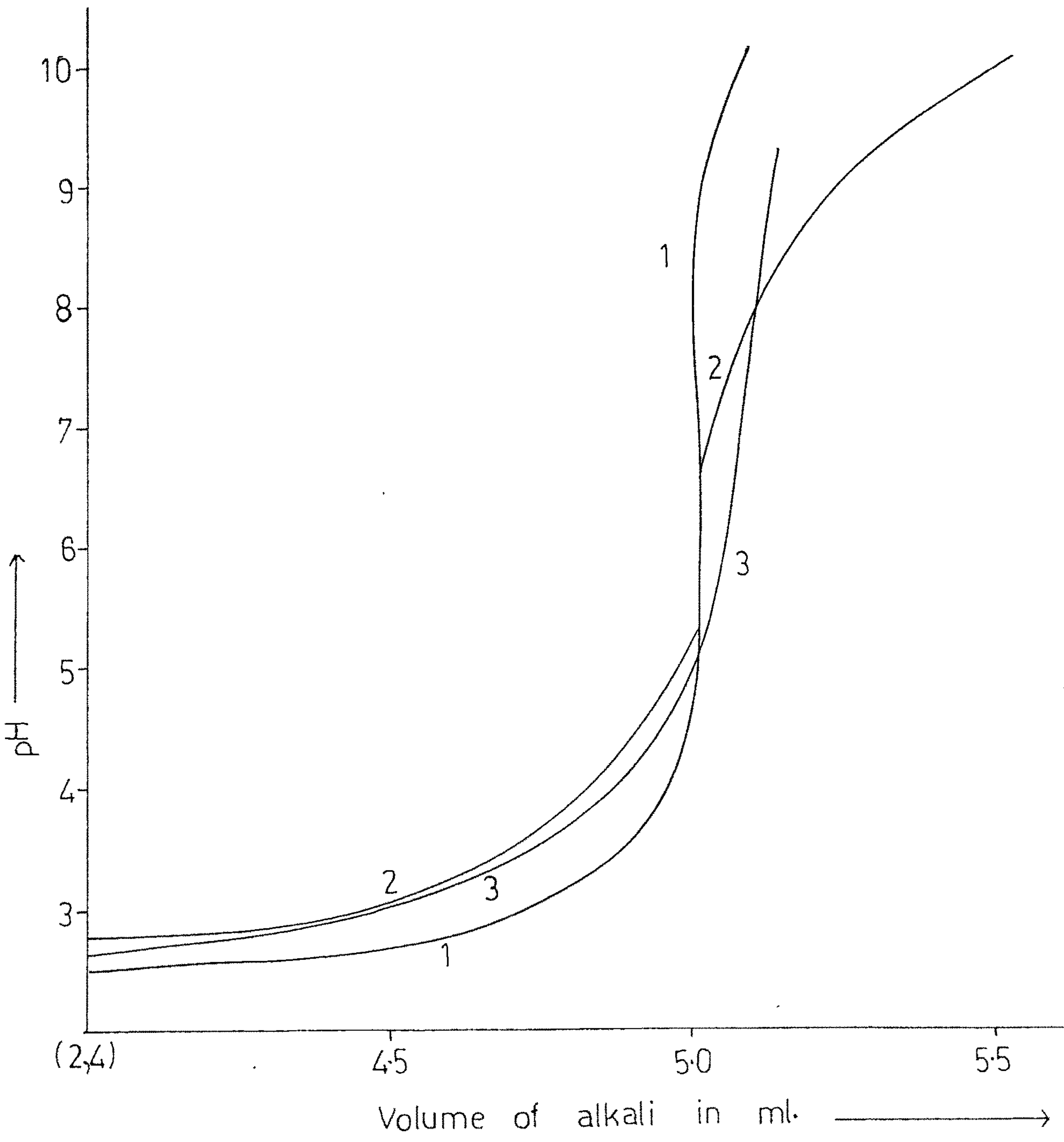


Fig III 12

$T_L^\circ = T_M^\circ = 0{\cdot}001\,M$

CuA³Glycine system at 30°c

1· Acid

2· Glycine

3· Cu + dpa + Glycine (1:1:1)

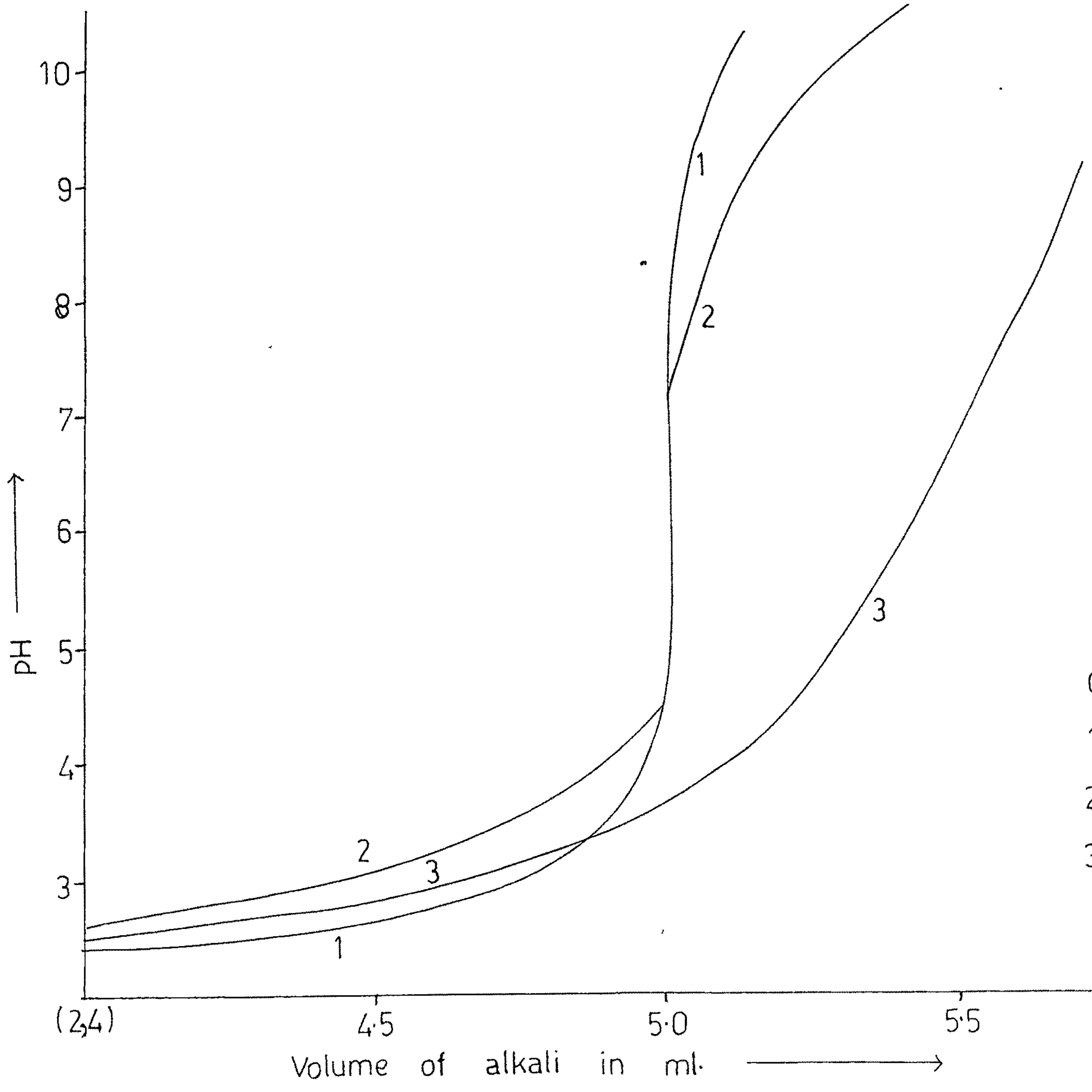


Fig III 13

$T_L^o = T_M^o = 0{\cdot}001M$

CuA^2 α-alanine system at 30°c

1 Acid

2 α-alanine

3 Cu + dpk + α-alanine (1:1:1)

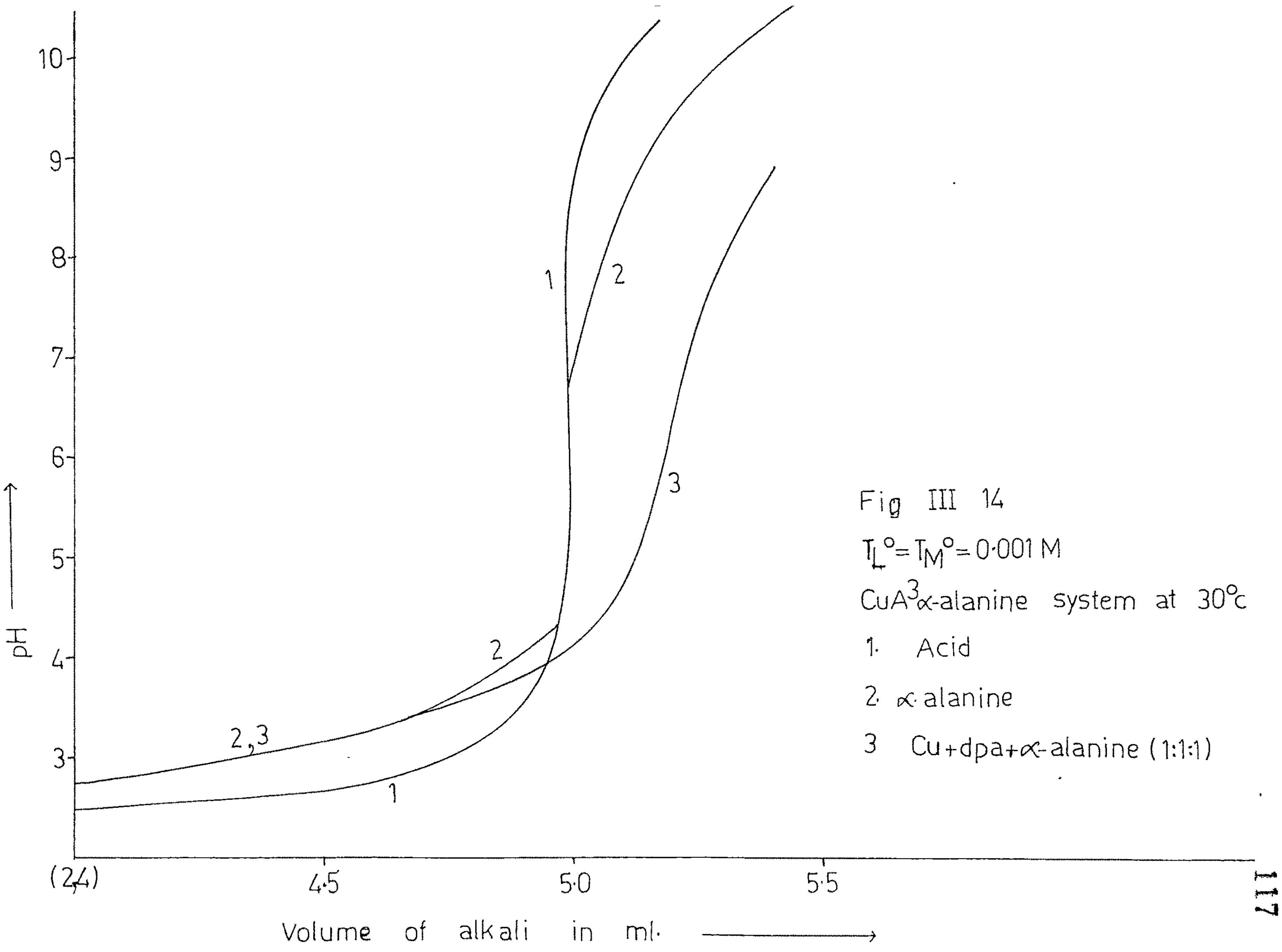


Fig III 14

$T_L^\circ = T_M^\circ = 0{\cdot}001$ M

CuA^{3}α-alanine system at 30°c

1. Acid

2. α-alanine

3. Cu+dpa+α-alanine (1:1:1)

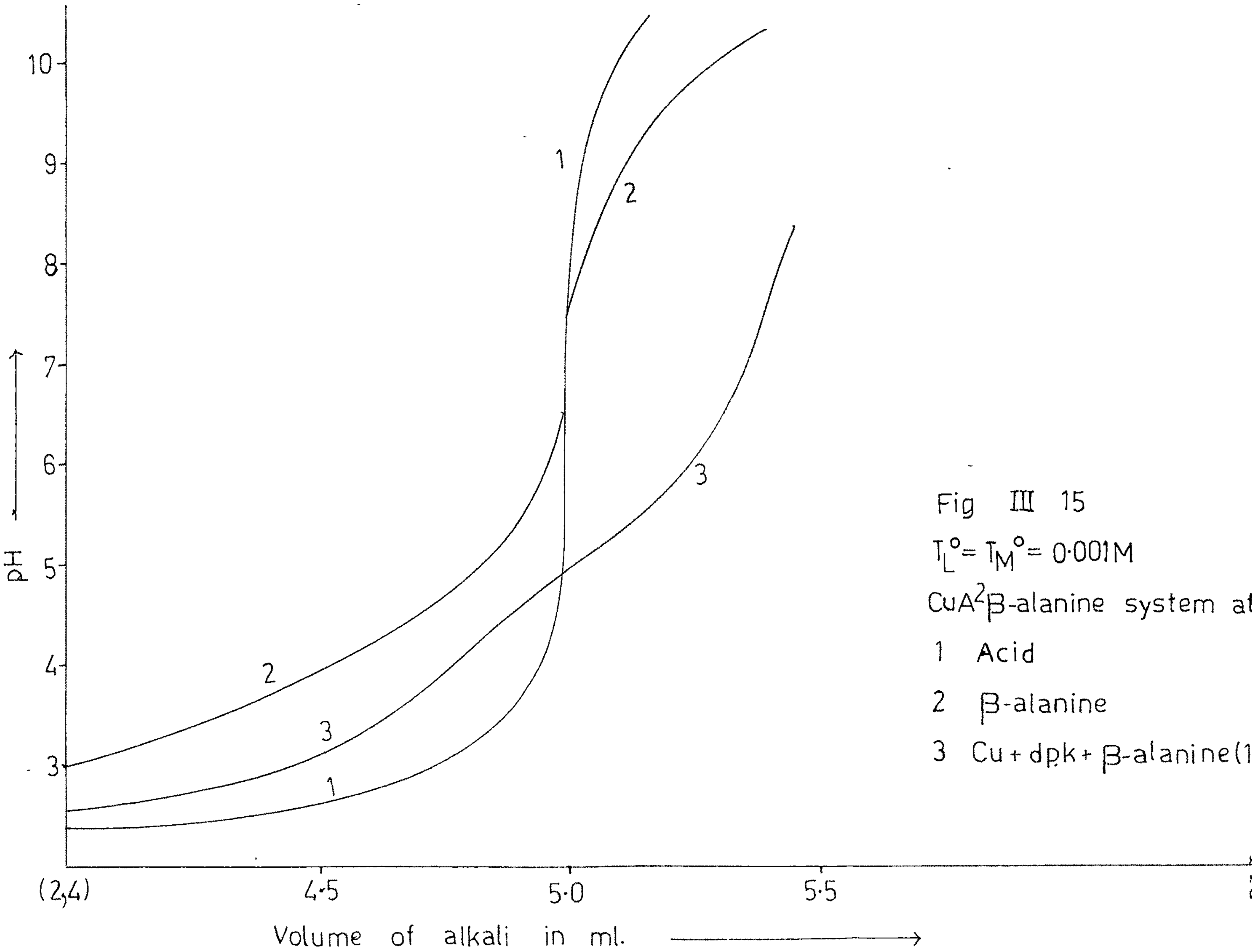


Fig III 15

$T_L^o = T_M^o = 0{\cdot}001M$

CuA^{2}β-alanine system at 30°c

1 Acid

2 β-alanine

3 Cu + dpk + β-alanine (1:1:1)

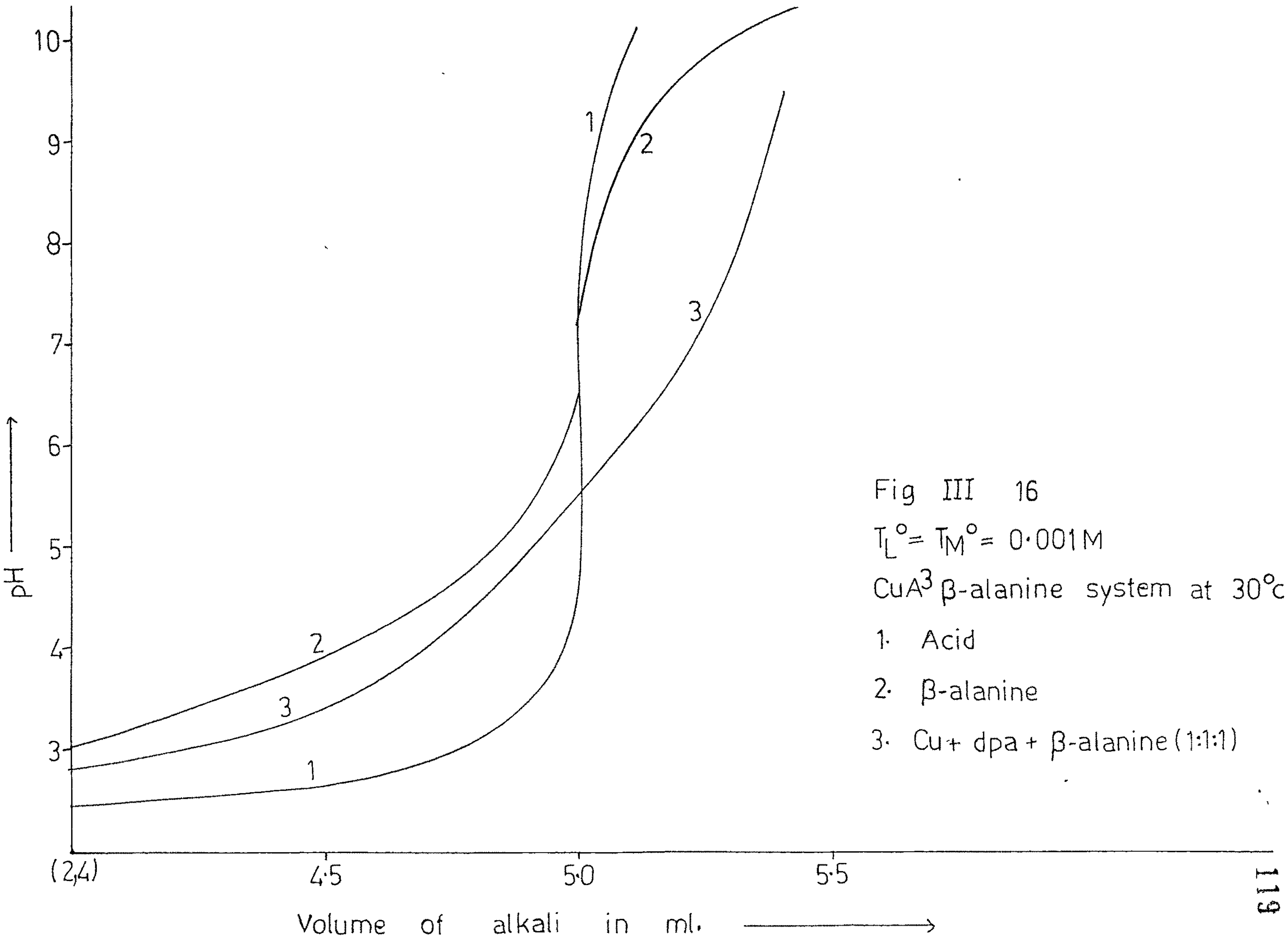


Fig III 16

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001\,M$

CuA^3 β-alanine system at 30°c

1· Acid

2· β-alanine

3· Cu+ dpa + β-alanine (1:1:1)

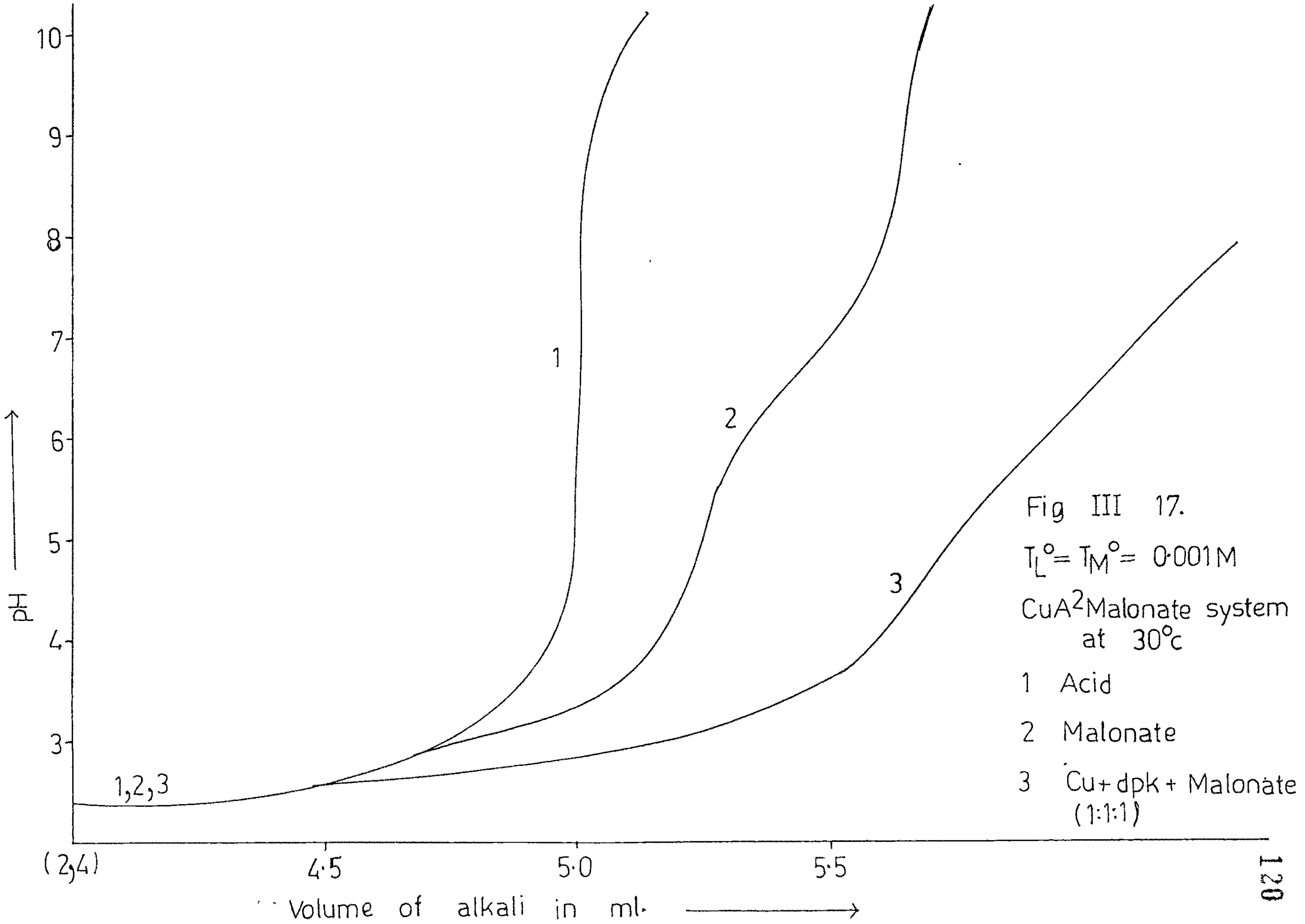


Fig III 17.

$T_L^\circ = T_M^\circ = 0{\cdot}001\,M$

CuA^2 Malonate system at 30°c

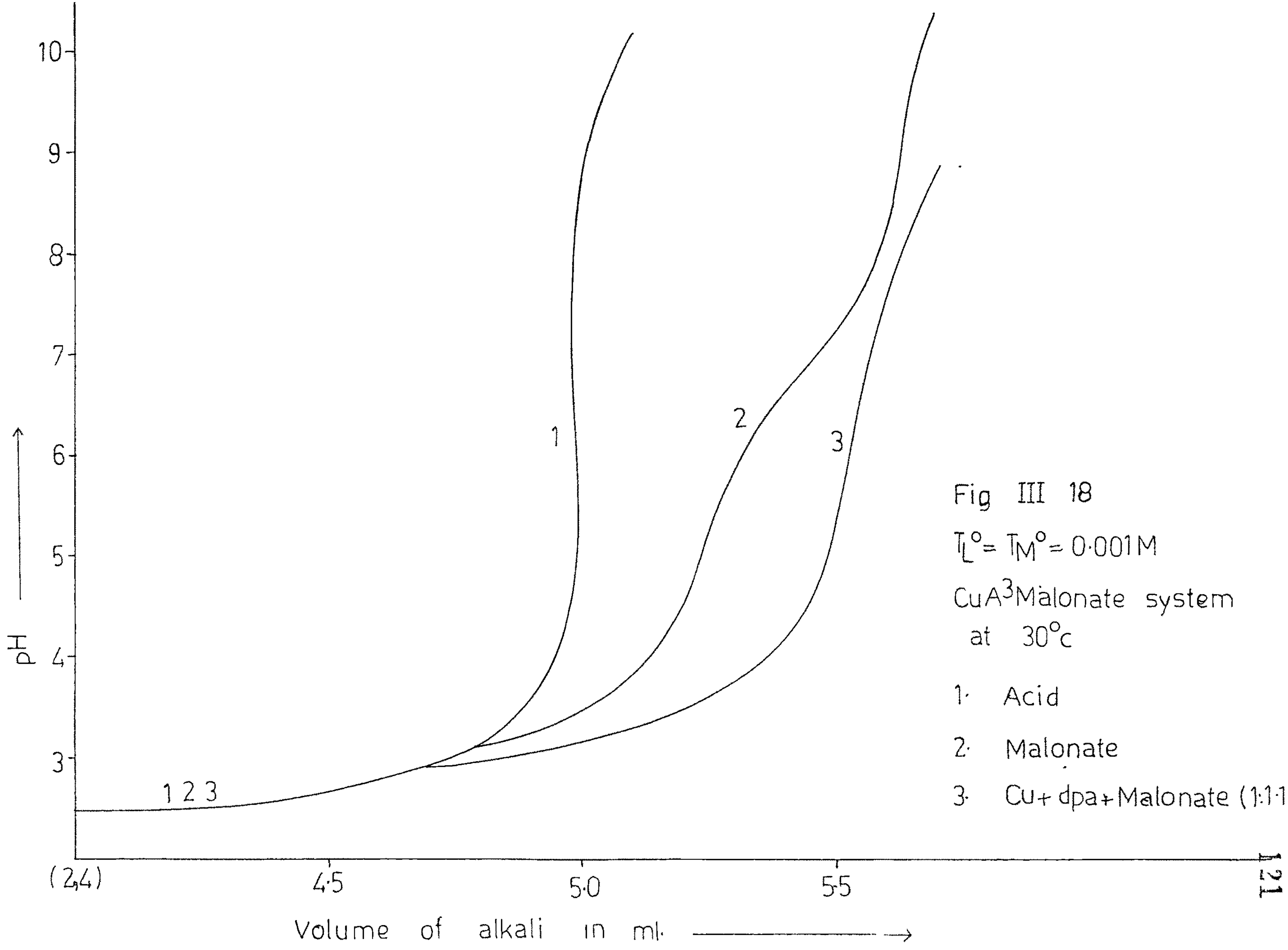


Fig III 18

$T_L^o = T_M^o = 0{\cdot}001M$

CuA^3Malonate system at 30°c

1· Acid
2· Malonate
3· Cu+dpa+Malonate (1:1:1)

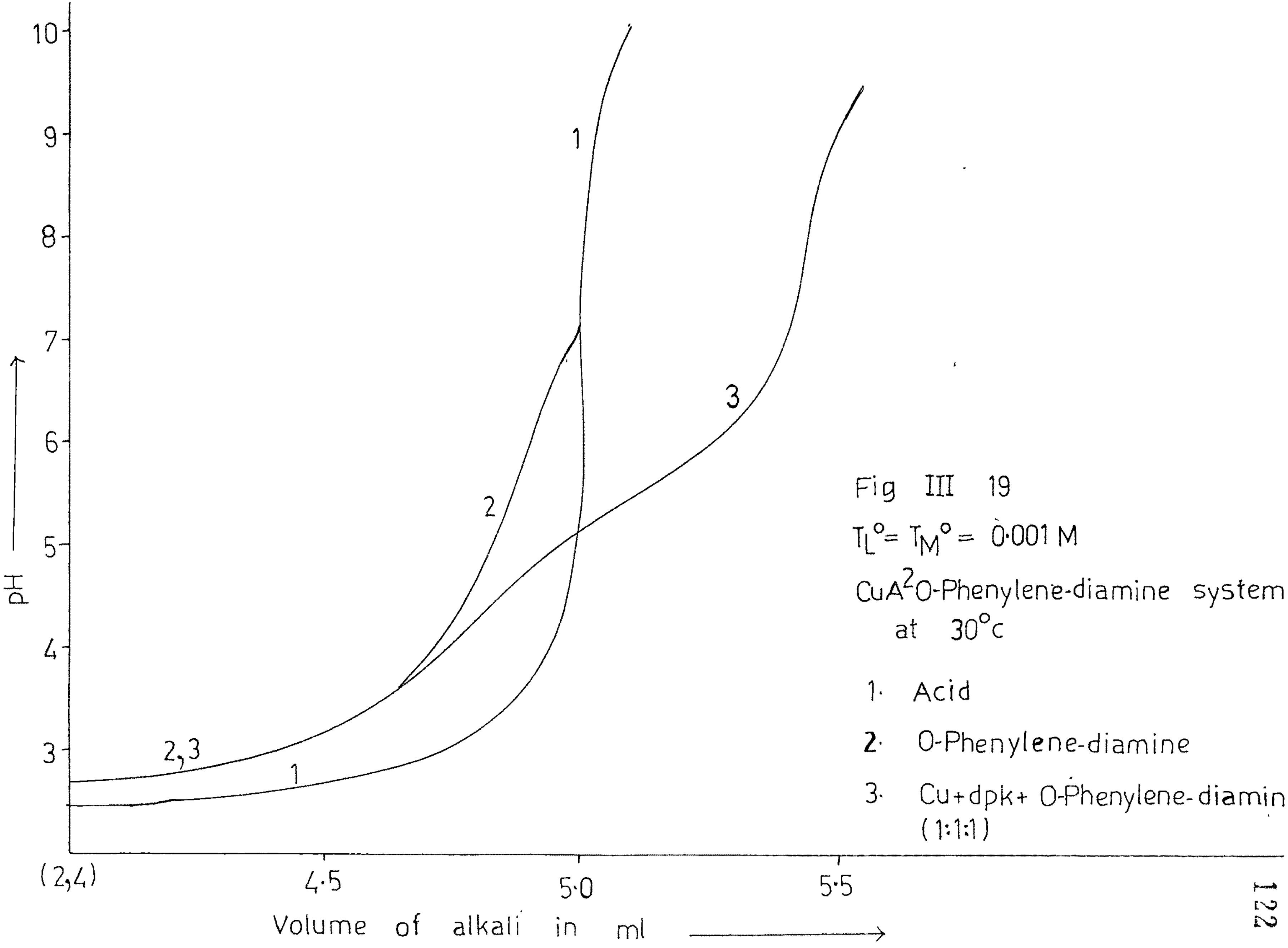


Fig III 19

$T_L^\circ = T_M^\circ = 0{\cdot}001$ M

CuA^2O-Phenylene-diamine system at 30°c

1· Acid

2· O-Phenylene-diamine

3· Cu+dpk+ O-Phenylene-diamine (1:1:1)

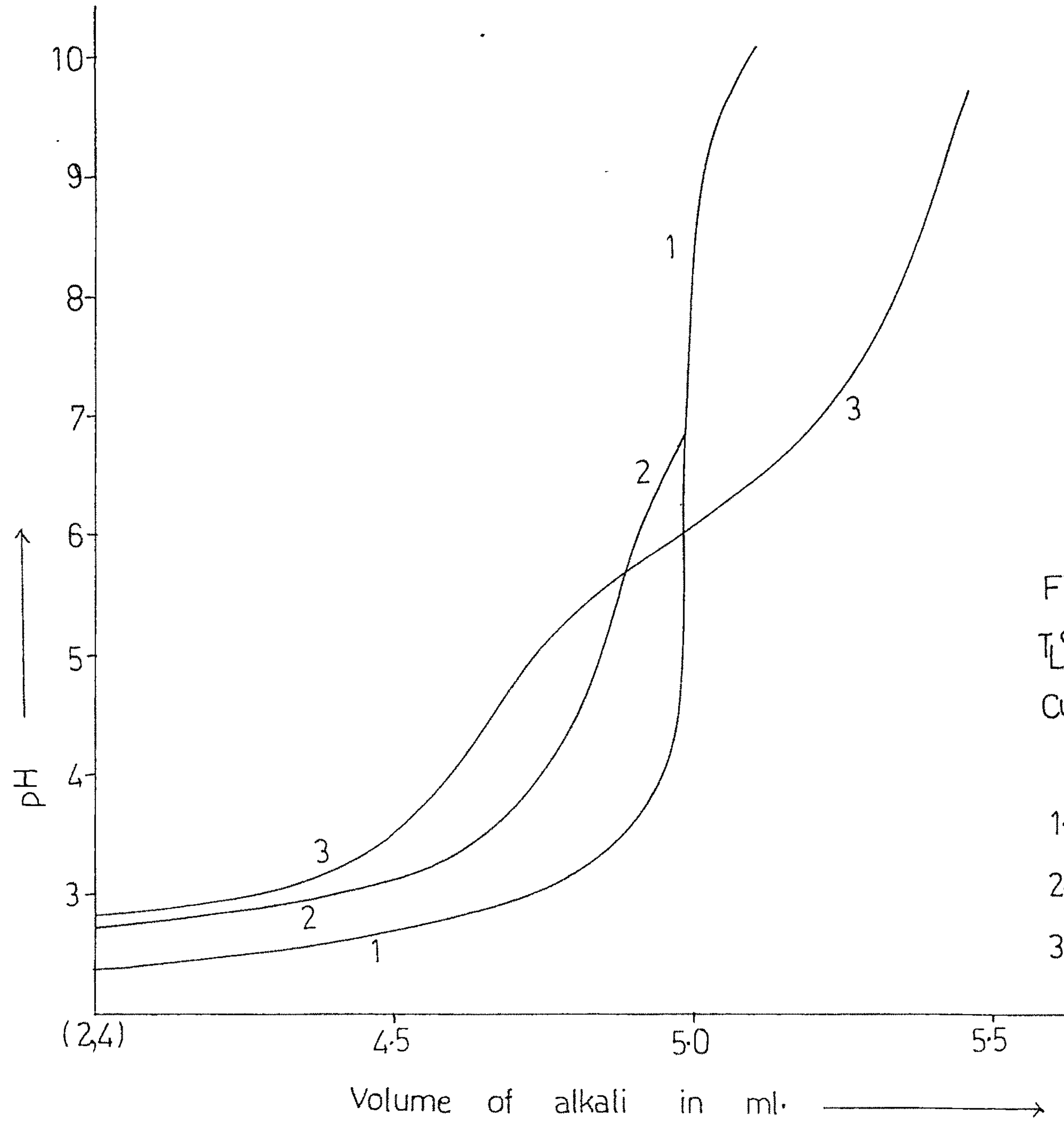


Fig III 20

$T_L^\circ = T_M^\circ = 0{\cdot}001\,M$

CuA^3 o Phenylene diamine system
at 30°c

1· Acid

2· o-Phenylene-diamine

3· Cu+dpa+o-Phenylene-diamine
(1:1:1)

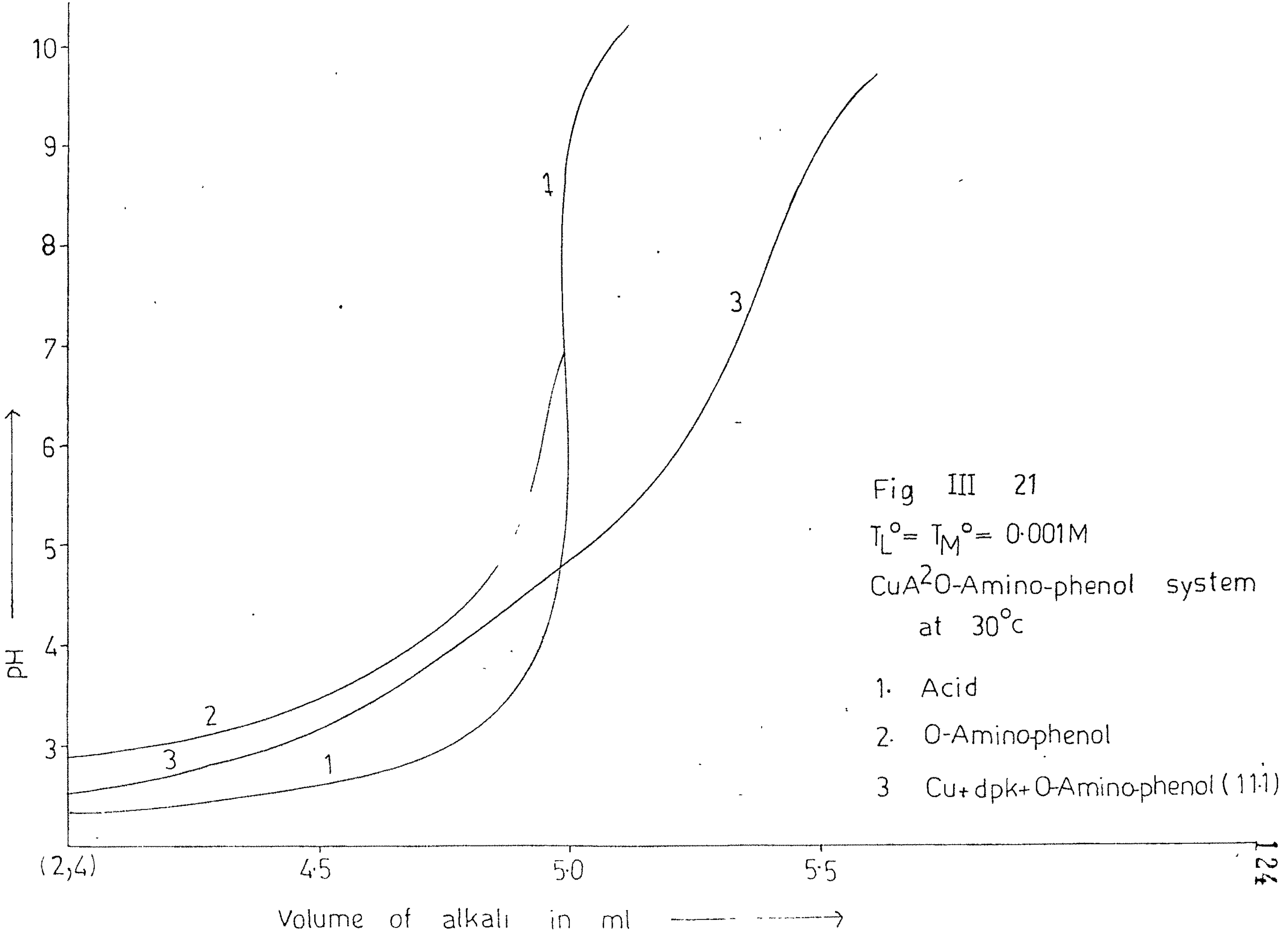


Fig III 21

$T_L^o = T_M^o = 0{\cdot}001M$

CuA^{2}O-Amino-phenol system at 30°c

1. Acid
2. O-Amino-phenol
3. Cu+dpk+O-Amino-phenol (1:1:1)

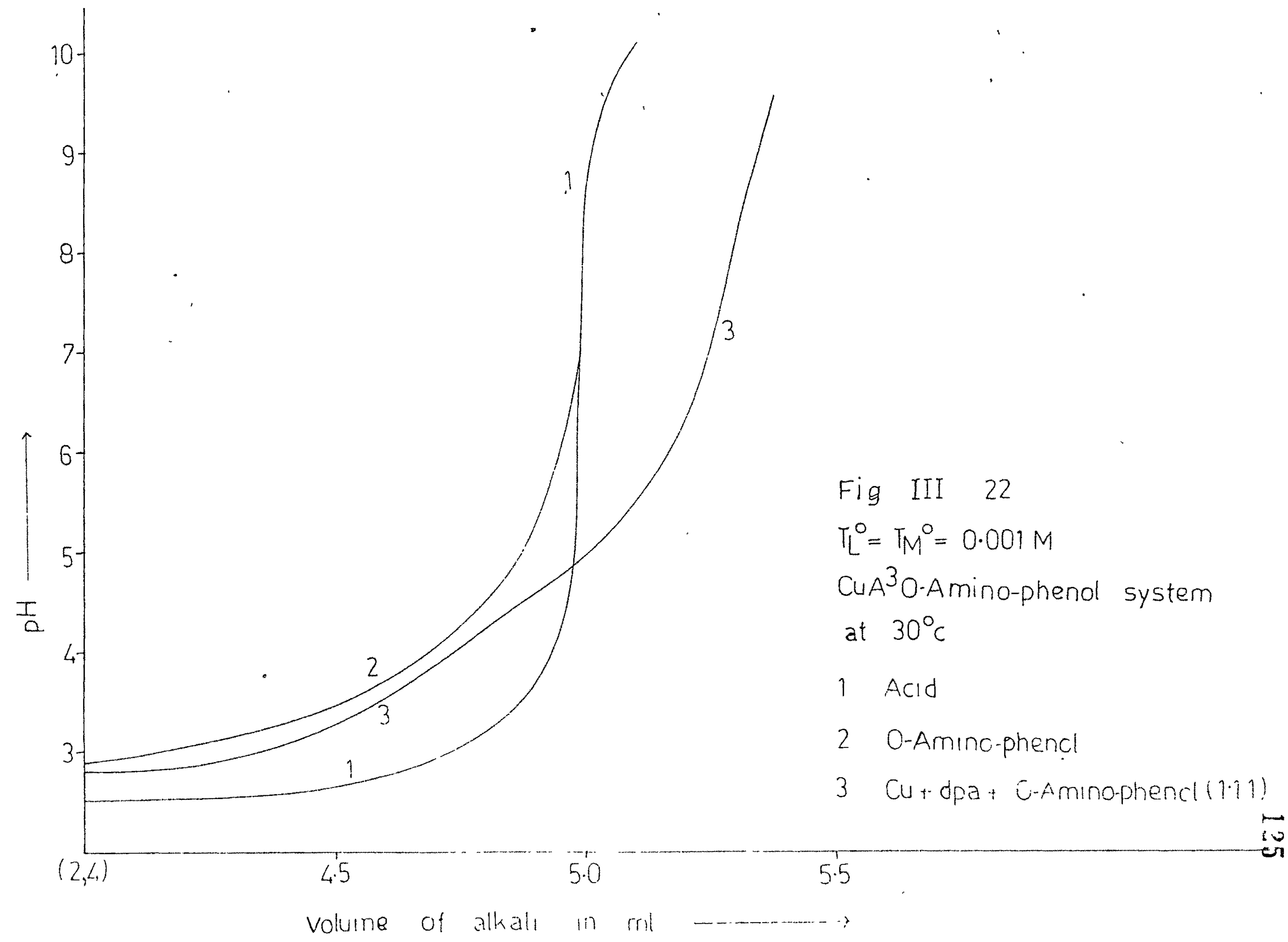


Fig III 22

$T_L^o = T_M^o = 0{\cdot}001$ M

CuA^3O-Amino-phenol system at 30°c

1 Acid

2 O-Amino-phenol

3 Cu + dpa + O-Amino-phenol (1:1:1)

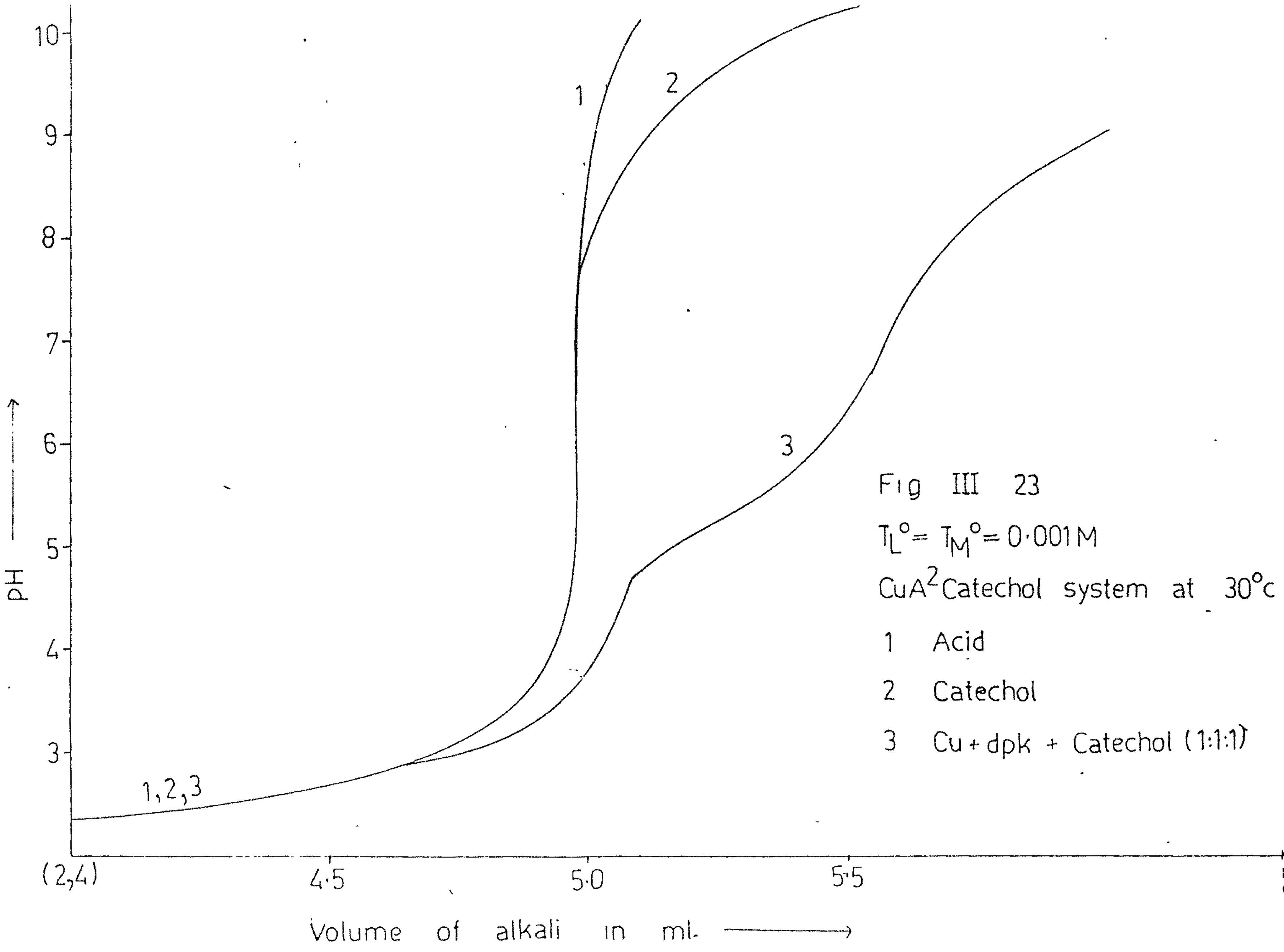


Fig III 23

$T_L^\circ = T_M^\circ = 0{\cdot}001\,M$

CuA^2Catechol system at 30°c

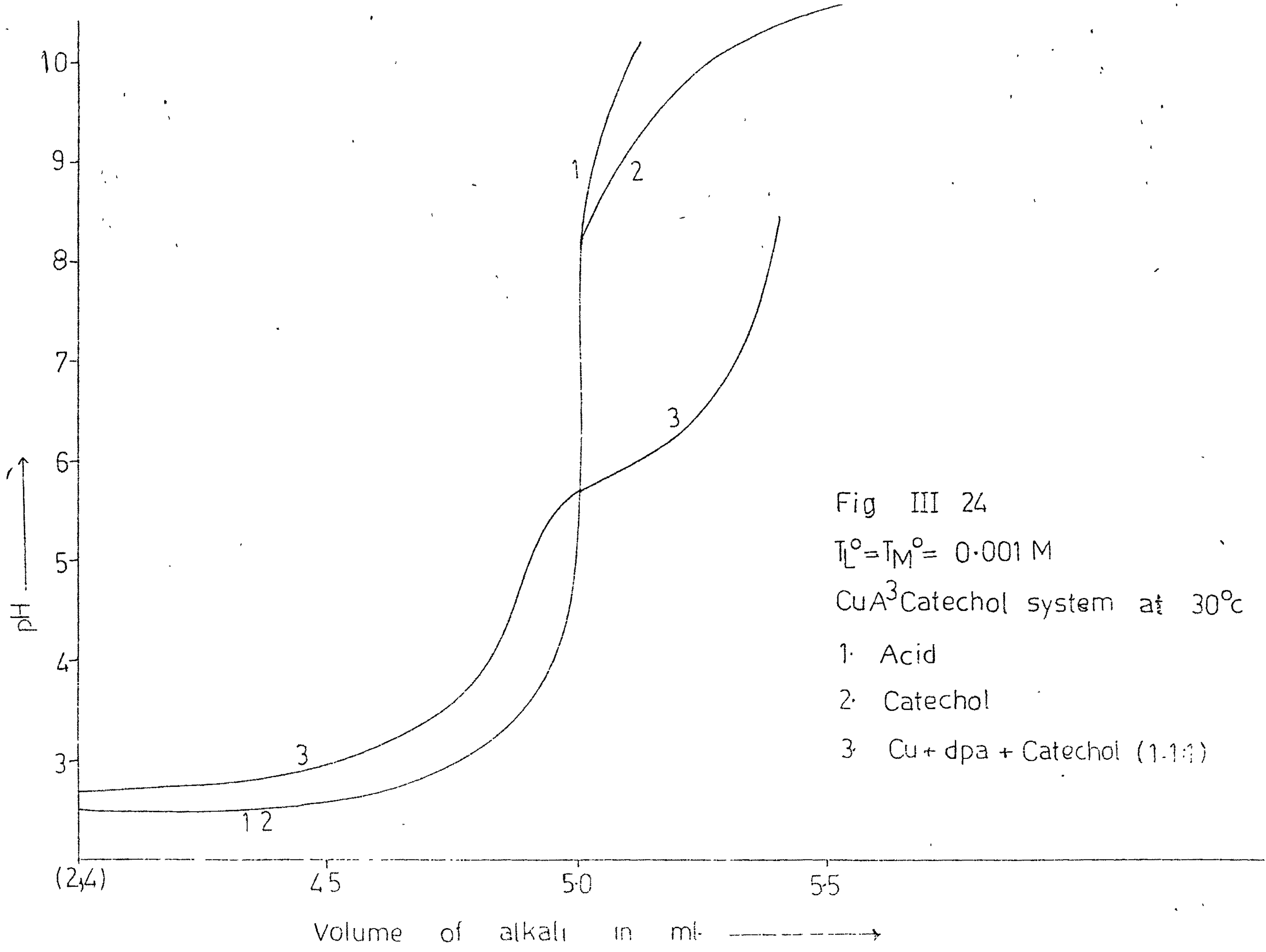


Fig III 24

$T_L^o = T_M^o = 0{\cdot}001$ M

CuA^{3}Catechol system at 30°c

1· Acid

2· Catechol

3· Cu + dpa + Catechol (1:1:1)

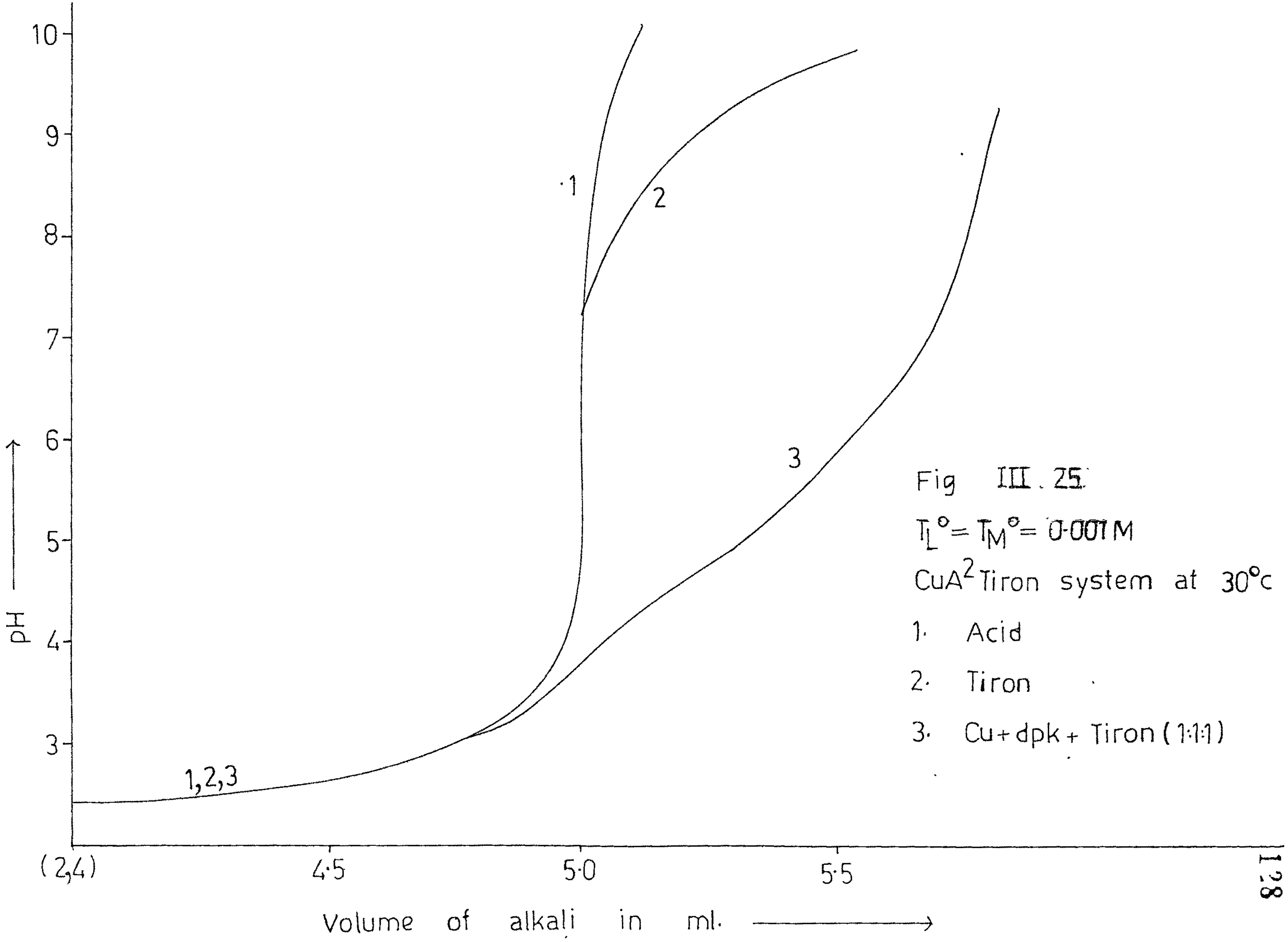


Fig III . 25

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001\,M$

CuA^{2}Tiron system at 30°c

1· Acid

2· Tiron

3· Cu+dpk+Tiron (1:1:1)

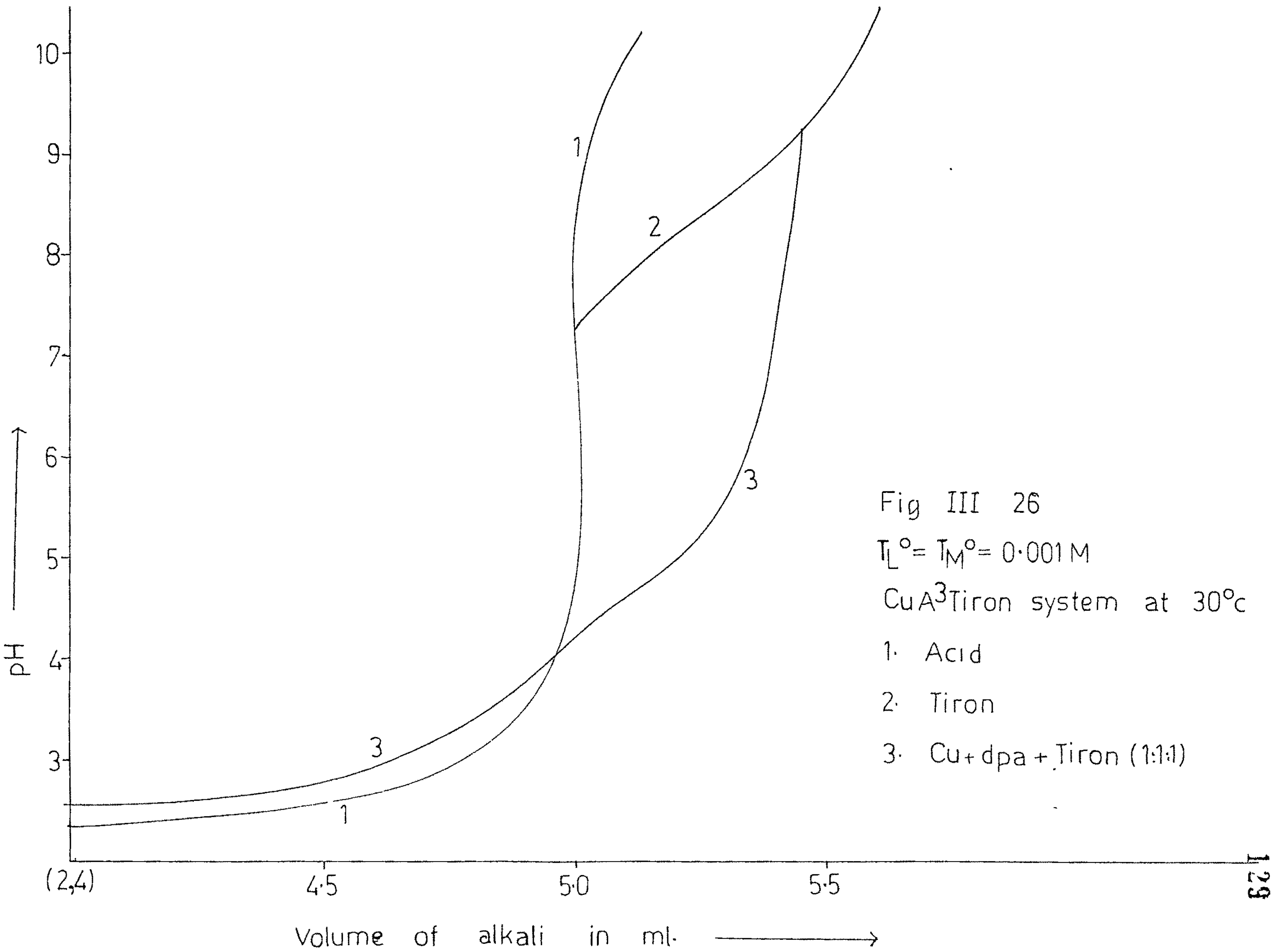


Fig III 26

$T_L^o = T_M^o = 0{\cdot}001\,M$

CuA^3Tiron system at 30°c

1· Acid

2· Tiron

3· Cu+dpa+Tiron (1:1:1)

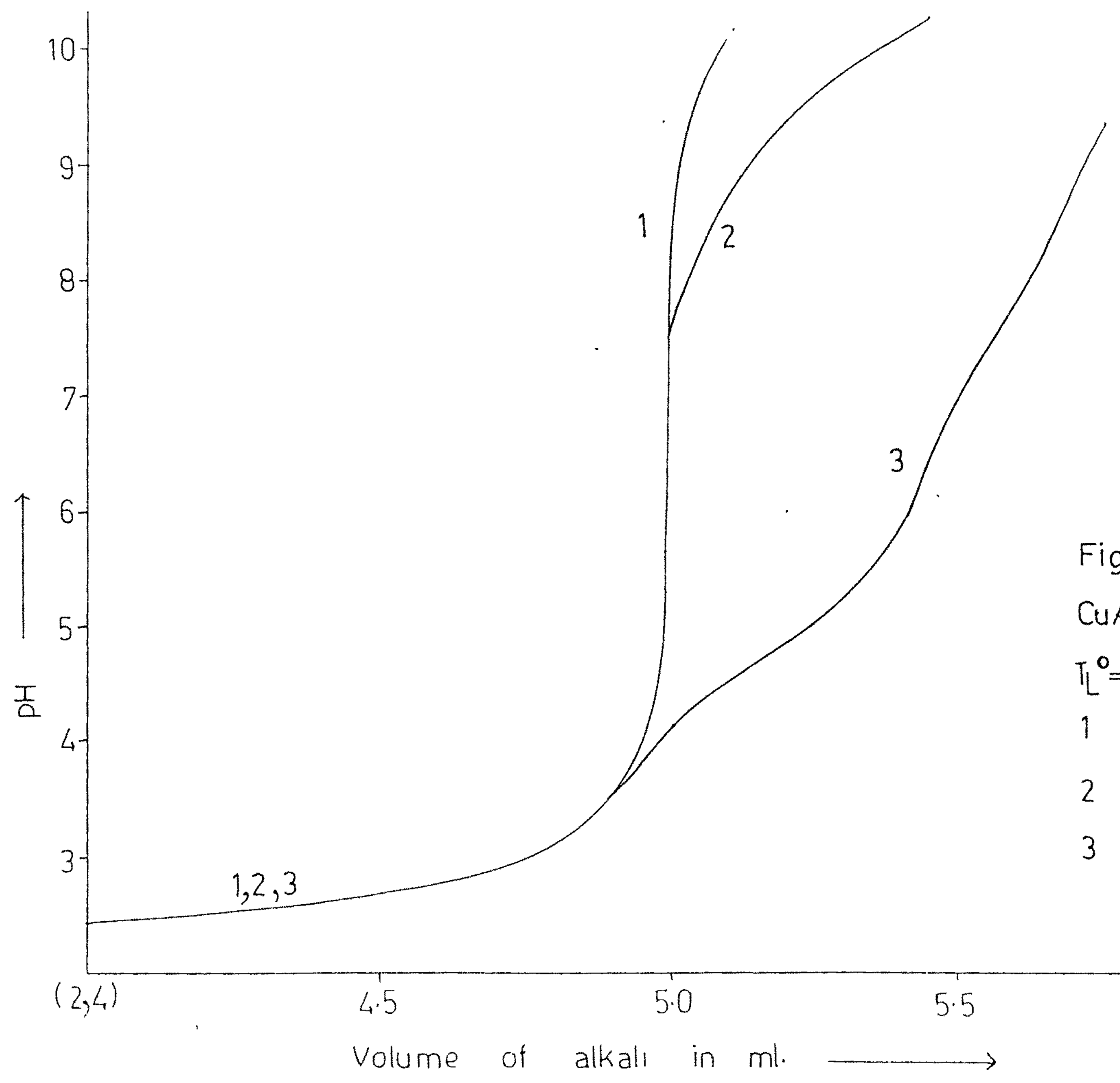


Fig III 27.

CuA^2 Pyrogallol system at 30°c

$T_L^o = T_M^o =$ 0·001 M

1 Acid

2 Pyrogallol

3 Cu + dpk + Pyrogallol (1:1:1)

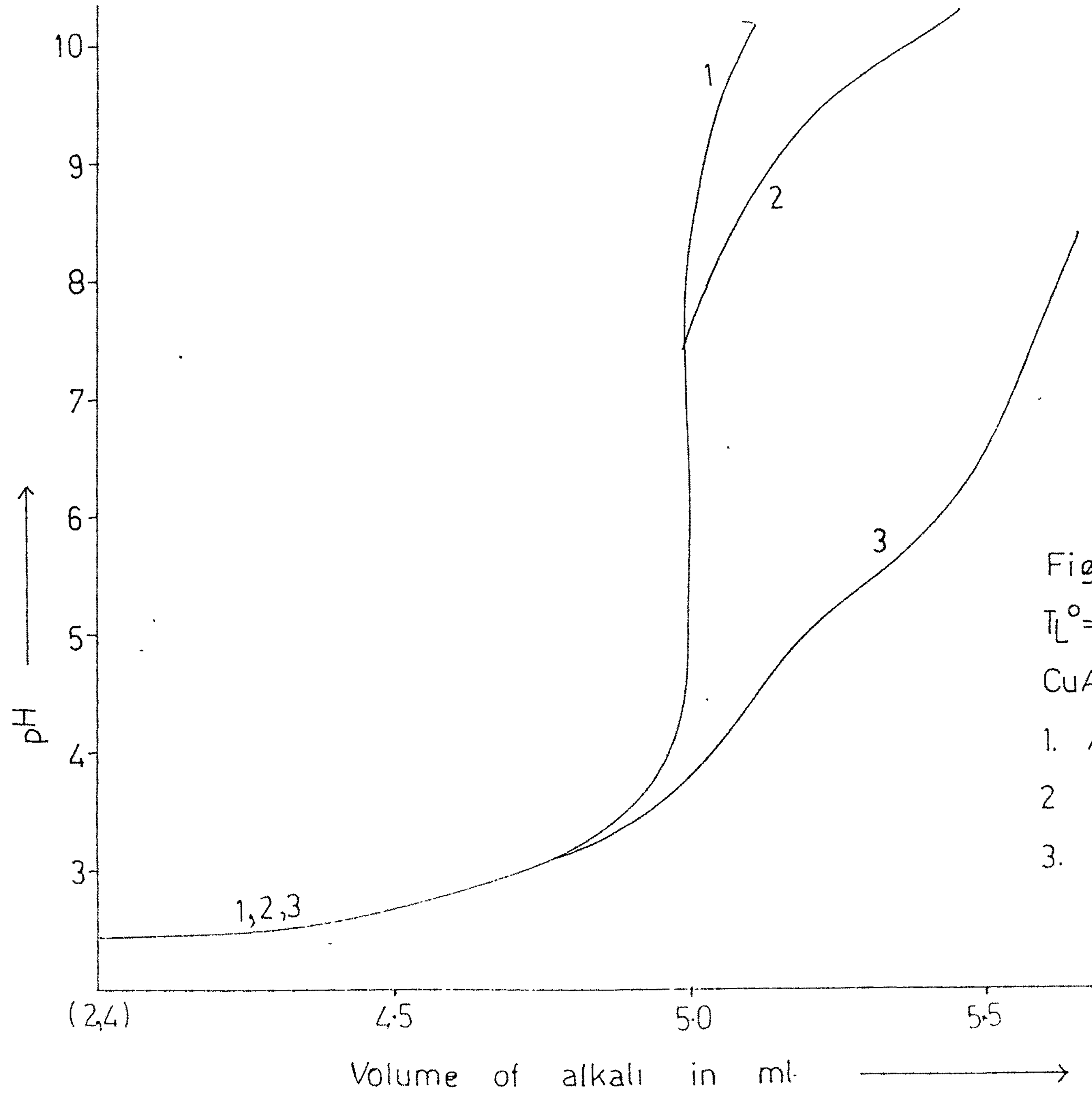


Fig III 28

$T_L^\circ = T_M^\circ = 0{\cdot}001\,M$

CuA^{3}Pyrogallol system at 30°c

1. Acid.

2 Pyrogallol.

3. Cu+ dpa + Pyrogallol (1:1:1)

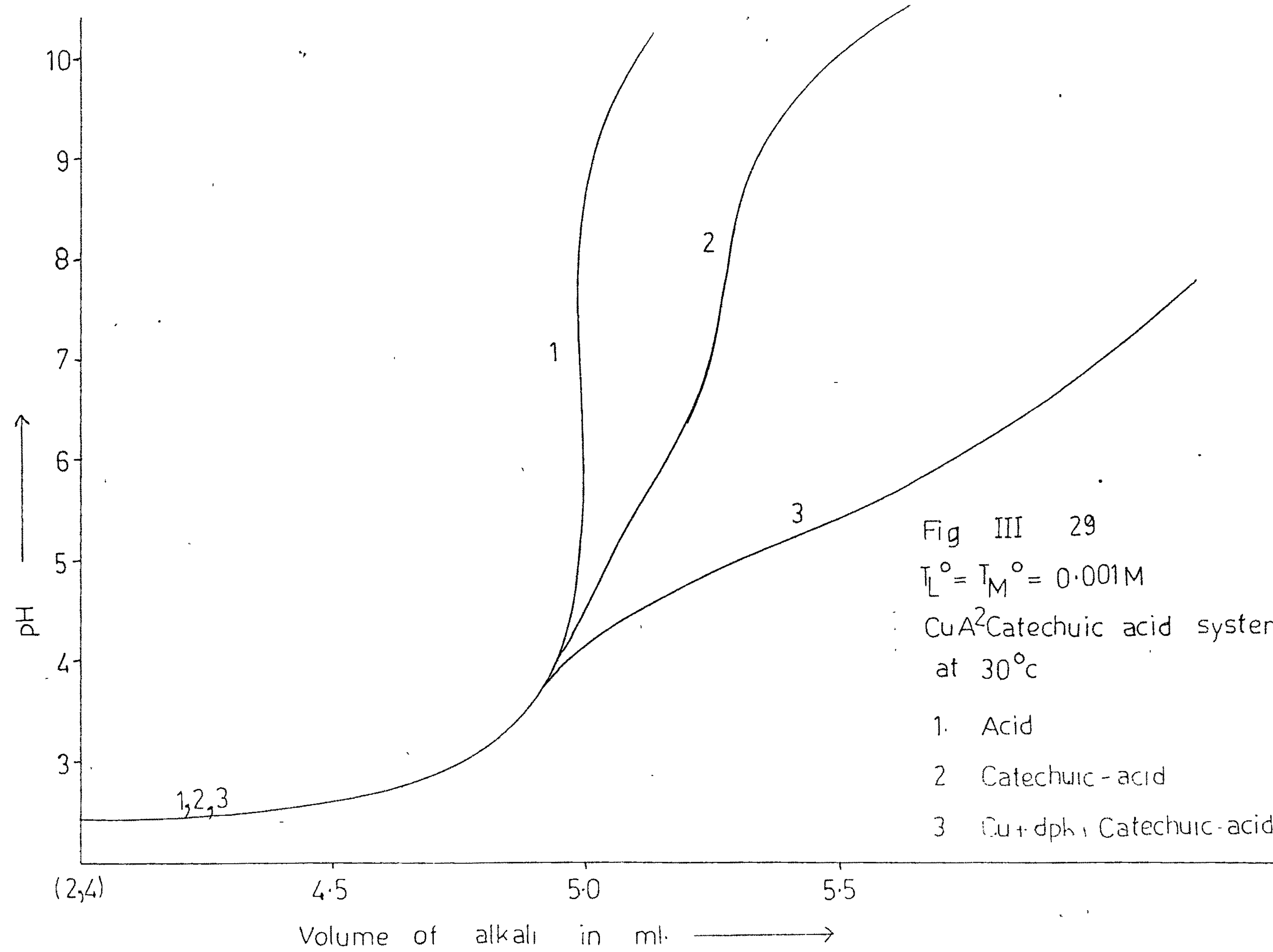


Fig III 29

$T_L^\circ = T_M^\circ = 0{\cdot}001M$

CuA^{2}Catechuic acid system at 30°c

1. Acid

2 Catechuic - acid

3 Cu + dph , Catechuic-acid(1·1·1)

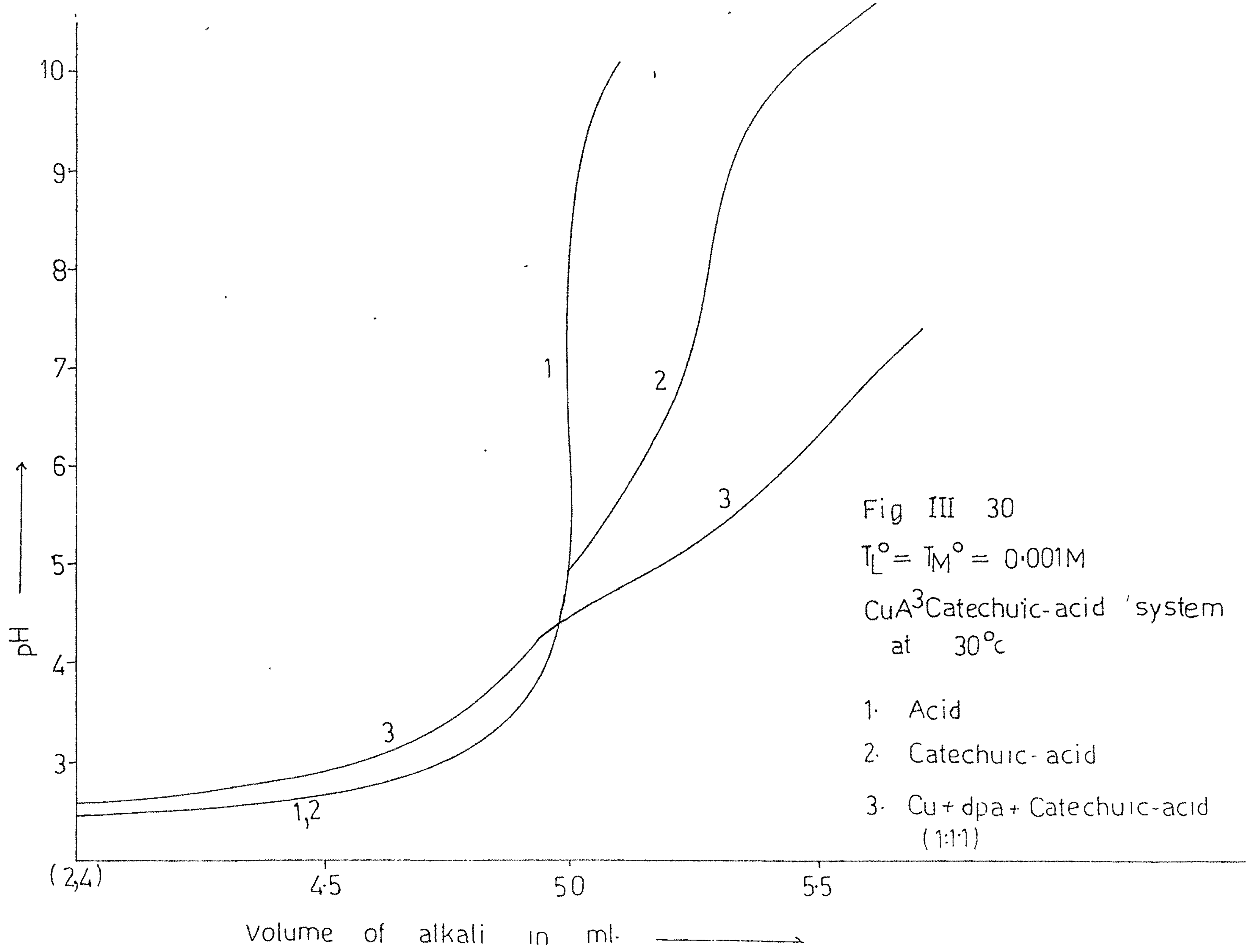


Fig III 30

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001M$

CuA^{3}Catechuic-acid 'system
at 30°c

1· Acid

2· Catechuic- acid

3· Cu + dpa + Catechuic-acid
(1:1:1)

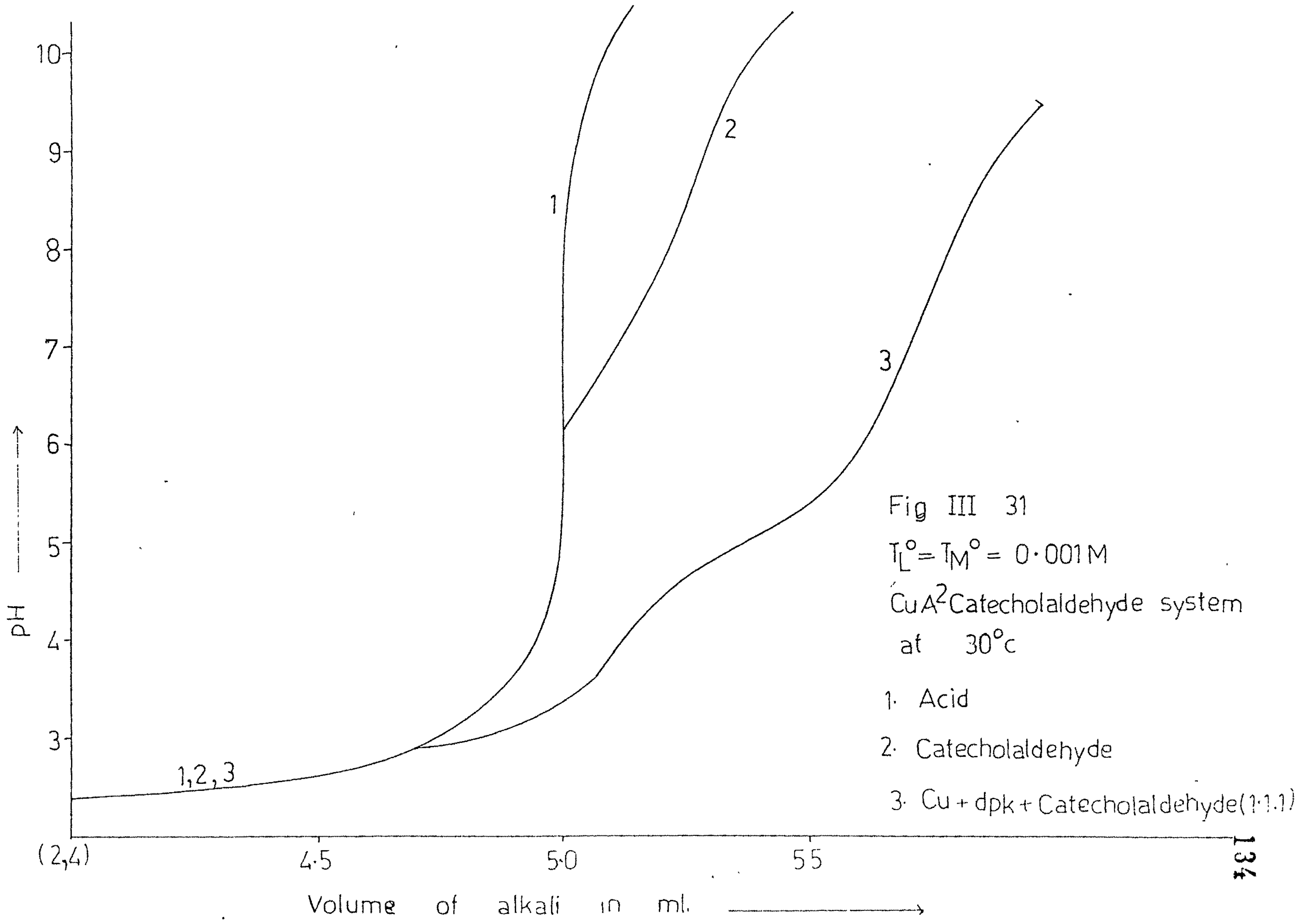


Fig III 31

$T_L^\circ = T_M^\circ = 0\cdot001\,M$

CuA^{2}Catecholaldehyde system at 30°c

1· Acid

2· Catecholaldehyde

3· Cu + dpk + Catecholaldehyde(1:1:1)

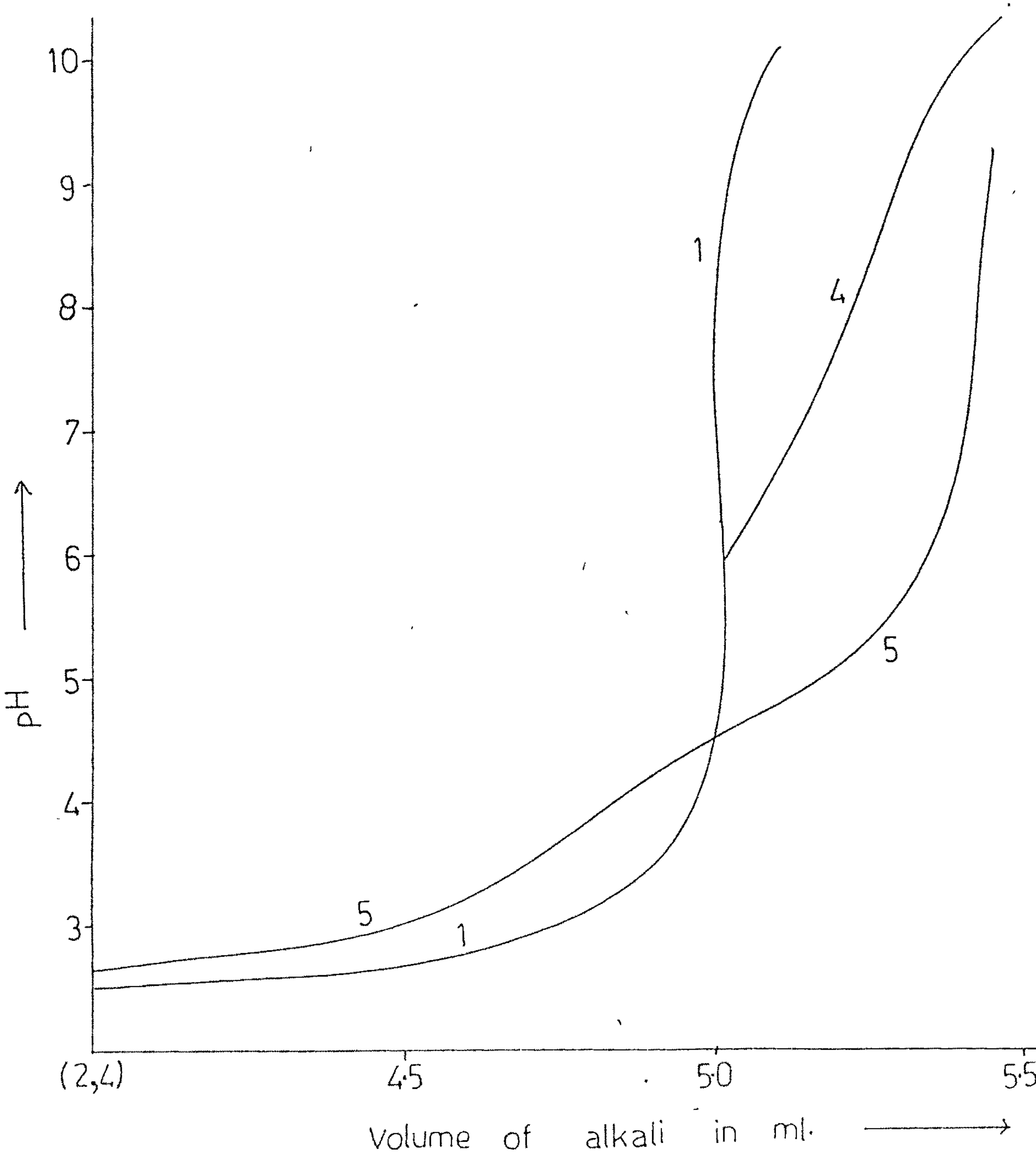


Fig III 32

$T_L^o = T_M^o = 0{\cdot}001\,M$

CuA^{3}Catecholaldehyde system
at 30°c

1· Acid

2· Catecholaldehyde

3· Cu + dpa + Catecholaldehyde (1:1:1)

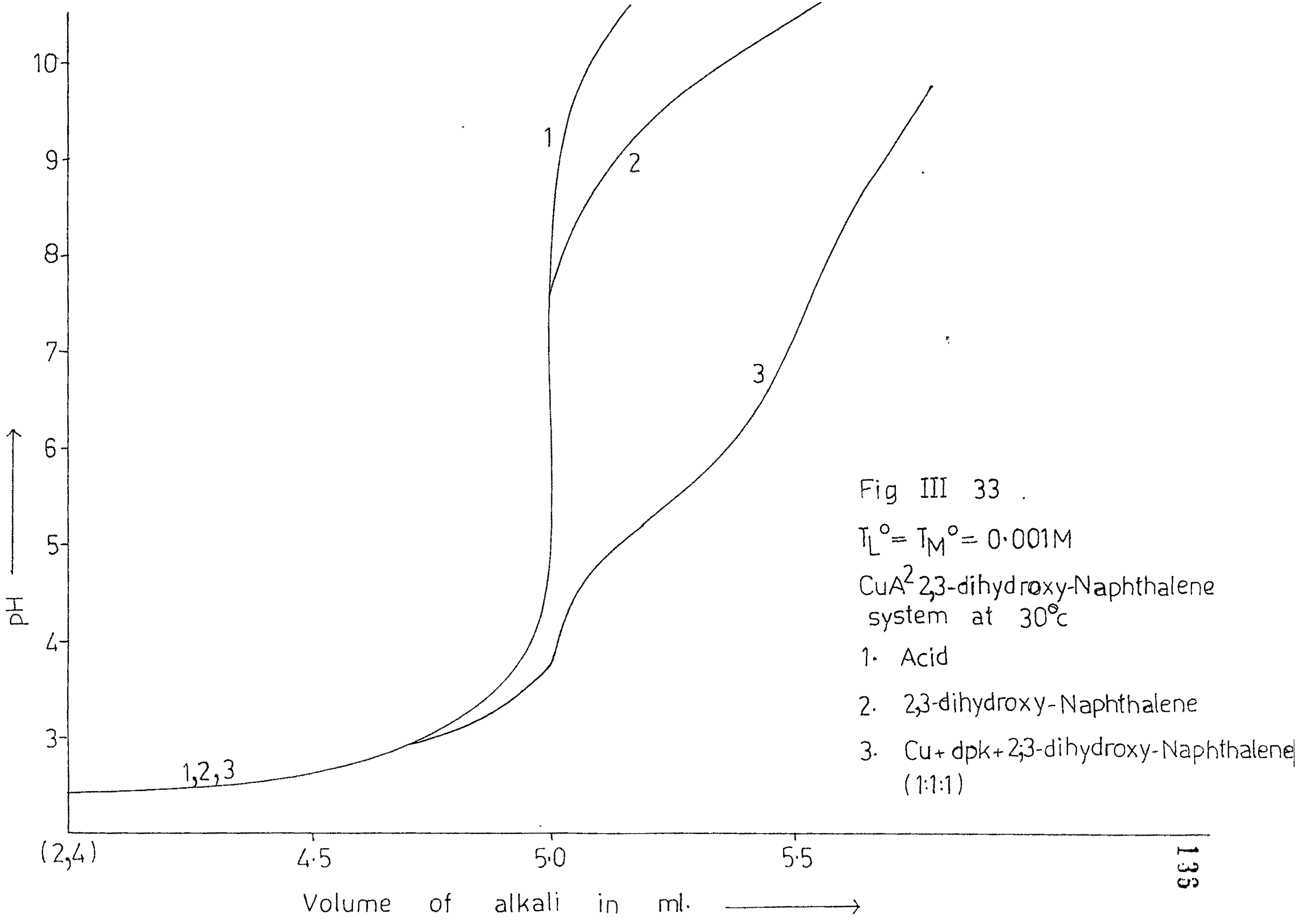


Fig III 33 .

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001M$

CuA^2 2,3-dihydroxy-Naphthalene system at 30°c

1· Acid

2· 2,3-dihydroxy-Naphthalene

3· Cu+ dpk+2,3-dihydroxy-Naphthalene (1:1:1)

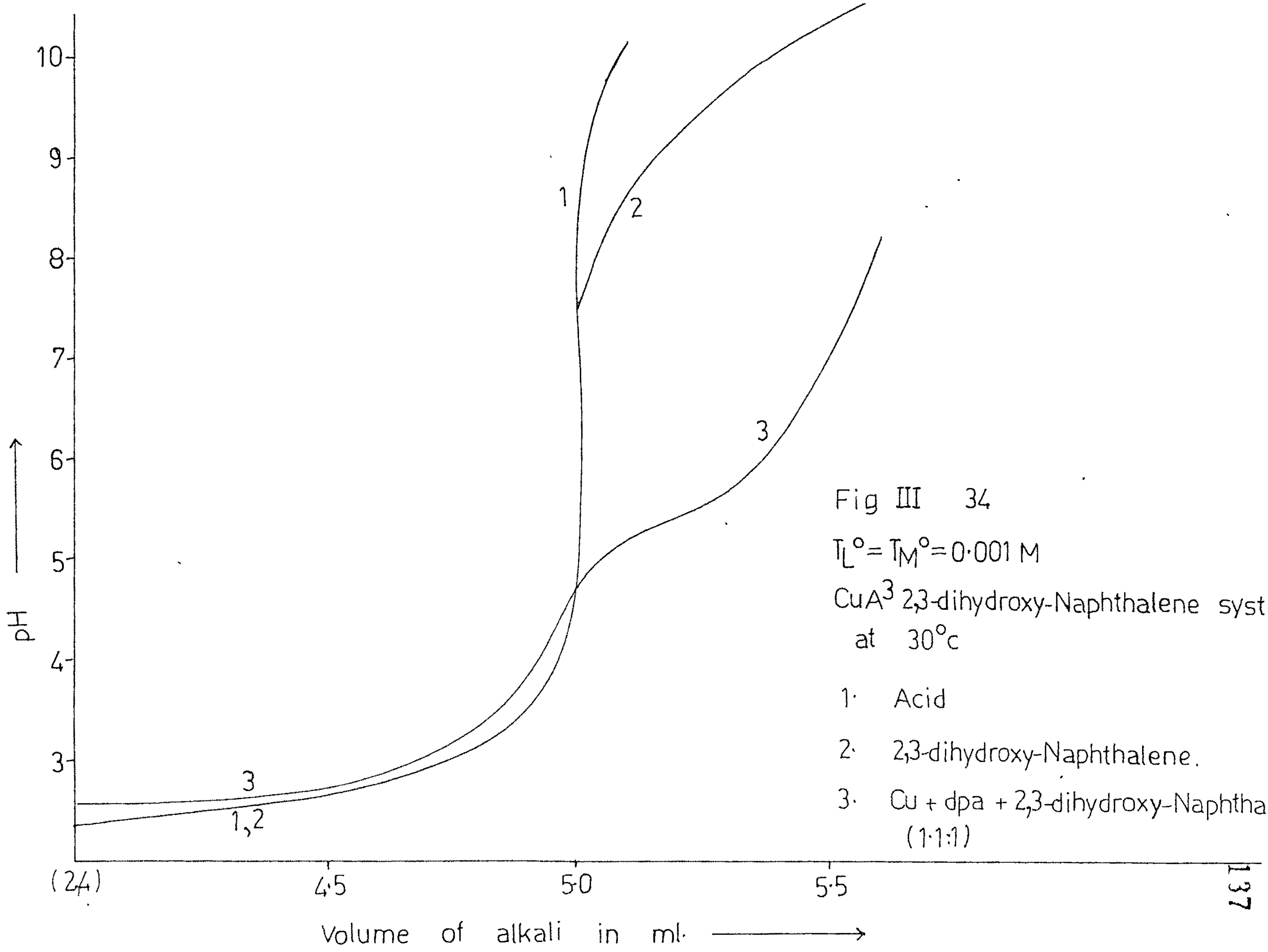


Fig III 34

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001$ M

CuA^3 2,3-dihydroxy-Naphthalene system at 30°c

1· Acid

2· 2,3-dihydroxy-Naphthalene.

3· Cu + dpa + 2,3-dihydroxy-Naphthalene. (1·1:1)

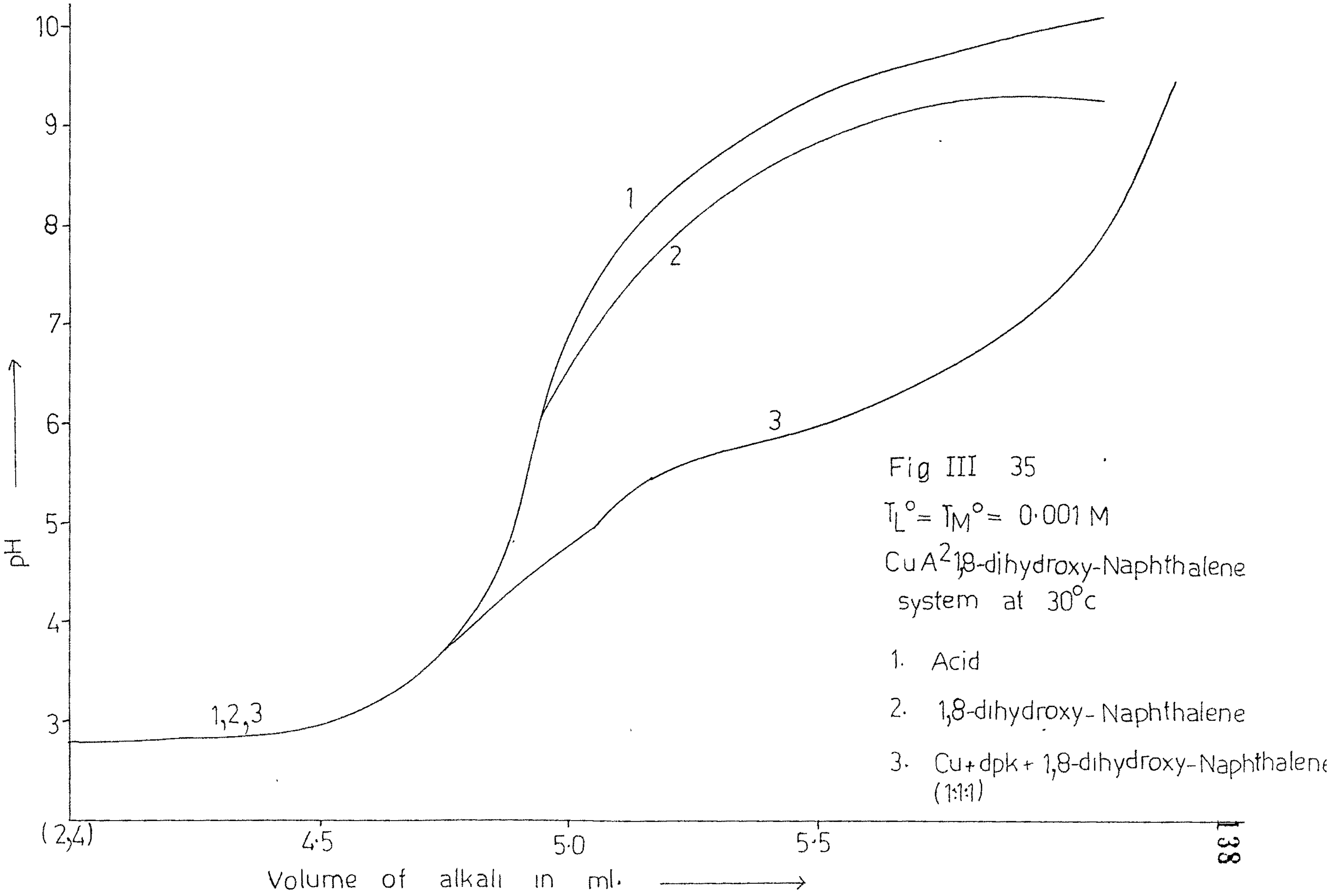


Fig III 35

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001$ M

$CuA^2$1,8-dihydroxy-Naphthalene system at 30°c

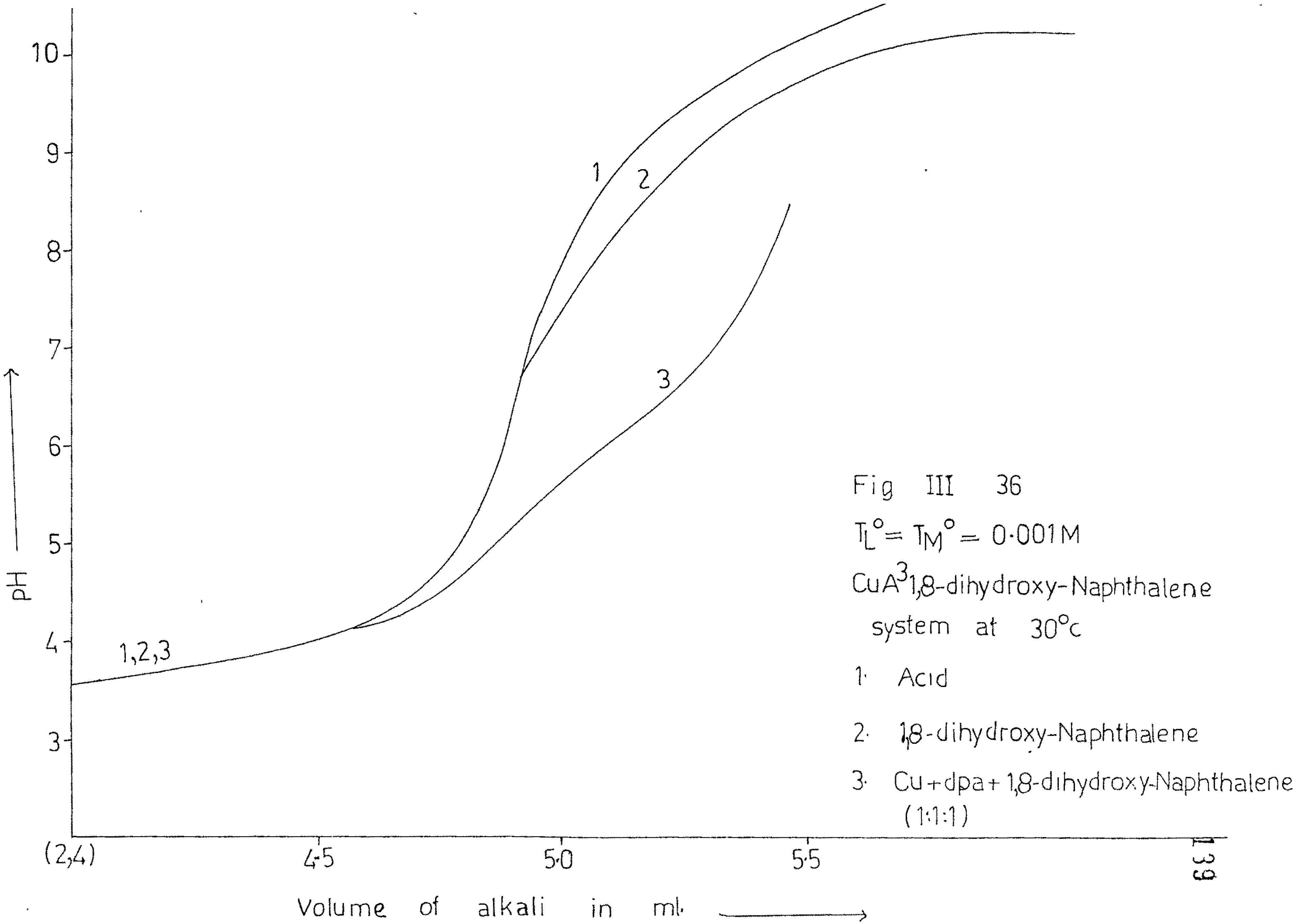


Fig III 36

$T_L^\circ = T_M^\circ = 0{\cdot}001\,M$

CuA^3 1,8-dihydroxy-Naphthalene system at 30°c

1· Acid

2· 1,8-dihydroxy-Naphthalene

3· Cu+dpa+1,8-dihydroxy-Naphthalene (1:1:1)

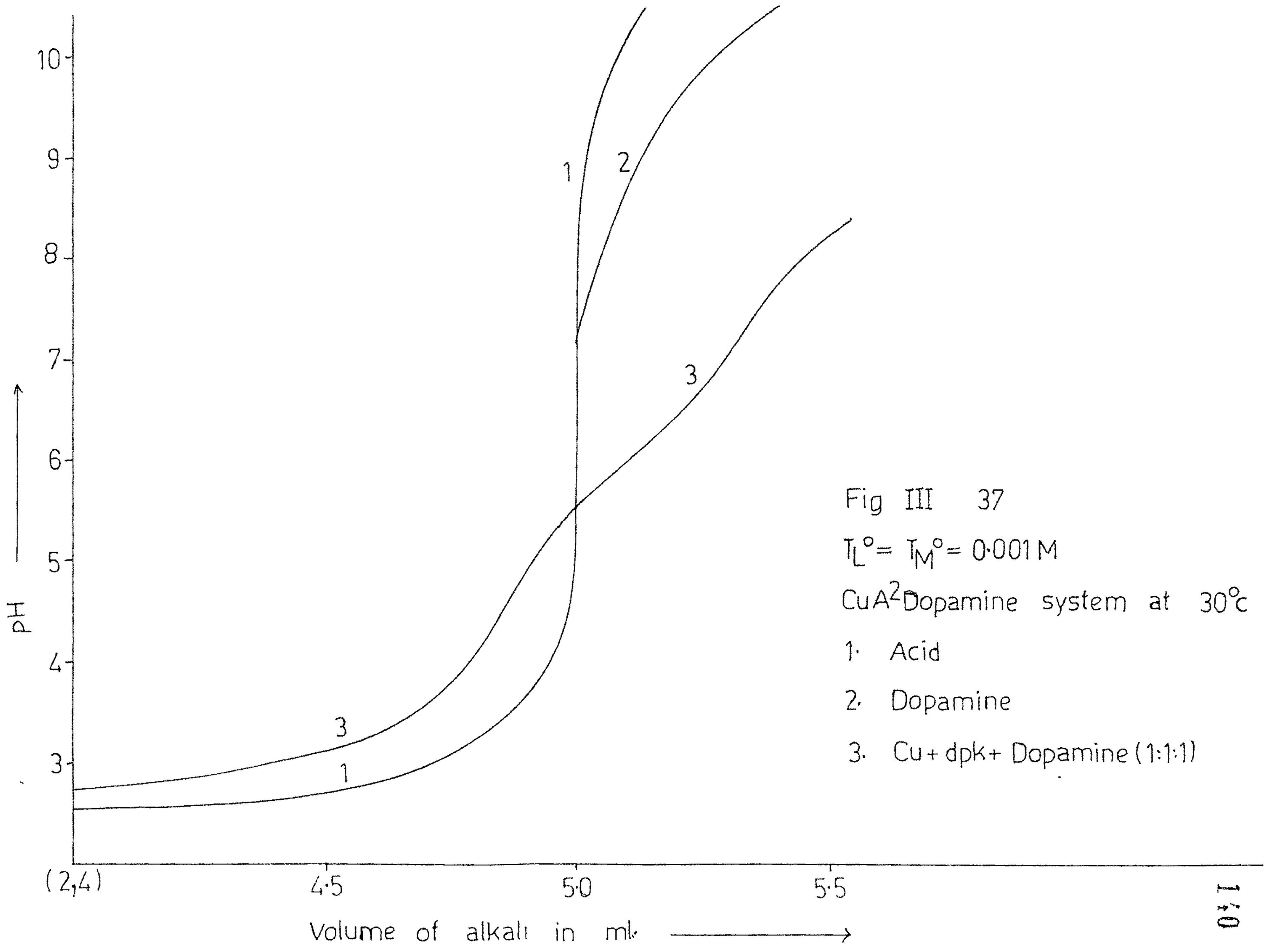


Fig III 37

$T_L^o = T_M^o = 0{\cdot}001\,M$

CuA²Dopamine system at 30°c

1· Acid

2· Dopamine

3· Cu + dpk + Dopamine (1:1:1)

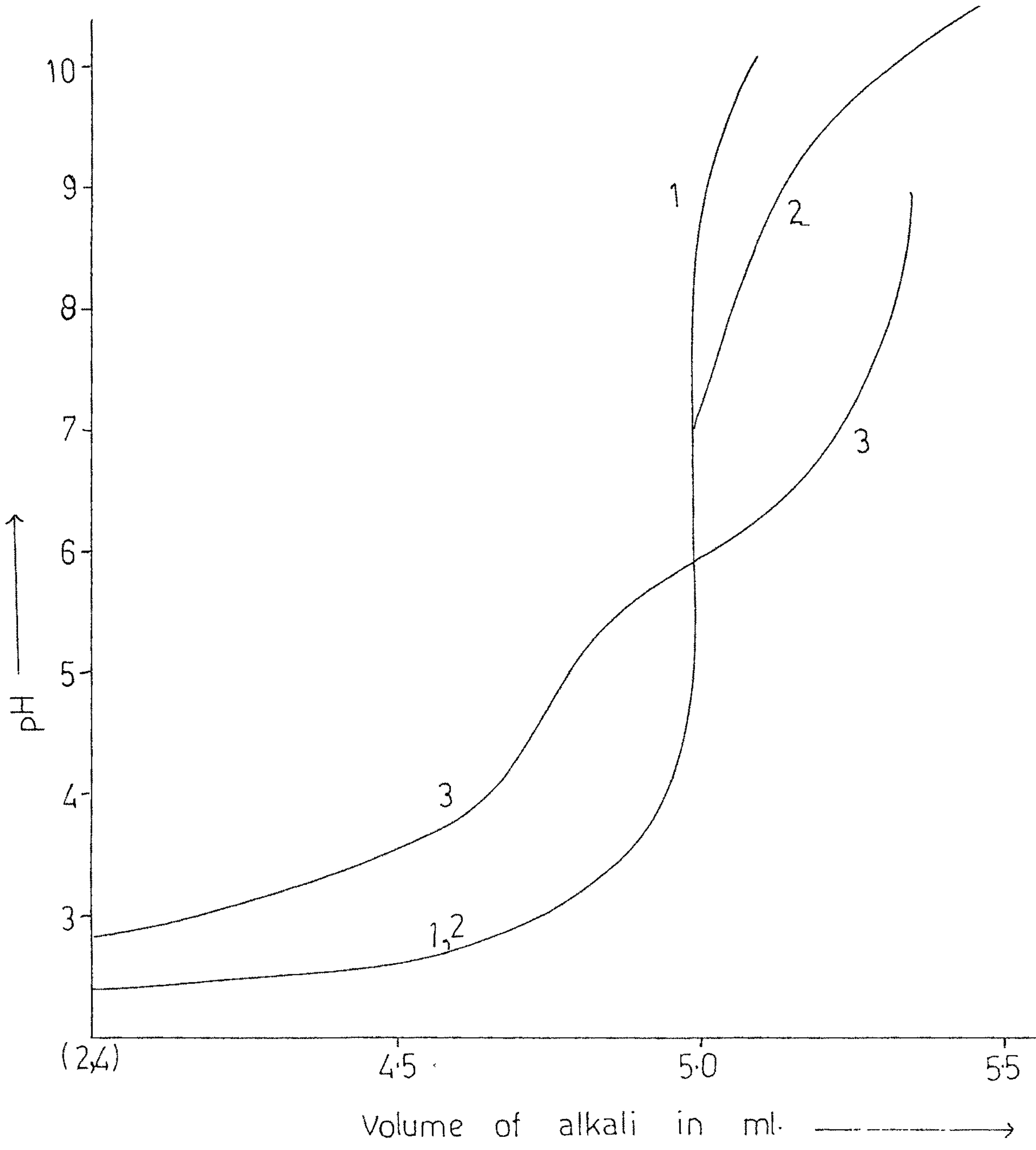


Fig III 38

$T_L^o = T_M^o = 0 \cdot 001$ M

CuA^3 Dopamine system at 30°c

1· Acid

2 Dopamine

3· Cu+dpa+Dopamine (1:1:1)

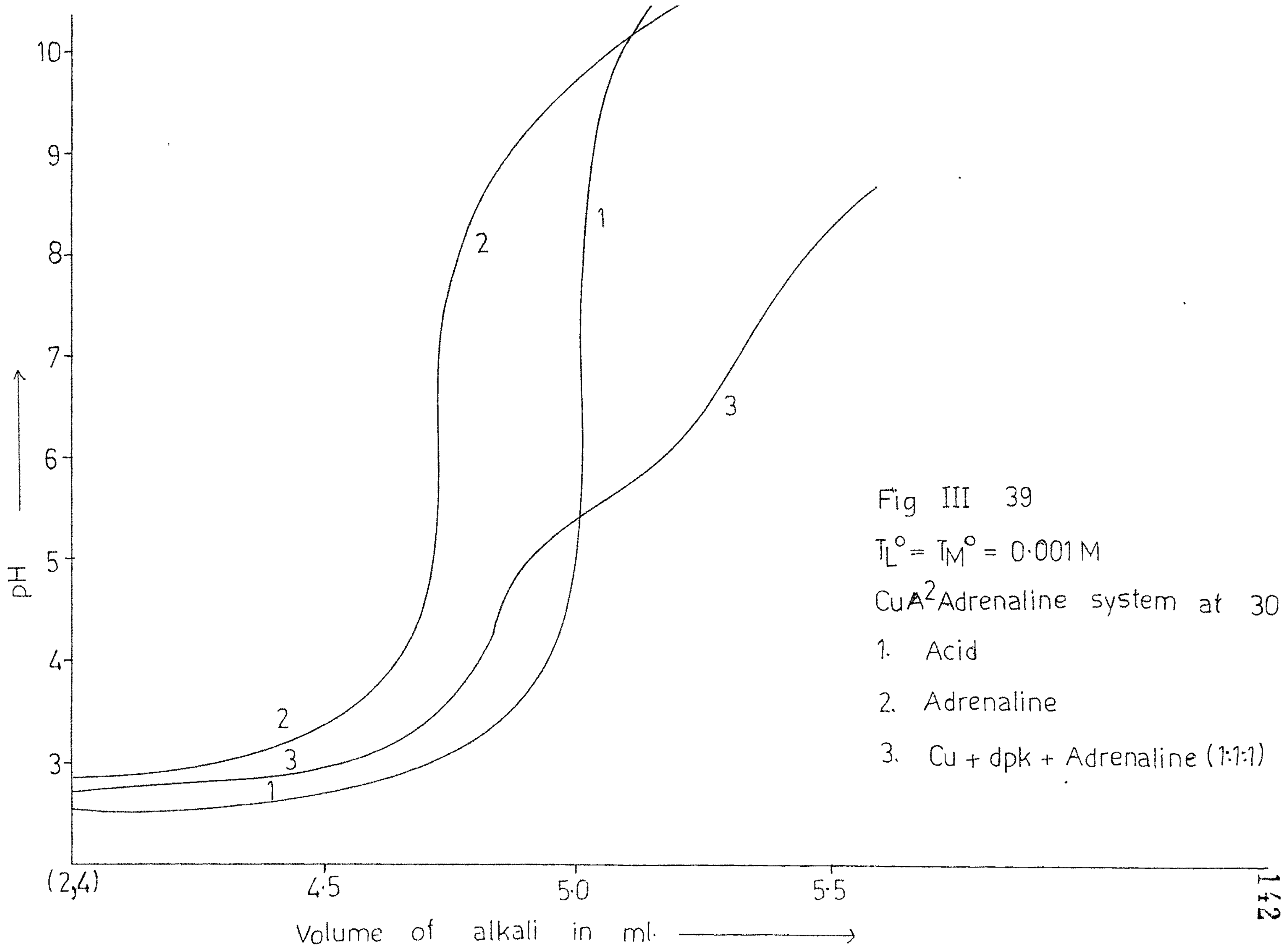


Fig III 39

$T_L^o = T_M^o = 0{\cdot}001$ M

CuA^2Adrenaline system at 30°c

1. Acid

2. Adrenaline

3. Cu + dpk + Adrenaline (1:1:1)

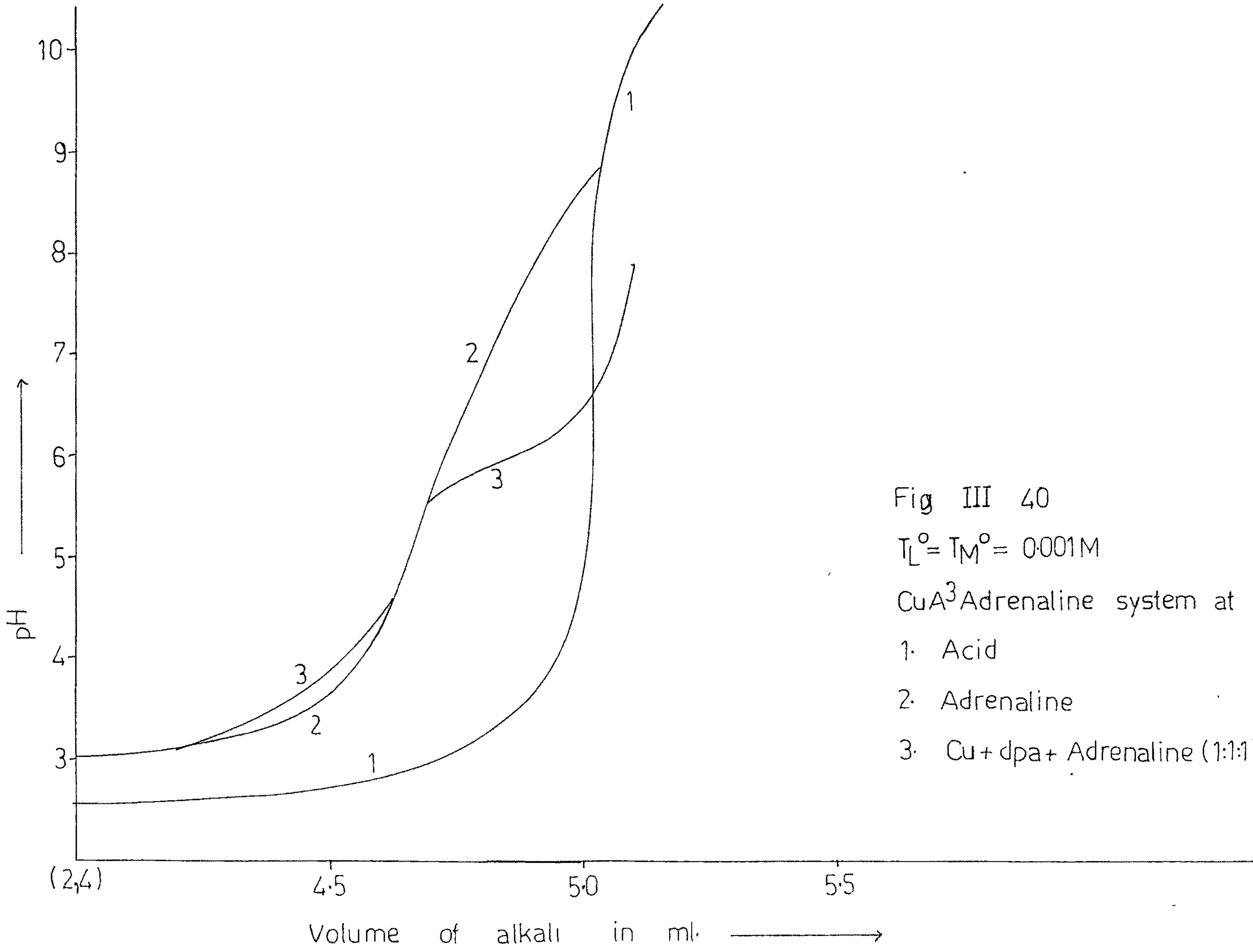


Fig III 40

$T_L^o = T_M^o = 0{\cdot}001M$

CuA^3 Adrenaline system at 30°c

1· Acid

2· Adrenaline

3· Cu + dpa + Adrenaline (1:1:1)

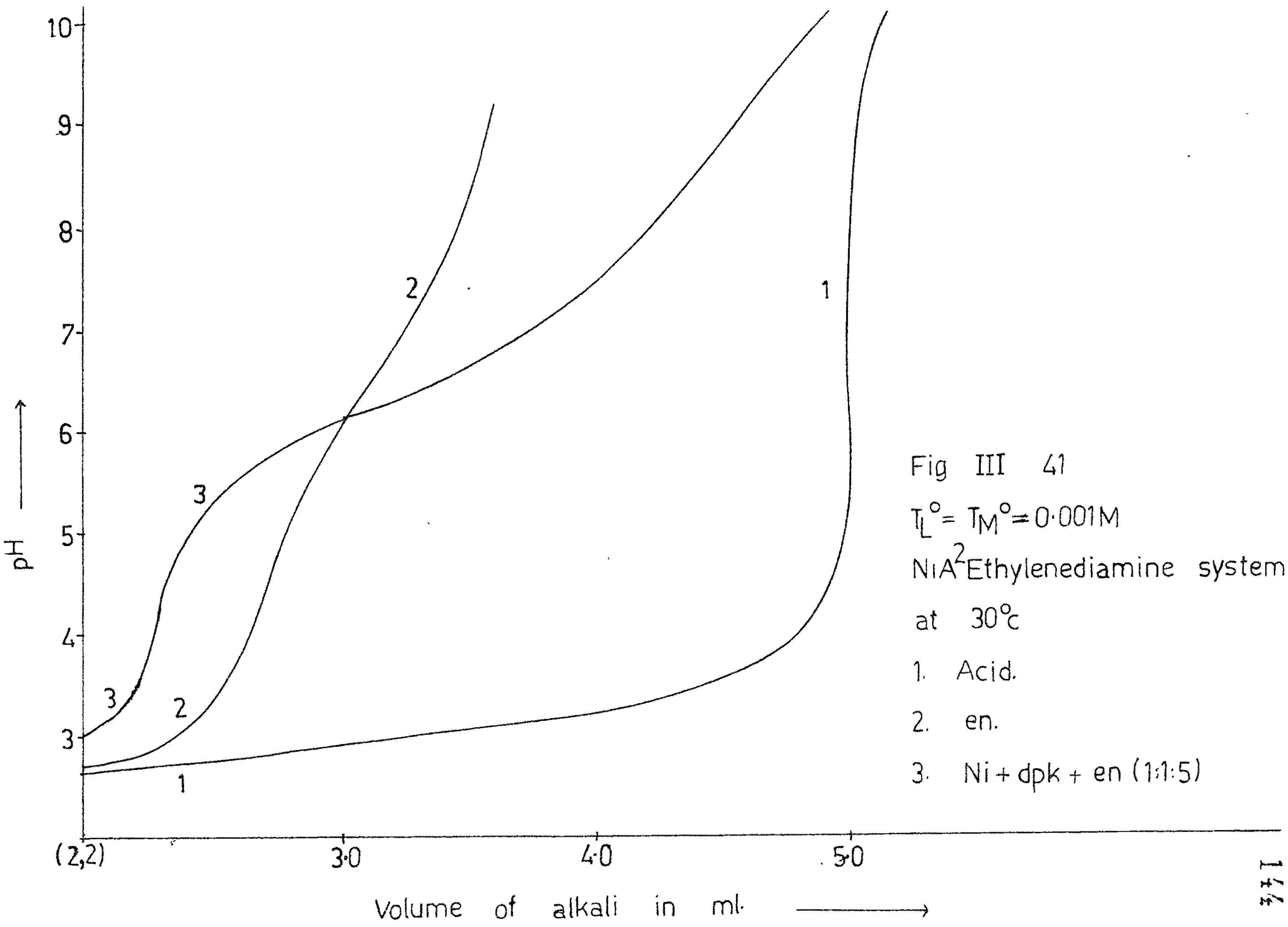


Fig III 41

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001M$

NiA^2 Ethylenediamine system

at 30°c

1. Acid.

2. en.

3. Ni + dpk + en (1:1:5)

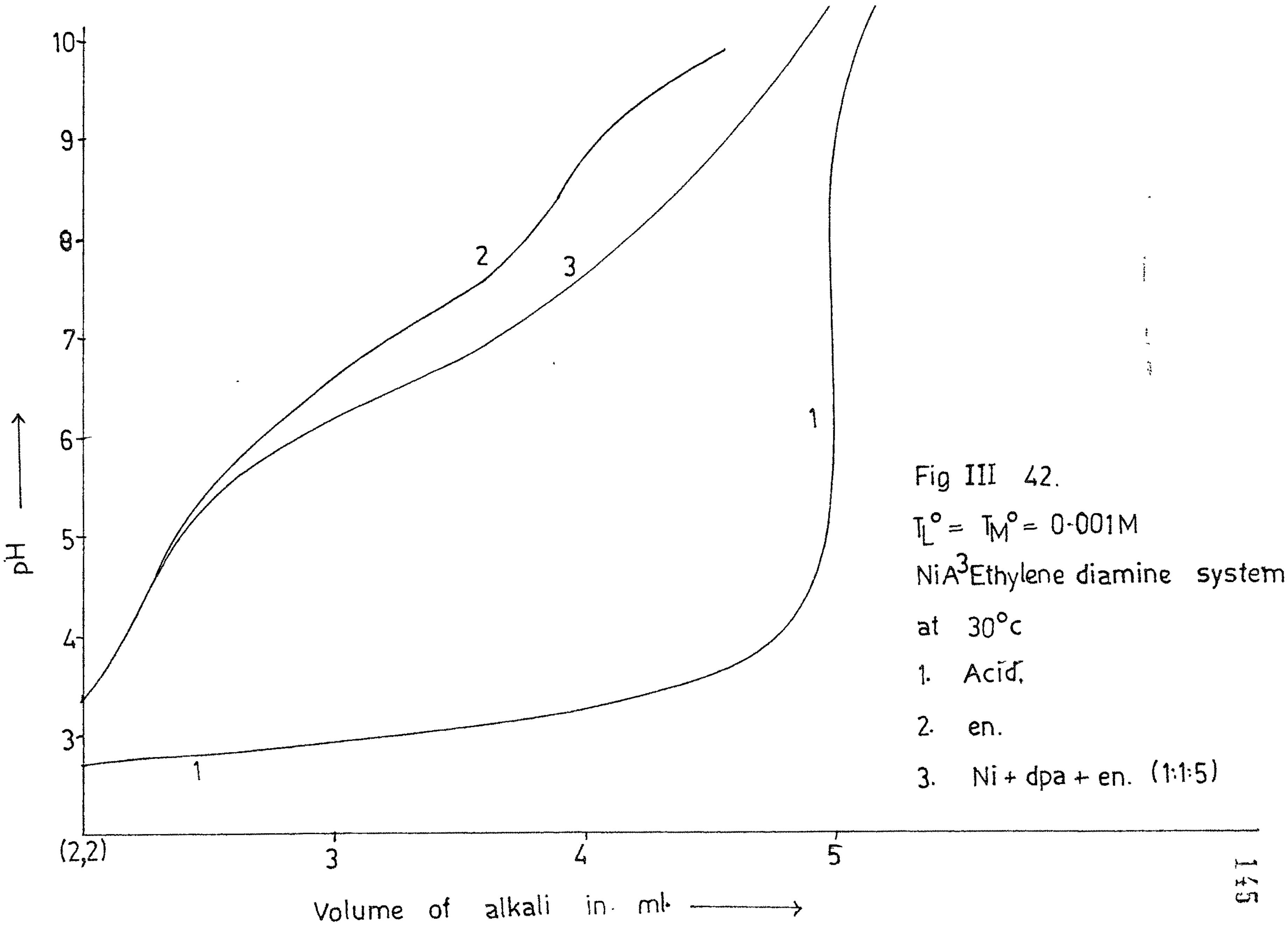


Fig III 42.

$T_L^\circ = T_M^\circ = 0{\cdot}001M$

NiA^{3}Ethylene diamine system

at 30°c

1. Acid.

2. en.

3. Ni + dpa + en. (1:1:5)

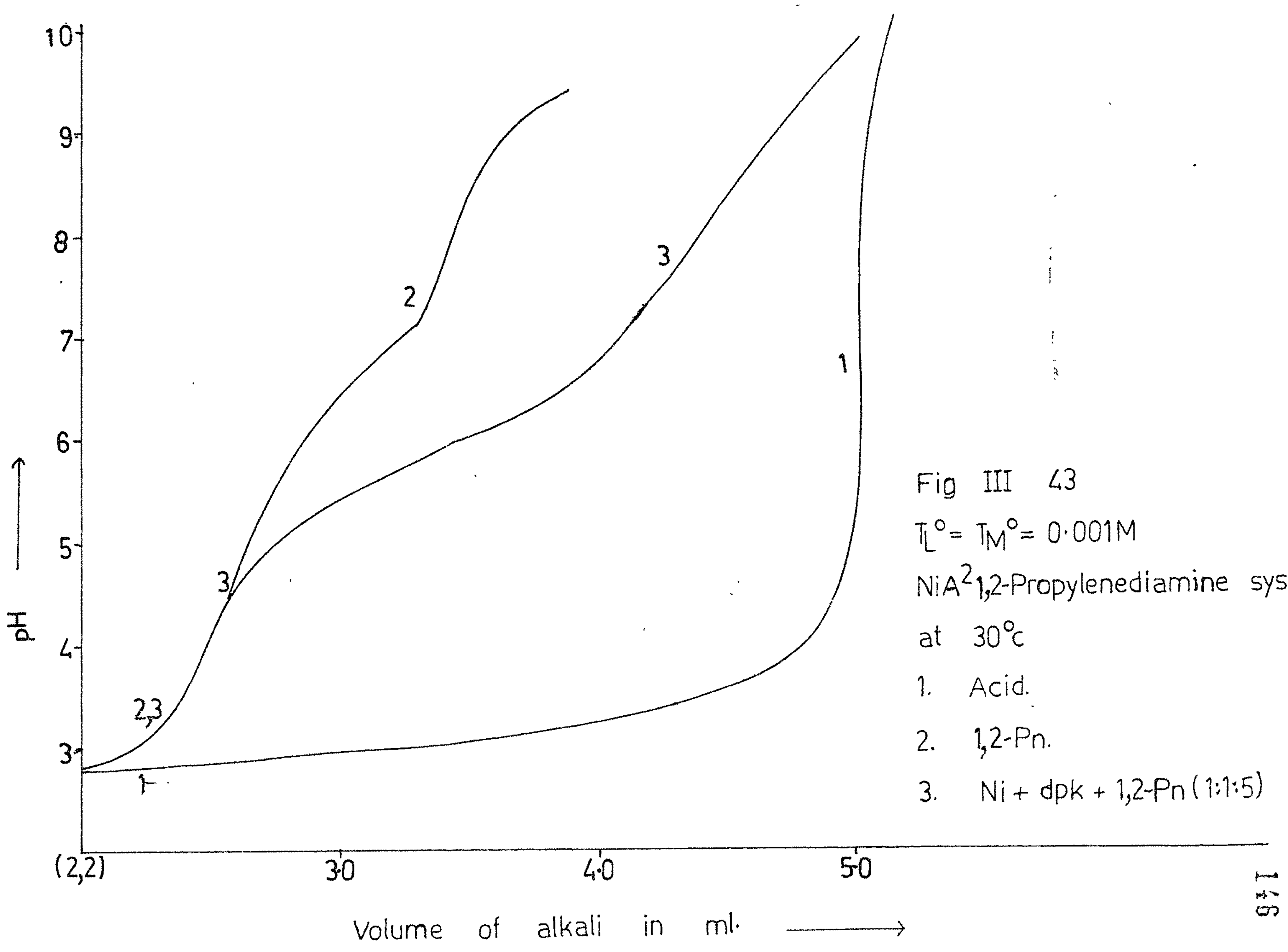


Fig III 43

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001M$

NiA^2 1,2-Propylenediamine system

at 30°c

1. Acid.
2. 1,2-Pn.
3. Ni + dpk + 1,2-Pn (1:1:5)

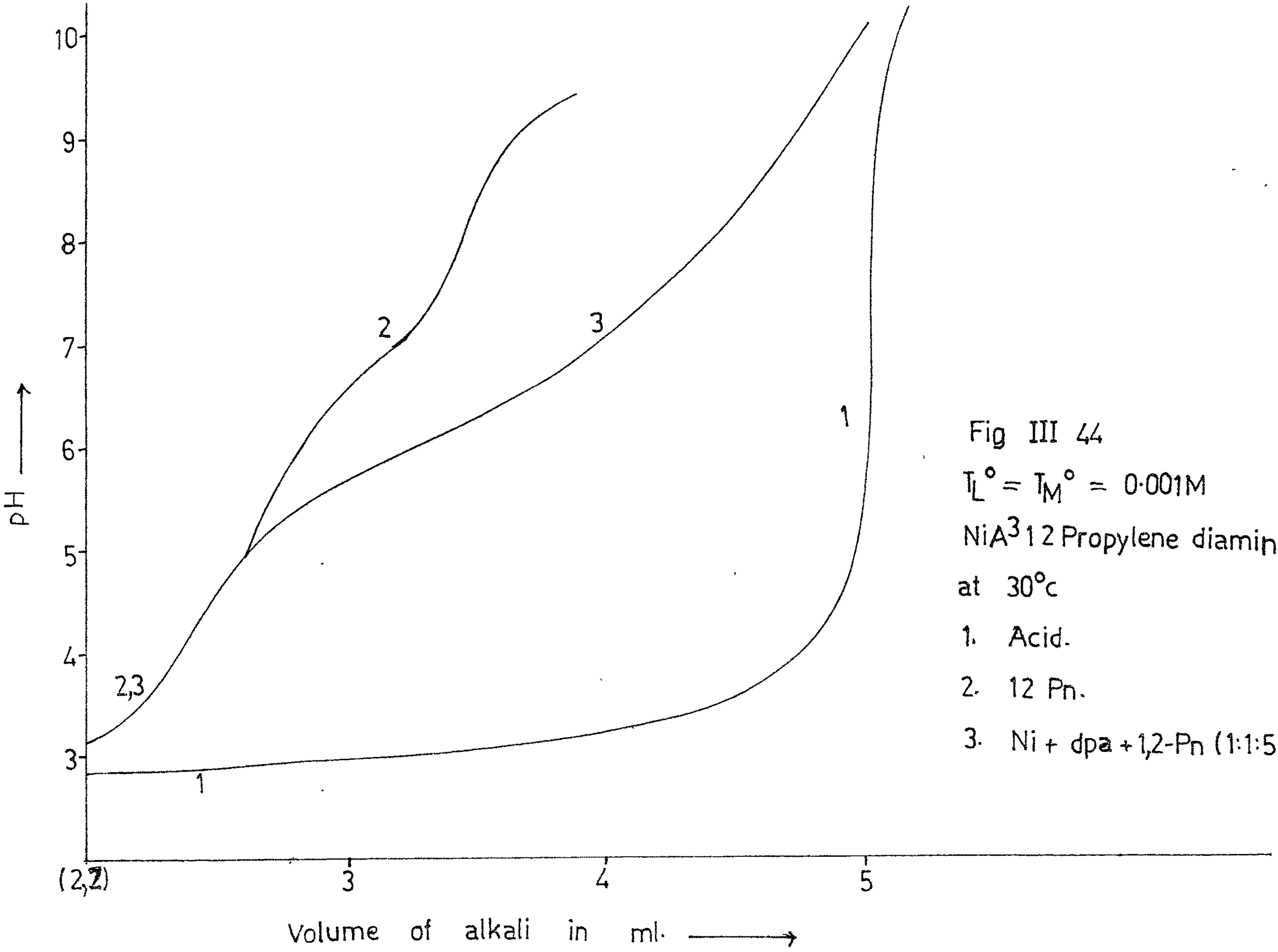


Fig III 44

$T_L^\circ = T_M^\circ = 0{\cdot}001M$

NiA^3 1 2 Propylene diamine system

at 30°c

1. Acid.
2. 12 Pn.
3. Ni + dpa + 1,2-Pn (1:1:5)

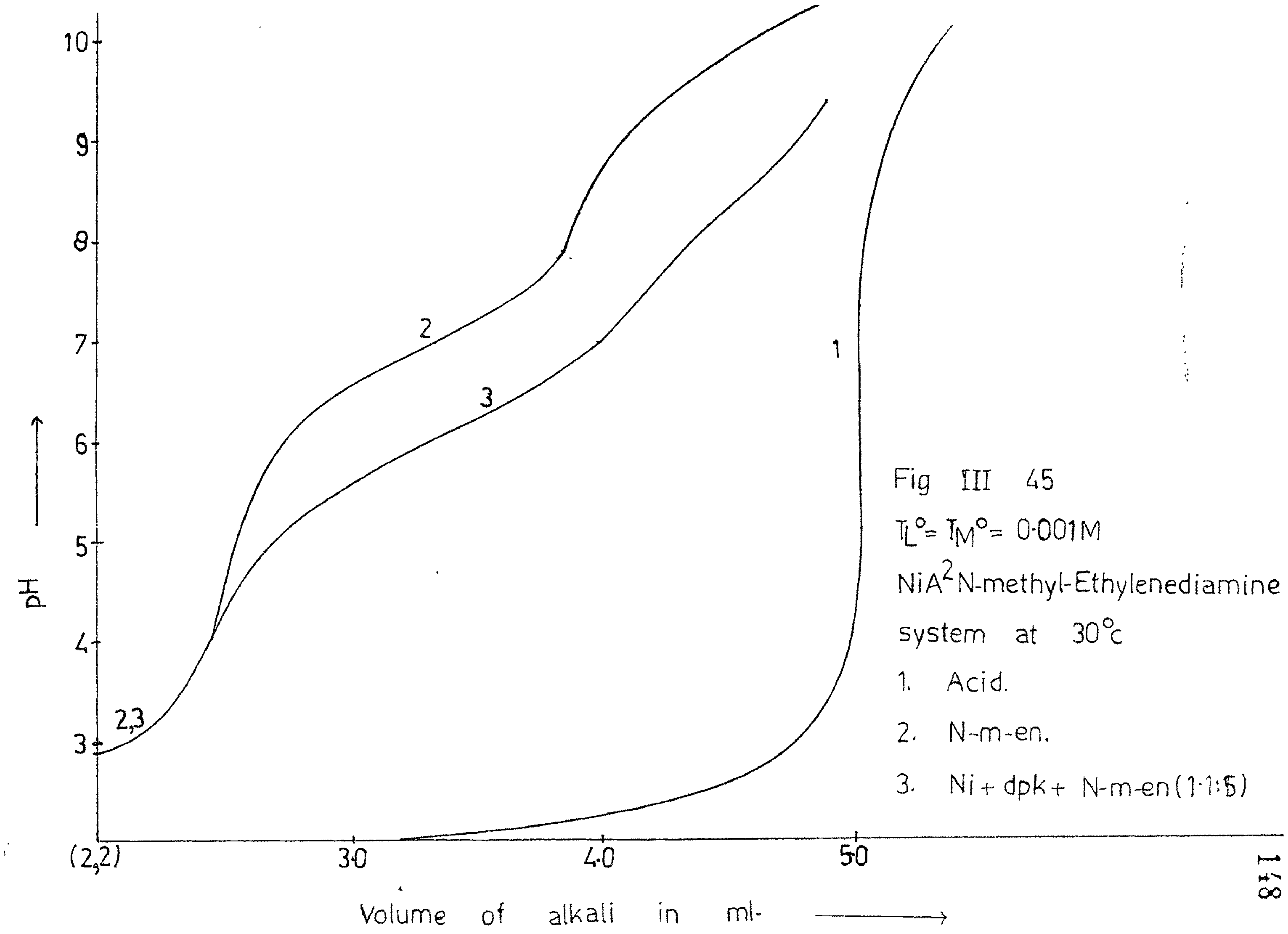


Fig III 45

$T_L^\circ = T_M^\circ = 0{\cdot}001M$

NiA^2 N-methyl-Ethylenediamine system at 30°c

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

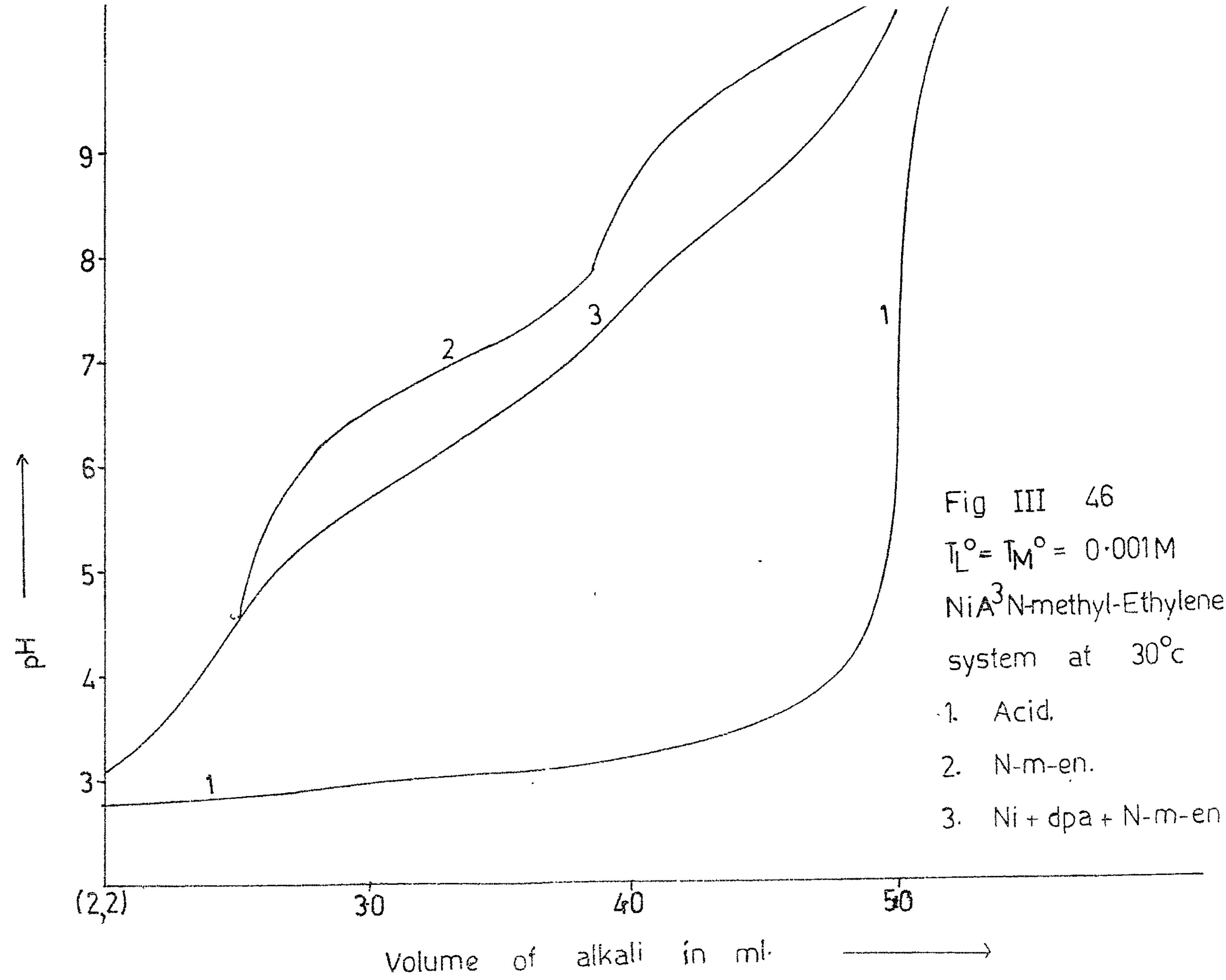


Fig III 46

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001M$

NiA^3N-methyl-Ethylene-diamine system at 30°c

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

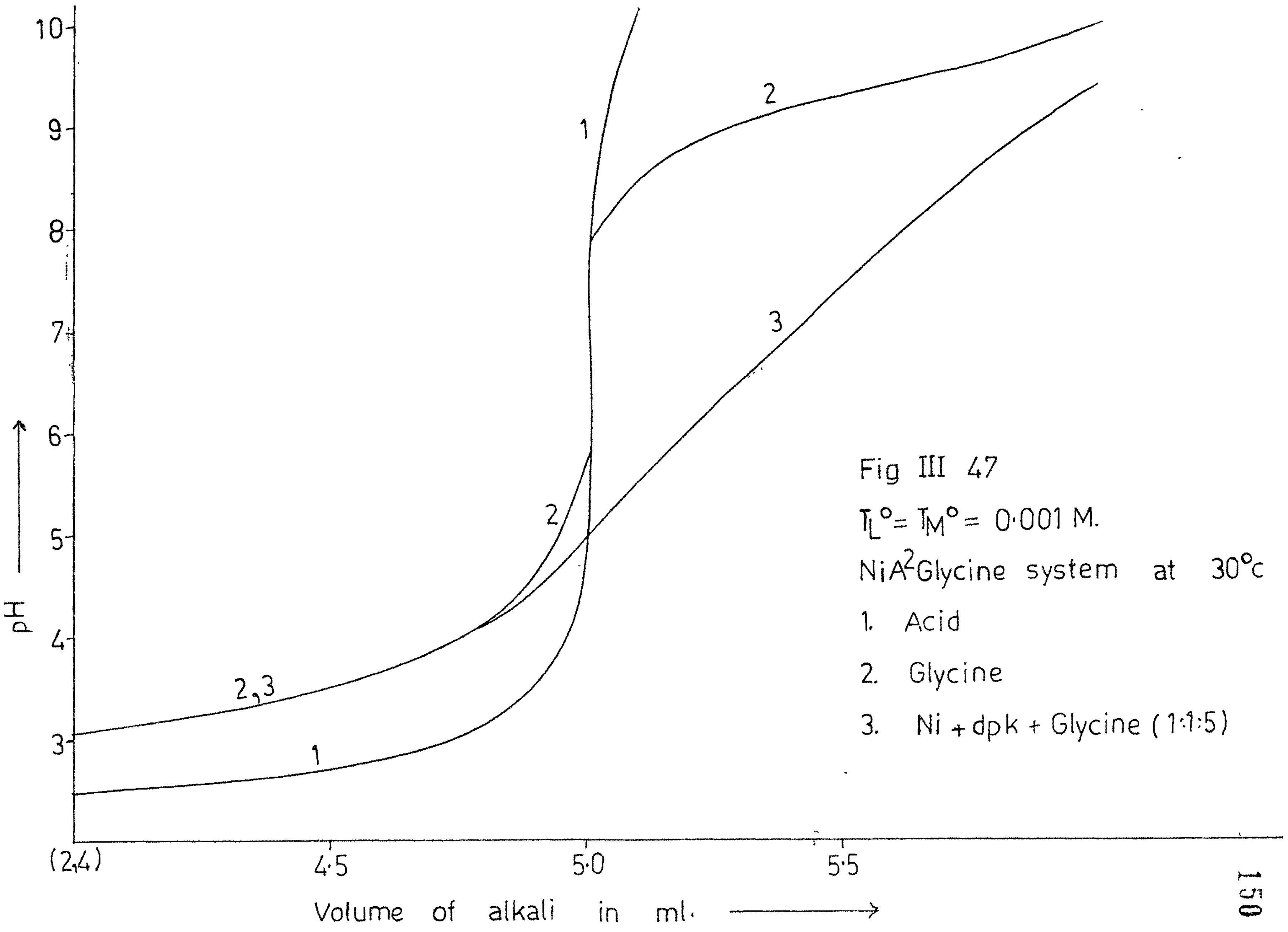


Fig III 47

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001$ M.

NiA^2Glycine system at 30°c

1. Acid
2. Glycine
3. Ni + dpk + Glycine (1:1:5)

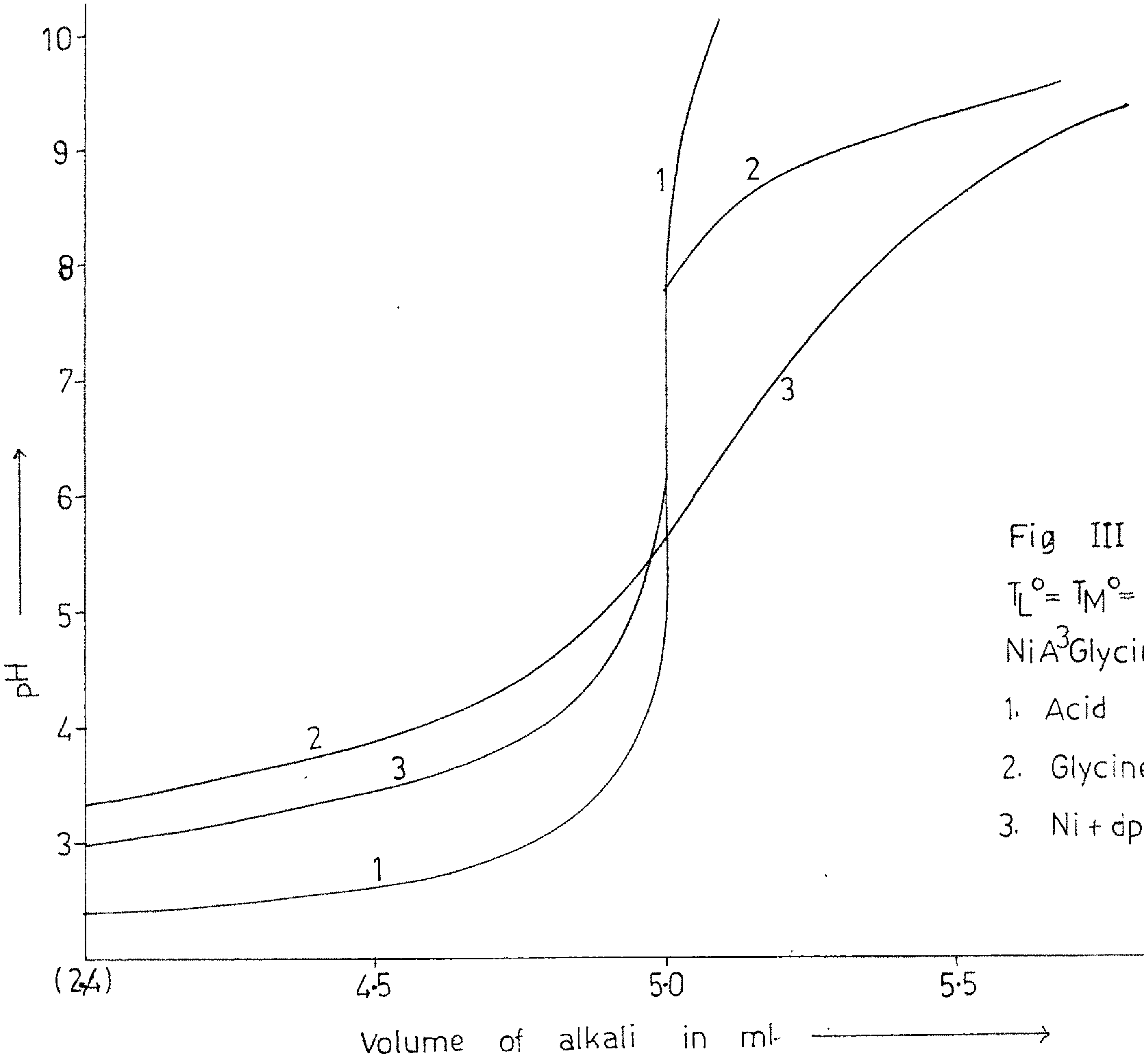


Fig III 48

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001$ M

NiA^3Glycine system at 30°c

1. Acid

2. Glycine

3. Ni + dpa + Glycine (1:1:5)

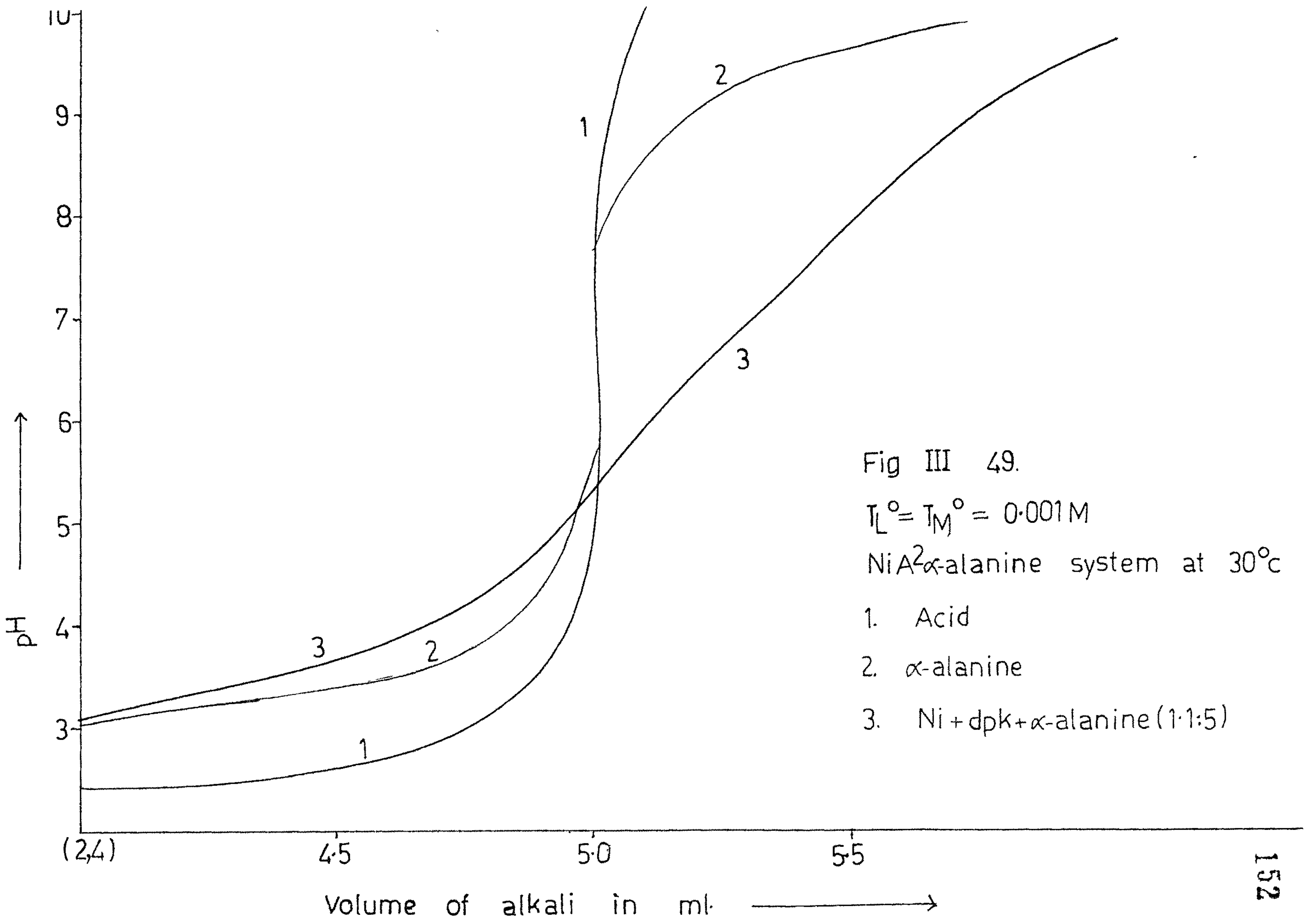


Fig III 49.

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001\,M$

NiA^2 α-alanine system at 30°c

1. Acid
2. α-alanine
3. Ni + dpk + α-alanine (1·1:5)

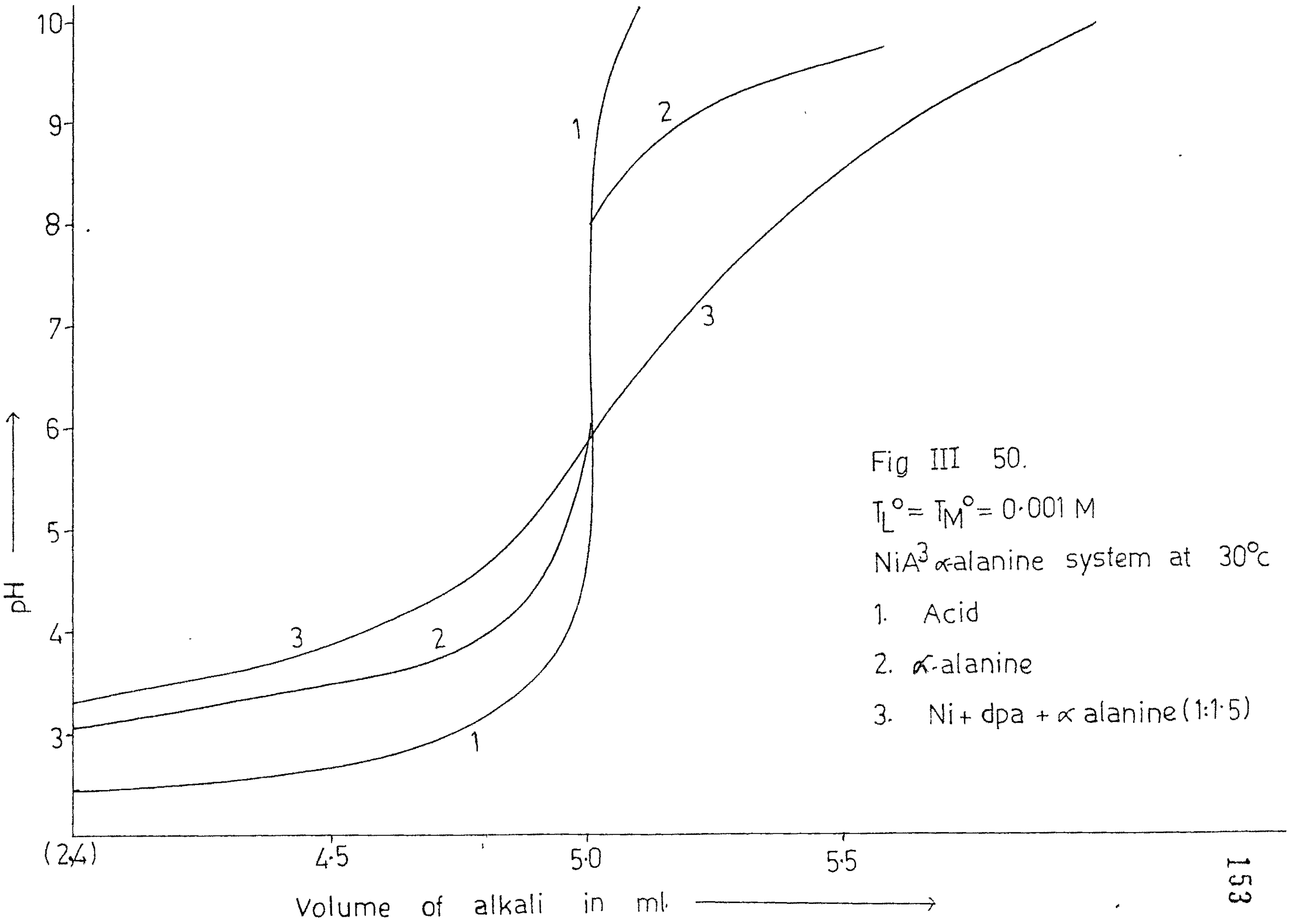


Fig III 50.

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001$ M

NiA^3 α-alanine system at 30°c

1. Acid

2. α-alanine

3. Ni + dpa + α alanine (1:1·5)

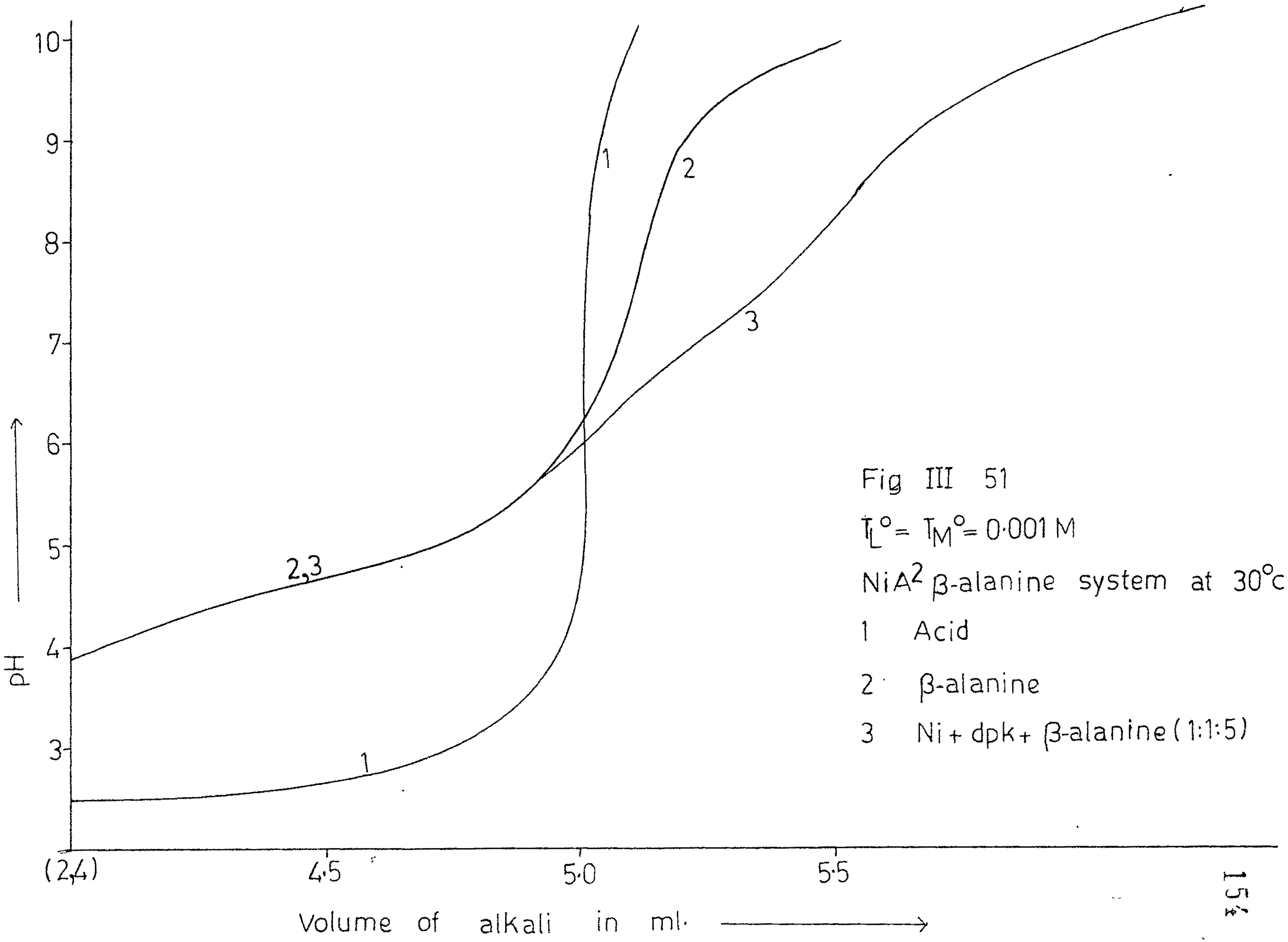


Fig III 51

$T_L^o = T_M^o = 0{\cdot}001\,M$

NiA^2 β-alanine system at 30°c

1 Acid

2 β-alanine

3 Ni + dpk + β-alanine (1:1:5)

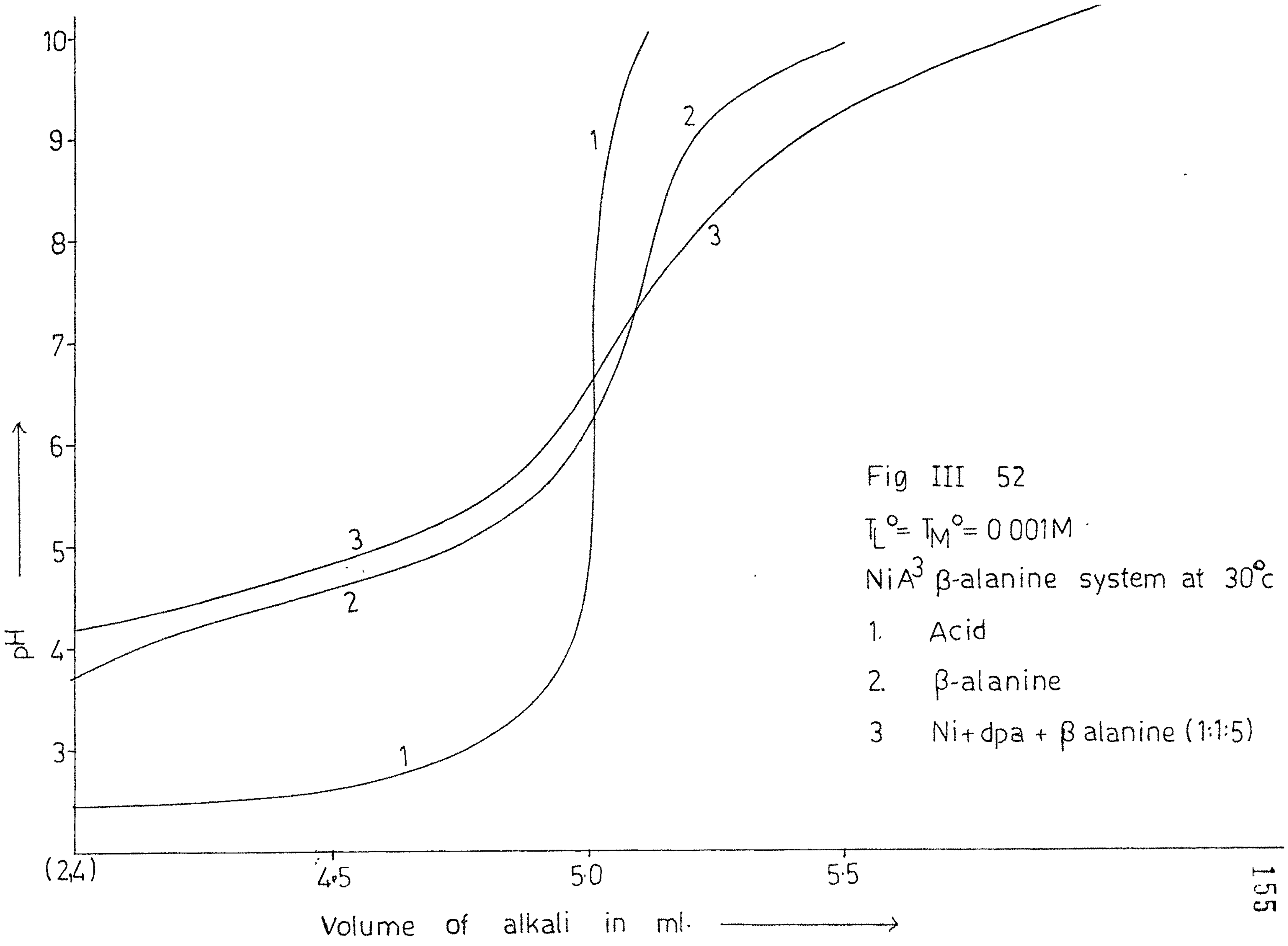


Fig III 52

$T_L^o = T_M^o = 0\ 001M$

NiA^3 β-alanine system at 30°c

1. Acid

2. β-alanine

3 Ni + dpa + β alanine (1:1:5)

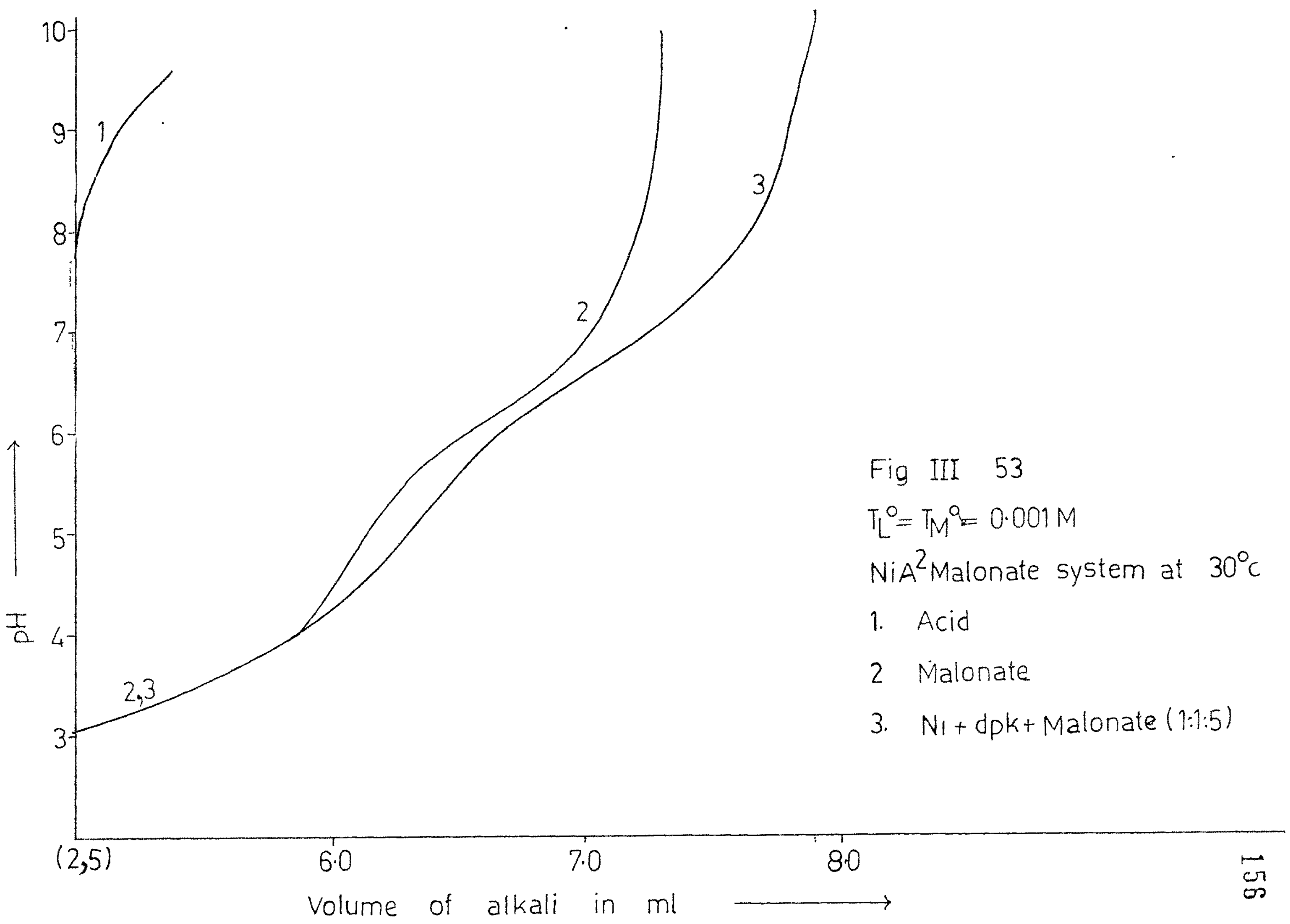


Fig III 53

$T_L^o = T_M^o = 0{\cdot}001\,M$

NiA^{2}Malonate system at 30°c

1. Acid

2 Malonate

3. Ni + dpk + Malonate (1:1:5)

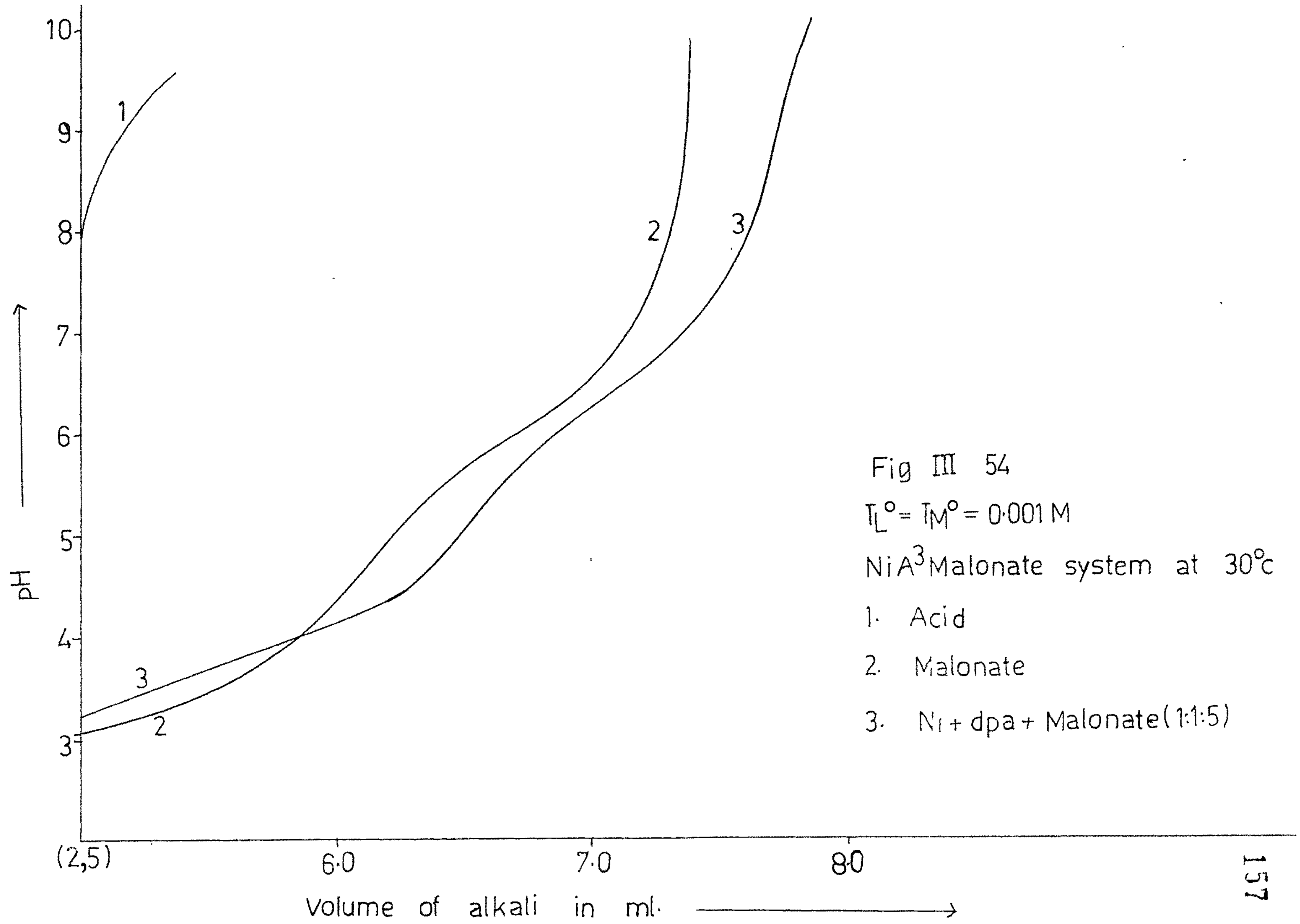


Fig III 54

$T_L^o = T_M^o = 0{\cdot}001\,M$

Ni A^3 Malonate system at 30°c

1· Acid

2. Malonate

3. Ni + dpa + Malonate (1:1:5)

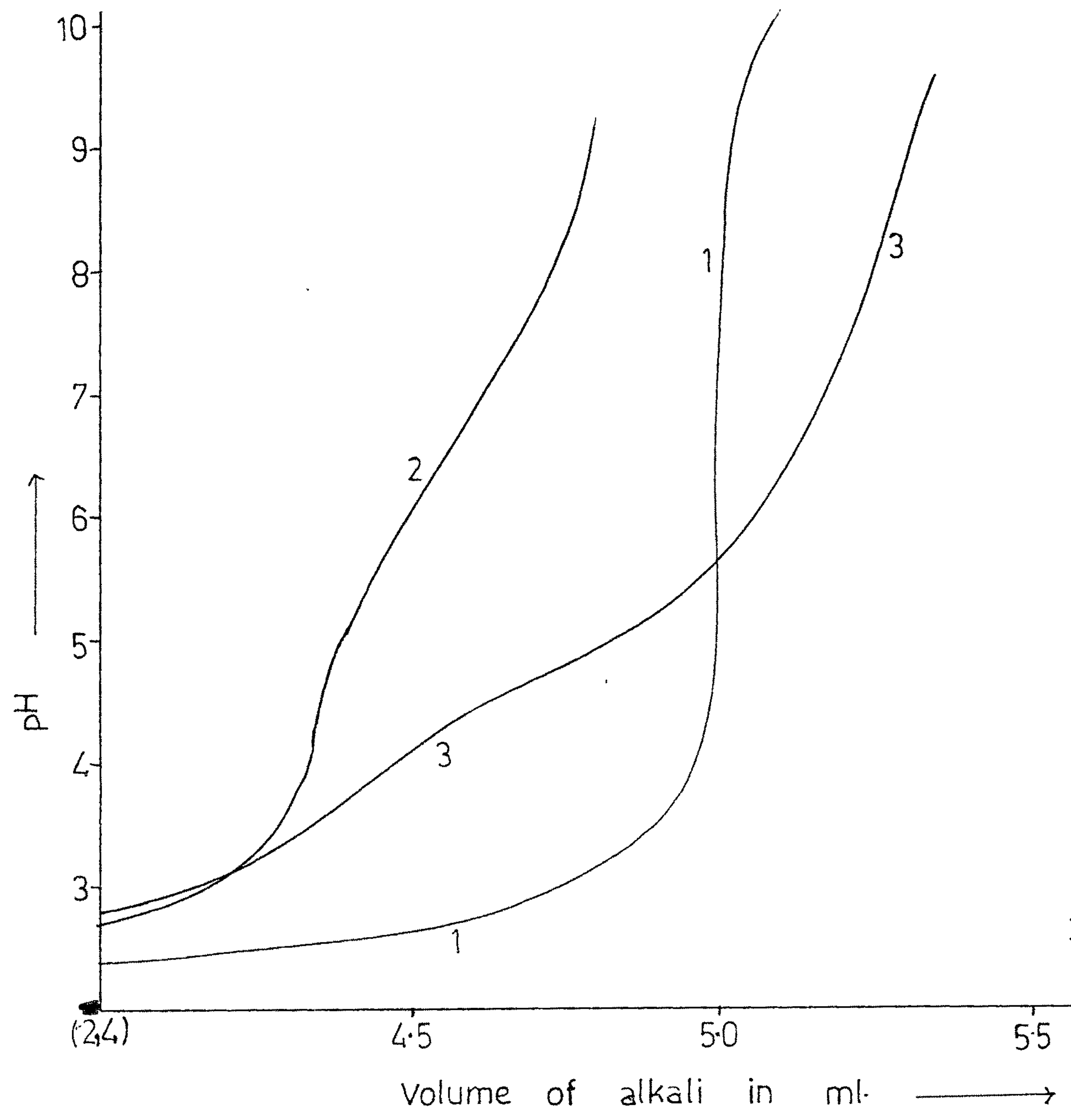


Fig III 55

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

CuA^2 Ethylene-diamine system at 30°C

aqueous medium

1. Acid.
2. Ethylenediamine.
3. Cu + dpk + Ethylenediamine (1:1:1)

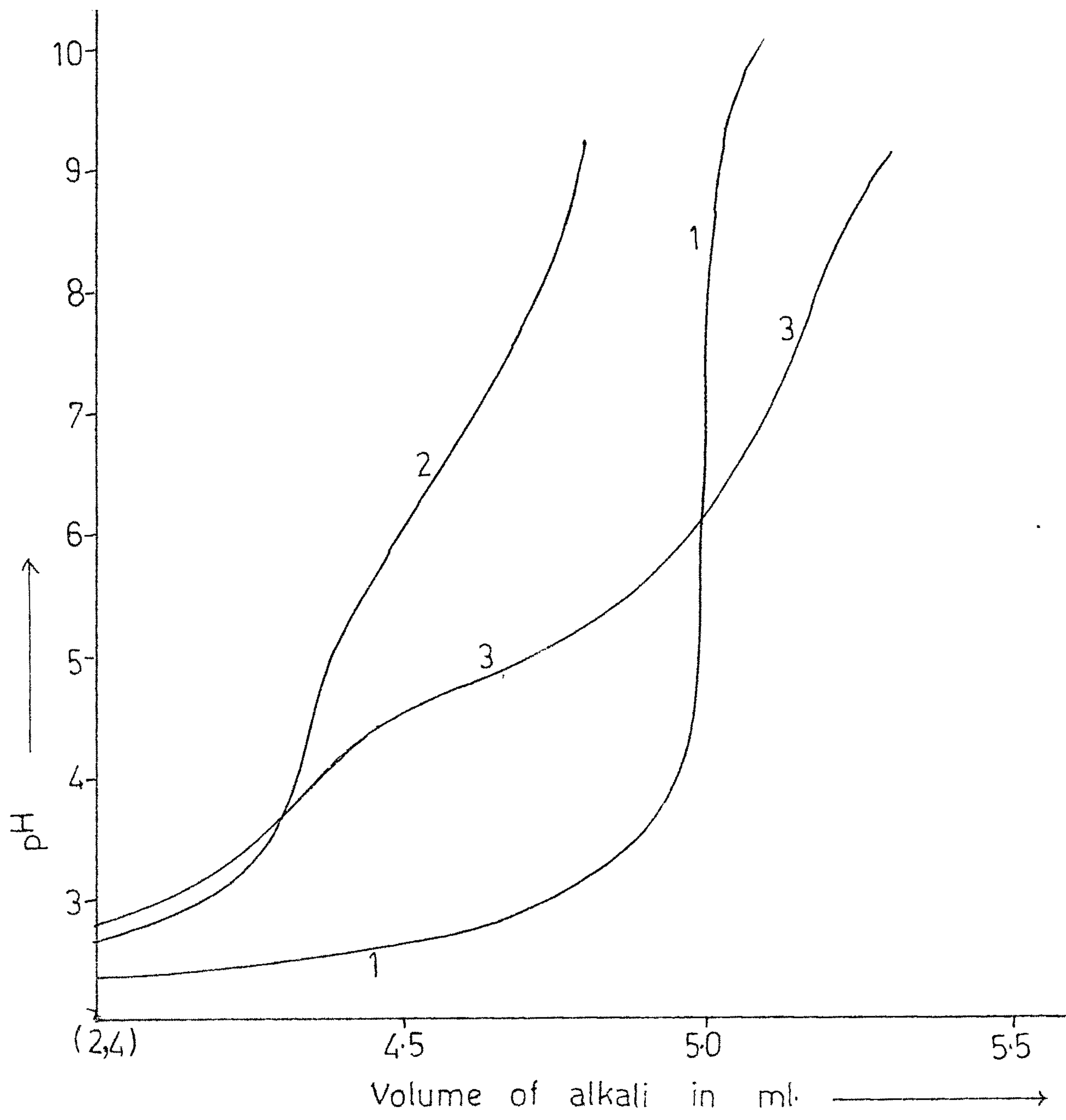


Fig III 56.

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001M$

CuA^2 Ethylenediamine system at 3C

25% dioxan-water medium

1. Acid.
2. Ethylenediamine.
3. Cu + dpk + Ethylenediamine (1:1:1)

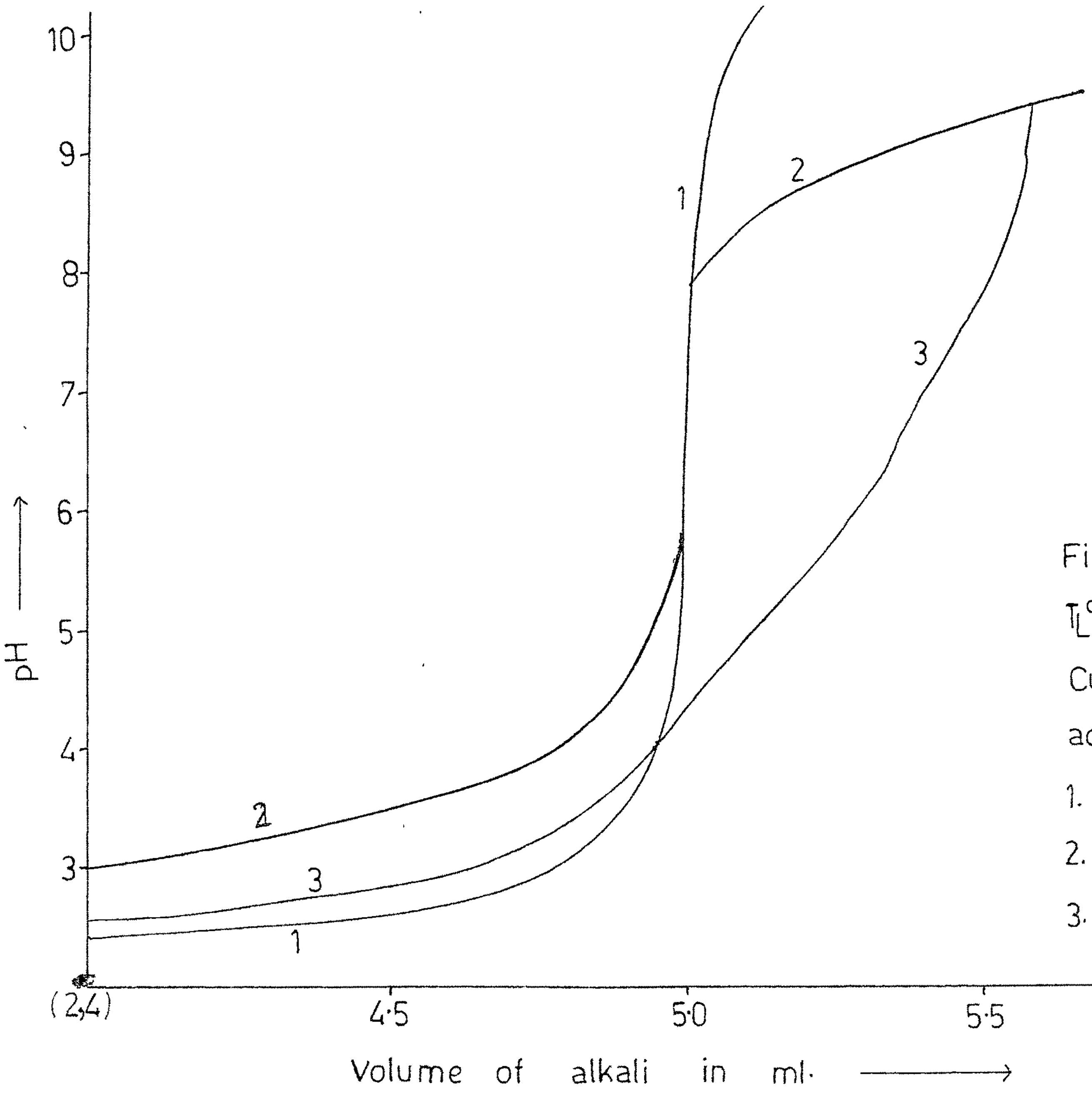


Fig III 57

$T_L^o = T_M^o = 0{\cdot}001\,M$

CuA^2Glycine system at 30°c aqueous medium.

1. Acid.
2. Glycine.
3. Cu + dpk + Glycine (1:1:1)

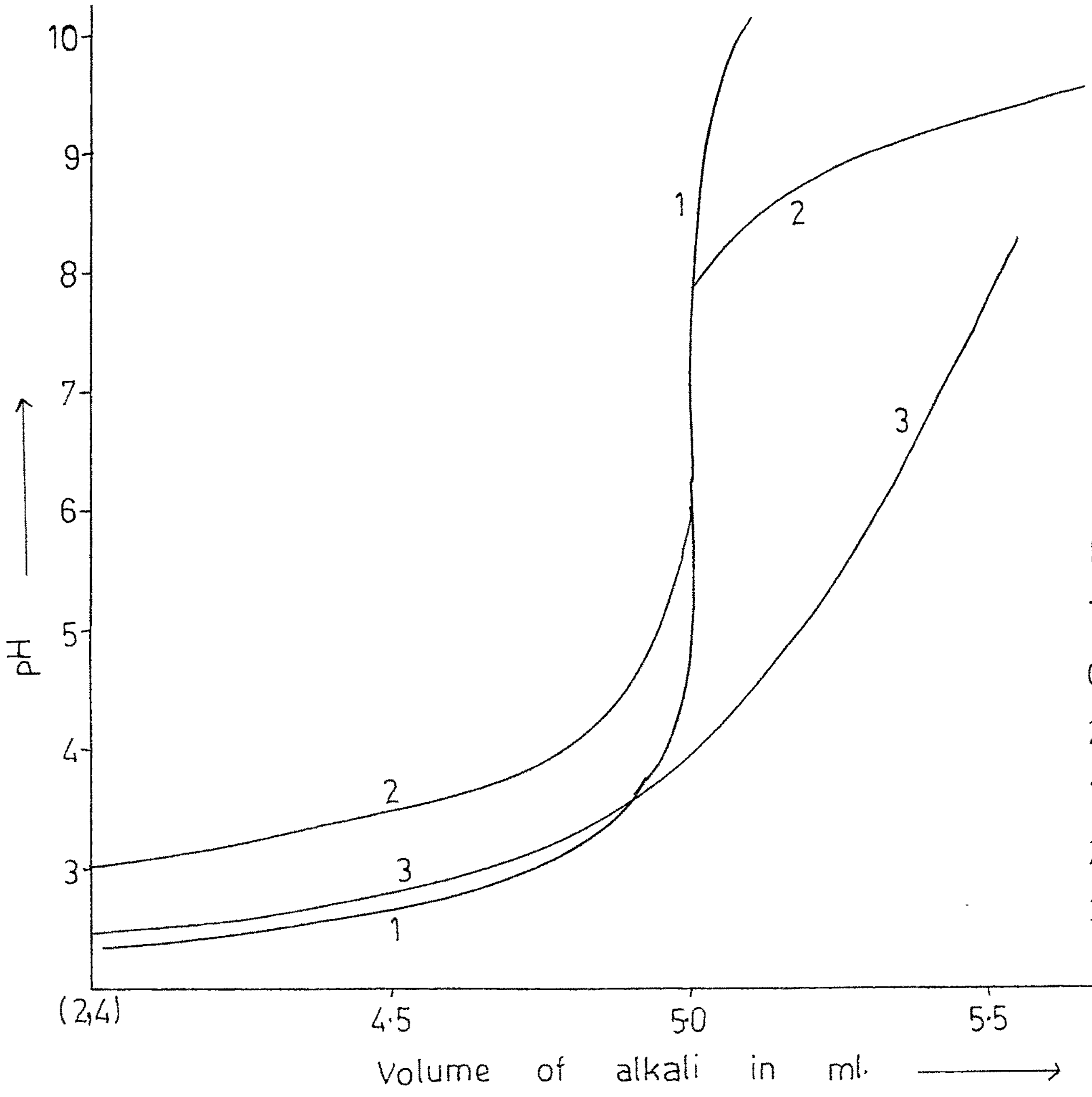


Fig III 58

$T_L^o = T_M^o = 0{\cdot}001M$

CuA^2Glycine system at 30°c

25% dioxan-water medium.

1. Acid.
2. Glycine.
3. Cu + dpk + Glycine. (1:1:1)

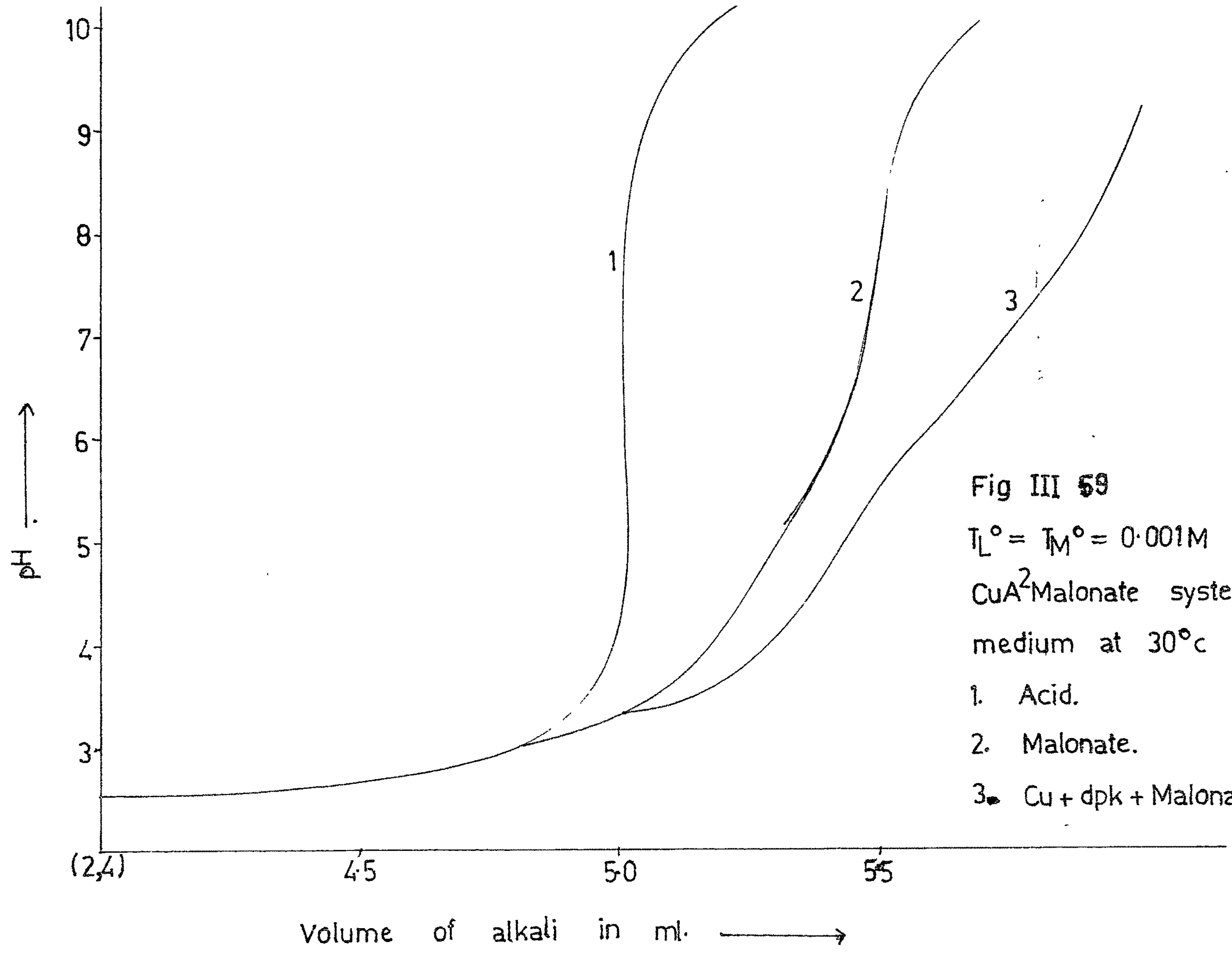


Fig III 59

$T_L^\circ = T_M^\circ = 0{\cdot}001M$

CuA^{2}Malonate system in aqueous medium at 30°c

1. Acid.
2. Malonate.
3. Cu + dpk + Malonate (1:1:1)

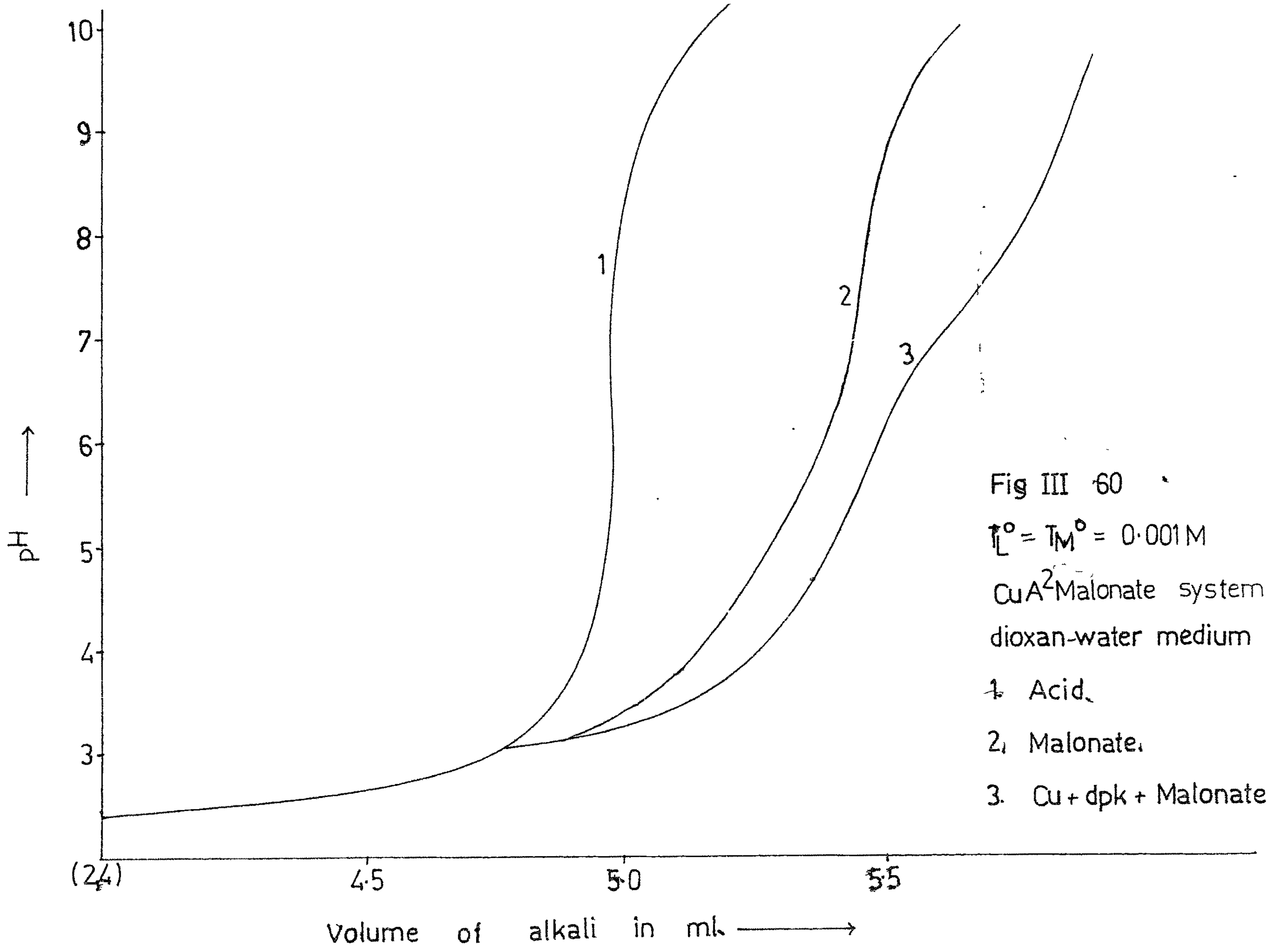


Fig III 60

$T_L^o = T_M^o = 0.001\,M$

CuA^2 Malonate system in 25% dioxan-water medium at 30°c

1. Acid.
2. Malonate.
3. Cu + dpk + Malonate. (1:1:1)

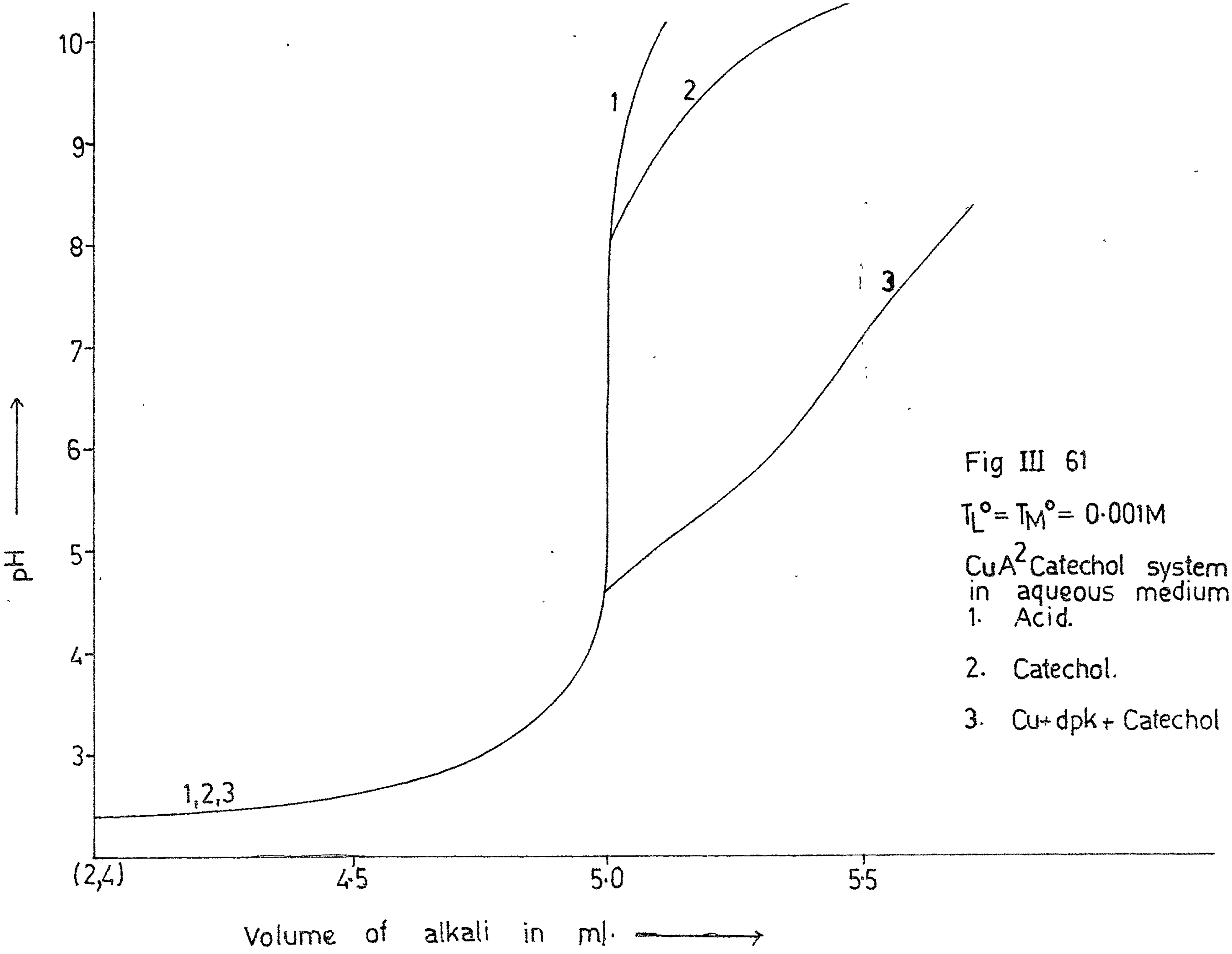


Fig III 61

$T_L^\circ = T_M^\circ = 0{\cdot}001M$

CuA^2Catechol system at 30°c in aqueous medium.

1. Acid.

2. Catechol.

3. Cu+dpk+Catechol (1:1:1)

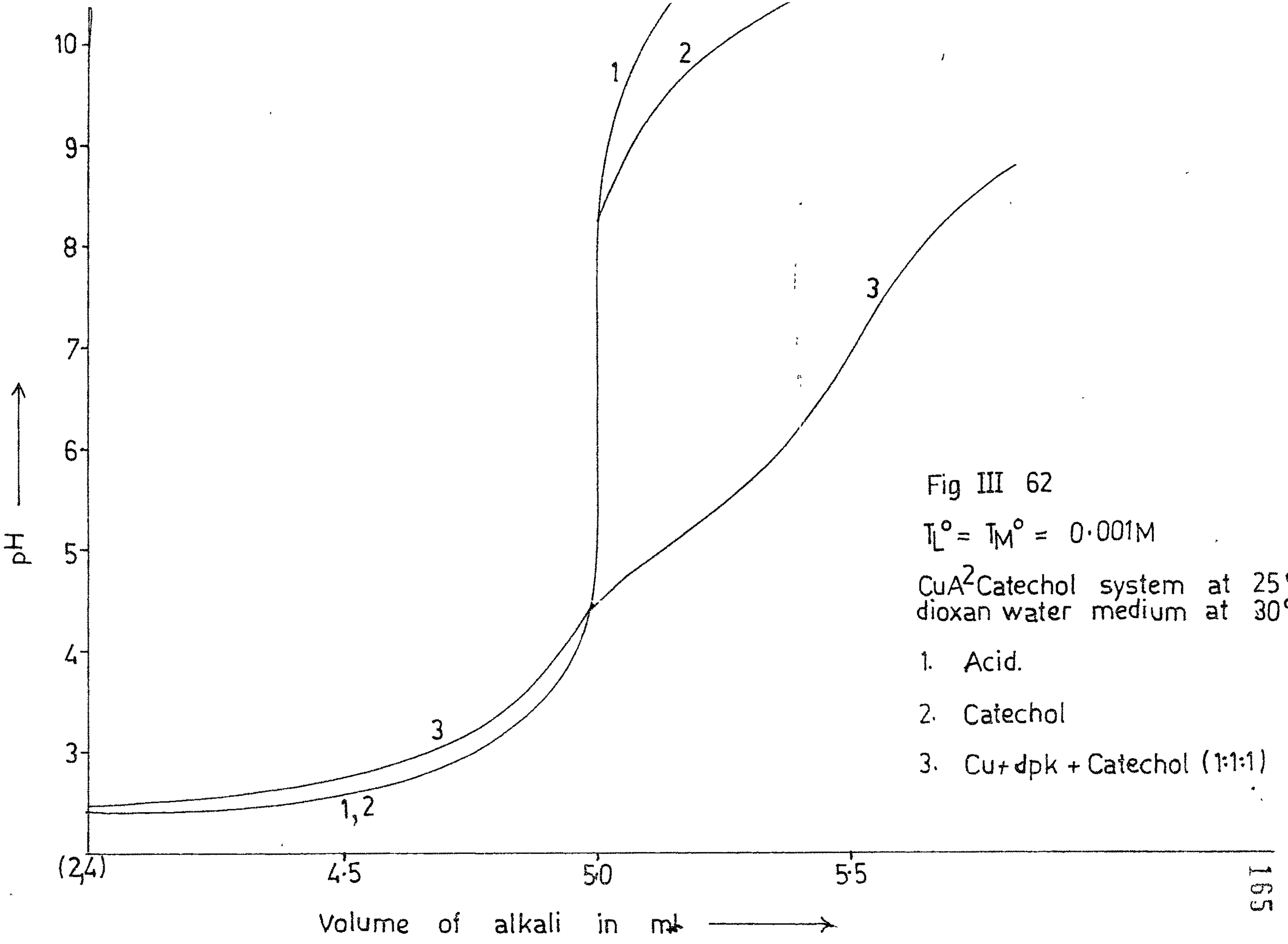


Fig III 62

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001M$

CuA^2Catechol system at 25% dioxan water medium at 30° c

1. Acid.
2. Catechol
3. Cu+dpk + Catechol (1:1:1)

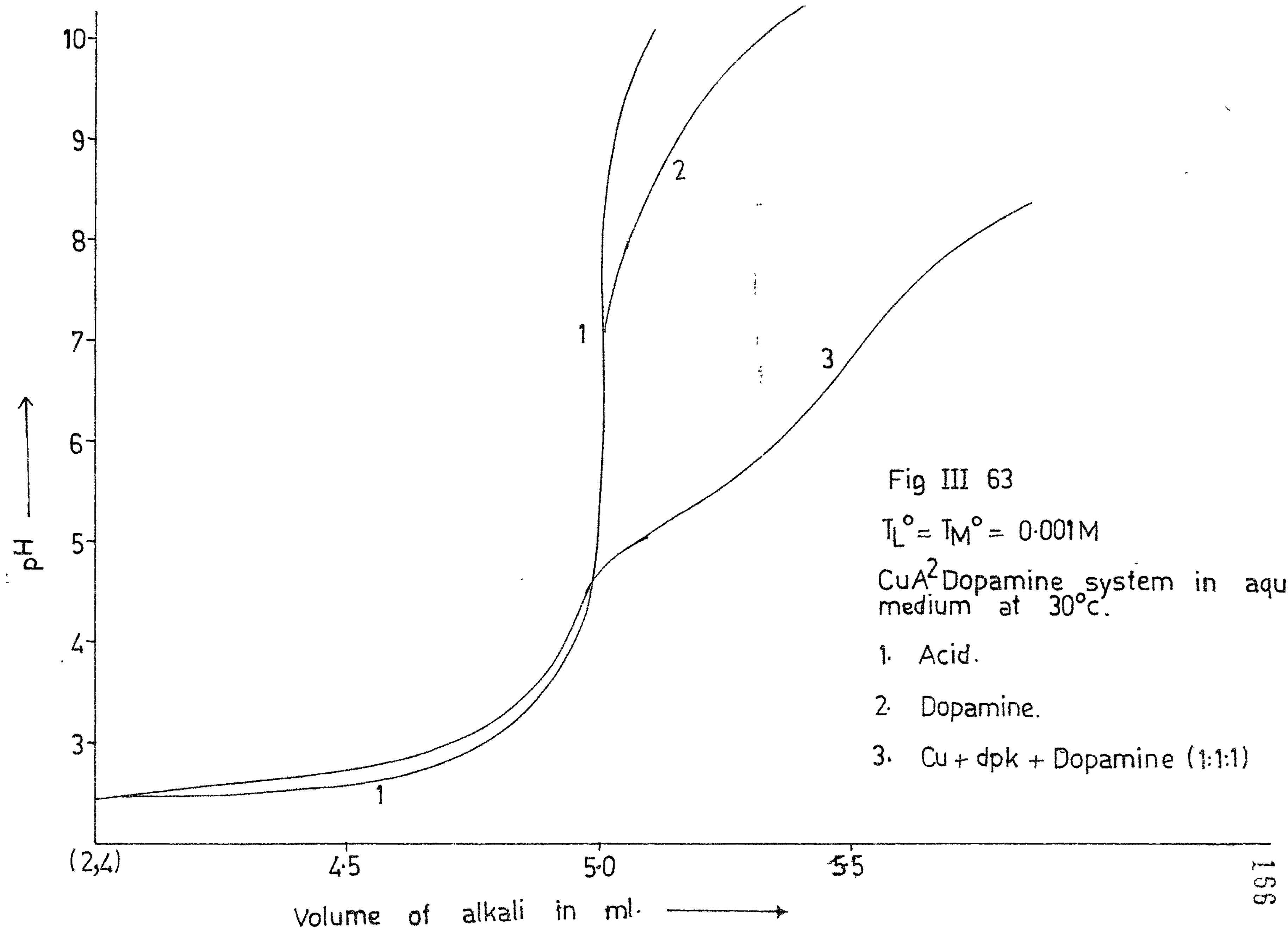


Fig III 63

$T_L^\circ = T_M^\circ = 0{\cdot}001\,M$

CuA^{2}Dopamine system in aqueous medium at 30°c.

1. Acid.

2. Dopamine.

3. Cu + dpk + Dopamine (1:1:1)

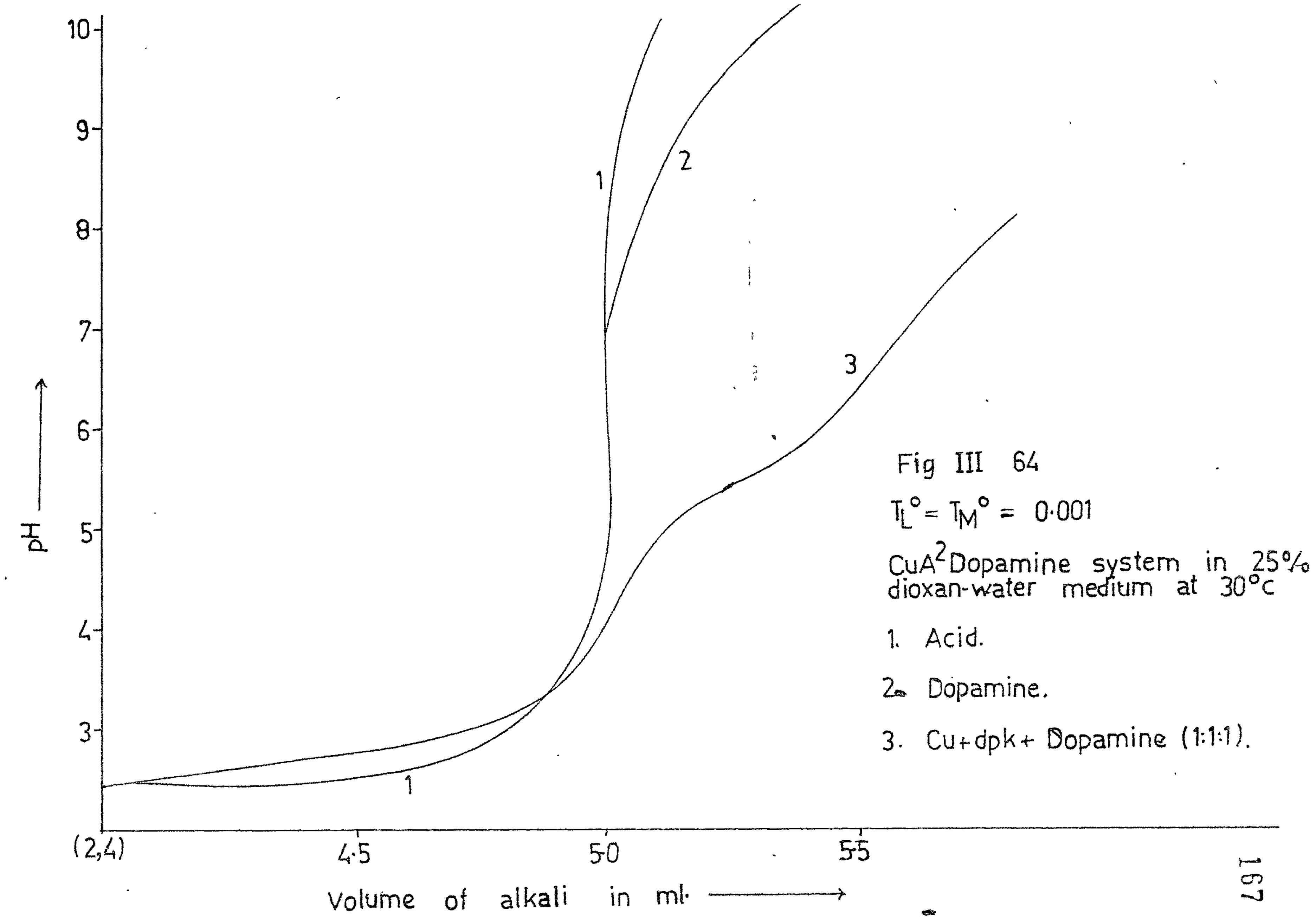


Fig III 64

$T_L^\circ = T_M^\circ = 0{\cdot}001$

CuA^{2}Dopamine system in 25% dioxan-water medium at 30°c

1. Acid.

2. Dopamine.

3. Cu+dpk+ Dopamine (1:1:1).

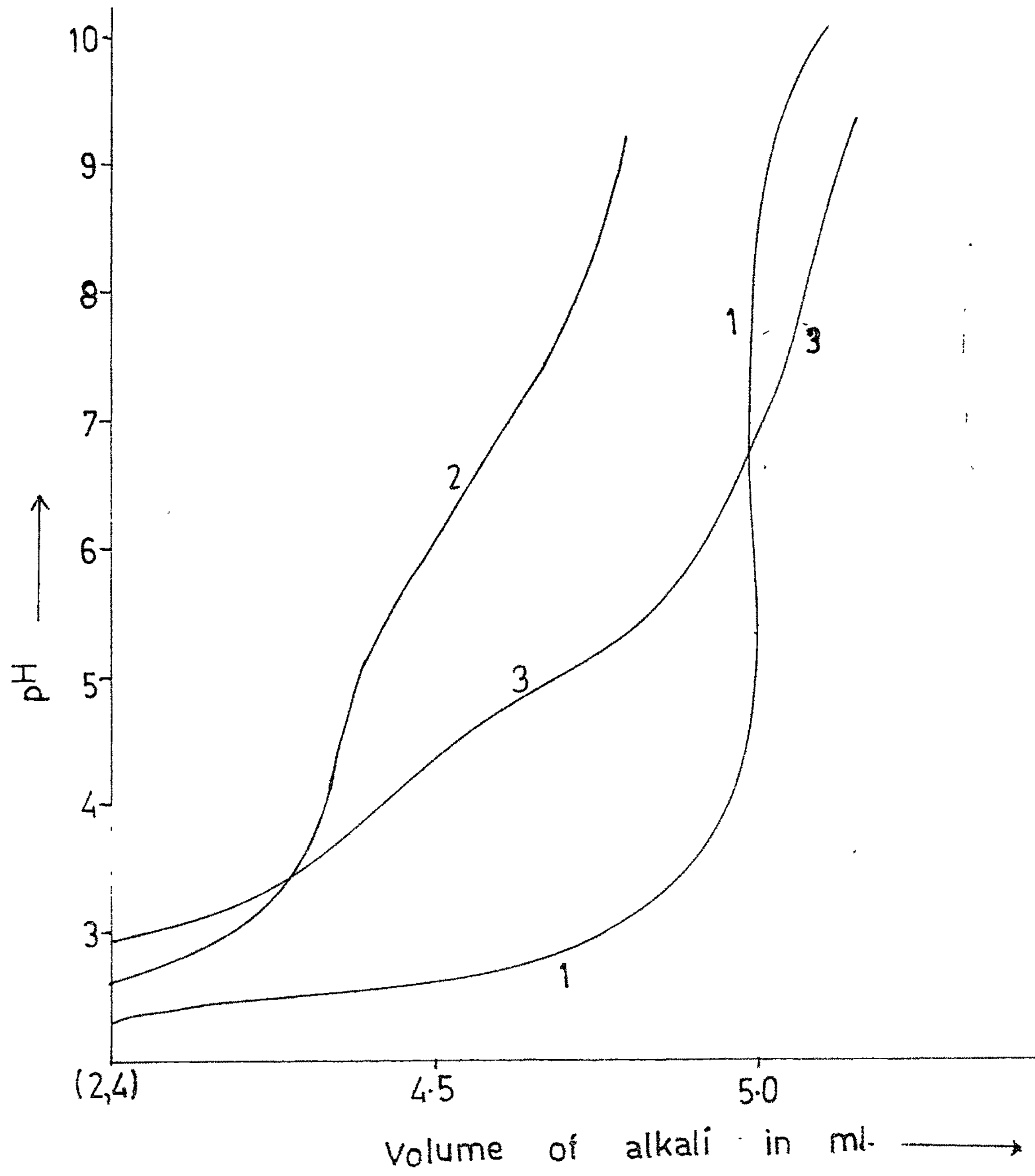


Fig III 65

$T_L^\circ = T_M^\circ = 0{\cdot}001M$

CuA^3 Ethylene-diamine system in 25% dioxan water medium at 30°c

1. Acid.

2. en.

3. Cu + dpa + en.(1:1:1)

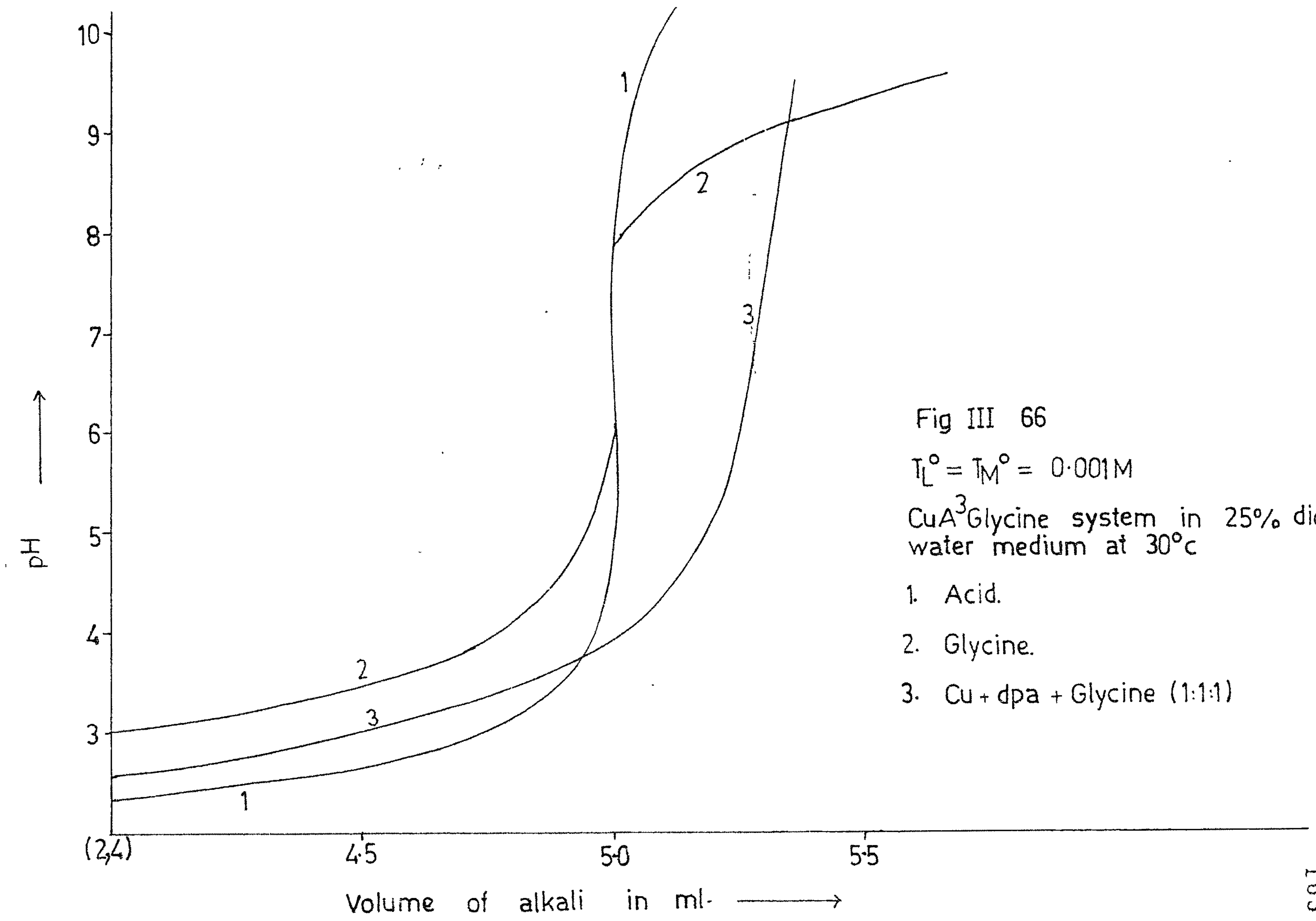


Fig III 66

$T_L^\circ = T_M^\circ = 0{\cdot}001M$

CuA^3Glycine system in 25% dioxan-water medium at 30°c

1. Acid.

2. Glycine.

3. Cu + dpa + Glycine (1:1:1)

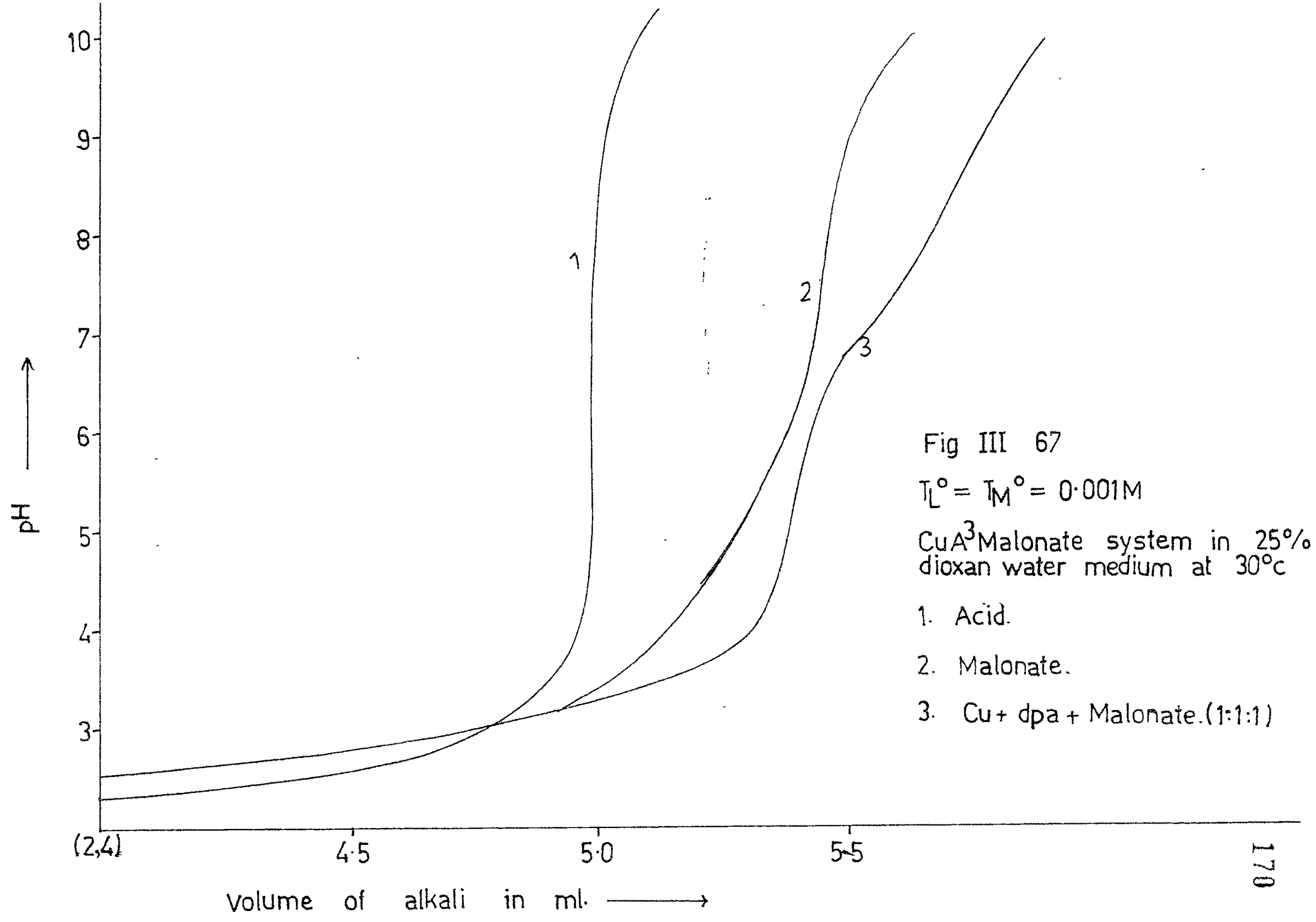


Fig III 67

$T_L^{\circ} = T_M^{\circ} = 0{\cdot}001M$

CuA^{3}Malonate system in 25% dioxan water medium at 30°c

1. Acid.
2. Malonate.
3. Cu + dpa + Malonate.(1:1:1)

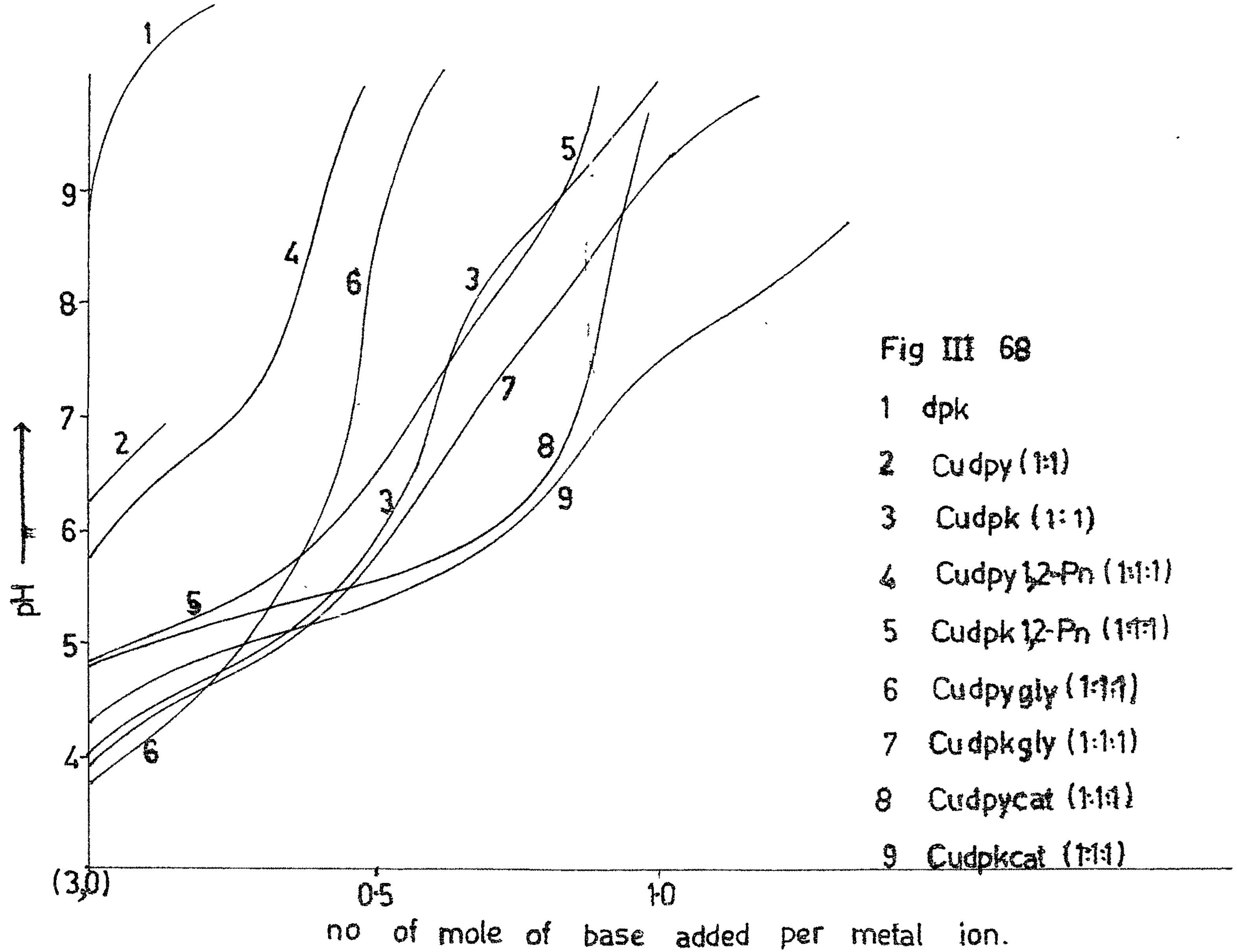
pH
9
8
7
6
5
4
(3,0)
0·5
1·0
no of mole of base added per metal ion.
1
2
3
4
5
6
7
8
9
1 dpk
2 Cudpy (1:1)
3 Cudpk (1:1)
4 Cudpy 1,2-Pn (1:1:1)
5 Cudpk 1,2-Pn (1:1:1)
6 Cudpygly (1:1:1)
7 Cudpkgly (1:1:1)
8 Cudpycat (1:1:1)
9 Cudpkcat (1:1:1)

Fig III 68

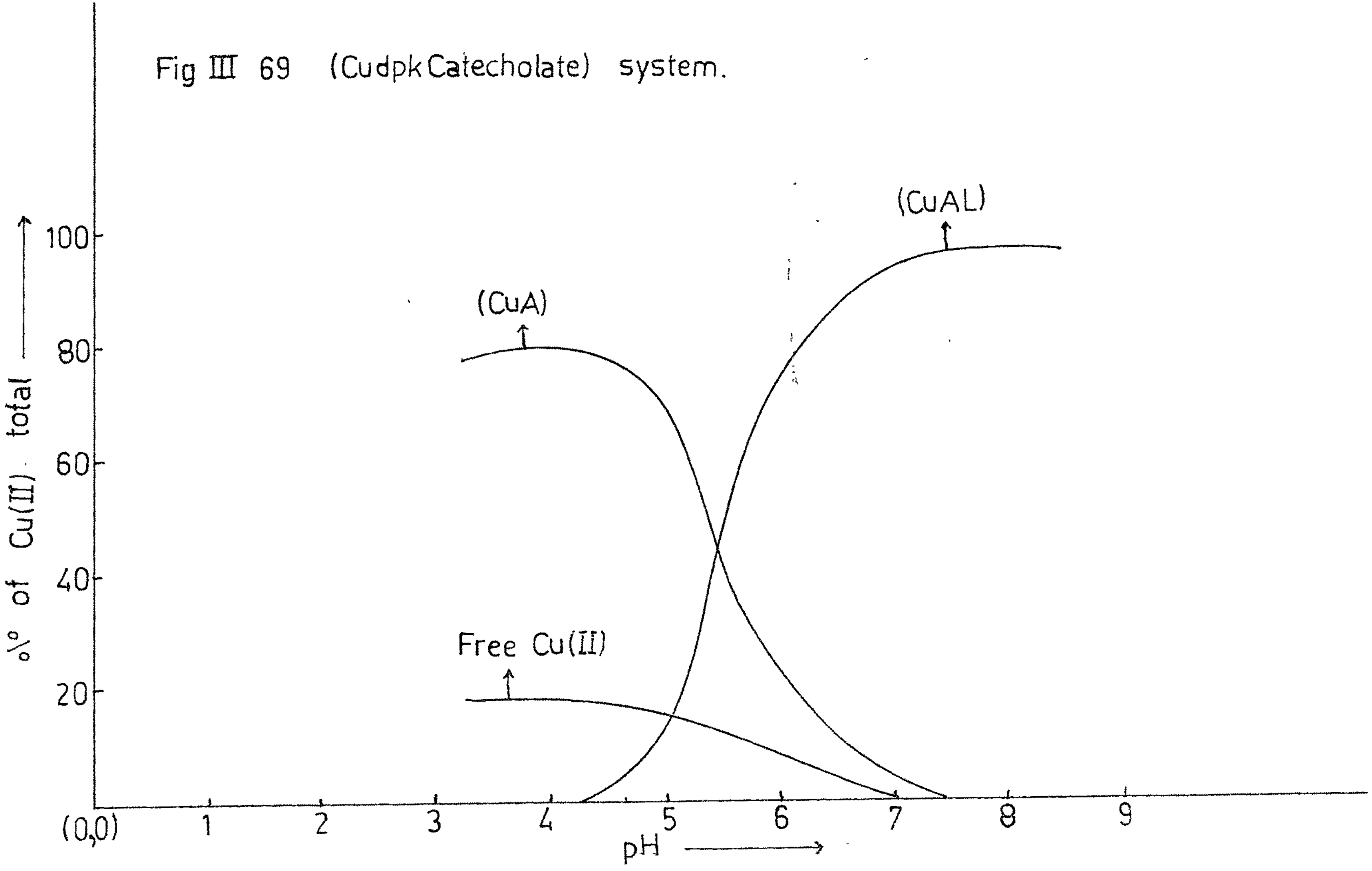
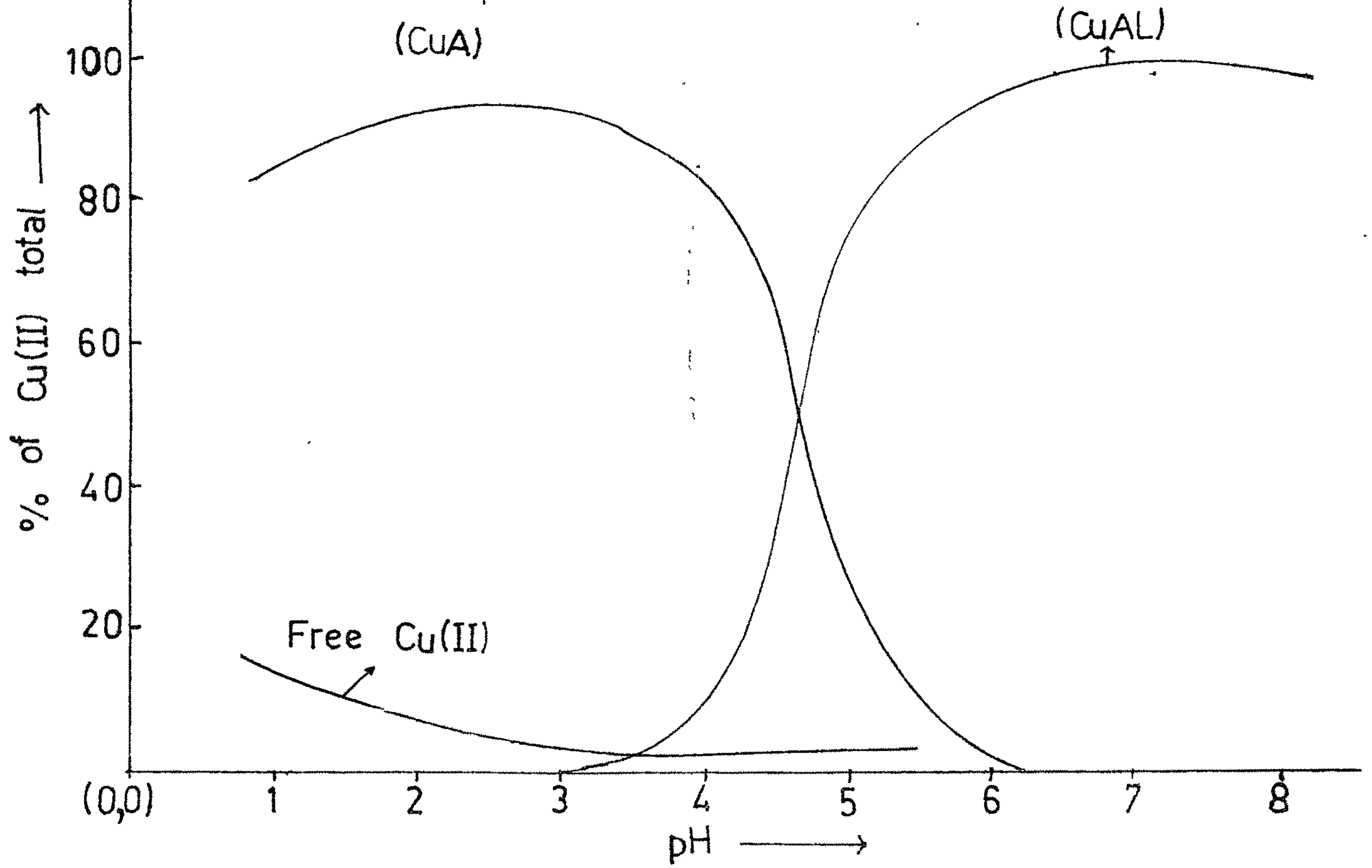


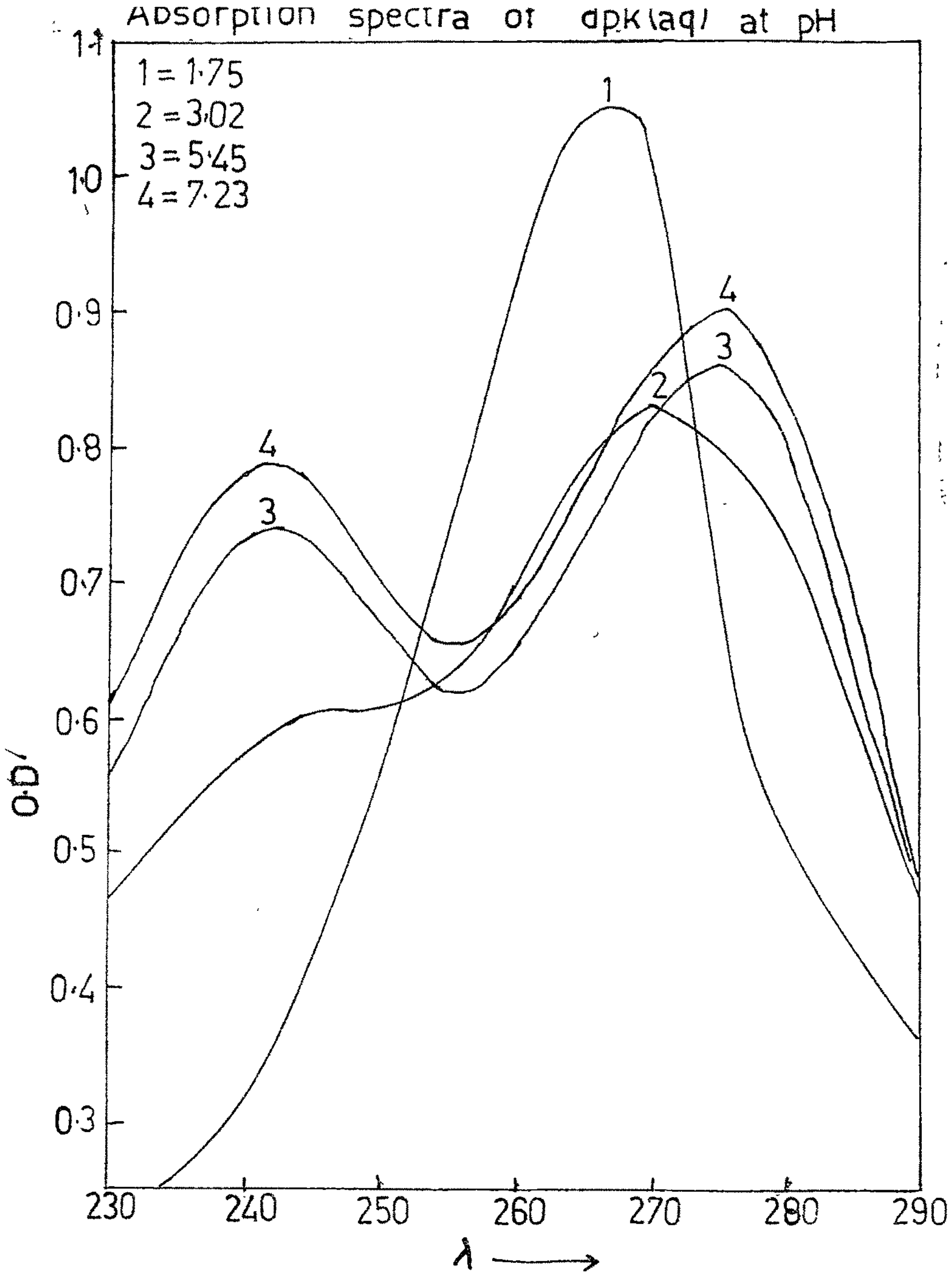
Fig III 69 (Cudpk Catecholate) system.

Variation of concentrations of different species with pH.

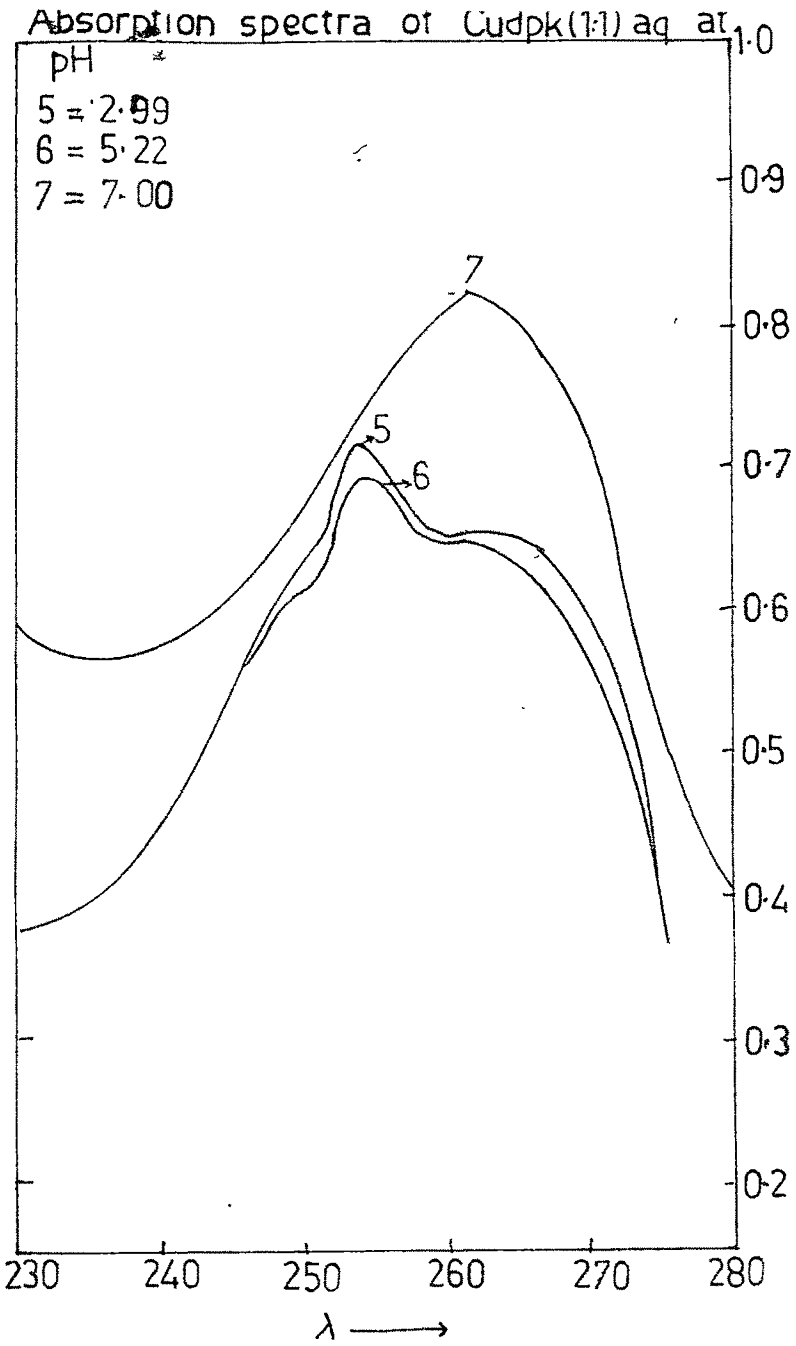
Fig III 70 (CudpaCatechol)



Variation of concentrations of different species with pH



Absorption spectra of dpk(aq) at pH



Absorption spectra of Cudpk(1:1) aq at pH

Results & Discussions

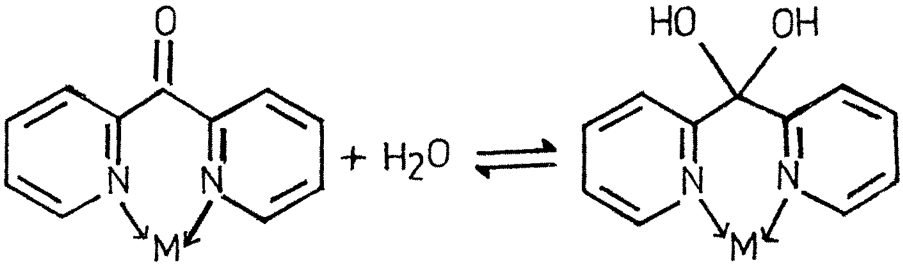
The fact whether [Cudpk] changes co-ordination sites from N-N to N-O^- at higher pH can be confirmed by observing the titration curve 1 fig. III 68. There is buffer region in the pH range 4 to 5 due to the neutralization of proton liberated as a results of O^- co-ordination of dpk. So in case of [CudpkCat] system, Sigel determined the formation constant in the pH range below 5 considering only N-N co-ordinated form of dpk. However, we observed that the values of the formation constant obtained by computer calculations in the range 3 to 4.5 or 3 to 7 are same. This indicates that in [CudpkL] systems probably dpk continues to co-ordinate from N-N end upto high pH.

This is confirmed by comparing the titration curves of [CudipyCat] and [CudpkCat] against NaOH (fig. 68). Similar curves are obtained in other [Cudpk O^--O^-] systems also. The two curves run parallel till pH ~ 7.0 indicating that in the ternary complex dpk continues to co-ordinate from N-N site only upto pH 7.0 as in case of 2,2'-dipyridyl. If in the ternary complex there was change in the co-ordination sites of dpk with liberation of -OH proton in the pH range 4 to 5 as in [Cudpk], [CudpkCat] curve should have been deviated from [CudipyCat] curve. A probable reason why dpk co-ordinates only from N-N sites in the present ternary complex $[Cudpk\ O^{-}-O^{-}]$, could be that $O^{-}-O^{-}$ co-ordinating ligands L favour second ligand A with N-N co-ordination,[26,27,29,31,45] with possibility of M ----→ A π interaction.

However, in case of [Cudpkamino acids] and [Cudpkdiamine] system buffer region in the pH range 4 to 5 is observed. The titration curves of [CudipyL] and [CudpkL] where L = amino acids or diamines against NaOH run parallel till pH ~ 5.0 indicating that in these ternary complexes dpk continues to co-ordinate from N-N site upto pH 5.0 only. Hence, computer calculations were done only upto pH 5.0 considering only N-N co-ordination of dpk.

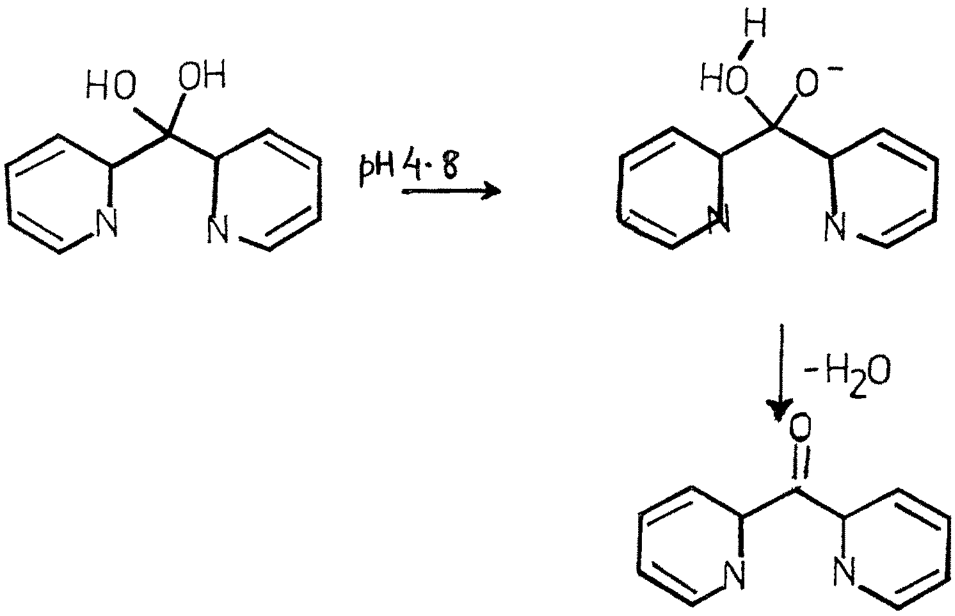
The values of the formation constants obtained by considering the species L, LH, LH_2, [MA] and [MAL] are nearly same as the value obtained by considering all the species in the computer method. This is further confirmed by observing the plot of the concentration of various species (as percentages of total Cu^{+2} present) against pH in case of $[Cudpk\ O^{-}-O^{-}]$ complex as shown in fig. III 69. It is observed that in the lower pH range (pH 1.8 to 3.0) Cu(II) and $[CuA]^{2+}$ are the major species and in higher pH range the species $[CuA]^{2+}$ and [CuAL] are in copiousness. Formation of $[CuA_2]^{2+}$, $[CuL]^{+}$ and $[CuL_2]$ are negligible and hence could not be plotted on the graph in fig. III 69. In cases of all the complexes 70 to 98% of mixed ligand is formed and the sum of percentages of [CuAL] and $[CuA]^{2+}$ total to almost 100%. In cases of $[Cudpk\ N\text{-}O^-]$ and [Cudpk N-N] complexes also in the range of calculations, Cu^{+2}, [CuA] and [CuAL] are the major species. In cases of [CudpaL] systems also calculations were done till pH 7.0. The species considered were same as in [CudipyL] system and it is observed that the major species are Cu(II), [Cudpa] and [CudpaL] (fig. 70).

Sigel[46] presumed that in $[Cudpk.H_2O]$, dpk is completely in gem diol form. Though isolation of only $[Cudpk.H_2O]$ has been reported,[138a] it has been recently shown[138b] that dpk can exist in both keto and gem diol forms even in solid complexes. Both type of complexes $[PdCl_2dpk.H_2O]$ and $[PdCl_2dpk]$, have been isolated in solid state. It can naturally be expected that in aqueous solution there has to be an equilibrium between keto and geminal diol form of co-ordinated dpk. Equation 2.



In the geminal diol form, -OH groups are electron withdrawing and hence increase back donation of dpk though not to the same extent as in keto form of dpk. However, in the geminal diol form there is sp^3 hybridization over carbon atom and hence the planarity of the ring will be lost. This should reduce M --> $dpk.H_2O$ π donation and hence the stability of [CudpkL] complexes should be significantly lowered. However, the ternary complexes [CudpkL] are more stable than [CudpaL]. This shows that dpk is not completely in gem-diol form in [CudpkL].

An observation of the spectrum of dpk and [Cudpk] (fig. III 71) at various pH supports this fact. In between pH 2 to 7 dpk exhibits two bands. The band at 245 nm. is due to $n \dashrightarrow \pi^*$ transition of C=O group of dpk and the band at 278 nm is due to $\pi \dashrightarrow \pi^*$ transition of dipyridyl ring. However, at lower pH 1 to 2, there is only one band observed at 268 nm. This may be due to following equilibrium. Equation-3.



At lower pH dpk may be in gem-diol form. On increasing pH, one -OH dissociates, resulting in the liberation of water molecule and it changes into keto form. With the increasing pH there is more of keto form as seen by the increasing intensity of the peak due to $n \dashrightarrow \pi^*$ transition of C=O (fig. 71). A similar observation was made by Martell and coworkers[138] in case of pyridine aldehyde.

In case of [Cudpk] there are two bands observed, at 256 nm corresponding to n $\longrightarrow \pi^*$ transition of C=O and the peak at 268 nm is due to $\pi \longrightarrow \pi^*$ transition of pyridyl ring. There is a shift in the band positions of the free ligand due to co-ordination with the metal ion.

The presence of C=O peak indicates that dpk in [Cudpk] is not completely in gem-diol form, but there is an equilibrium between the keto and gem-diol form of the co-ordinated ligands as shown in equation 2.

At higher pH ($>$ 5) the intensity of C=O peak becomes less compared to the peak at 268 nm. This is because of the dissociation of the gem-diol form leading to the formation of the species with dpk co-ordinated from N-O end (equation-1).

Thus in the lower pH range co-ordinated dpk exists significantly in the keto form. The stability of the complex [CuA^{2}L] is found to be much greater than [Cu 2,2'-dipyridyl L], due to the presence of electron withdrawing group C=O over A^2. The keto form of dpk is a stronger π acid than 2,2'-dipyridyl and hence stabilizes the ternary complexes.

It is interesting to observe that in ternary complexes containing O^--O^- co-ordinating ligands, dpk co-ordinates from N-N end over the whole pH range, whereas in case of ternary complexes containing O^--N, N-N or aliphatic O^--O^- co-ordinating ligands co-ordination of dpk is from N-N at lower pH and it changes to O^--N at higher pH.

This supports the fact that [MA] complexes, where A = heteroaromatic base co-ordinating from N-N, prefer O^{-}-O^{-} co-ordinating aromatic ligand. In case of [CuA catecholate and derivatives], therefore, N-N co-ordination of dpk continues till higher pH.

In case of dpa, an electron donating imino group (-NH group) attached between the two pyridine moieties enhances the eldctron density on the ring due to the presence of a lone pair of electrons on nitrogen atom. However, the delocalization of electron density in dpa is over a larger area than in 2,2'-dipyridyl. Hence the values of the ternary complex stabilities are comparable for [CuAL] with A = 2,2'-dipyridyl or 2,2'-dipyridylamine.

In both [CudpaL] and [CudpkL] systems the order of stabilization of ternary complexes with L's co-ordinating from different atom is O^{-}-O^{-} > O^{-}-N > N-N. This can be explained as discussed in chapter I. The size of the chelate ring L also affects the stability of the ternary complexes as in [Cu 5-nitro-1,10-phenanthroline L] systems. Therefore, [$CuAL^1$] and [$CuAL^6$] have higher stability than corresponding [$CuAL^3$] and [$CuAL^8$]. In cases of L^4, L^5 there is greater lowering in the ternary complex formation constants because of the steric effect due to substituted groups on the co-ordinating N-diamines as explained in chapter IIa.

In case of L^{13}, L^{14}, L^{15}, L^{16} complexes, Δ log K values are less positive than in case of $[CuAL^{12}]$. This is due to substituted electron withdrawing groups like sulfonates, carboxylates or aldehyde on the ring of ligands L^{13}, L^{15}, L^{16}, respectively, as discussed in case of $[CuA^{1}L]$ complexes.

The value of Δ log K of the mixed ligand complexes of $[CuAL^{17}]$ is also less than $[CuAL^{12}]$ as observed in $[CuA^{1}L]$ complexes. In case of $[CuAL^{18}]$ the Δ log K value is still less than $[CuAL^{17}]$ as discussed in case of $[CuA^{1}L]$.

In cases of the dopamine and adrenaline, the protonated amino group is withdrawing the electron density from the ring and making the Δ log K value less positive in $[CuAL^{19}H]$ and $[CuAL^{20}H]$ than in case of $[CuAL^{12}]$.

The discriminating effect of $[CuA]$ has been observed in $[CuAL]$ complexes also where $L = L^{10}$ to L^{12}. In these aromatic ligands the order is same as in case of N-N, $N-O^{-}$ and $O^{-}-O^{-}$ co-ordinating aliphatic (en, gly, malonate) ligands. The values of Δ log K are, however, more positive or less negative in $[CuAL]$ complexes where the co-ordinating atom N-N, $N-O^{-}$ or $O^{-}-O^{-}$ are over aromatic ring of L, compared to that when they are over aliphatic ligands L as explained in chapter IIb.

It has been observed earlier that in cases of $[CudipyL]$ complexes the values of K^{M}_{ML} and K^{M}_{MAL} are affected to the same extent by the nature of the solvent and consequently Δ log K is almost same in different solvents.[30,45]

A similar observation is made in the cases of [CudpaL] complexes in the present study. However, it is observed that in case of [CudpkL], Δ log K value does not remain same when different percentages of dioxan are used. It becomes more positive with the increase in the percentage of the organic solvent. In case of [Cudpk malonate] in aqueous and 10% dioxan the value of Δ log K is found to be negative while in 25% and 50% dioxan, Δ log K value is positive. In the 50% dioxan solution the values of the Δ log K for [Cudpk glycine] (O^--N) and [Cudpk en] (N-N) are also positive. This is the first observation of positive Δ log K in the complexes of ligands with N-N co-ordination.

The value of Δ log K is more positive in 50% aqueous-dioxan solvents compared to the value in aqueous solution. This can be explained by considering the equilibrium between keto and geminal-diol form. In aqueous-dioxan solution of the complex, geminal diol formation may be less (equation-2 shifting more to the left) and dpk is more in keto form, with greater π accepting ability than the geminal-diol form. This results in greater stability of log K^{Cudpk}_{CudpkL} complexes compared to log K^{Cu}_{CuL} in aqueous-dioxan solution and hence Δ log K is more positive. However, with decreasing amount of dioxan content, the values of Δ log K become less positive. This is because with increase in aqueous solvent, diol form is more. Thus the keto character is reduced and the ligand becomes less π acid in character in aqueous solution.

The Δ log K values of Ni(II) complexes are more negative than in cases of Cu(II) complexes. This is due to lesser release of electron repulsion in the ternary complexes of Ni(II) as discussed in chapter IIA.

The order of stability constants of [NiAL] complexes is same as that of [CuAL] complexes. The complexes of [NiA] also discriminate the ligand L in the order O^{-}-O^{-} > O^{-}-N > N-N though not to the same extent as in case of [CuA].