CHAPTER - IV

COMPLEX FORMATION BETWEEN BIVALENT METAL IONS AND 3-RESORCYLALDEHYDE OXIME

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4.1 INTRODUCTION

Dimethylglyoxime was introduced by Tschugaeff[1] in 1905 as an analytical reagent. A large number of oximes have been used since then as analytical reagents. Consequently the problems related to the structures of solid coordination compounds were taken up for study. Study of structures of solid complexes is quite interesting but equally interesting is the area of complexes in solution phase. Chemical reactions can be studied by using two approaches, related to kinetics on one hand and the equilibrium on the other. The reaction between metal ions and coordinating ligands provides interesting and challanging problems related to kinetics and equilibria.

Isolation of a well characterisable single compound in a pure form is a final goal of a synthetic chemist. However, he cannot ignore the existance of complexes or chelate species in ~~the~~ the solution phase.

Well crystallisable oxime derivatives of aldehydes and ketones can be prepared which are having favourable structural

features and are available in very pure form, so as to be used as ligands. The structure of oxime group was not clearly known upto 1961. In the year 1961 the neutron diffraction work by Hamilton[2] ended the controversy regarding the structure of the oxime group. And now it is established that the structure of the oxime group is C = NOH. The structural chemistry of metal complexes of oximes have been reviewed by Chakravorty[3]. The molecular structures of several bis-(salicylaldoximato) metal(II) complexes ~~of~~ have been studied [4-15].

In case of 3-resocylaldehyde oxime, one proton is available for complexation from phenolic OH group and second proton from oxime OH group. The proton from oxime OH group is not easily abstracted. Nitrogen atom present in the oxime group provides pair of stable electrons, for the formation of the chelate rings. ML_2 type of complex is formed at low pH in solution, whereas proton from phenolic OH group is lost. Second proton from oxime OH group is lost at higher pH to give ML type of complex. The pH metric studies of these complexes are possible.

The chemical equilibria of oximes are not investigated up to mark and much more work can be carried out in this branch.

Ramesh and his co-workers studied thermal stabilities of 2 Hydroxyl napthaldoxime[16] with transition metal ions. The stability constants of rare earth elements is studied with β-resorcylaldehyde oxime[17] in 50 % aquous dioxane mixture.

In the present work 3-resorcylaldehyde oxime has been studied in ethanol-water mixture at 25°, 35° and 45°C temperatures for first time to determine stability constants and thermodynamic parameters.

3.2 EXPERIMENTAL

Preparation of 3-Resorcylaldehyde Oxime [18]

In a 250 ml flask 2 g of the 2:4 dihydroxybenzaldehyde was taken and it was dissolved in sufficient ethanol. Then 5 g of hydroxylamine hydrochloride in 20 ml of water and 2 g of NaOH were added to the aldehyde solution. The mixture was refluxed for about 2 hours on water bath. After cooling, ice cold water was added to it and the solution was neutralised with acid. It was kept in a refrigerator for a few hours. The precipitated oxime was filtered out and recrystalised from ethanol. The melting point of 3-resorcylaldehyde is 201-2°C.

3.3 INSTRUMENTATION

Potentiometric titrations were carried out at temperature 25°, 35° and 45° C as described in the second chapter by using Elico Digital pH meter Model LI-120 and Philips glass calomel combination electrode.

Table 4.A.1

3 Resorcylaldehyde oxime used as a ligand

N' = 0.98 M t = 25°C μ = 0.1 M
Medium = 50 % v/v Ethanol-water V^o = 40.00 ml

I $[HClO_4]$ vs NaOH E^o = 0.02 M		II $[HClO_4+L]$ vs NaOH T_L^o = 0.01 M			III $[HClO_4+L+Mg^{++}]$ vs NaOH $T_{Mg^{++}}^o$ = 0.001 M		
Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH		Vol. of NaOH(ml)	pH	
0.00	2.10	0.00	2.09		0.00	2.09	
0.20	2.19	0.20	2.18		0.20	2.18	
0.40	2.33	0.40	2.30		0.40	2.30	
0.60	2.58	0.60	2.56		0.60	2.54	
0.70	2.85	0.70	2.85		0.70	2.81	
0.74	3.07	0.74	3.07		0.74	3.06	
0.78	3.66	0.78	3.66		0.78	3.66	
0.82	9.60	0.82	7.41	yellow	0.82	7.00	yellow
0.86	10.24	0.86	7.91		0.86	7.60	
0.90	10.49	0.90	8.15		0.90	7.85	
0.94	10.63	0.94	8.36		0.94	8.10	
0.98	10.73	0.98	8.50		0.98	ppt.	
1.02	10.81	1.02	8.66				
1.06	10.89	1.06	8.79				
1.10	10.94	1.10	8.93				
1.14	10.98	1.14	9.07				
1.18	11.01	1.18	9.19				
1.22	11.05	1.22	9.35				
1.26	11.07	1.26	9.45				
1.30	11.09	1.30	9.58				
1.34	11.12	1.34	9.70				
1.38	11.14	1.38	9.81				
1.42	11.16	1.42	9.92				
1.46	11.18	1.46	10.03				
		1.50	10.13				
		1.54	10.26				
		1.58	10.42				
		1.62	10.52				
		1.66	10.63				
		1.70	10.72				
		1.74	10.81				
		1.78	10.88				
		1.82	10.93				
		1.86	10.98				
		1.90	11.02				
		1.94	11.06				
		1.98	11.09				
		2.02	11.12				

Table 4.A.1 (contd.)

3 Resorcylaldehyde oxime used as a ligand

N' = 0.98 M t = 25°C μ = 0.1 M

Medium = 50 % v/v Ethanol-water V^o = 40.00 ml

IV $[HClO_4+L+Cd^{++}]$ vs NaOH $T^o_{Cd^{++}}$ = 0.001 M		V $[HClO_4+L+Zn^{++}]$ vs NaOH $T^o_{Zn^{++}}$ = 0.001 M		VI $[HClO_4+L+Mn^{++}]$ vs NaOH $T^o_{Mn^{++}}$ = 0.001 M	
Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH
0.00	2.09	0.00	2.09 colour-	0.00	2.09 colour-
0.20	2.18	0.20	2.18 less	0.20	2.18 less
0.40	2.30	0.40	2.30	0.40	2.32
0.60	2.55	0.60	2.54	0.60	2.55 yellow
0.70	2.82	0.70	2.82	0.70	2.82
0.74	3.06	0.74	3.00	0.74	3.08
0.78	3.66	0.78	3.30	0.78	3.66
0.82	7.00	0.82	5.79 red-	0.82	6.40
0.86	7.51	0.86	6.41 yellow	0.86	6.96 dark-
0.90	7.86	0.90	6.94	0.90	7.33 yellow
0.94	8.09	0.94	7.46	0.94	7.87
0.98	gelatenous ppt.	0.98	7.87	0.98	7.10
		1.02	8.13	1.02	turbidity
		1.06	8.30 turbidity		

VII $[HClO_4+L+Ni^{++}]$ vs NaOH $T^o_{Ni^{++}}$ = 0.001 M		VIII $[HClO_4+L+Co^{++}]$ vs NaOH $T^o_{Co^{++}}$ = 0.001 M		IX $[HClO_4+L+Cu^{++}]$ vs NaOH $T^o_{Cu^{++}}$ = 0.001 M	
Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH
0.00	2.10 colour-	0.00	2.10 colour-	0.00	2.09 colour-
0.20	2.18 less	0.20	2.18 less	0.20	2.18 less
0.40	2.30	0.40	2.30	0.40	2.29
0.60	2.54	0.60	2.53 red-	0.60	2.51
0.70	2.82	0.70	2.75 brown	0.70	2.71
0.74	3.03	0.74	2.92	0.74	2.86
0.78	3.52	0.78	3.15	0.78	3.07
0.82	5.10	0.82	4.03 dark-	0.82	3.66 yellow
0.86	5.60 yellow	0.86	5.15 dark	0.86	ppt.
0.90	turbidity	0.90	6.59 very dark red		

Table 4.A.1'

3 Resorcylaldehyde oxime used as a ligand

N' = 0.98 M t = 35°C μ = 0.1 M

Medium = 50 % v/v Ethanol-water V^{o} = 40.00 ml

I $[HClO_4]$ vs NaOH E^{o} = 0.02 M		II $[HClO_4+L]$ vs NaOH T_L^{o} = 0.01 M		III $[HClO_4+L+Mg^{++}]$ vs NaOH $T_{Mg^{++}}^{o}$ = 0.001 M	
Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH
0.00	2.21	0.00	2.21 colour-	0.00	2.21 colour-
0.20	2.30	0.20	2.30 less	0.20	2.30 less
0.40	2.41	0.40	2.43	0.40	2.43
0.60	2.64	0.60	2.67	0.60	2.67
0.70	2.88	0.70	2.92	0.70	2.92
0.74	3.03	0.74	3.11	0.74	3.20
0.78	3.55	0.78	3.58	0.78	3.60
0.82	8.60	0.82	6.61	0.82	6.34 yellow
0.86	10.10	0.86	7.59 yellow	0.86	7.20
0.90	10.33	0.90	7.97	0.90	7.65
0.94	10.49	0.94	8.19	0.94	8.00
0.98	10.60	0.98	8.38	0.98	turbidity
1.02	10.69	1.02	8.52		
1.06	10.76	1.06	8.64		
1.10	10.81	1.10	8.76		
1.14	10.86	1.14	8.88		
1.18	10.90	1.18	9.03		
1.22	10.94	1.22	9.17		
1.26	10.97	1.26	9.31		
1.30	11.01	1.30	9.40		
1.34	11.03	1.34	9.54		
1.38	11.05	1.38	9.62		
1.42	11.08	1.42	9.73		
1.46	11.10	1.46	9.82		
1.50	11.11	1.50	9.97		
1.54	11.13	1.54	10.05		
1.58	11.15	1.58	10.18		
1.62	11.17	1.62	10.30		
1.66	11.19	1.66	10.40		
1.70	11.21	1.70	10.49		
		1.74	10.56		
		1.78	10.62		
		1.82	10.70		
		1.86	10.74		
		1.90	10.78		
		1.94	10.83		
		1.98	10.86		
		2.02	10.93		
		2.06	10.96		

contd..III

II contd.

Vol. of NaOH(ml)	pH
2.10	10.98
2.14	11.00
2.18	11.02
2.22	11.05
2.26	11.07
2.30	11.09
2.34	11.11 dark yellow

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Table 4.A.1' (contd.)

3 Resorcylaldehyde oxime used as a ligand

N' = 0.98 M t = 35°C μ = 0.1 M

Medium = 50 % v/v Ethanol-water V^{o} = 40.00 ml

IV $[HClO_4+L=Cd^{++}]$vs NaOH $T^{o}_{Cd^{++}}$ = 0.001 M		V $[HClO_4+L+Zn^{++}]$vs NaOH $T^{o}_{Zn^{++}}$ = 0.001 M		VI $[HClO_4+L+Mn^{++}]$vs NaOH $T^{o}_{Mn^{++}}$ = 0.001 M	
Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH
0.00	2.20 colour-	0.00	2.20 colour-	0.00	2.20 colour-
0.20	2.29 less	0.20	2.29 less	0.20	2.30 less
0.40	2.43	0.40	2.43	0.40	2.43 faint-
0.60	2.69	0.60	2.69	0.60	2.70 yellow
0.70	2.93	0.70	2.93	0.70	2.93
0.74	3.22	0.74	3.11	0.74	3.20
0.78	4.03	0.78	3.58	0.78	3.60
0.82	6.74	0.82	5.31 red-	0.82	6.02 yellow
0.86	white	0.86	6.27 yellow	0.86	7.00
	turbidity	0.90	6.95	0.90	7.50
		0.94	7.39	0.94	7.75 dark
		0.98	gelatenous ppt.	0.98	yellow

VII $[HClO_4+L+Ni^{++}]$vs NaOH $T^{o}_{Ni^{++}}$ = 0.001 M		VIII $[HClO_4+L+Co^{++}]$vs NaOH $T^{o}_{Co^{++}}$ = 0.001 M		IX $[HClO_4+L+Cu^{++}]$vs NaOH $T^{o}_{Cu^{++}}$ = 0.001 M	
Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH
0.00	2.20 colour-	0.00	2.21 colourless	0.00	2.21 colour-
0.20	2.31 less	0.20	2.29 faint-	0.20	2.30 less
0.40	2.43	0.40	2.41 yellow	0.40	2.44
0.60	2.69	0.60	2.64	0.60	2.65
0.70	2.93	0.70	2.88	0.70	2.82
0.74	3.12	0.74	3.02	0.74	2.91
0.78	3.58 yellow	0.78	3.25	0.78	3.07
0.82	4.97	0.82	4.22 dark red	0.82	3.50 yellow
0.86	5.55	0.86	5.82 yellow	0.86	4.41
0.90	6.81	0.90	6.40	0.90	brown
0.94	7.40	0.94	7.42 dark red		ppt.
0.98	8.30				
1.02	8.56				
1.06	8.70				
1.10	8.89 dark yellow				

Table 4.A.1*

3 Resorcylaldehyde oxime used as a ligand

N' = 0.98 M t = 45°C μ = 0.1 M

Medium = 50 % v/v Ethanol-water V^{o} = 40.00 ml

I $[HClO_4]$ vs NaOH E^{o} = 0.02 M		II $[HClO_4+L]$ vs NaOH T_L^{o} = 0.01 M			III $[HClO_4+L+Mg^{++}]$ vs NaOH $T_{Mg^{++}}^{o}$ = 0.001 M		
Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH		Vol. of NaOH(ml)	pH	
0.00	2.34	0.00	2.34	colour-	0.00	2.35	colour-
0.20	2.43	0.20	2.40	less	0.20	2.43	less
0.40	2.54	0.40	2.53		0.40	2.54	
0.60	2.79	0.60	2.78		0.60	2.80	
0.70	3.07	0.70	3.07		0.70	3.07	
0.74	3.26	0.74	3.32		0.74	3.30	
0.78	3.79	0.78	3.80	yellow	0.78	3.80	
0.82	9.75	0.82	7.26		0.82	6.80	yellow
0.86	10.14	0.86	7.65		0.86	7.40	
0.90	10.30	0.90	7.97		0.90	7.65	
0.94	10.44	0.94	8.12		0.94	7.85	
0.98	10.56	0.98	8.26		0.98	turbidity	
1.02	10.63	1.02	8.45				
1.06	10.69	1.06	8.60				
1.10	10.73	1.10	8.76				
1.14	10.77	1.14	8.90				
1.18	10.81	1.18	9.11				
1.22	10.84	1.22	9.23				
1.26	10.86	1.26	9.37				
1.30	10.90	1.30	9.45				
1.34	10.93	1.34	9.52				
1.38	10.95	1.38	9.66				
1.42	10.97	1.42	9.77				
1.46	11.00	1.46	9.97				
1.50	11.02	1.50	10.09				
1.54	11.04	1.54	10.10				
1.58	11.05	1.58	10.25				
1.62	11.07	1.62	10.40				
1.66	11.08	1.66	10.58				
1.70	11.10	1.70	10.55				
		1.74	10.62				
		1.78	10.68				
		1.82	10.72				
		1.86	10.76				
		1.90	10.80				

contd..III

II contd.

vol. of NaOH(ml)	pH
1.94	10.83
1.98	10.86
2.02	10.89
2.06	10.92
2.10	10.95
2.14	10.97
2.18	10.99
2.22	11.01

αα..

Table 4.A.1" (contd.)

3 Resorcylaldehyde oxime used as a ligand

N' = 0.98 t = 45°C μ = 0.1 M

Medium = 50 % v/v Ethanol-water V^{o} = 40.00 ml

IV $[HClO_4+L+Cd^{++}]$vs NaOH $T^{o}_{Cd^{++}}$ = 0.001 M		V $[HClO_4+L+Zn^{++}]$vs NaOH $T^{o}_{Zn^{++}}$ = 0.001 M		VI $[HClO_4+L+Mn^{++}]$vs NaOH $T^{o}_{Mn^{++}}$ = 0.001 M	
Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH
0.00	2.34 colour-	0.00	2.35 colour-	0.00	2.35 colour-
0.20	2.42 less	0.20	2.43 less	0.20	2.42 less
0.40	2.58	0.40	2.54	0.40	2.55
0.60	2.90	0.60	2.80	0.60	2.80
0.70	3.37	0.70	3.09	0.70	3.08
0.74	5.42	0.74	3.30	0.74	3.32
0.78	(6.91) turbidity	0.78	3.80	0.78	3.80 yellow
		0.82	5.60 red-	0.82	6.45
		0.86	6.70 yellow	0.86	7.31
		0.90	7.23	0.90	7.50 dark red colour
		0.94	7.22		
		0.98	8.05		
		1.02	dark yellow		

VII $[HClO_4+L+Ni^{++}]$vs NaOH $T^{o}_{Ni^{++}}$ = 0.001 M		VIII $[HClO_4+L+Co^{++}]$vs NaOH $T^{o}_{Co^{++}}$ = 0.001 M		IX $[HClO_4+L+Cu^{++}]$vs NaOH $T^{o}_{Cu^{++}}$ = 0.001 M	
Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH
0.00	2.35 colour-	0.00	2.35 colour-	0.00	2.35 colour-
0.20	2.42 less	0.20	2.42 less	0.20	2.42 less
0.40	2.55	0.40	2.56	0.40	2.56
0.60	2.80	0.60	2.81	0.60	2.80
0.70	3.10	0.70	3.11	0.70	3.10
0.74	3.30	0.74	3.30	0.74	3.22
0.78	3.80	0.78	3.60	0.78	3.42
0.82	5.08 yellow	0.82	4.40 yellow	0.82	3.73 yellow
0.86	5.76	0.86	ppt.	0.86	4.46
0.90	green yellow ppt.			0.90	ppt.

Table 4.B.1

3 Resorcylaldehyde oxime used as a ligand

N^{1} = 0.98 M μ = 0.1 M V^{o} = 40.00 ml

E^{o} = 0.02 M t = 25°C T_L^{o} = 0.01

Medium = 50 % v/v Ethanol-water

pH	V'	V''	$\bar{n}_A$	log $\bar{n}_A F$
4.5	0.7812	0.7875	1.9845	- 1.8029
5.0	0.7825	0.7925	1.9754	- 1.5983
5.5	0.7837	0.7975	1.9661	- 1.4548
6.0	0.7850	0.8025	1.9571	- 1.3484
6.5	0.7862	0.8075	1.9477	- 1.2581
7.0	0.7875	0.8125	1.9387	- 1.2050
7.5	0.7887	0.8275	1.9046	- 0.9770
8.0	0.7900	0.8725	1.7978	- 0.5959
8.5	0.7950	0.9875	1.5800	- 0.1402
9.0	0.8025	1.1125	1.2402	+ 0.5001
9.5	0.8175	1.2800	0.867	- 0.8141
9.6	0.8200	1.3200	0.7750	- 0.5371
9.8	0.8300	1.3900	0.6280	- 0.2275
10.0	0.8425	1.4600	0.4880	+ 0.0209
10.2	0.8550	1.5300	0.3490	+ 0.3908
10.4	0.8800	1.5800	0.288	+ 0.4037
10.5	0.9000	1.6200	0.093	+ 0.9891

Proton-ligand stability constants

Method	log K_1^H	log K_2^H
Half integral (values from fig.4.1.2)	9.725	8.425
Graphical (values from fig.4.1.3)	9.740	8.4

Table 4.B.1'

3 Resorcylaldehyde oxime used as a ligand

$N' = 0.98$ M $\mu = 0.1$ M $V^o = 40.00$ ml

$E^o = 0.02$ M $t = 35^oC$ $T_L^o = 0.01$ M

Medium = 50 % v/v Ethanol-water

pH	V'	V''	$\bar{n}_A$	log $\bar{n}_A F$
3.5	0.7725	0.7730	1.9908	- 3.6989
4.0	0.7816	0.7850	1.9794	- 1.6771
4.5	0.7856	0.7950	1.9769	- 1.6262
5.0	0.7900	0.8010	1.9730	- 1.5567
5.5	0.7932	0.8062	1.9681	- 1.4821
6.0	0.7965	0.8125	1.9618	- 1.4014
6.5	0.7997	0.8175	1.9563	- 1.3401
7.0	0.8030	0.8225	1.9522	- 1.2993
7.5	0.8062	0.8500	1.8926	- 0.9196
7.6	0.8069	0.8600	1.8699	- 0.8253
7.8	0.8082	0.8800	1.8240	- 0.6188
8.0	0.8100	0.9000	1.7795	- 0.4396
8.2	0.8120	0.9300	1.7100	- 0.3889
8.4	0.8180	0.9800	1.6179	- 0.2087
8.6	0.8200	1.0500	1.4363	+ 0.0956
8.8	0.8220	1.1000	1.2945	+ 0.3795
9.0	0.8240	1.1700	1.1524	+ 0.7453
9.4	0.8280	1.3000	0.8440	- 0.7360
9.6	0.8300	1.3800	0.6530	- 0.2746
10.0	0.8500	1.5200	0.3600	+ 0.2499
10.2	0.8800	1.5900	0.2630	+ 0.4475
10.4	0.9100	1.6600	0.1670	+ 0.6979
10.5	0.9400	1.7000	0.1430	+ 0.7777

Proton-ligand stability constants

Method	log K_1^H	log K_2^H
Half integral (values from fig.4.1.2)	9.8	8.525
Graphical (values from fig.4.1.3)	9.825	8.475

Table 4.B.1"

3 Resorcylaldehyde oxime used as a ligand

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 45°C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water

pH	V'	V"	$\bar{n}_A$	log $\bar{n}_A F$
4.5	0.7840	0.7875	1.9845	- 1.8029
5.0	0.7875	0.7925	1.9816	- 1.7227
5.5	0.7912	0.7975	1.9705	- 1.5172
6.0	0.7950	0.8025	1.9595	- 1.3745
6.5	0.7962	0.8075	1.9497	- 1.2870
7.0	0.7975	0.8125	1.9460	- 1.2435
7.5	0.8012	0.8400	1.9047	- 0.9774
8.0	0.8025	0.9150	1.7850	- 0.5625
8.2	0.8030	0.9825	1.6420	- 0.2536
8.4	0.8040	1.0100	1.4951	+ 0.0077
8.5	0.8042	1.0300	1.4460	+ 0.0942
8.6	0.8045	1.0600	1.3752	+ 0.2216
8.8	0.8055	1.1125	1.2585	+ 0.4575
9.0	0.8060	1.1700	1.01079	+ 0.9233
9.4	0.8100	1.3100	0.8020	- 0.6175
9.5	0.8125	1.3400	0.7080	- 0.3846
9.6	0.8150	1.3800	0.5900	- 0.1581
9.8	0.8275	1.4500	0.4510	0.0854
10.0	0.8375	1.5000	0.3770	0.2182
10.2	0.8775	1.5600	0.3310	0.3056
10.5	0.9500	1.6700	0.2420	0.4959
10.8	1.1800	1.9300	0.1780	0.6645

Proton-ligand stability constants

Method		log K_1^H	log K_2^H
Half integral	(values from fig.4.1.2)	9.975	8.650
Graphical	(values from fig.4.1.3)	9.950	8.550

Table 4.C.1.1

Stability constant of Magnesium-3 Resocylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 25°C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T^o_{Mg^{++}}$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\frac{\bar{n}}{F}$
6.8	0.7870	0.8105	0.8150			
7.0	0.7875	0.8125	0.8225	0.1265	3.6241	0.8391
7.2	0.7880	0.8175	0.8325	0.1908	3.4340	0.6274
7.4	0.7885	0.8200	0.8425	0.2871	3.2481	0.3949
7.6	0.7890	0.8350	0.8650	0.3889	3.0676	0.1963
7.8	0.7895	0.8525	0.8950	0.5648	2.8983	-0.1132
8.0	0.7900	0.8725	0.8250	0.7161	2.7391	-0.4018
8.2	0.7920	0.8950	0.8625	0.9471	2.5788	-1.2528

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig. 4.1.4)	3.00
Graphical (value from fig. 4.1.5)	3.00

Table 4.C.1.2

Stability constant of Manganese-3 Resocylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 25°C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T^o_{Mn^{++}}$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\frac{\bar{n}}{F}$
6.0	0.7850	08025	0.8125	0.1253	4.6139	0.8439
6.2	0.7855	0.8045	0.8175	0.1632	4.4155	0.7099
6.4	0.7860	0.8065	0.8225	0.1967	4.2437	0.6110
6.6	0.7865	0.8085	0.8300	0.2709	4.0621	0.4311
6.8	0.7870	0.8105	0.8425	0.4040	3.8416	0.1688
7.0	0.7875	0.8125	0.8600	0.6010	3.6534	-0.1777
7.2	0.7880	0.8175	0.8725	0.6998	3.4568	-0.3678
7.4	0.7885	0.8200	0.8950	0.9570	3.2737	-1.3474
7.6	0.7890	0.8350	0.9150	1.037	3.0974	-

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.4.1.4)	3.225
Graphical (value from fig.4.1.5)	3.250

Table 4.C.1.3

Stability constant of Zinc-3 Resorcylaldehyde oxime system

$N' = 0.98$ M $\mu = 0.1$ M $V^o = 40.00$ ml

$E^o = 0.02$ M $t = 25^oC$ $T_L^o = 0.01$ M

Medium = 50 % v/v Ethanol-water $T^o_{Zn^{++}} = 0.001$ M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\frac{\bar{n}}{F}$
5.0	0.7825	0.7925	0.8050	0.1552	5.6152	0.7359
5.2	0.7830	0.7945	0.8085	0.1742	5.4161	0.6760
5.4	0.7835	0.7965	0.8125	0.1993	5.2172	0.6040
5.6	0.7840	0.7985	0.8175	0.2372	5.0233	0.5073
5.8	0.7845	0.8005	0.8225	0.2752	4.8285	0.4206
6.0	0.7850	0.8025	0.8325	0.3846	4.6254	0.2042
6.2	0.7855	0.8045	0.8475	0.5399	4.4342	-0.0694
6.4	0.7860	0.8065	0.8650	0.7485	4.2689	-0.4736
6.6	0.7865	0.8085	0.8800	0.9005	4.0908	-0.9567

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.4.1.4)	4.5
Graphical (value from 4.1.5)	4.5

Table 4.C.1.4

Stability constant of Nickel-3 Resorcylaldehyde oxime system

$N' = 0.98$ M $\mu = 0.1$ M $V^o = 40.00$ ml

$E^o = 0.02$ M $t = 25^oC$ $T_L^o = 0.01$ M

Medium = 50 % v/v Ethanol-water $T^o_{Ni^{++}} = 0.001$ M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\frac{\bar{n}}{F}$
4.0	0.78	0.7825	0.7925	0.1885	6.6167	0.6339
4.2	0.7805	0.7845	0.8020	0.2155	6.4179	0.5612
4.4	0.7810	0.7865	0.8060	0.2407	6.2190	0.4990
4.6	0.7815	0.7885	0.8100	0.2660	6.0201	0.4408
4.8	0.7820	0.7905	0.8140	0.2912	5.8213	0.3863
5.0	0.7825	0.7925	0.8175	0.3098	5.6221	0.3478
5.2	0.7830	0.7945	0.8275	0.4105	5.4266	0.1572
5.4	0.7835	0.7965	0.8375	0.5109	5.2312	-0.0190
5.6	0.7840	0.7985	0.8550	0.7051	5.0402	-0.3787
5.8	0.7845	0.8005	0.8775	0.9521	4.8519	-1.2983

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.4.1.4)	5.26
Graphical (value from fig.4.1.5)	5.25

Table 4.C.1.5

Stability constant of Cobalt-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 25° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T^o_{Co^{++}}$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
3.4	0.7750	0.7750	0.7900	0.1840	7.2169	0.6469
3.6	0.7800	0.7800	0.7975	0.2147	7.0179	0.5623
3.8	0.7800	0.7800	0.8115	0.2638	6.8200	0.4456
4.0	0.7800	0.7825	0.8185	0.3199	6.6225	0.3276
4.2	0.7805	0.7845	0.8250	0.4999	6.4307	0.0002
4.4	0.7810	0.7865	0.8315	0.5555	6.2332	-0.0968
4.6	0.7815	0.7885	0.8380	0.6124	6.0359	-0.1987
4.8	0.7820	0.7905	0.8450	0.6751	5.8388	-0.3177
5.0	0.7825	0.7925	0.8525	0.7449	5.6421	-0.4654
5.2	0.7830	0.7945	0.8610	0.8271	5.4459	-0.6799
5.4	0.7835	0.7965	0.8725	0.9469	5.2517	-1.2512

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.4.1.4)	6.2
Graphical (value from fig.4.1.5)	6.2

Table.4.C.1.6

Stability constant of Copper-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 25° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T^o_{Cu^{++}}$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
3.0	0.7300	0.7300	0.7550	0.3069	7.6220	0.3538
3.2	0.7575	0.7575	0.7850	0.3375	7.4233	0.2930
3.4	0.7750	0.7750	0.8050	0.3679	7.2247	0.2351
3.6	0.7775	0.7775	0.8200	0.5214	7.0317	-0.0373
3.8	0.7800	0.7800	0.8300	0.6138	6.8359	-0.2012
4.0	0.7800	0.7825	0.8425	0.7381	6.6418	-0.4500

Metal ligand stability constant

Method	log K_1
Half integral (value from fig.4.1.4)	7.1
Graphical (value from fig.4.1.5)	7.025

Table 4.C.1'.1

Stability constant of Magnesium-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 35° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T_{Mg^{++}}^o$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\frac{\bar{n}}{F}$
6.8	0.8017	0.8305	0.8375	0.09414	3.7214	0.9832
7.0	0.8030	0.8350	0.8475	0.1575	3.5290	0.7299
7.2	0.8043	0.8400	0.8575	0.2217	3.3395	0.5454
7.4	0.8056	0.8425	0.8675	0.3193	3.1559	0.3287
7.6	0.8069	0.8600	0.8950	0.4590	2.9805	0.0714
7.8	0.8082	0.8800	0.9250	0.6198	2.8154	-0.2123
8.0	0.8100	0.9000	0.9575	0.8241	2.6653	-0.6708
8.2	0.8120	0.9300	0.9975	1.024	2.5320	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.4.1.4)	2.90
Graphical	(value from fig.4.1.5)	2.91

Table 4.C.1'.2

Stability constant of Manganese-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 35° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T_{Mn^{++}}^o$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\frac{\bar{n}}{F}$
6.4	0.7991	0.8165	0.8325	0.2005	4.1208	0.6007
6.6	0.8004	0.8185	0.8425	0.3009	3.9274	0.3662
6.8	0.8017	0.8205	0.8500	0.3695	3.7336	0.2320
7.0	0.8030	0.8225	0.8600	0.4700	3.5431	0.0505
7.2	0.8043	0.8300	0.8750	0.5693	3.3553	-0.1211
7.4	0.8056	0.8400	0.8925	0.6720	3.1720	-0.3115
7.6	0.8069	0.8500	0.9175	0.7541	2.9941	-0.4867
7.8	0.8082	0.8800	0.9450	0.8954	2.7284	-0.9325

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.4.1.4)	3.500
Graphical	(value from fig.4.1.5)	3.450

Table 4.C.1'.3

Stability constant of Zinc-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 35° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T_{Zn^{++}}^o$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\frac{\bar{n}}{F}$
5.0	0.7900	0.8010	0.8125	0.1429	5.5148	0.7780
5.2	0.7913	0.8025	0.8175	0.1865	5.3167	0.6398
5.4	0.7926	0.8050	0.8225	0.2179	5.1181	0.5550
5.6	0.7939	0.8075	0.8300	0.2806	4.9209	0.4088
5.8	0.7952	0.8100	0.8375	0.3435	4.7237	0.2814
6.0	0.7965	0.8125	0.8450	0.4188	4.5271	0.1423
6.2	0.7978	0.8145	0.8525	0.4756	4.3233	0.0415
6.4	0.7991	0.8165	0.8625	0.5754	4.1477	-0.1320
6.6	0.8004	0.8185	0.8750	0.7211	3.9457	-0.4126
6.8	0.8017	0.8205	0.8900	0.8726	3.7571	-0.8356
7.0	0.8030	0.8225	0.9200	001.225	3.589	-

Metal ligand stability constant

Method		log K_1
Half integral	(value from fig.4.1.4)	4.375
Graphical	(value from fig.4.1.5)	4.2

Table 4.C.1'.4

Stability constant of Nickel-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 35° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T_{Ni^{++}}^o$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\frac{\bar{n}}{F}$
4.2	0.7832	0.7860	0.7950	0.1115	6.3232	0.9014
4.4	0.7848	0.7850	0.8000	0.1550	6.1152	0.7366
4.6	0.7864	0.7900	0.8075	0.2172	5.9180	0.5567
4.8	0.7880	0.7925	0.8150	0.2794	5.7211	0.4115
5.0	0.7900	0.7950	0.8225	0.3418	5.5236	0.2845
5.2	0.7913	0.7975	0.8350	0.4662	5.3293	0.0585
5.4	0.7926	0.8025	0.8500	0.5916	5.1350	-0.1609
5.6	0.7939	0.8050	0.8650	0.7484	4.9424	-0.4734
5.8	0.7952	0.8075	0.8775	0.8744	4.7483	-0.8427
6.0	0.7965	0.8125	0.8900	0.9690	4.5528	-0.9694

Metal-Ligand stability constant

Method		log K_1
Half integral	(value from fig.4.1.4)	5.250
Graphical	(value from fig.4.1.5)	5.175

Table 4.C.1'.5

Stability constant of Cobalt-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 45° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T_{Co}^{o\,++}$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
3.4	0.7750	0.7750	0.7875	0.1534	7.1151	0.7419
3.6	0.7800	0.7800	0.7975	0.2151	6.9179	0.5622
3.8	0.7808	0.7825	0.8075	0.3080	6.7220	0.3516
4.0	0.7816	0.7850	0.8150	0.3716	6.5248	0.2282
4.2	0.7832	0.7860	0.8225	0.4525	6.3286	0.0828
4.4	0.7848	0.7875	0.8275	0.4962	6.1306	0.0067
4.6	0.7864	0.7900	0.8350	0.5585	5.9334	-0.1021
4.8	0.7880	0.7925	0.8425	0.6209	5.7361	-0.2143
5.0	0.7900	0.7950	0.8525	0.7147	5.5408	-0.3988
5.2	0.7913	0.7975	0.8675	0.8704	5.3481	-0.8270

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.4.1.4)	6.15
Graphical (value from fig.4.1.5)	6.15

Table 4.C.1'.6

Stability constant of Copper-3 Rssorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 35° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T_{Cu}^{o\,++}$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
3.0	0.7425	0.7425	0.7725	0.3682	7.5248	0.2344
3.2	0.7625	0.7625	0.7950	0.3988	7.3261	0.1782
3.4	0.7750	0.7750	0.8125	0.4598	7.1289	0.0699
3.6	0.7800	0.7800	0.8275	0.5838	6.9345	-0.1470
3.8	0.7808	0.7825	0.8375	0.6776	6.7389	-0.3226
4.0	0.7816	0.7850	0.8475	0.7743	6.5435	-0.5355
4.2	0.7842	0.7860	0.8525	0.8243	6.3458	-0.6714

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.4.1.4)	7.25
Graphical (value from fig.4.1.5)	7.00

Table 4.C.1".1

Stability constant of Magnesium-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 45° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T^o_{Mg^{++}}$ = 0.001 M

pH	V'	V"	V"'	$\bar{n}$	pL	log $\bar{n}$ F
7.0	0.7925	0.8125	0.8275	0.1890	3.4338	0.6325
7.2	0.8000	0.8200	0.8400	0.2522	3.2463	0.4721
7.4	0.8010	0.8325	0.8600	0.3505	3.0655	0.2677
7.6	0.8015	0.8550	0.8900	0.4593	2.8930	0.0709
7.8	0.8020	0.8825	0.9250	0.5763	2.7317	-0.1336
8.0	0.8025	0.9125	0.9650	0.7209	2.5866	-0.4120
8.2	0.8030	0.9825	1.0450	0.9328	2.4637	-1.1424

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.4.1.4)	2.825
Graphical (value from fig.4.1.5)	2.825

Table 4.C.1".2

Stability constant of Manganese-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 45° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T^o_{Mn^{++}}$ = 0.001 M

pH	V'	V"	V"'	$\bar{n}$	pL	log $\bar{n}$ F
6.2	0.7955	0.8045	0.8125	0.1003	4.2157	0.9462
6.4	0.7960	0.8065	0.8175	0.1383	4.0189	0.7945
6.6	0.7965	0.8085	0.8240	0.1951	3.8240	0.6156
6.8	0.7970	0.8085	0.8300	0.2707	3.6312	0.4304
7.0	0.7975	0.8105	0.8400	0.3716	3.4418	0.2282
7.2	0.8000	0.8125	0.8550	0.5358	3.2591	-0.0625
7.4	0.8010	0.8200	0.8775	0.7333	3.0831	-0.4393
7.6	0.8015	0.8325	0.9175	0.8517	2.9112	-0.7591

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.4.1.4)	3.350
Graphical (value from fig.4.1.5)	3.280

Table 4.C.1".3

Stability constant of Zinc-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 45° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T^o_{Zn^{++}}$ = 0.001 M

pH	V'	V"	V"'	$\bar{n}$	pL	log $\bar{n}$ F
5.0	0.7875	0.7925	0.8050	0.1229	5.4138	0.8535
5.2	0.7890	0.7945	08100	0.1526	5.2151	0.7446
5.4	0.7905	0.7965	0.8150	0.2424	5.0192	0.4949
5.6	0.7920	0.7985	0.8200	0.2679	4.8203	0.4466
5.8	0.7935	0.8005	0.8275	0.3373	4.6234	0.2934
6.0	0.7950	0.8025	0.8325	0.3756	4.4251	0.2208
6.2	0.7955	0.8045	0.8400	0.4452	4.2311	0.0955
6.4	0.7960	0.8065	0.8475	0.5039	4.0352	-0.0068
6.6	0.7965	0.8085	0.8575	0.6167	3.8431	-0.2066
6.8	0.7970	0.8105	0.8700	0.7492	3.6536	-0.4753
7.0	0.7975	0.8125	0.8875	0.9452	3.4686	-1.2067

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.4.1.4)	4.1
Graphical	(value from fig.4.1.5)	4.075

Table 4.C.1".4

Stability constant of Nickel-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 35° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T^o_{Ni^{++}}$ = 0.001 M

pH	V'	V"	V"'	$\bar{n}$	pL	log $\bar{n}$ F
4.4	0.7830	0.7865	0.7950	0.1047	6.0130	0.9320
4.6	0.7845	0.7885	0.8025	0.1731	5.8160	0.6793
4.8	0.7860	0.7905	0.8100	0.2413	5.6190	0.4976
5.0	0.7875	0.7925	0.8175	0.3094	5.4221	0.3486
5.2	0.7890	0.7945	0.8260	0.3904	5.2257	0.1935
5.4	0.7905	0.7965	0.8375	0.5098	5.0312	-0.0170
5.6	0.7920	0.7985	0.8475	0.6105	4.8359	-0.1952
5.8	0.7935	0.8005	0.8600	0.7432	4.6391	-0.4615
6.0	0.7950	0.8025	0.8725	0.8764	4.4484	-0.8507

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.4.1.4)	5.05
Graphical	(value from fig.4.1.5)	5.05

Table 4.C.1".5

Stability constant of cobalt-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 45° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T^o_{Co^{++}}$ = 0.01 M

pH	V'	V"	V"'	$\bar{n}$	pL	log $\frac{\bar{n}}{F}$
3.4	0.7550	0.7550	0.7650	0.1228	7.0135	0.8542
3.6	0.7725	0.7725	0.7850	0.1533	6.8149	0.7420
3.8	0.7800	0.7800	0.7950	0.1839	6.6163	0.6474
4.0	0.7800	0.7825	0.8050	0.2757	6.4205	0.4194
4.2	0.7815	0.7850	0.8125	0.3370	6.2233	0.2941
4.6	0.7845	0.7885	0.8375	0.6059	5.8355	-0.1868
4.8	0.7860	0.7905	0.8500	0.7362	5.6417	-0.4457
5.0	0.7875	0.7925	0.8650	0.8974	5.4493	-0.9429

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.4.1.4)	6.00
Graphical	(value from fig.4.1.5)	5.98

Table 4.C.1".6

Stability constant of Copper-3 Resorcylaldehyde oxime system

N' = 0.98 M μ = 0.1 M V^o = 40.00 ml

E^o = 0.02 M t = 45° C T_L^o = 0.01 M

Medium = 50 % v/v Ethanol-water $T^o_{Cu^{++}}$ = 0.001 M

pH	V'	V"	V"'	$\bar{n}$	pL	log $\frac{\bar{n}}{F}$
3.4	0.7550	0.7550	0.7800	0.3011	7.0214	0.3657
3.6	0.7725	0.7725	0.8075	0.4292	6.8273	0.1238
3.8	0.7800	0.7800	0.8250	0.5514	6.6349	-0.0896
4.0	0.7800	0.7825	0.8400	0.7047	6.4402	-0.3778
4.2	0.7815	0.7850	0.8500	0.8500	0.7966	-0.5929
4.4	0.7830	0.7885	0.8675	0.9614	6.0523	-1.3963

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.4.1.4)	6.750
Graphical	(value from fig.4.1.5)	6.750

Table 4.D.1 : 3-Resorcylaldehyde oxime used as a ligand

Metal	Stability constant	Temperature			ΔG° K joules/mole			ΔH° K joules/mole		ΔS° Joules/mole		
		25°C	35°C	45°C	25°C	35°C	45°C	Graphical	Calculated	25°C	35°C	45°C
H^{+}	$\log K_1^H$	9.962	9.812	9.732	56.69	57.69	59.07	-19.15	-16.99	+125.94	+125.10	+125.82
H^{+}	$\log K_2^H$	8.6	8.5	8.412	48.94	49.15	51.08	-19.15	-20.82	+ 99.94	+ 99.70	+100.36
Mg^{++}	$\log K_1$	3.0	2.905	2.825	17.07	17.08	17.15	-16.11	-15.80	+ 3.0203	+ 3.153	+ 3.265
Mn^{++}	$\log K_1$	3.237	3.475	3.315	18.40	20.40	20.12	-30.90	-29.92	- 41.91	- 34.06	- 33.90
Zn^{++}	$\log K_1$	4.5	4.287	4.087	25.60	25.21	24.82	-38.33	-37.36	- 42.74	- 42.58	- 42.49
Ni^{++}	$\log K_1$	5.25	5.212	5.05	29.87	30.65	30.66	-20.83	-18.48	- 30.38	- 31.90	- 30.92
Co^{++}	$\log K_1$	6.2	6.15	5.99	35.27	36.18	36.36	-18.24	-19.35	- 57.19	- 58.24	- 56.98
Cu^{++}	$\log K_1$	7.062	7.12	6.750	40.17	41.87	40.98	-23.94	-30.05	- 54.47	- 58.19	- 53.34

3.4 RESULTS AND DISCUSSION

3-Resorcylaldehyde Oxime (3-RAO)

The experimental observations of 3-RAO are given in Table 4.A.1, 4.A.1' and 4.A.1". The ligand is used to study complexations with bivalent metal ions Mg^{++}, Cd^{++}, Zn^{++}, Mn^{++}, Ni^{++}, Co^{++} and Cu^{++}. In acidic medium it is colourless but acquires yellow colour which deepens with addition of sodium hydroxide. In case of Mg^{++} and Cd^{++} slight white coloured precipitate is formed. In case of Zn^{++}, Mn^{++} and Ni^{++} initial colourless solution becomes yellow with addition of sodium hydroxide. In case of cobalt colourless solution becomes faint yellow, dark yellow and finally dark red with addition of alkali. In case of copper slightly brownish coloured precipitate is obtained. The titration curves are shown in figs.4.1.1.a, 4.1.1'.a, 4.1.1".a, 4.1.1.b, 4.1.1'.b, and 4.1.1"b. The Table 4.B.1, 4.B.1' and 4.B.1" gives the data for proton-ligand stability constant. Figs. 4.1.2 and 4.1.3 are the plots of half integral and graphical methods used for proton-ligand stability constant. Tables 4.C.1.1 to 4.C.1.6, 4.C.1'.1 to 4.C.1'.6 and 4.6.1".1 to 4.C.1".6 cover the six metal ions and their stability constants. The metal ligand stability constants are determined by using half integral and graphical methods by using figs.4.1.4 and 4.1.5. The values of overall changes in free energy (ΔG^{o}) enthalpy (ΔH^{o}) and entropy (ΔS^{o}) accompanying complexation have been determined by using the temperature . Co-efficient

and Gibbs-Helmholtz equation ΔH is also determined with the help of an isobar equation,

$$\frac{d\ (\log B)}{d(\ 1/T\ )} = -\frac{\Delta H}{4.576}$$

The values of ΔH are determined by using Fig. No.4.1.6. The stability constants and thermodynamic parameters are tabulated in Table No.4.D.1.

The complex formation has been investigated in the present work in ethanol-water mixture. This ligand is studied at 25°, 35° and 45°C to calculate thermodynamic parameters by us.

Complexation with Oxime Ligands

The term "oxime" is a short form of oxy-imine, C = NOH. The oxime group is amphiprotic with a slightly basic nitrogen atom and a mildly acidic hydroxyl group. Tschugaeff correctly identified[19] the bidentate nature of vic-dioximes. The chelate ring size, however, remained uncertain and went through the incorrect seven-membered and six membered formulation to the now well established five-membered formulation. The detailed accounts of these and other historical developments are well documented at several places[20-23]. Interesting chemistry of oxime complexes has been developed during the last few decades and necessarily more studies on bonding and stability constants

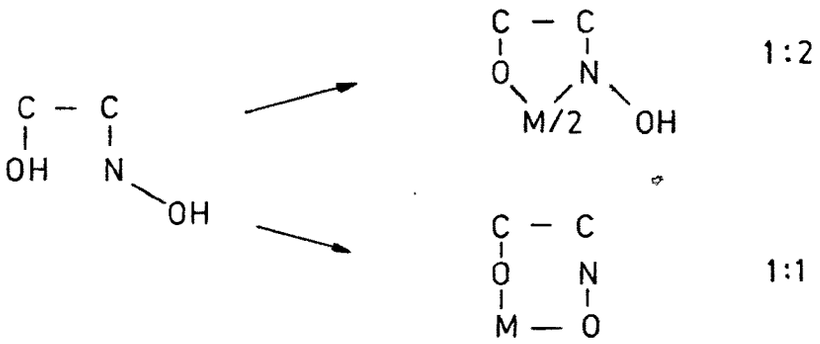
of the complexes is helpful in furthering the applied aspects of this class of ligands.

Structure of the Oxime Group

There are two possible structures for oxime group

I II

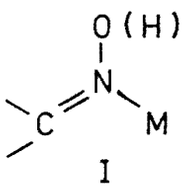
Neutron diffraction work by Hamilton[24] on dimethylgloxime definitely established the presence of O-H bonds, therefore Structure I is the correct one. 3-Resorcylaldehyde oxime contains two dissociable protons. One coming from phenolic -OH and other from oxime OH. In case of oximes the bond formation is through phenolic O and the N of the oxime group acts as the donor. But dideprotonation is also possible. Both the hydroxyl groups lose protons and nitrogen acts as a donor.



Oxime can form 1:1 and 1:2 complexes.

Modes of Bonding in Complexes

As a ligand the oxime group is potentially ambident with possibilities of coordination through nitrogen and/or oxygen atom (s). In the majority of complexes coordination actually occurs at nitrogen. The following modes of metal-oxime linking are proved.



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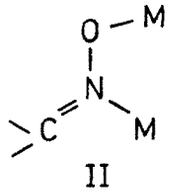
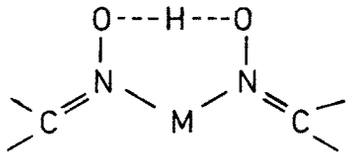
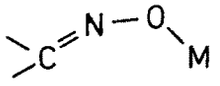


II



III



IV

Oximes can react either as such or in the form of the conjugate base. The hydrogen atom in structure I is kept in parenthesis because this atom may or may not be present. In second structure, one oxime group is present as such while the second group is present as the conjugate base; the single hydrogen atom is then shared the O--H--O bridge. The I and II structural types are quite common. Several polynuclear species containing III are also known. In IV the oximate anion is linked to the metal through oxygen. Only a limited number of complexes belonging to this type are known at present.

Order of Log K_1 Values

Stability orders for different metal ions have been reported by several workers and they were found to follow some definite sequence. Thus, Irving and Williams[25] have observed the stability order for the metal ions of the first transition series as,

$$Zn^{++} > Cu^{++} > Ni^{++} > Co^{++} > Fe^{++} > Mn^{++}$$

Maley and Mellor[26] obtained stability order for the bivalent metal ions as,

$$Pd^{++} > Cu^{++} > Ni^{++} > Pb^{++} > Co^{++} > Zn^{++} > Cd^{++} > Fe^{++} > Mn^{++} > Mg^{++}$$

In the present work order of stability for divalent metal ions with 3-Resorcylaldehyde oxime is as

$$Cu^{++} > Co^{++} > Ni^{++} > Zn^{++} > Mn^{++} > Mg^{++}$$

In the present work there is reversal of order of Ni^{++} and Co^{++} from Irving and Rossottis order. Many workers[27-30] have reported $Co^{++} > Ni^{++}$ for N, O donors and the same is observed in the present study also. For O, O doners the order is reported as $Ni^{++} > Co^{++}$ by many workers[31-34]. These observations lead to author to conclude that the order of log K values will depend both on the nature of the metal ion and on the nature of the donor atoms in particular. Thus there is no abnormality in the results obtained.

Effect of Temperature

Log K_1^H and log K_2^H values for proton-ligand stability constants and log K_1 values for metal-ligand stability constants increases with increase temperature as shown in Table 4.D.1.

Thermodynamic Parameters

The enthalpy change for all metal ions under w study is negative and entropy change is also negative except Mg^{++}. Thus, for Mg^{++}, both heat and entropy changes are favourable for complex formation. But for Mn^{++}, Zn^{++}, Ni^{++}, Co^{++} and Cu^{++} entropy change and enthalpy change opposes the formation of the complex as noted by Bent.[35]

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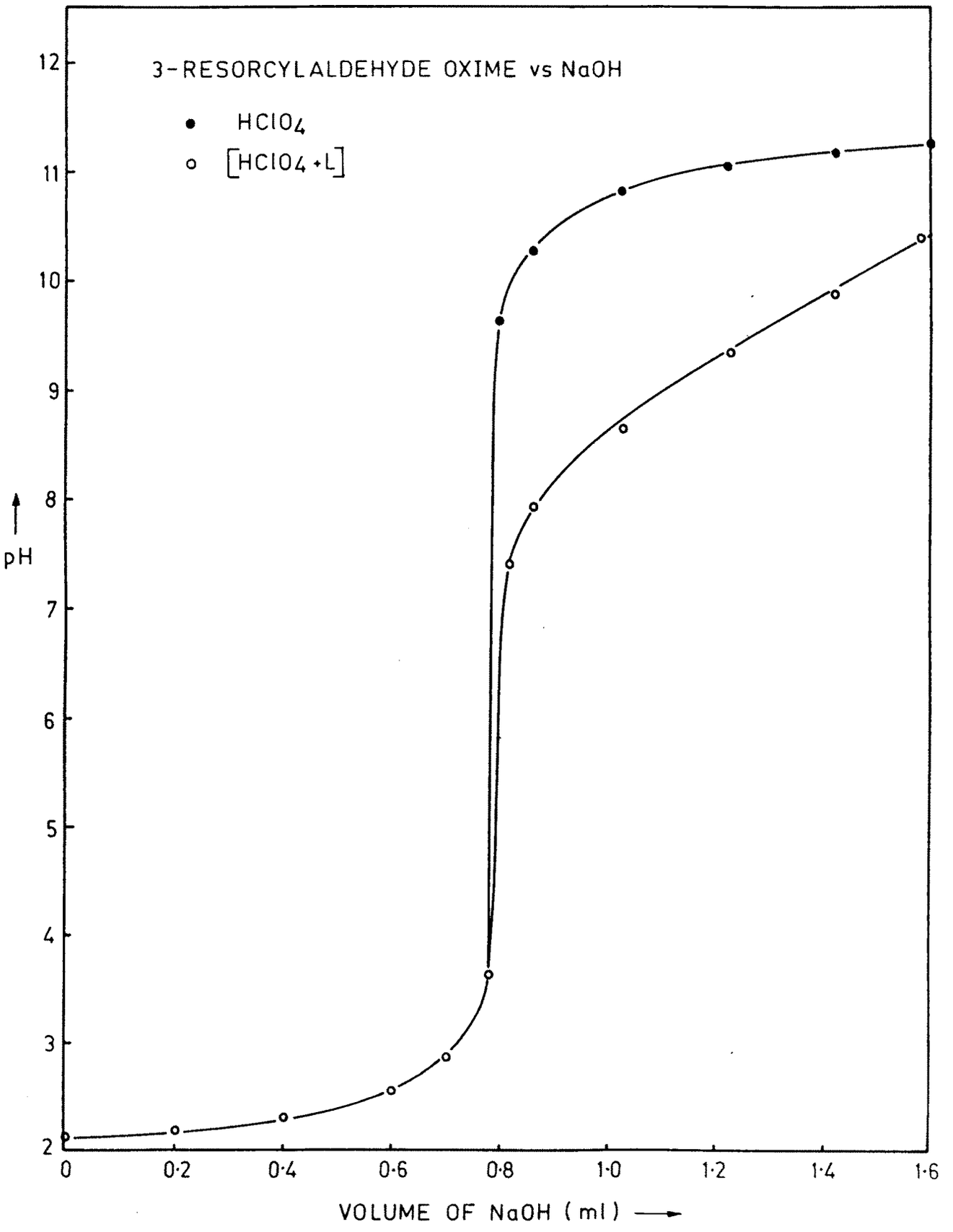

Fig. 4·1·1a : TITRATION CURVES

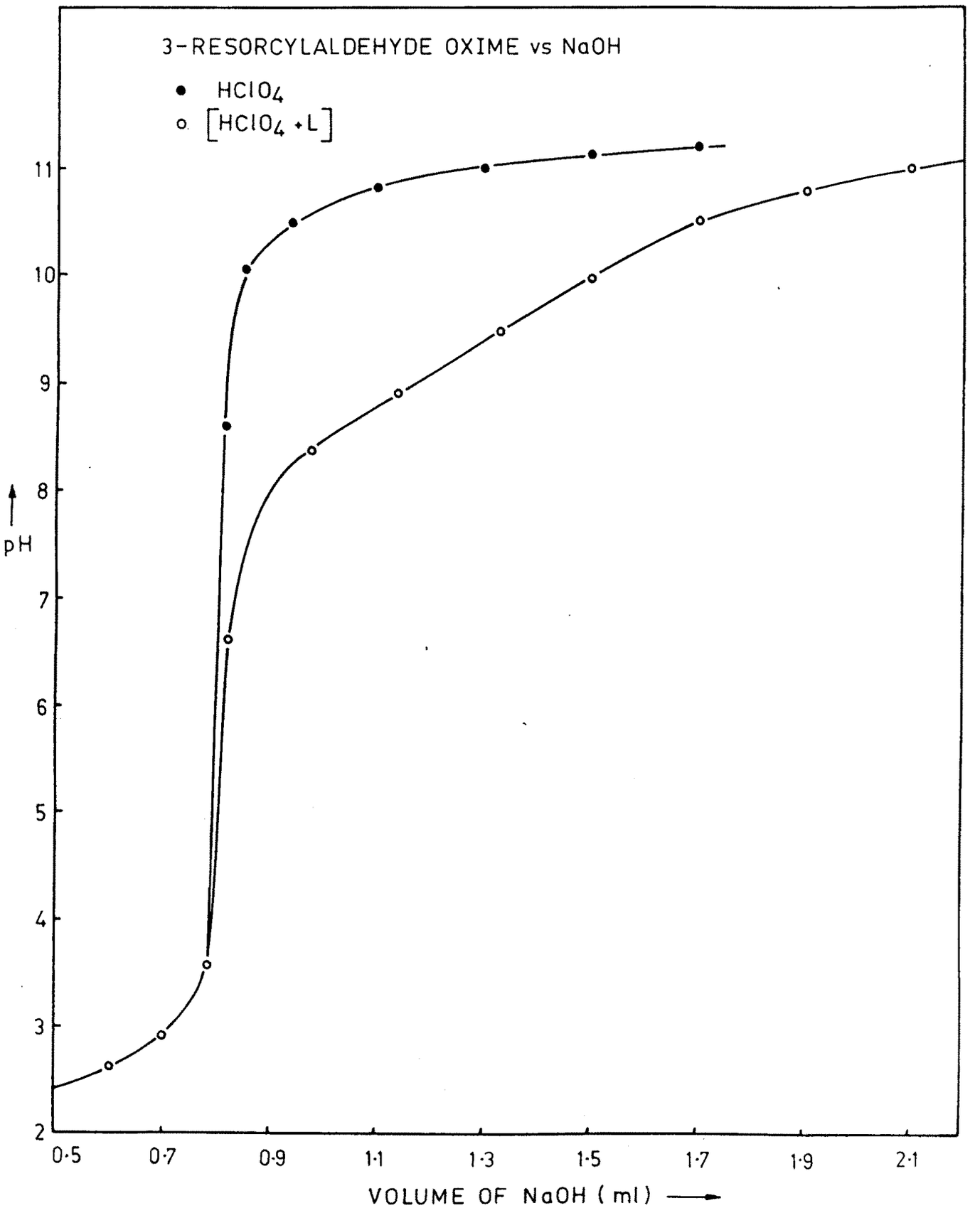

Fig. 4·1·1a : TITRATION CURVES

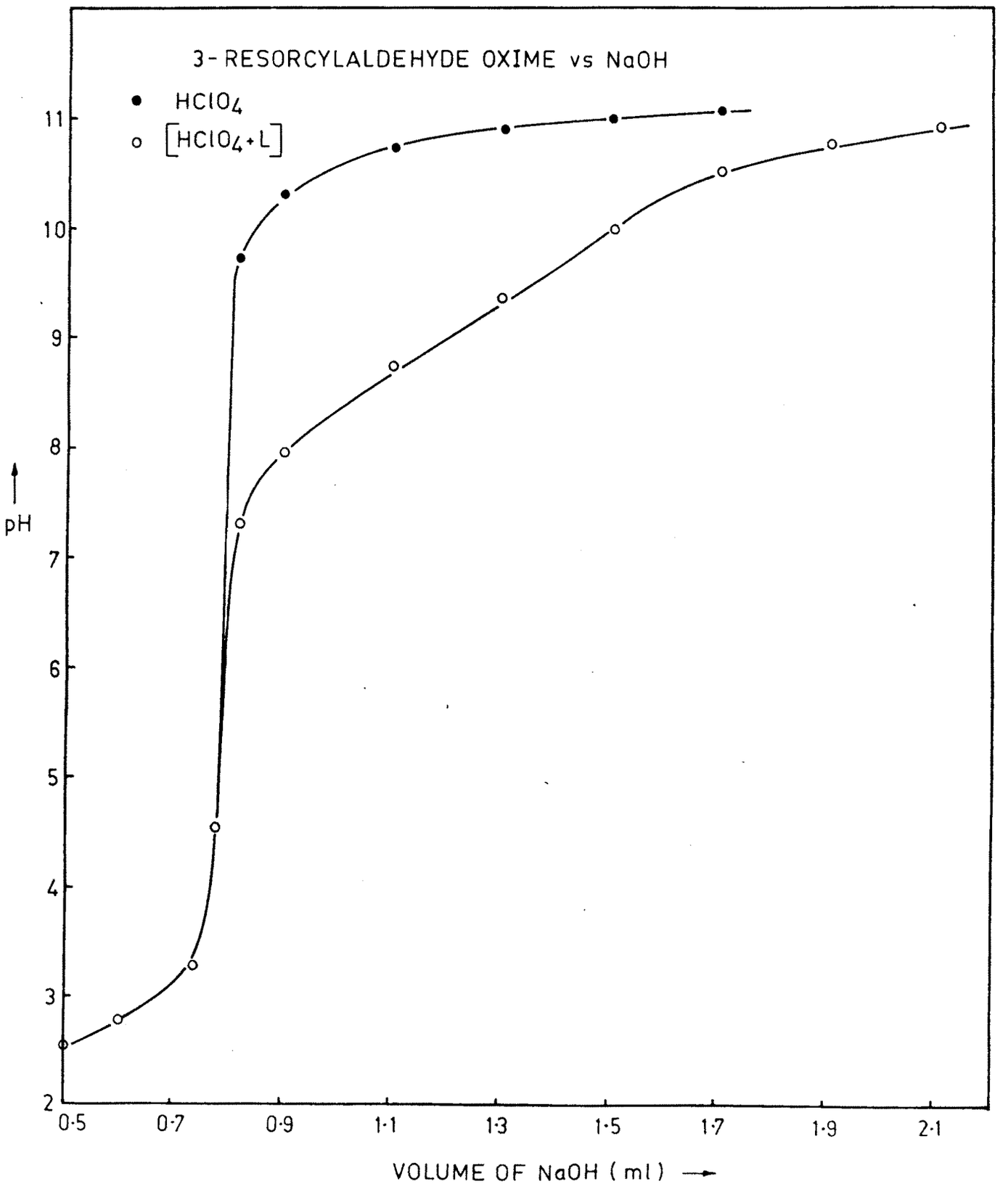

Fig. 4·1·1a : TITRATION CURVES

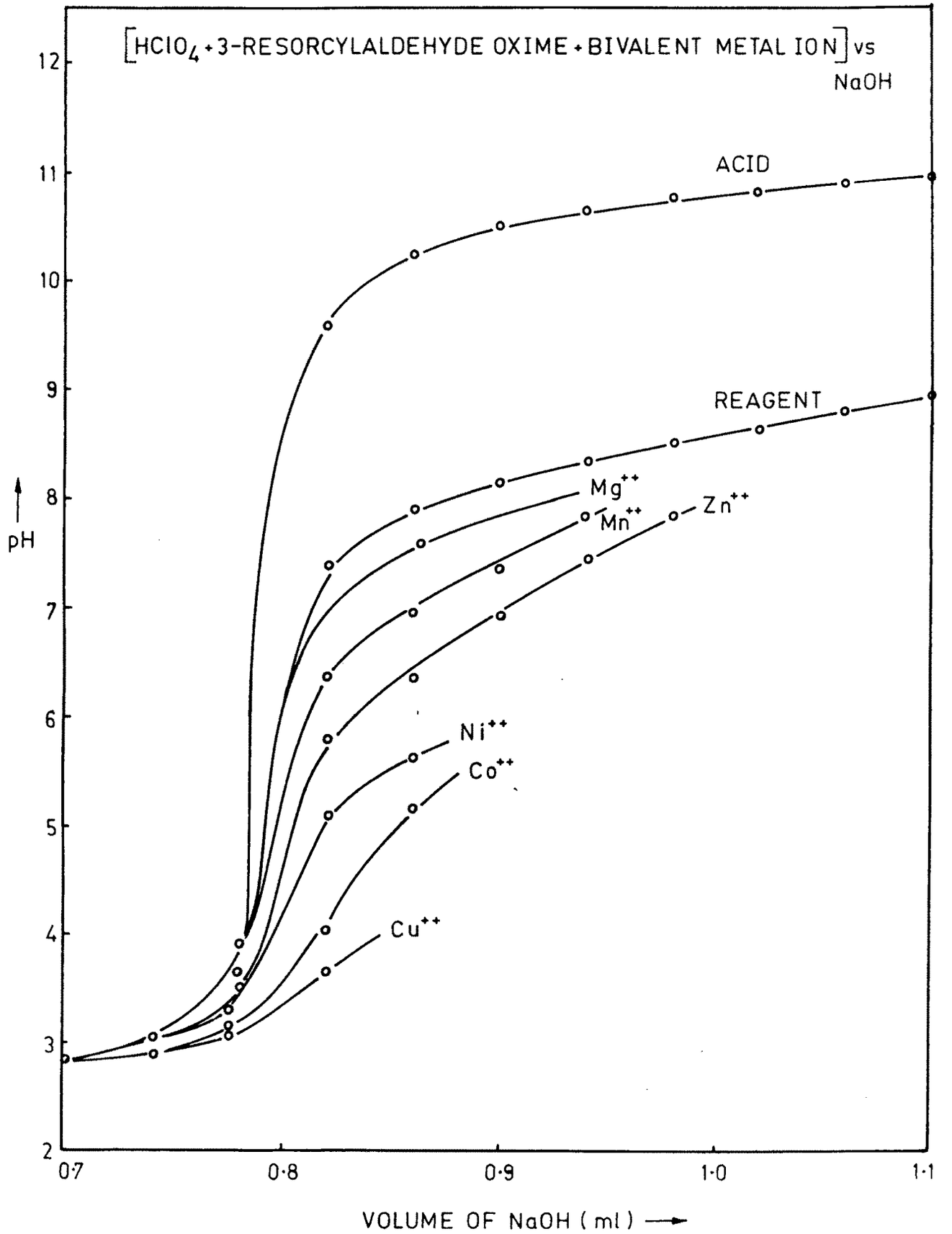

Fig. 4·1·1 b : TITRATION CURVES

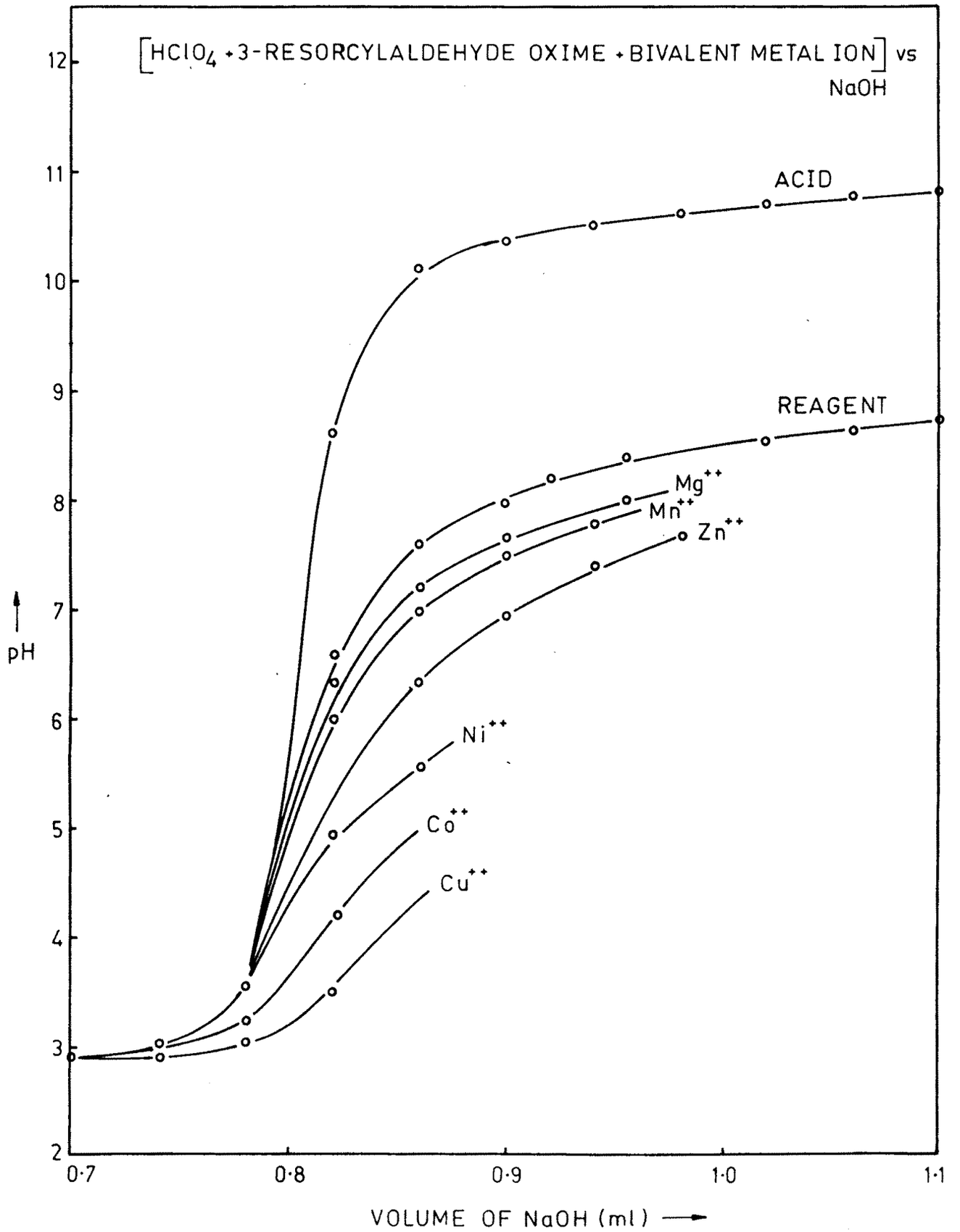

Fig. 4·1·1b : TITRATION CURVES

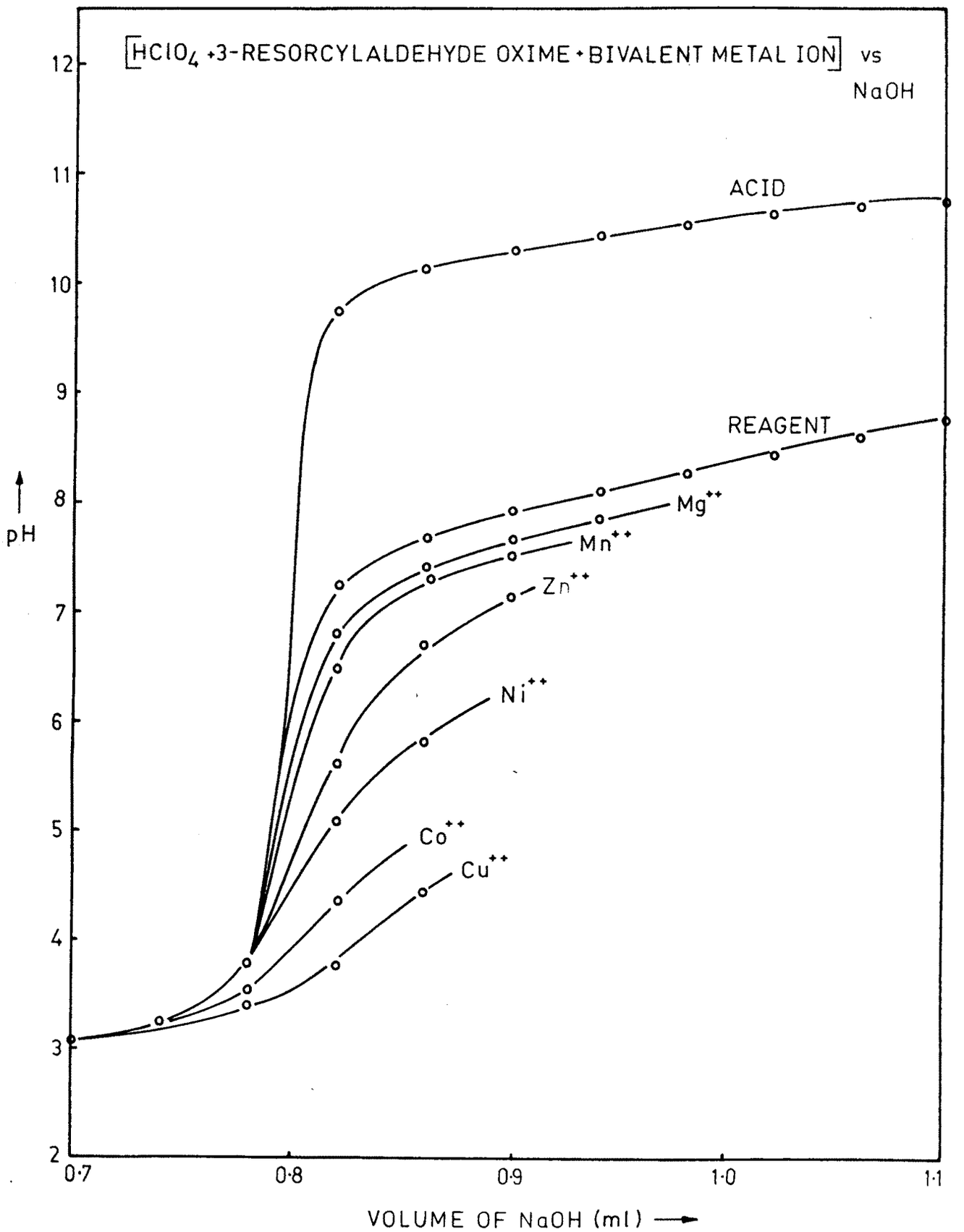

Fig. 4·1·1"b: TITRATION CURVES

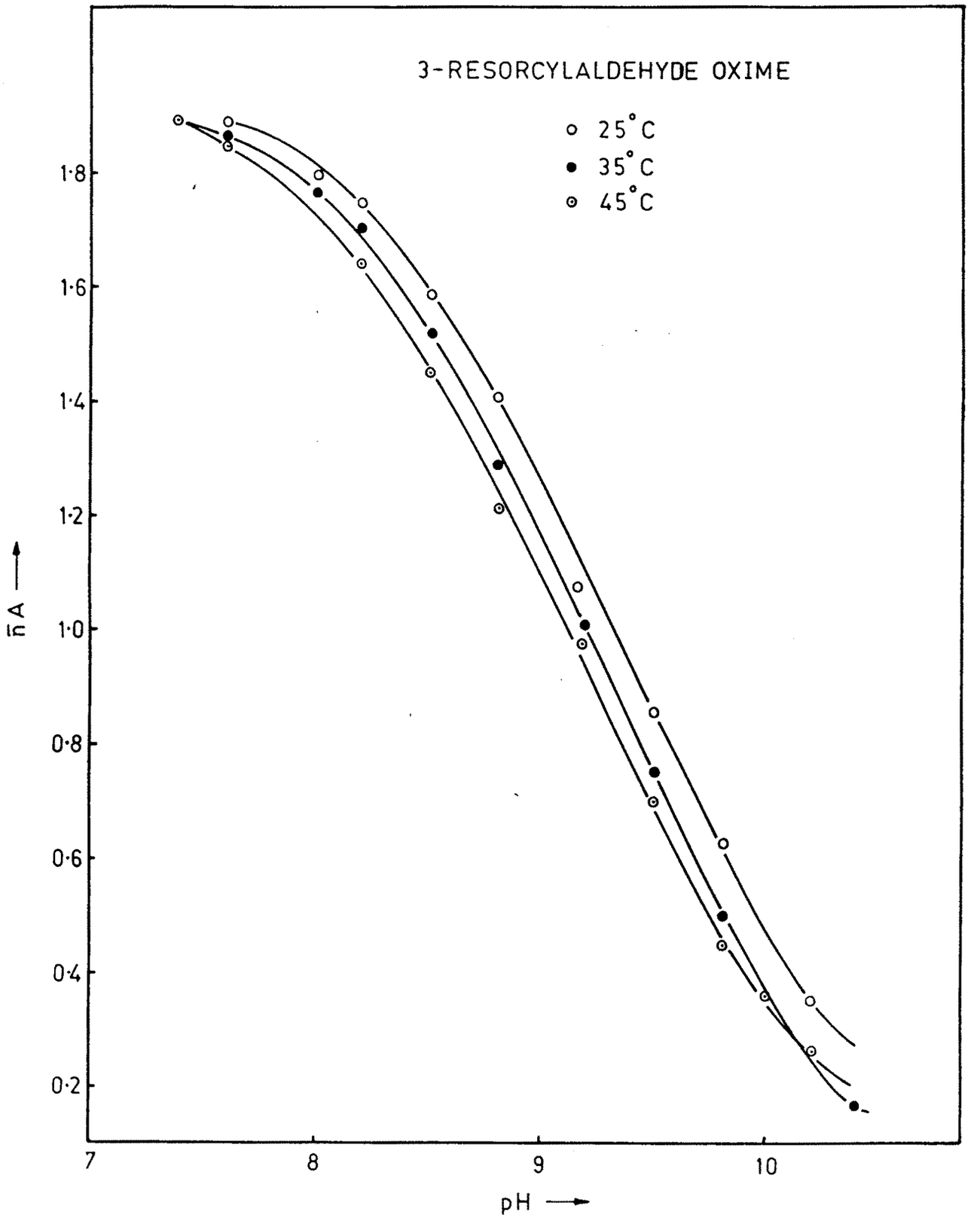

Fig. 4·1·2 : FORMATION CURVES FOR PROTON LIGAND SYSTEMS

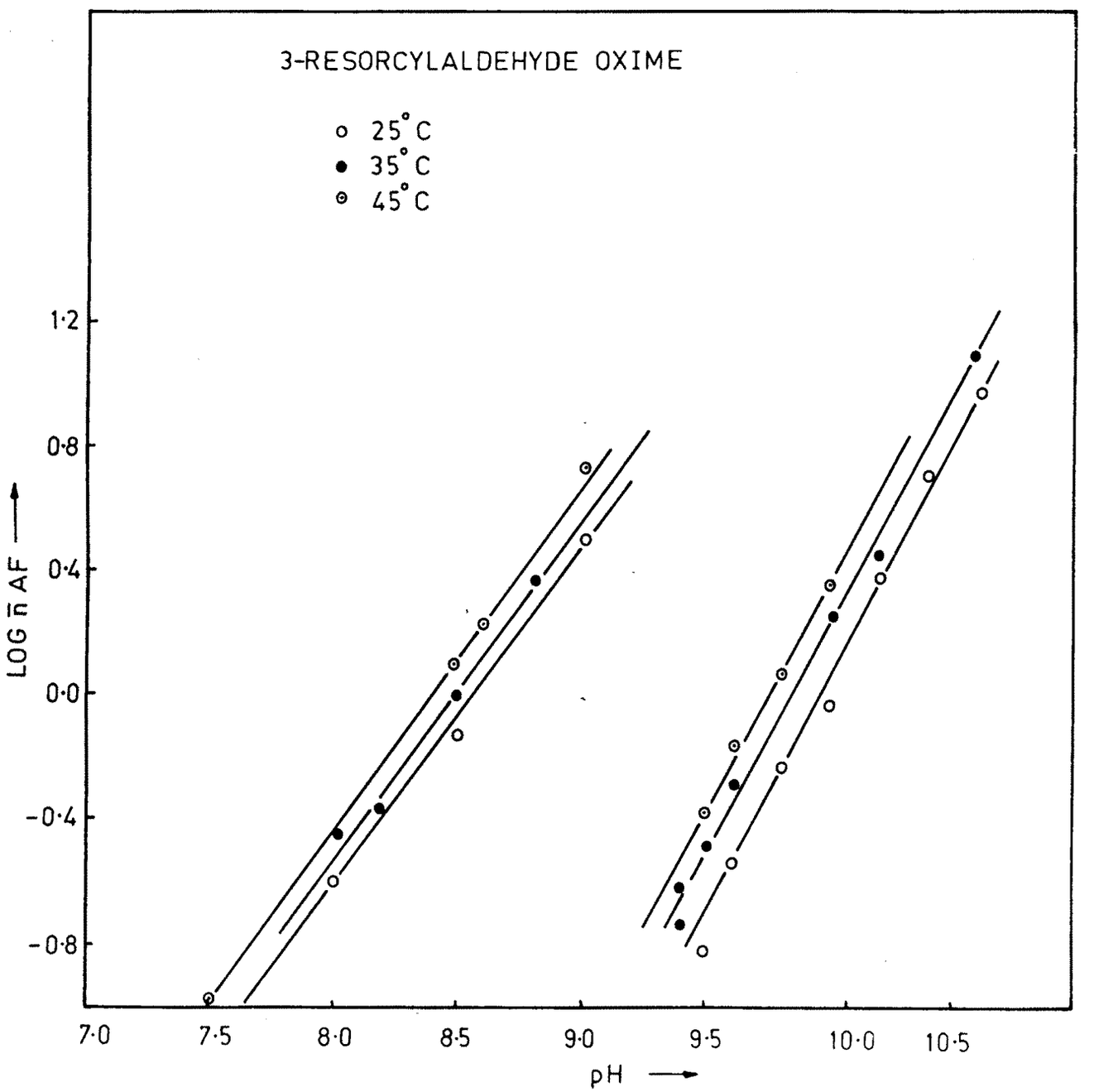

Fig. 4·1·3 : FORMATION CURVES FOR PROTON-LIGAND SYSTEMS

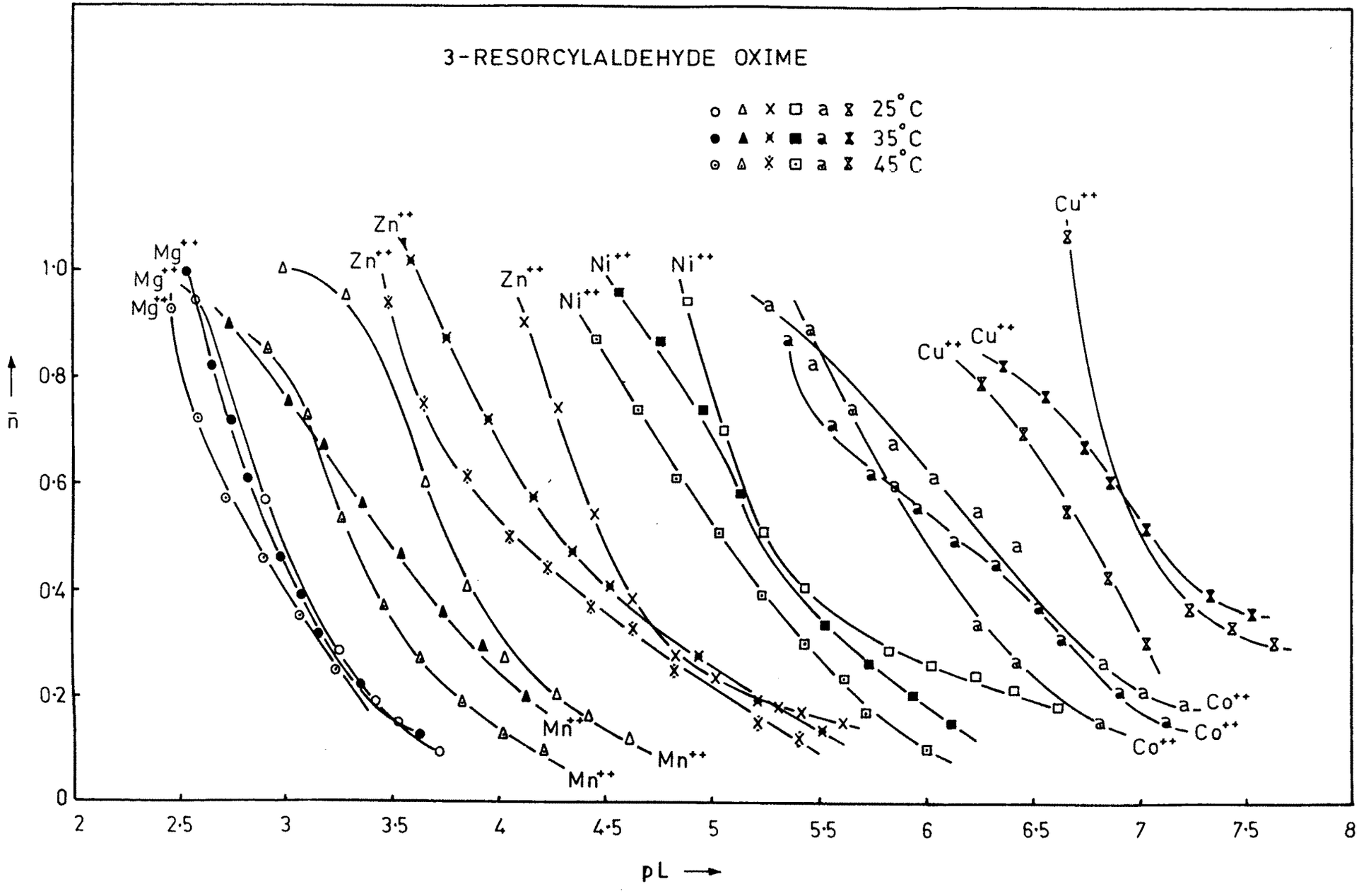

Fig. 4·1·4 : FORMATION CURVES FOR METAL LIGAND SYSTEMS

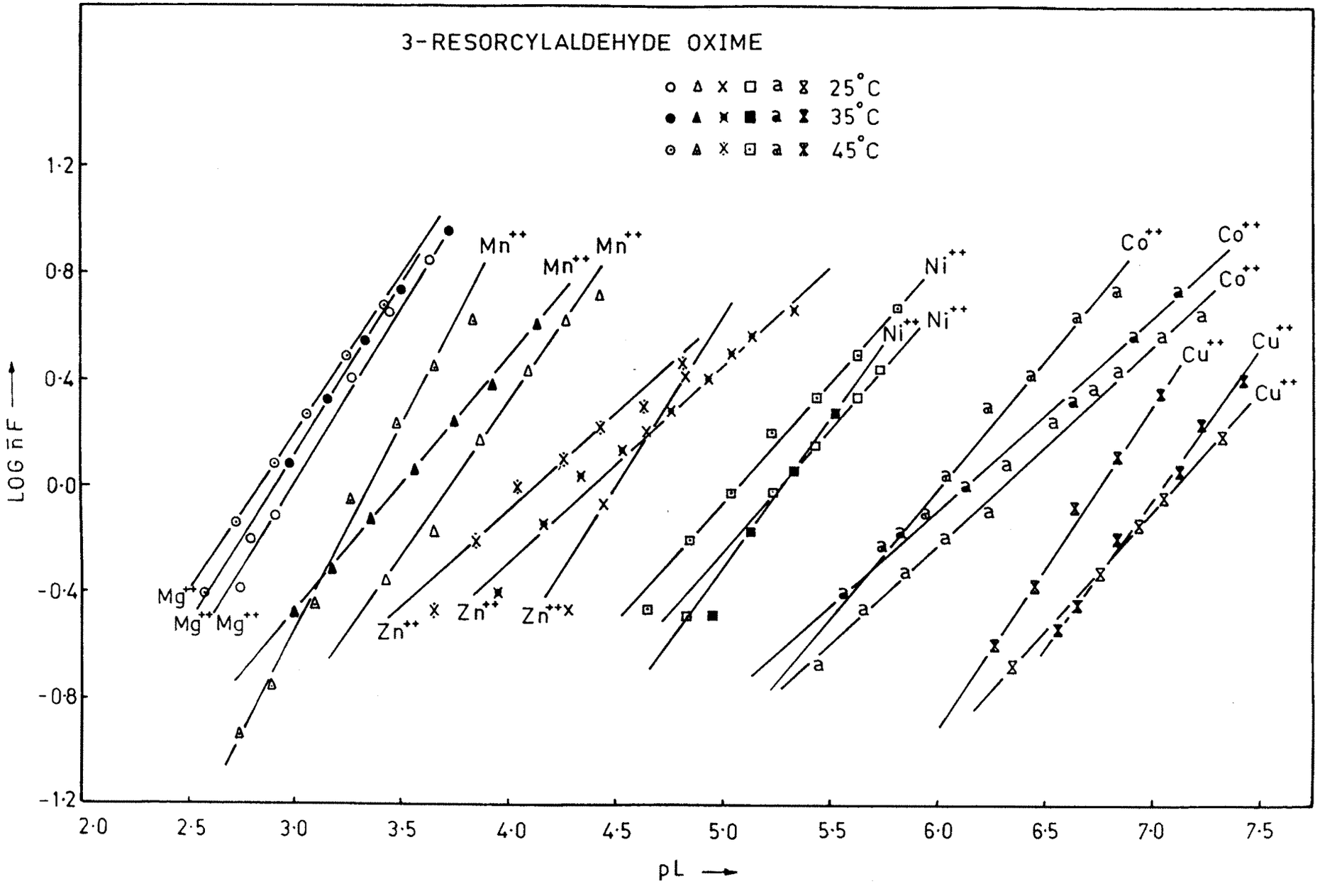

Fig. 4·1·5 : FORMATION CURVES FOR METAL LIGAND SYSTEMS

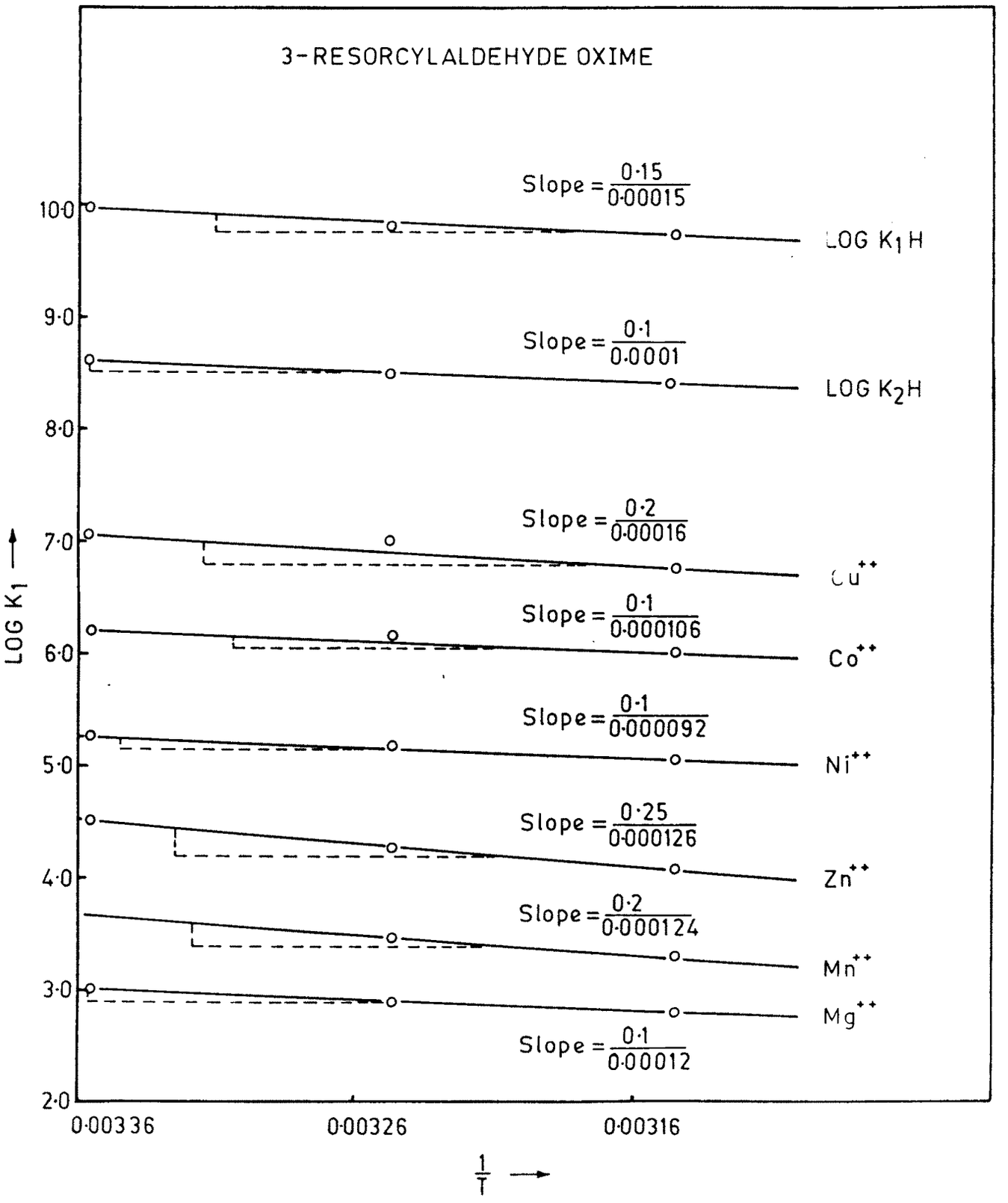

Fig. 4·1·6 : ΔH BY ISOBAR EQUATION