CHAPTER-3

CHAPTER - III

COMPLEX FORMATION BETWEEN BIVALENT METAL IONS AND vic-HYDROXY ALDEHYDES

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COMPLEX FORMATION BETWEEN BIVALENT METAL IONS AND WEAK vic-HYDROXY ALDEHYDES

3.1 INTRODUCTION

Chemical reactions can be studied by using two approaches related to kinetics on one hand and the equilibrium on the other. Simple inorganic reactions are generally instantaneous, proceed in one direction and yield quantitatively the end products. However many reactions between metal ions and coordinating ligands offer interesting and challanging problems related to kinetics and equilibria. Again the nature of kinetic behaviour may be simple to complex and same is true for chemical equilibria involved in such reactions. In the solution phase the formation of complex molecule depends on several experimental parameters. Isolation and identification of each of these species formed in a chemical reaction is often possible but sometimes difficult. In the light of bonding and reactivity a proper understanding of overall reaction is possible. It is known now that the processes of life involve a host of such complicated reactions and therefore importance of a detailed study of equilibria in solution phase cannot be overestimated.

It is obvious that the important types of ligands may have suitable geometry and convenient framework so as to form a

complex molecule without involving undue strain. The vic-hydroxy aldehydes possess an -OH group capable of donating a proton and form an ionic bond at the same time the -CO from aldehyde function has doner O atom and the same is repeated on the other side giving ML_2 type complexes of bidentate monobasic ligands. The equilibrium depends on temperature and concentrations of reacting species. Although in literature there is extensive reporting on complex formation with simple aldehydes[1-8]. The reports of thermodynamic aspects are lacking.

3.2 EXPERIMENTAL

3-nitrosalicylaldehyde, and 5-nitrosalicylaldehyde are prepared by Hach et al. method[9].

In a 5 litre flask equipped with a morter-stirrer place 2000 g glacical HOAC and 500 g salicylaldehyde. Cool to 25°C and add, during 2.5 hours, 400 g of 98 % HNO_3 (sp.gr. 1.50). After the first 100 g of HNO_3 has been added, the temperature must be kept below 15°C. After all HNO_3 has been added, let the temperature rise during 1-2 hours to 45°C, then pore immediately into 10 litre of H_2O containing 1 lb. of cracked ice. Let the mixture stand for 5 hours. The yield should be 90 % of mixed 3-nitro and 5-nitro isomers. These isomers (400 g.) were dissolved in 3 litre H_2O and 100 g NaOH by warming. On standing overnight the 5-nitro isomer pptd out. The 3-nitro isomer behaved like a mixture. It melts from 85° to 100°C until

it was dissolved in boiling alcohol and were slowly precipited by addition of H_2O and cooling in thermos bottle. The resulting tan crystals melts at 108.5 - 9.9°C. The purified 3 nitrosalicylaldehyde is having melting point 109° to 10°C and that of 5-nitrosalicylaldehyde is 126°C. 5-nitrosalicylaldehyde can be also prepared by Deton et al. method[10].

3.3 INSTRUMENTATION

Potentiometric titrations were carried out as described in Chapter Two at temperatures 25°, 35° and 45°C by using Elico Digital pH Meter, Model LI-120 and Philips glass calomel combination electrode.

Table 3.A.1

3 Nitro salicylaldehyde used as a ligand

N^1 = 0.98 M $t = 25^{o}C$ μ = 0.1 M

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

I		II		III	
$[HClO_4]$ vs NaOH		$[HCO_4+L]$ vs NaOH		$[HCO_4+L+Mg^{++}]$ vs NaOH	
E^{o} = 0.02 M		T_L^{o} = 0.01 M		$T_{Mg^{++}}^{o}$ = 0.001 M	
Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH	Vol. of NaOH(ml)	pH
0.00	2.14	0.00	2.15	0.00	2.15
0.20	2.25	0.20	2.25	0.20	2.23
0.40	2.37	0.40	2.38	0.40	2.35
0.60	2.59	0.60	2.64	0.60	2.62
0.70	2.91	0.70	2.93	0.70	2.89
0.74	3.13	0.74	3.13	0.74	3.15
0.78	3.66	0.78	3.66	0.78	3.65
0.82	9.60	0.82	4.20	0.82	4.19
0.86	10.24	0.86	4.91	0.86	4.72
0.90	10.49	0.90	5.27	0.90	5.09
0.94	10.63	0.94	5.52	0.94	5.30
0.98	10.73	0.98	5.67	0.98	5.49
1.02	10.81	1.02	5.90	1.02	5.75
1.06	10.89	1.06	6.24	1.06	6.09
1.10	10.94	1.10	6.38	1.10	ppt.
1.14	10.98	1.14	6.92		
1.18	11.01	1.18	7.96		
1.22	11.05	1.22	10.41		
1.26	11.07	1.26	10.82		
1.28	11.09	1.28			
1.32	11.12	1.32			
1.36	11.14	1.36			

Table 3.A.1 (contd.)

3 Nitro salicylaldehyde used as a ligand

N' = 0.98 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 $[HClO_4+Mn^{++}]$ 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	2.15	0.00	2.16	0.00	2.14
0.20	2.24	0.20	2.26	0.20	2.25
0.40	2.36	0.40	2.36	0.40	2.37
0.60	2.63	0.60	2.58	0.60	2.61
0.70	2.90	0.70	2.86	0.70	2.90
0.74	3.09	0.74	3.05	0.74	3.12
0.78	3.65	0.78	3.35	0.78	3.35
0.82	4.15	0.82	3.75	0.82	3.96 yellow
0.86	4.58	0.86	4.20	0.86	ppt.
0.90	4.90	0.90	4.75		
0.94	5.15	0.94	5.05 yellow		
0.98	5.35	0.98	5.20		
1.02	5.53	1.02	5.37		
		1.06	5.76		
		1.10	ppt.		

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	2.16 colour-	0.00	2.16 colour-	0.00	2.17 colour-
0.20	2.23 less	0.20	2.23 less	0.20	2.26 less
0.40	2.37	0.40	2.37	0.40	2.38
0.60	2.63	0.60	2.63	0.60	2.62
0.70	2.84	0.70	2.84	0.70	2.83
0.74	3.01	0.74	3.09	0.74	3.02
0.78	3.14	0.78	3.44	0.78	3.20
0.82	3.04 yellow	0.82	4.48 yellow	0.82	3.65 yellow
0.86	4.36	0.86	4.88	0.86	4.20
0.90	4.80	0.90	5.11	0.90	4.52
0.94	5.10	0.94	5.30	0.94	4.79
0.98	5.32	0.98	5.50	0.98	5.00
1.02	5.51	1.02	5.70	1.02	ppt.
1.06	5.75	1.06	5.95		
1.10	ppt.	1.10	ppt.		

Table 3.A.1'

3 Nitro salicylaldehyde used as a ligand

N' = 0.98 $t = 35^{o}C$ $\mu = 0.1$ 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	2.31 less	0.20	2.31 less
0.40	2.44	0.40	2.44	0.40	2.44
0.60	2.64	0.60	2.64	0.60	2.66
0.70	2.91	0.70	2.92	0.70	2.91
0.74	3.08	0.74	3.10	0.74	3.08
0.78	3.40	0.78	3.44	0.78	3.40
0.82	8.60	0.82	4.23	0.82	4.20 yellow
0.86	10.10	0.86	4.75 yellow	0.86	4.68
0.90	10.30	0.90	5.12	0.90	4.98
0.94	10.49	0.94	5.34	0.94	5.20
0.98	10.60	0.98	5.51	0.98	5.38
1.02	10.69	1.02	5.70	1.02	5.52
1.06	10.76	1.06	6.00	1.06	5.71
1.10	10.81	1.10	6.20	1.10	5.90
1.14	10.86	1.14	6.80	1.14	ppt.
1.18	10.90	1.18	8.82		
1.22	10.94	1.22	9.60		
1.26	10.97	1.26	10.12		
1.30	11.01	1.30	10.36		
1.34	11.03	1.34	10.53		
1.38	11.05	1.38	10.65		
1.42	11.08	1.42	10.74		
1.46	11.10	1.46	10.81		
1.50	11.11	1.50	10.86		
1.54	11.13	1.54	10.91		
1.58	11.15	1.58	10.95		
1.62	11.17	1.62	10.99		
1.66	11.19	1.66	11.02		
1.70	11.21	1.70	11.05		
		1.74	11.08		
		1.78	11.10		
		1.82	11.12		
		1.86	11.14		
		1.90	11.16		
		1.94	11.17		
		1.98	11.19		
		2.02	11.21 orange yellow		

contd.

Table 3.A.1' (contd.)

'3 Nitro salicylaldehyde used as a ligand

N' = 0.98 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	2.21 colour-	0.00	2.20 colour-	0.00	2.20 colour-
0.20	2.30 less	0.20	2.29 less	0.20	2.28 less
0.40	2.43	0.40	2.42	0.40	2.41
0.60	2.65	0.60	2.63	0.60	2.63
0.70	2.88	0.70	2.84	0.70	2.85
0.74	3.05	0.74	3.00	0.74	2.98
0.78	3.31	0.78	3.22	0.78	3.20
0.82	4.18 yellow	0.82	3.78 yellow	0.82	3.95 yellow
0.86	4.52	0.86	4.36	0.86	ppt.
0.90	4.88	0.90	4.70		
0.94	5.10	0.94	4.90		
0.98	5.28	0.98	5.08		
1.02	5.40	1.02	5.26		
1.06	ppt.	1.06	5.46		
		1.10	5.63		
		1.14	ppt.		

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	2.21 colour-	0.00	2.20 colour-	0.00	2.21 colour-
0.20	2.29 less	0.20	2.29 less	0.20	2.31 less
0.40	2.43	0.40	2.42	0.40	2.44
0.60	2.66	0.60	2.62	0.60	2.67
0.70	2.90	0.70	2.84	0.70	2.89
0.74	3.05	0.74	3.00	0.74	3.00
0.78	3.37	0.78	3.26 yellow	0.78	3.20
0.82	4.00 yellow	0.82	3.86	0.82	3.64 yellow
0.86	4.41	0.86	4.35	0.86	4.21
0.90	4.65	0.90	4.70	0.90	4.55
0.94	5.05	0.94	4.89	0.94	4.83
0.98	5.25	0.98	5.10	0.98	5.00
1.02	5.73	1.02	5.31	1.02	ppt.
1.06	6.17	1.06	5.62		
1.10	ppt.	1.10	ppt.		

Table 3.A.1"

3 Nitro salicylaldehyde 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

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	2.35 colour-	0.00	2.35 colour-	0.00	2.35 colour-
0.20	2.42 less	0.20	2.43 less	0.20	2.44 less
0.40	2.55	0.40	2.55	0.40	2.57
0.60	2.80	0.60	2.80	0.60	2.81
0.70	3.04	0.70	3.04	0.70	3.05
0.74	3.20	0.74	3.24	0.74	3.24
0.78	3.57	0.78	3.60	0.78	3.64
0.82	9.50	0.82	4.36 yellow	0.82	4.35 yellow
0.86	10.10	0.86	4.75	0.86	4.65
0.90	10.30	0.90	4.98	0.90	5.88
0.94	10.44	0.94	5.17	0.94	5.05
0.98	10.53	0.98	5.35	0.98	5.20
1.02	10.61	1.02	5.50	1.02	5.32
1.06	10.70	1.06	5.74	1.06	5.52
1.10	10.74	1.10	5.97	1.10	5.69
1.14	10.79	1.14	6.68	1.14	6.46
1.18	10.83	1.18	9.55	1.18	ppt.
1.22	10.86	1.22	10.10		
1.26	10.90	1.26	10.30		
1.30	10.92	1.30	10.40		
1.34	10.94	1.34	10.52		
1.38	10.96	1.38	10.60		
1.42	10.99	1.42	10.68		
1.46	11.00	1.46	10.74		
1.50	11.02	1.50	10.79		
1.54	11.03	1.54	10.82		
1.58	11.04	1.58	10.86		
1.62	11.06	1.62	10.89		
1.66	11.07	1.66	10.91		
1.70	11.09	1.70	10.94		
1.74	11.10	1.74	10.96		
1.78	11.11	1.78	10.98		
1.82	11.12	1.82	11.00		
1.86	11.13	1.86	11.01		
1.90	11.14	1.90	11.03		
		1.94	11.04		
		1.98	11.05		
		2.02	11.06		
		2.06	11.08		
		2.10	11.09		

contd..

Table 3.A.1" (contd.)

3 Nitro salicylaldehyde 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	
0.00	2.35 colour-	0.00	2.35 colour-	0.00	2.35 colour-
0.20	2.44 less	0.20	2.43 less	0.20	2.43 less
0.40	2.579	0.40	2.56	0.40	2.56
0.60	2.81	0.60	2.78	0.60	2.79
0.70	3.05	0.70	3.04	0.70	3.00
0.74	3.23	0.74	3.20	0.74	3.20
0.78	3.60	0.78	3.38	0.78	3.50 yellow
0.82	4.36 yellow	0.82	3.72 yellow	0.82	4.00
0.86	4.57	0.86	4.30	0.86	ppt.
0.90	4.79	0.90	4.62		
0.94	4.97	0.94	4.80		
0.98	5.10	0.98	4.98		
1.02	5.22	1.02	5.12		
1.06	5.34	1.06	5.56		
1.10	5.93	1.10	5.73		
1.14	ppt	1.14	6.00		
		1.18	ppt.		

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	2.34 colour-
0.20	2.43 less	0.20	2.43 less	0.20	2.42 less
0.40	2.57	0.40	2.56	0.40	2.55
0.60	2.80	0.60	2.78	0.60	2.78
0.70	3.04	0.70	3.00	0.70	2.99
0.74	3.21	0.74	3.16	0.74	3.12
0.78	3.48 yellow	0.78	3.44	0.78	3.38 yellow
0.82	4.02	0.82	3.94	0.82	3.69
0.86	4.56	0.86	4.55	0.86	4.18
0.90	4.82	0.90	4.85	0.90	4.48
0.94	5.03	0.94	5.05	0.94	4.68
0.98	5.23	0.98	5.23	0.98	4.82
1.02	5.40	1.02	5.40	1.02	5.02
1.06	5.60	1.06	5.60	1.06	ppt.
1.10	5.84	1.10	5.83		
1.14	ppt.	1.14	ppt.		

Table 3.A.2

5 Nitro salicylaldehyde used as a ligand

N' = 0.98 $t = 25^{o}C$ $\mu = 0.1$ 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	2.09	0.00	2.09	colour-	0.00	2.09	colour-
0.20	2.17	0.20	2.18	less	0.20	2.18	less
0.40	2.30	0.40	2.32		0.40	2.31	
0.60	2.53	0.60	2.54		0.60	2.55	
0.70	2.87	0.70	2.90		0.70	2.88	
0.74	3.13	0.74	3.15		0.74	3.14	
0.78	3.66	0.78	3.67		0.78	3.66	
0.82	11.00	0.82	4.55	yellow	0.82	4.45	yellow
0.86	11.41	0.86	4.91		0.86	4.75	
0.90	11.66	0.90	5.15		0.90	4.97	
0.94	11.77	0.94	5.38		0.94	5.25	
0.98	11.87	0.98	5.56		0.98	5.42	
1.02	11.94	1.02	5.65		1.02	5.52	
1.06	12.03	1.06	5.90		1.06	5.76	
1.10	12.10	1.10	6.13		1.10	6.08	
1.14	12.16	1.14	6.51		1.14	6.49	
		1.18	7.45		1.18	7.02	
		1.22	11.13		1.22	ppt.	
		1.26	11.57				
		1.30	11.76				
		1.34	11.90				
		1.38	12.01				

Table 3.A.2

5 Nitro salicylaldehyde 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	colour-	0.00	2.09	colour-	0.00	2.09	colour-
0.20	2.18	less	0.20	2.18	less	0.20	2.18	less
0.40	2.31		0.40	2.30		0.40	2.30	
0.60	2.55		0.60	2.56		0.60	2.54	
0.70	2.88		0.70	2.70		0.70	2.85	
0.74	3.14		0.74	2.85		0.74	2.99	
0.78	3.60		0.78	3.08		0.78	3.33	
0.82	4.30	yellow	0.82	3.47	yellow	0.82	3.92	yellow
0.86	4.65		0.86	4.30		0.86	4.31	
0.90	4.90		0.90	4.74		0.90	4.58	
0.94	5.04		0.94	5.03		0.94	ppt.	
0.98	5.25		0.98	5.15				
1.02	5.42		1.02	5.42				
1.06	5.60		1.06	5.58				
1.10	5.77		1.10	5.90				
1.14	6.05		1.14	6.03				
1.18	6.50		1.18	ppt.				
1.22	ppt.							

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	2.09	colour-	0.00	2.09	colour-	0.00	2.09	colour-
0.20	2.19	less	0.20	2.20	less	0.20	2.19	less
0.40	2.31		0.40	2.33		0.40	2.33	
0.60	2.54		0.60	2.55		0.60	2.56	
0.70	2.80		0.70	2.75		0.70	2.75	
0.74	3.0		0.74	2.90		0.74	2.90	
0.78	3.45		0.78	3.15		0.78	3.10	
0.82	3.80	yellow	0.82	3.69	yellow	0.82	3.25	
0.86	4.18		0.86	4.14		0.86	green ppt.	
0.90	4.39		0.90	4.45				
0.94	4.63		0.94	4.62				
0.98	4.79		0.98	4.80				
1.02	4.96		1.02	4.99				
1.06	5.10		1.06	5.12				
1.10	ppt		1.10	ppt				

Table 3.A.2'

5 Nitro salicylaldehyde used as a ligand

N' = 0.98 t = 35°C μ = 0.1 M

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

I		II		III	
$[HClO_4]$ vs NaOH		$[HClO_4+L]$ vs NaOH		$[HClO_4+L+Mg^{++}]$ vs NaOH	
E^{o} = 0.02 M		T_L^{o} = 0.01 M		$T_{Mg^{++}}^{o}$ = 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-
0220	2.30	0.20	2.30 less	0.20	2.28 less
0.40	2.44	0.40	2.42	0.40	2.42
0.60	2.64	0.60	2.62	0.60	2.64
0.70	2.88	0.70	2.81	0.70	2.85
0.74	3.03	0.74	2.93	0.74	2.98
0.78	3.35	0.78	3.13	0.78	3.33
0.82	8.60	0.82	4.40 yellow	0.82	3.85 yellow
0.86	10.10	0.86	4.74	0.86	4.74
0.90	10.33	0.90	5.10	0.90	5.01
0.94	10.49	0.94	5.25	0.94	5.18
0.98	10.60	0.98	5.42	0.98	5.30
1.02	10.69	1.02	5.56	1.02	5.45
1.06	10.76	1.06	5.70	1.06	5.55
1.10	10.81	1.10	5.88	1.10	5.70
1.14	10.86	1.14	6.08	1.14	5.95
1.18	10.90	1.18	6.38	1.18	6.84
1.22	10.94	1.22	8.72	1.22	ppt.
1.26	10.97	1.26	10.07		
1.30	11.01	1.30	10.34		
1.34	11.03	1.34	10.52		
1.38	11.05	1.38	10.66		
1.42	11.08	1.42	10.76		
1.46	11.10	1.46	10.84		
1.50	11.11	1.50	10.90		
1.54	11.13	1.54	10.95		
1.58	11.15	1.58	10.99		
1.62	11.17	1.62	10.04		
1.66	11.19	1.66	11.07		
1.70	11.21	1.70	11.10		
		1.74	11.12		
		1.78	11.14		
		1.82	11.16		
		1.86	11.18		
		1.90	11.20		
		1.94	11.22		
		1.98	11.24		
		2.02	11.25		
		2.06	11.27		
		2.10	11.29		

Table 3.A.2' (contd.)

5 Nitro salicylaldehyde used as a ligand

N' = 0.98 $\quad$ t = 35°C $\quad$ μ = 0.1 M

Medium = 50 % v/v ethanol-water $\quad$ 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	
0.00	2.21 colour-	0.00	2.21 colour-	0.00	2.21 colour-
0.20	2.30 less	0.20	2.29 less	0.20	2.30 less
0.40	2.43	0.40	2.42	0.40	2.42
0.60	2.67	0.60	2.65	0.60	2.64
0.70	2.90	0.70	2.83	0.70	2.85 yellow
0.74	3.02	0.74	2.97	0.74	2.95
0.78	2.34	0.78	3.19	0.78	3.28
0.82	4.28 yellow	0.82	3.65 yellow	0.82	3.72
0.86	4.60	0.86	4.33	0.86	4.35
0.90	4.85	0.90	4.59	0.90	ppt.
0.94	4.99	0.94	4.82		
0.98	5.12	0.98	5.00		
1.02	5.25	1.02	5.18		
1.06	5.47	1.06	5.34		
1.10	5.65	1.10	5.53		
1.14	5.94	1.14	5.77		
1.18	6.75	1.18	6.18		
1.22	ppt	1.22	ppt		

VII $[HClO_4+L+Ni^{++}]$vs NaOH $T^{o}_{Ni^{++}}$ = 0.001 M		VIII $[HClO_4+L+Co^{++}]$vs NaOH $T^{o}_{Cd^{++}}$ = 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	2.21 colour-	0.00	2.21 colour-	0.00	2.21 colour-
0.20	2.30 less	0.20	2.30 less	0.20	2.30 less
0.40	2.42	0.40	2.43	0.40	2.42
0.60	2.64	0.60	2.67	0.60	2.64
0.70	2.85	0.70	2.90	0.70	2.84
0.74	2.90	0.74	3.06	0.74	2.97
0.78	3.04	0.78	3.31	0.78	3.13
0.82	3.25 yellow	0.82	3.95 yellow	0.82	3.38
0.86	3.63	0.86	4.43	0.86	3.60 green
0.90	4.15	0.90	4.71	0.90	ppt
0.94	4.46	0.94	4.92		
0.98	4.73	0.98	5.11		
1.02	4.94	1.02	5.25		
1.06	ppt	1.06	ppt		

Table 3.A.2"

5 Nitro-salicylaldehyde 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	2.35	0.00	2.35 colour-	0.00	2.35 colour-
0.20	2.43	0.20	2.44	0.20	2.43
0.40	2.56	0.40	2.57	0.40	2.55
0.60	2.76	0.60	2.76	0.60	2.78
0.70	2.93	0.70	2.93	0.70	2.94
0.74	3.16	0.74	3.17	0.74	3.16
0.78	3.40	0.78	3.41	0.78	3.40
0.82	4.25	0.82	4.11 yellow	0.82	4.10 yellow
0.86	9.97	0.86	4.66	0.86	4.58
0.90	10.24	0.90	4.86	0.90	4.78
0.94	10.39	0.94	5.05	0.94	4.95
0.98	10.50	0.98	5.20	0.98	5.12
1.02	10.59	1.02	5.34	1.02	5.25
1.06	10.66	1.06	5.50	1.06	5.35
1.10	10.73	1.10	5.74	1.10	5.49
1.14	10.77	1.14	6.15	1.14	6.40
1.18	10.82	1.18	7.30	1.18	ppt.
1.22	10.87	1.22	9.88		
1.26	10.90	1.26	10.19		
1.30	10.93	1.30	10.33		
1.34	10.96	1.34	10.44		
1.38	10.99	1.38	10.54		
1.42	11.01	1.42	10.62		
1.46	11.03	1.46	10.68		
1.50	11.05	1.50	10.72		
1.54	11.07	1.54	10.77		
1.58	11.08	1.58	10.80		
1.62	11.10	1.62	10.83		
1.66	11.11	1.66	10.86		
1.70	11.12	1.70	10.89		
		1.74	10.91		
		1.78	10.93		
		1.82	10.95		
		1.86	10.97		
		1.90	10.99		
		1.94	11.02		
		1.98	11.04		
		2.02	11.06		
		2.06	11.07		
		2.10	11.08		
		2.14	11.09		
		2.18	11.10		

Table 3.A.2[#]

5 Nitro salicylaldehyde 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

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	2.34 colour-
0.20	2.42 less	0.20	2.41 less	0.20	2.41 less
0.40	2.55	0.40	2.53	0.40	2.55
0.60	2.78	0.60	2.75	0.60	2.76
0.70	2.95	0.70	2.98	0.70	2.98
0.74	3.15	0.74	3.09	0.74	3.11
0.78	3.42	0.78	3.35	0.78	3.40
0.82	4.00 yellow	0.82	3.99 yellow	0.82	3.85 yellow
0.86	4.42	0.86	4.46	0.86	4.25
0.90	4.65	0.90	4.72	0.90	ppt.
0.94	4.84	0.94	4.93		
0.98	5.00	0.98	ppt.		
1.02	5.12				
1.06	5.50				
1.10	5.71				
1.14	6.04				
1.18	ppt.				

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	2.34 colour-
0.20	2.44 less	0.20	2.44 less	0.20	2.40 less
0.40	2.56	0.40	2.57	0.40	2.53
0.60	2.78	0.60	2.79	0.60	2.75
0.70	2.94	0.70	2.98	0.70	2.95
0.74	3.10	0.74	3.15	0.74	3.09
0.78	3.32	0.78	3.35	0.78	3.28
0.82	3.68 yellow	0.82	3.85 yellow	0.82	3.60
0.86	4.15	0.86	4.45	0.86	3.85
0.90	4.40	0.90	4.62	0.90	ppt.
0.94	4.70	0.94	4.90		
0.98	4.85	0.98	5.07		
1.02	ppt.	1.02	ppt.		

Table 3.B.1

3 Nitro salicylaldehyde used as ligand

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

pH	V'	V''	$\bar{n}_A$	log $\bar{n}_A F$
4.0	0.7866	0.8066	0.04904	- 1.2913
4.5	0.7891	0.8400	0.1248	- 0.8459
5.0	0.7916	0.8700	0.1922	- 0.6236
5.2	0.7916	0.8966	0.2549	- 0.4659
5.4	0.7936	0.9200	0.3098	- 0.3417
5.5	0.7941	0.9400	0.3577	- 0.2542
5.6	0.7946	0.9633	0.4135	- 0.1518
5.8	0.7956	1.0066	0.5172	.0.0300
6.0	0.7966	1.0400	0.5967	0.1701
6.2	0.7976	1.0800	0.6921	0.3521
6.4	0.7986	1.1040	0.7487	0.4741
6.5	0.7991	1.1140	0.7716	0.5288
6.6	0.7996	1.1233	0.7938	0.5854
6.8	0.8006	1.1366	0.8233	0.6684
7.0	0.8016	1.1466	0.8455	0.7382
7.5	0.8041	1.1700	0.8969	0.9395
8.0	0.8066	1.1800	0.9152	1.0331

Proton-ligand stability constant

Method	log K_1^H
Half integral (value from fig. 3.1.2)	5.766
Graphical (value from fig. 3.1.3)	5.8

Table 3.b.1'

3 Nitro salicylaldehyde used as ligand

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

pH	V'	V"	$\bar{n}_A$	log $\bar{n}_A F$
3.5	0.78	0.7833	0.9919	- 2.0880
4.0	0.7832	0.8066	0.9426	- 1.2137
4.5	0.7872	0.8400	0.8706	- 0.8277
4.6	0.7880	0.8466	0.8564	- 0.7753
4.8	0.7896	0.8633	0.8193	- 0.6555
5.0	0.7912	0.8866	0.7662	- 0.5154
5.2	0.7928	0.9133	0.7047	- 0.3777
5.4	0.7944	0.9500	0.6186	- 0.2100
5.5	0.7952	0.9700	0.5715	- 0.1251
5.6	0.7960	0.9966	0.5083	- 0.0145
5.8	0.7976	1.0400	0.4059	0.3949
6.0	0.7992	1.0800	0.2871	0.3949
6.2	0.8008	1.1000	0.2660	0.4408
6.4	0.8024	1.1166	0.2300	0.5248
6.5	0.8032	1.1233	0.2157	0.5607
6.6	0.8040	1.1300	0.2011	0.5991
6.8	0.8056	1.1400	0.1806	0.6568
7.0	0.8072	1.1466	0.1682	0.6942
7.2	0.8088	1.1533	0.1557	0.7342
7.5	0.8112	1.1666	0.1292	0.8286
8.0	0.8150	1.1800	0.0813	1.0531

Proton-Ligand stability constant

Method	log K_1^H
Half integral (value from fig. 3.1.2)	5.6
Graphical (value from fig. 3.1.3)	5.64

Table 3.B.1"

3 Nitro salicylaldehyde 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	0.8018	0.8333	0.9280	- 1.0875
5.0	0.8035	0.9033	0.7555	- 0.4910
5.2	0.8042	0.9466	0.6511	- 0.2709
5.4	0.8056	0.9966	0.5323	- 0.0562
5.5	0.8060	1.0200	0.4756	0.0425
5.6	0.8063	1.0400	0.4272	0.1274
5.8	0.8070	1.0740	0.3457	0.2771
6.0	0.8077	1.1033	0.2759	0.4191
6.2	0.8084	1.1200	0.2363	0.5094
6.4	0.8091	1.1300	0.2137	0.5658
6.5	0.8094	1.1333	0.2062	0.5854
6.6	0.8098	1.1366	0.1991	0.6045
6.8	0.8105	1.1400	0.1936	0.6212
7.0	0.8112	1.1430	0.1872	0.6377
7.5	0.8130	1.1505	0.1732	0.6789
8.0	0.8147	1.1580	0.1588	0.7242
8.5	0.8165	1.1655	0.1449	0.7709
9.0	0.8183	1.1730	0.1308	0.8226
9.5	0.8200	1.1800	0.1192	0.8691
10.0	0.8500	1.2140	0.1090	0.9125
10.5	0.9600	1.3300	0.0965	0.9714

Proton-ligand stability constant

Method	log K_1^H
Half integral (value from fig. 3.1.2)	5.44
Graphical (value from fig. 3.1.3)	5.47

Table 3.B.2

5 Nitro-salicylaldehyde used as a ligand

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

pH	V'	V''	$\bar{n}_A$	log $\bar{n}_A F$
4.0	0.7833	0.7900	0.9835	-1.7772
4.2	0.7845	0.8000	0.9698	-1.5069
4.4	0.7857	0.8100	0.9404	-1.1982
4.5	0.7862	0.8167	0.9252	-1.0924
4.6	0.7868	0.8266	0.9024	-0.9660
4.8	0.7879	0.8500	0.8477	-0.7457
5.0	0.7891	0.8733	0.7935	-0.5848
5.2	0.7903	0.9100	0.7066	-0.3817
5.4	0.7915	0.9466	0.6198	-0.2123
5.5	0.7922	0.9666	0.5720	-0.1260
5.6	0.7927	0.9933	0.5083	-0.0145
5.8	0.7939	1.0400	0.3967	0.1820
6.0	0.7949	1.0767	0.3093	0.3489
6.2	0.7961	1.1100	0.2307	0.4831
6.4	0.7973	1.1333	0.1765	0.5690
6.5	0.7980	1.1400	0.1617	0.7148
6.6	0.7985	1.1500	0.1384	0.7941
6.8	0.7996	1.1666	0.1003	0.9529
7.0	0.8007	1.1766	0.0790	1.0667

Proton-ligand stability constant

Method	log K_1^H
Half integral (value from fig.3.2.2)	5.6
Graphical (value from fig.3.2.3)	5.666

Table 3.B.2'

5 Nitro-salicylaldehyde 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 $\bar{n}_A F$
4.0	0.7866	0.7910	0.9892	-1.9623
4.2	0.7881	0.8033	0.9627	-1.4122
4.4	0.7896	0.8166	0.9337	-1.1493
4.5	0.7904	0.8233	0.9194	-1.0569
4.6	0.7911	0.8300	0.9046	-0.9772
4.8	0.7926	0.8500	0.1407	-0.7859
5.0	0.7941	0.8600	0.8385	-0.7152
5.2	0.7956	0.9233	0.6870	-0.3414
5.4	0.7971	0.9733	0.5681	-0.1190
5.5	0.7989	1.0066	0.4663	0.0605
5.6	0.7986	1.0333	0.4247	0.1318
5.8	0.8001	1.0866	0.2977	0.3727
6.0	0.8016	1.1300	0.1952	0.6153
6.2	0.8031	1.1633	0.1174	0.8761
6.4	0.8046	1.1833	0.0719	1.1109
6.5	0.8054	1.1875	0.0635	1.1687

Proton-ligand stability constant

Method	log K_1^H
Half integral (value from fig.3.2.2)	5.5
Graphical (value from fig.3.2.3)	5.5

Table 3.B.2"

5 Nitro salicylaldehyde 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 $\bar{n}_A F$
4.4	0.8220	0.8366	0.9642	-1.4307
4.5	0.8225	0.8433	0.9490	-1.2701
4.6	0.8230	0.8533	0.9257	-1.0959
4.8	0.8240	0.8900	0.8384	-0.7148
5.0	0.8250	0.9333	0.7347	-0.4424
5.2	0.8260	0.9800	0.6888	-0.2615
5.4	0.8270	1.0366	0.4865	0.0235
5.6	0.8280	1.0800	0.3825	0.2078
5.8	0.8290	1.1066	0.3355	0.2969
6.0	0.8300	1.1266	0.2736	0.4241
6.2	0.8310	1.1433	0.2351	0.5123
6.4	0.8320	1.1533	0.2122	0.5692
6.6	0.8330	1.1600	0.1993	0.5912
6.8	0.8340	1.1650	0.1894	0.6321
7.0	0.8350	1.1720	0.1748	0.6741
7.5	0.8375	1.1850	0.1491	0.7564
8.0	0.8400	1.1923	0.1374	0.7978
8.5	0.8427	1.1981	0.1298	0.8262
9.0	0.8455	1.2038	0.1226	0.8547
9.5	0.8482	1.2096	0.1110	0.9036
10.0	0.8650	1.2400	0.0827	1.0450
10.5	0.9700	1.3650	0.0360	1.2278

Proton-ligand stability constant

Method		log K_1^H
Hlaf integral	(value from fig.3.2.2)	5.38
Graphical	(value from fig.3.2.3)	5.38

Table 3.C.1.1

Stability constant of magnesium-3 nitro-salicylaldehyde 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 $\bar{n}$ F
4.6	0.7896	0.8433	0.85	0.1842	3.2437	0.6464
4.8	0.7906	0.8566	0.8666	0.2924	3.0634	0.3838
5.0	0.7916	0.8700	0.8900	0.6068	2.9004	-0.1885
5.2	0.7926	0.8966	0.9233	0.8782	2.7469	-0.8580
5.4	0.7936	0.9200	0.9566	1.3000	2.6158	-

Metal-Ligand Stability Constant

Method	log K_1
Half integral (value from fig.3.1.4)	2.9
Graphical (value from fig.3.1.5)	2.970

Table 3.C.1.2

Stability constant of cadmium-3 nitro salicylaldehyde 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 $T^o_{Cd^{++}}$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
4.2	0.7876	0.82	0.8240	0.1064	3.6233	0.9239
4.4	0.7886	0.8333	0.8433	0.3003	3.4391	0.3673
4.6	0.7896	0.8433	0.8633	0.4366	3.2550	0.1107
4.8	0.7906	0.8566	0.8866	0.8772	3.0904	-0.8539
5.0	0.7916	0.8700	0.9133	1.314	2.9350	-

Metal-Ligand stability constant

Method	log K_1
Half integral (value from fig. 3.1.4)	3.242
Graphical (value from fig. 3.1.5)	3.314

Table 3.C.1.3

Stability constant of Manganese-3 Nitro salicylaldehyde 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 $\bar{n}$ F
3.5	0.7716	0.7716	0.7766	0.1471	4.3360	0.7632
3.6	0.7766	0.7766	0.7866	0.2452	4.2457	0.4884
3.8	0.7866	0.79	0.8060	0.3832	4.0670	0.2067
4.0	0.7876	0.8066	0.8266	0.4901	3.8367	0.0172
4.2	0.7886	0.8200	0.8450	0.6653	3.6495	-0.2984
4.4	0.7891	0.8333	0.8666	0.9158	3.4675	-1.0365

Metal ligand stability constant

Method	log K_1
Half integral (value from fig.3.1.4)	3.828
Graphical (value from fig.3.1.5)	3.828

Table 3.C.1.4

Stability constant of Zinc-3 Nitrosalicylaldehyde 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 % Ethanol-water $T^o_{Zn^{++}}$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
3.2	0.7466	0.7466	0.7566	0.2455	4.6187	0.4877
3.4	0.7643	0.7643	0.7833	0.4462	4.4458	0.0587
3.6	0.7766	0.7766	0.8050	0.6965	4.2663	-0.3608
3.8	0.7866	0.7900	0.8240	0.8335	4.1078	-0.6995
4.0	0.7876	0.82	0.8580	0.9313	3.8573	-1.1321

Metal ligand stability constant

Method	log K_1
Half integral (value from fig. 3.1.4)	4.4
Graphical (value from fig. 3.1.5)	4.4

Table 3.C.1.5

Stability constant of copper-3 Nitro-salicylaldehyde 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 $T_{Cu^{++}}^o = 0.001$ M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
3.0	0.7180	0.7180	0.7250	0.1720	4.8152	0.6821
3.1	0.7366	0.7366	0.7500	0.3291	4.7224	0.3095
3.2	0.7466	0.7466	0.7633	0.4100	4.6261	0.1582
3.3	0.7566	0.7566	0.7800	0.5742	4.5337	-0.1299
3.4	0.7650	0.7650	0.7966	0.7754	4.4432	-0.5381
3.5	0.7700	0.7700	0.8033	0.8166	4.3454	-0.6486
3.6	0.7766	0.7766	0.8166	0.9811	4.2532	-1.7152

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.3.1.4)	4.570
Graphical (value from fig.3.1.5)	4.570

Table 3.C.1'.1

Stability constant of Magnesium-3 Nitrosalicylaldehyde 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 $\bar{n}$ F
4.6	0.7880	0.8466	0.8533	0.1918	3.0588	0.6246
4.8	0.7896	0.8633	0.8766	0.3980	2.8906	0.1797
5.0	0.7912	0.8866	0.9033	0.5318	2.7305	-0.0553
5.2	0.7928	0.9133	0.9366	0.8106	2.5920	-0.6318
5.4	0.7944	0.9500	0.9833	1.3190	2.4840	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.1.4)	2.743
Graphical	(value from fig.3.1.5)	2.842

Table 3.C.1'.2

Stability constant of Cadmium-3 Nitro salicylaldehyde 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 % Ethanol-water $T_{Cd}^{o\,++}$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
4.2	0.7848	0.8200	0.8240	0.1074	3.4304	0.9199
4.4	0.7864	0.8333	0.8433	0.2771	3.2477	0.4164
4.6	0.7880	0.8466	0.8633	0.4780	3.0717	0.0382
4.8	0.7896	0.8833	0.9033	0.5984	2.9003	-0.1733
5.0	0.7912	0.8833	0.9200	1.169	2.7608	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.1.4)	3.000
Graphical	(value from fig.3.1.5)	3.056

Table 3.C.1'.3

Stability constant of Manganese-3 Nitro salicylaldehyde system

$N' = 0.98$ 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 $T_{Mn^{++}}^o = 0.001$ M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
3.5	0.7800	0.7833	0.7900	0.1656	4.1488	0.7023
3.6	0.7808	0.7866	0.7955	0.2015	4.0586	0.5980
3.8	0.7816	0.7966	0.8090	0.3256	3.8286	0.3362
4.0	0.7832	0.80669	0.8240	0.4525	3.6396	0.0787
4.2	0.7848	0.8200	0.8400	0.5369	3.4497	-0.0642
4.4	0.7864	0.8333	0.8600	0.7398	3.2423	-0.4538

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.3.1.4)	3.485
Graphical (value from fig.3.1.5)	3.600

Table 3.C.1'.4

Stability constant of Zinc-3 Nitro salicylaldehyde system

$N' = 0.98$ 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 $T_{Zn^{++}}^o = 0.001$ M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
3.2	0.7633	0.7633	0.7733	0.2443	4.4192	0.4880
3.4	0.7800	0.7800	0.7933	0.3261	4.2229	0.3152
3.6	0.7808	0.7866	0.8070	0.5075	4.0724	-0.0130
3.8	0.7816	0.7966	0.8200	0.5957	3.9414	-0.1683
4.0	0.7832	0.8066	0.8366	0.7802	3.6547	-0.5502
4.2	0.7848	0.8200	0.8533	0.8935	3.4664	-0.9287
4.4	0.7864	0.8333	0.8700	1.1017	3.2821	-

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.3.1.4)	4.070
Graphical (value from fig.3.1.5)	4.056

Table 3.C.1'.5

Stability constant of copper-3 Nitro salicylaldehyde system

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

$E^o = 0.02$ M $t = 35^oC$ $T_L^o = 0.001$ 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	0.7366	0.1620	4.6149	0.7136
3.2	0.7650	0.7650	0.7800	0.3681	4.4414	0.2347
3.4	0.7800	0.7800	0.8000	0.4904	4.2569	0.0167
3.6	0.7808	0.7900	0.8166	0.6618	4.0796	-0.4915
3.8	0.7816	0.8033	0.8400	0.9241	3.8484	-1.0855
4.0	0.7832	0.8066	0.8466	1.040	3.6671	-

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.3.1.4)	4.29
Graphical (value from fig.3.1.5)	4.25

Table 3.C.1".1

Stability constant of Magnesium-3 Nitro salicylaldehyde 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
4.6	0.8014	0.8233	0.83	0.1740	2.9238	0.6766
4.8	0.8021	0.8433	0.8533	0.4360	2.7661	0.1218
5.0	0.8028	0.8666	0.8866	0.6159	2.6186	-0.2051
5.2	0.8035	0.9033	0.9300	0.8668	2.4927	-0.8134
5.4	0.8042	0.9466	0.9800	1.2370	2.3941	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.1.4)	2.67
Graphical	(value from fig.3.1.5)	2.70

Table 3.C.1".2

Stability constant of Cadmium-3 Nitro-salicylaldehyde 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 $T^o_{Cd^{++}}$ = 0.001 M

pH	V'	V"	V"'	$\bar{n}$	pL	log $\bar{n}$ F
4.4	0.8014	0.8233	0.8266	0.08273	3.0995	1.0448
4.6	0.8021	0.8433	0.8533	0.2590	2.9277	0.4565
4.8	0.8028	0.8666	0.8866	0.5501	2.7715	-0.0874
5.0	0.8035	0.9033	0.9400	1.131	2.6436	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.1.4)	2.785
Graphical	(value from fig.3.1.5)	2.795

Table 3.C.1".3

Stability constant of Manganese-3 Nitro salicylaldehyde 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
3.6	0.7800	0.7800	0.7847	0.1153	3.8694	0.8852
3.8	0.7933	0.7933	0.8008	0.1840	3.6762	0.6471
4.0	0.8000	0.8000	0.8133	0.3261	3.4882	0.3152
4.2	0.8007	0.8100	0.8315	0.5271	3.2960	-0.0472
4.4	0.8014	0.8233	0.8545	0.7823	3.1313	-0.5555
4.6	0.8021	0.8433	0.8833	1.0360	-	-

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.3.1.4)	3.314
Graphical (value from fig.3.1.5)	3.314

Table 3.C.1".4

Stability constant of zinc-3 Nitro salicylaldehyde 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
3.2	0.7460	0.7460	0.7500	0.09809	4.2627	0.9635
3.4	0.7633	0.7633	0.7766	0.3261	4.0728	0.3152
3.6	0.7810	0.7810	0.8033	0.5468	3.8889	-0.0815
3.8	0.7966	0.7966	0.8220	0.6227	3.6962	-0.2177
4.0	0.8000	0.8000	0.8366	0.8974	3.5106	-0.9419
4.2	0.8007	0.8100	0.8533	1.062	3.3301	-
4.4	0.8014	0.8233	0.8733	1.226	3.1527	-

Metal ligand stability constant

Method	log K_1
Half integral (value from fig.3.1.4)	3.928
Graphical (value from fig.3.1.5)	3.914

Table 3.C.1".5

Stability constant of copper-3 Nitro salicylaldehyde 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 $T_{Cu^{++}}^o$ = 0.001 M

pH	V'	V"	V"'	$\bar{n}$	pL	log $\bar{n}$ F
3.2	0.7400	0.7400	0.7533	0.3265	4.2960	0.3144
3.4	0.7650	0.7650	0.7866	0.5301	4.1189	-0.0523
3.6	0.7833	0.7833	0.8133	0.7355	3.9076	-0.4442
3.8	0.7933	0.7933	0.8300	0.8997	3.7092	-0.9529
4.0	0.8000	0.8000	0.8466	1.142	3.5264	-

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.3.1.4)	4.142
Graphical (value from fig.3.1.5)	4.142

Table 3.C.2.1

Stability constant of Magnesium-5 Nitro salicylaldehyde system

N' = 0.98 M μ = 0.1 M V^o = 40 ml

E^o = 0.02 M t = 25°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 $\bar{n}$ F
4.6	0.7911	0.8300	0.8400	0.2763	3.0625	0.4181
4.8	0.7926	0.8500	0.8650	0.4513	2.9031	0.0849
5.0	0.7941	0.8700	0.8900	0.6184	2.7344	-0.2097
5.2	0.7956	0.9033	0.9266	0.8002	2.5914	-0.5977
5.4	0.7971	0.9333	0.9733	1.532	-	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.2.4)	2.832
Graphical	(value from fig.3.2.5)	2.864

Table 3.C.2.2

Stability constant of Cadmium-5 Nitro salicylaldehyde 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 $T_{Cd^{++}}^o$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
4.2	0.7845	0.8033	0.8100	0.1742	3.4332	0.6759
4.4	0.7857	0.8133	0.8300	0.4620	3.2557	0.0662
4.6	0.7862	0.8300	0.8500	0.5411	3.0742	-0.0615
4.7	0.7868	0.8366	0.8600	0.6750	2.9029	-0.3174
4.8	0.7879	0.8600	0.8900	0.9033	2.7471	-0.9706
5.0	0.7871	0.8700	0.9233	1.6490	-	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.2.4)	3.2
Graphical	(value from fig.3.2.5)	3.216

Table 3.C.2.3

Stability constant of Manganese-5 Nitro salicylaldehyde system

$N' = 0.98$ M $\mu = 0.1$ M $V^o = 40$ ml

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

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

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
3.4	0.7700	0.7700	0.7766	0.1618	4.2181	0.7144
3.6	0.7766	0.7766	0.7900	0.3285	4.0272	0.3104
3.8	0.7866	0.7866	0.8066	0.5334	3.8392	-0.0589
4.0	0.7833	0.7933	0.8266	0.8424	3.6575	-0.6290
4.2	0.7845	0.8066	0.8466	1.040	-	-

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.3.2.4)	3.864
Graphical (value from fig.3.2.5)	3.9

Table 3.C.2.4

Stability constant of Nickel-5 Nitro salicylaldehyde 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 $T_{Ni^{++}}^o = 0.001$ M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
3.2	0.7500	0.7500	0.7533	0.07362	4.4280	1.0997
3.4	0.7670	0.7670	0.7733	0.1644	4.2181	0.7071
3.6	0.7800	0.7800	0.7933	0.3261	4.0271	0.2957
3.8	0.7870	0.7866	0.8166	0.7474	3.8494	-0.4711
4.0	0.7833	0.7933	0.8400	1.196	-	-

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.3.2.4)	3.932
Graphical (value from fig.3.2.5)	4.0

Table 3.C.2.5

Stability constant of Copper- 5 Nitro salicylaldehyde 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 $T^o_{Cu^{++}} = 0.001$ M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
2.8	0.7000	0.7000	0.7166	0.2573	5.2190	0.4604
2.9	0.7100	0.7100	0.7333	0.5724	5.0332	-0.1267
3.0	0.7266	0.7266	0.7566	0.7283	4.8407	-0.4282
3.1	0.7400	0.7400	0.7733	0.8174	4.6449	-0.6509
3.2	0.7500	0.7500	0.7933	1.4730	-	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.2.4)	4.732
Graphical	(value from fig.3.2.5)	4.716)

Table 3.C.2'.1

Stability constant of Magnesium-5 Nitro salicylaldehyde system

$N' = 0.98$ 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 $T^o_{Mg^{++}} = 0.001$ M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
4.6	0.7911	0.8366	0.8466	0.2681	2.9722	0.4360
4.8	0.7926	0.8500	0.8666	0.4735	2.8002	0.0461
5.0	0.7941	0.8800	0.9000	0.5846	2.6550	-0.1485
5.2	0.7956	0.9233	0.9466	0.8335	2.5240	-0.6994
5.4	0.7971	0.9733	1.0066	1.4360	2.4316	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.2.4)	2.72
Graphical	(value from fig.3.2.5)	2.78

Table 3.C.2'.2

Stability constant of Cadmium-5 Nitro salicylaldehyde 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 $T^o_{Cd^{++}}$ = 0.001 M

pH	V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$ F
4.2	0.7881	0.8200	0.8280	0.2124	3.3394	0.5691
4.4	0.7896	0.8266	0.8466	0.4385	3.1615	0.1074
4.6	0.7911	0.8300	0.8566	0.7139	2.9925	-0.3970
4.8	0.7926	0.8500	0.8866	1.044	2.8360	-
5.0	0.7941	0.8600	0.9066	1.362	2.6894	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.2.4)	3.120
Graphical	(value from fig.3.2.5)	3.150

Table 3.C.2'.3

Stability constant of Manganese-5 Nitro salicylaldehyde 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 $T^o_{Mn^{++}}$ = 0.001 M

pH	8 V'	V''	V'''	$\bar{n}$	pL	log $\bar{n}$F
3.6	0.7850	0.8033	0.8100	0.1684	3.9215	0.6937
3.8	0.7858	0.8100	0.8233	0.3373	3.7322	0.2934
4.0	0.7866	0.8166	0.8333	0.4417	3.5418	0.1017
4.2	0.7881	0.8200	0.8466	0.7057	3.3618	-0.3803
4.4	0.7896	0.8266	0.8633	0.9891	3.1873	-1.9578

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.2.4)	3.5
Graphical	(value from fig.3.2.5)	3.565

Table 3.C.2'.4

Stability constant of Nickel-5 Nitro salicylaldehyde 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 $\bar{n}$ F
3.4	0.7766	0.7900	0.8000	0.2472	4.1194	0.4837
3.6	0.7850	0.8033	0.8166	0.3342	3.9289	0.2993
3.8	0.7858	0.8100	0.8300	0.5071	3.7399	-0.0123
4.0	0.7866	0.8166	0.8466	0.7934	3.5581	-0.5856
4.2	0.7881	0.8200	0.8633	1.1490	3.3831	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.2.4)	3.748
Graphical	(value from fig.3.2.5)	3.8

Table 3.C.2'.5

Stability constant of Copper-5 Nitro salicylaldehyde 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	0.7333	0.7333	0.7466	0.3266	4.5225	0.3143
3.2	0.7633	0.7667	0.7900	0.5765	4.3341	-0.1340
3.3	0.7733	0.7800	0.8100	0.7418	4.2419	-0.4584
3.4	0.7850	0.7900	0.8266	0.9010	4.1494	-0.9611
3.5	0.7966	0.7980	0.8466	1.2010	4.1410	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.2.4)	4.364
Graphical	(value from fig.3.2.5)	4.416

Table 3.C.2".1

Stability constant of Magnesium-5 Nitro salicylaldehyde 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
4.6	0.8230	0.8533	0.8633	0.2646	2.8847	0.4438
4.8	0.8240	0.8900	0.9066	0.4856	2.7285	0.0250
5.0	0.8250	0.9333	0.9533	0.6668	2.5854	-0.3013
5.2	0.8260	0.9800	1.0066	0.9461	2.4663	-1.0443
5.4	0.8270	1.0366	1.0733	1.848	2.4007	-

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.3.2.4)	2.7
Graphical (value from fig.3.2.5)	2.7

Table 3.C.2".2

Stability constant of Cadmium-5 Nitro salicylaldehyde 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 $T^o_{Cd^{++}}$ = 0.001 M

pH	V'	V"	V"'	$\bar{n}$	pL	log $\bar{n}$ F
4.0	0.8166	0.8166	0.8200	0.08083	3.4291	1.0557
4.2	0.8233	0.8233	0.8333	0.4131	3.2536	0.1525
4.4	0.8220	0.8366	0.8566	0.5081	3.0730	-0.0140
4.6	0.8230	0.8533	0.8833	0.7939	2.9089	-0.5857
4.8	0.8240	0.8900	0.9266	1.0710	2.7561	-

Metal-ligand stability constant

Method	log K_1
Half integral (value from fig.3.2.4)	3.0
Graphical (value from fig.3.2.5)	3.1

Table 3.C."'.3

Stability constant of Manganese-5 Nitro salicylaldehyde 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 $T_{Mn}^{o\,++}$ = 0.001 M

pH	V'	V"	V'"	$\bar{n}$	pL	log $\bar{n}$ F
3.6	0.8000	0.8000	0.8033	0.08085	3.8190	0.9556
3.8	0.8100	0.8100	0.8167	0.1642	3.6267	0.7169
4.0	0.8166	0.8166	0.8300	0.3283	3.4402	0.3110
4.2	0.8233	0.8233	0.8500	0.6606	3.2650	-0.2892
4.4	0.8220	0.8366	0.8733	0.9576	3.0930	-1.0513

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.2.4)	3.365
Graphical	(value from fig.3.2.5)	3.365

Table 3.C.2".4

Stability constant of Nickel-5 Nitro salicylaldehyde 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 $T_N^{o\,++}$ = 0.001 M

pH	V'	V"	V"'	$\bar{n}$	pL	log $\bar{n}$ F
3.4	0.7800	0.7800	0.7900	0.2452	4.0192	0.4884
3.6	0.8000	0.8000	0.8133	0.3259	3.8299	0.3157
3.8	0.8100	0.8100	0.8300	0.4899	3.6413	0.0176
4.0	0.8166	0.8166	0.8466	0.7422	3.4592	-0.4594
4.2	0.8233	0.8233	0.8700	1.1870	3.2902	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.2.4)	3.632
Graphical	(value from fig.3.2.5)	3.680

Table 3.C.2".5

Stability constant of Copper-5 Nitro salicylaldehyde 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 $\frac{\bar{n}}{F}$
3.2	0.7533	0.7533	0.7667	0.3293	4.226	0.3091
3.4	0.7800	0.7800	0.8000	0.4914	4.0257	0.0929
3.5	0.7900	0.7900	0.8133	0.5715	3.9395	-0.1251
3.6	0.8000	0.8000	0.8300	0.7352	3.8411	-0.4435
3.7	0.8033	0.8033	0.8400	0.8995	3.7617	-0.9519
3.8	0.8100	0.8100	0.8533	1.0610	3.6683	-

Metal-ligand stability constant

Method		log K_1
Half integral	(value from fig.3.2.4)	4.00
Graphical	(value from fig.3.2.5)	4.00

Table 3.D.1 : 3-Nitro salicylaldehyde used as a ligand

Metal	Stability constant	Temperature			$-\Delta G^{o}$ K joules/mole			ΔH^{o} K joules/mole		ΔS^{o} Joules/mole		
		25°C	35°C	45°C	25°C	35°C	45°C	Graphical	Calculated	25°C	35°C	45°C
H^{+}	$\log K_1^H$	5.783	5.62	5.45	32.92	33.05	33.08	- 28.73	- 30.17	+ 14.03	+ 14.009	+ 13.6
Mg^{++}	$\log K_1$	2.935	2.792	2.685	16.69	16.42	16.29	- 23.94	- 22.53	- 24.33	- 24.44	- 24.4
Cd^{++}	$\log K_1$	3.278	3.028	2.790	18.64	17.80	16.94	- 43.7	- 44.17	- 81.81	- 81.85	- 82.1
Mn^{++}	$\log K_1$	3.828	3.542	3.314	21.78	20.83	20.11	- 46.07	- 46.39	- 96.46	- 82.86	- 82.4
Zn^{++}	$\log K_1$	4.4	4.063	3.921	25.03	23.89	23.80	- 43.04	- 42.04	- 60.41	- 62.17	- 63.3
Cu^{++}	$\log K_1$	4.570	4.271	4.142	27.44	25.11	25.14	- 40.10	- 38.25	- 47.31	- 48.62	- 47.0

Table 3.D.2 : 5-Nitro salicylaldehyde used as a ligand

Metal	Stability constant	Temperature			$-\Delta G^{o}$ K joules/mole			ΔH^{o} K joules/mole		ΔS^{o} Joules/mole		
		25°C	35°C	45°C	25°C	35°C	45°C	Graphical	Calculated	25°C	35°C	45°C
H^{+}	$\log K_1^H$	5.632	5.5	5.38	32.04	32.35	32.66	- 23.36	- 23.36	+ 29.12	+ 29.16	+ 29.24
Mg^{++}	$\log K_1$	2.848	2.75	2.7	16.20	16.17	16.39	- 11.05	- 12.56	+ 17.28	+ 16.62	+ 16.78
Cd^{++}	$\log K_1$	3.208	3.135	3.05	18.25	18.43	18.51	- 14.37	- 14.34	+ 13.01	+ 13.18	+ 13.03
Mn^{++}	$\log K_1$	3.882	3.532	3.365	22.08	20.77	20.42	- 46.93	- 46.26	- 83.40	- 84.95	- 83.36
Ni^{++}	$\log K_1$	3.966	3.774	3.656	22.62	22.19	22.19	- 29.03	- 27.86	- 21.50	- 22.18	- 21.49
Cu^{++}	$\log K_1$	4.724	4.39	4.00	26.87	25.82	24.28	- 64.73	- 65.73	-127.03	-126.27	-125.86

3.4 PRESENT WORK : RESULTS AND DISCUSSION

The values of the proton-ligand and metal-ligand stability constants are obtained by using Calvin-Bjerrum technique as modified by Irving and Rossotti[11].

3-Nitro salicylaldehyde (3-NSA)

The ligand was used to study complexations with bivalent metal ions Mg^{++}, Cd^{++}, Zn^{++}, Mn^{++}, Ni^{++}, Co^{++} and Cu^{++}. Tables 3.A.1, 3.A.1' and 3.A.1" contains the experimental observations of titration of 3-NSA at temperature 25^{o}, 35^{o} and $45^{o}C$. In acidic medium it is colourless but acquires yellow colour which deepens with addition of alkali. The metal ions get precipitated due to addition of sodium hydroxide during titration. All these metal ions get precipitated below pH 7. The titration curves are shown in figs. 3.1.1.a, 3.1.1'.a, 3.1.1".a, 3.1.1.b, 3.1.1'b and 3.1.1".b. The tables 3.B.1, 3.B.1' and 3.B.1" gives the data for proton-ligand stability constants. Figs. 3.1.2 and 3.1.3 are the plots of half integral and graphical methods for determination of proton-ligand stability constants. Tables 3.C.1.1 to 3.C.1.5, 3.C.1'.1 to 3.C.1'.5 and 3.C.1".1 to 3.C.1".5 cover the five metal ions and their stability constants. The metal-ligand stability constants are determined by using half integral and graphical methods by using figs.3.1.4 and 3.1.5. 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 coefficient and Gibbs Helmholtz equation. H is also determined with the help of an isobar equation

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

The value of ΔH are determined by using fig.3.1.6. The stability constants and thermodynamic parameter are tabulated in Table 3.D.1.

Some work has been already reported for this ligand in dioxane-water mixtures. The complex formation has been investigated in the present work in ethanol-water mixture for first time and this ligand is studied at 25°, 35° and 45°C temperature in detail to calculate thermodynamic parameters by us.

5-Nitro-salicylaldehyde (5-NSA)

Table 3.A.2, 3.A.2' and 3.A.2'' gives the experimental observations of titrations of 5-NSA. The ligand is used to study complexations with bivalent ions Mg^{++}, Cd^{++}, Zn^{++}, Mn^{++}, Ni^{++}, Co^{++} and Cu^{++}. In acidic medium it is colourless, but acquires, yellow colour which deepens with addition of alkali. The metal ions get precipitate due to addition of sodium hydroxide during titration. All metal ions get precipitate in acidic medium. The titration curves are shown in figs.3.2.1.a, 3.2.1'.a, 3.2.1''.a, 3.2.1.b, 3.2.1'.b and 3.2.1''.b. Table 3.B.2, 3.B.2' and 3.B.2'' gives the data for proton-ligand

stability constants. Figs.3.2.2 and 3.2.3 are the plots of half integral and graphical methods used to determine proton-ligand stability constants. Tables 3.C.2.1 to 3.C.2.5, 3.C.2'.1 to 3.C.2'.5 and 3.C.2".1 to 3.C.2".5 covers the five metal ions and their stability constants at 25°, 35° and 45°C. temperature. The metal-ligand stability constants are determinec by using half integral and graphical methods by using figs.3.2.4 and 3.2.5. 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 coefficient and Gibbs. Helmholtz equation H is also determined with the help of an isobar equation.

The values of ΔH are determined by using fig.3.2.6. The stability constants and thermodynamic parameters tabulated in Table 3.D.2.

Salicylaldehyde and substituted salicylaldehydes are vic-hydroxy aldehydes, possessing suitable structural characteristics require for formation of chelate ring with a metal ion. The phenolic -OH group attributes weakly acidic character to this compound and the metal ion can abstract a proton to form M-O bond. The vicinal carbony part of the aldehyde group is capable of donating an electron pair on oxygen to form coordinate bond. This ligand is therefore basically a monoprotic bidentate unit giving rise to ML_2 type chelates with bivalent metal ions. The nature of bonding, structure and thermodynamic

stability of the complex is important. It is well known that substituents in ligand aromatic ring at various sites bring about change in electron density near the bonding sites and therefore use of substituted salicylaldehydes as ligands in the study of thermodynamic stability constant and the pertinent parameters will be useful. The substituents like $-NO_2$, -Cl, -Br, -OH are electron attracting groups and act as electrophilic substituents. They pull the electron cloud towards themselves as a consequence of which electron densities around the active sites lower. This leads to a negative inductive effect. The $-NO_2$ group in position 3 or 5 in nitrosalicylaldehyde has therefore, thiner electron cloud around the carbonyl oxygen compare with that of salicylaldehyde. It is obvious that the hydrogen bond formation between phenolic -OH and aldehydic carbonyl will be weaker in nitro-salicylaldehydes. The phenolic -OH proton in nitrosalicylaldehyde therefore will have lower ionisation energy.[12] On the contrary the presence of electrophobic or electron repelling group such as $-CH_3$ or $-NH_2$ push the electron cloud away from themselves and this results in increased electron density around the active centres leading to positive inductive effect, as such in aminosalicylaldehydes. We except increased electron density around carbonyl oxygen compared as that of salicylaldehyde obviously the hydrogen bond formation between carbonyl and phenolic groups will be stronger. The extend of substituent effect can be judged fairly accurately by comparing the properties in the light of the substituent

constants proposed by Hammet. However, the ortho substitution and also hydrogen bonding make the picture somewhat obscure. The electron withdrawing tendency of $-NO_2$ group occuring in position 3 or 5 has Hammet 6 value of 0.71. The pK values of 3-nitro salicylaldehyde and 5-nitro salicylaldehyde are 6 and 5.9 in dioxane-water.[18] This indicates that in nitro derivatives the phenol is more dissociated. This also means that the nitro derivatives form the phenolic bonds faster than the parent aldehyde. However the coordinate bond closing the chelate ring should form more easily in the parent compound. Thus leading to more stable complex. It appears that the coordination step has more influence on the stability of complex than the phenolic bond formation.

Proton-Ligand Stability Constants

Ligand	$\log K_1^H$		
	Temperature		
	25°C	35°C	45°C
Salicylaldehyde	9.5[18]	-	-
3-nitrosalicylaldehyde	5.783	5.62	5.45
5-nitrosalicylaldehyde	5.632	5.5	5.38

Irving and Williams[13] correlated the data of Mellor and Maley[14] on the successive stability constants of divalent ions of the

first transition series by plotting stability constants against the atomic numbers of the metals. They showed that log K value increases with increase in atomic number except in zinc. The zinc chelates are less stable than copper chelates. In the present work order of stability constants for divalent transition metals is as shown below.

(1) 3-Nitrosalicylaldehyde

$$Mn < Cu > Zn$$

(2) 5-Nitrosalicylaldehyde

$$Mn < Ni < Cu$$

The order of stability constants of divalent transition metals agree with Irvong and Williams order.
This sequence is identical for all temperature.

The stability sequence for various divalent metals with a given reagent is rather inflexible regardless of the reagent used as shown below.

The stability order given by Irving and Williams[13]

$$Cu > Ni > Co > Zn > Pb > Cd > Mn > Mg.$$

Stability order given by Calvin[15] for sodium 5-salicylaldehyde sulphonate.

$$Cu > Ni > Co > Zn > Pb > Cd > Mn > Mg.$$

Maley found same order for salicylaldehyde[16] with exception of Pb.

In the present work we found following order :

3-Nitrosalicylaldehyde

Cu > Zn > Mn > Cd > Mg.

5-Nitrosalicylaldehyde

Cu > Ni > Mn > Cd > Mg.

There is reversal of order for Mn and Cd.

Calvin and Melchior[17] found the correlation in between stability constants of chelate formed by 5-salicylaldehyde sulfonate and second ionisation potential of the gaseous atoms of transition metals. They showed that stability constant increases with increase in second ionisation potentials.

In the present work we also found similar relation to be valid.

Heat changes (ΔH^{o}) are negative for 3-NO_2 and 5-NO_2 salicylaldehyde therefoe complex formation is favoured, and complexes are stable.

There is decrease in log K_1^H and log K_1 values with increase in temperature for 3-nitro and 5-nitro salicylaldehyde.

Ionization Potentials and Stability Constants

for Transition Metals

Ion	E_1 volts	E_2 volts	Log Stability Constant			
			Salicylaldehyde [6]	5-Sulposalicylaldehyde [6]	3-Nitrosalicylaldehyde	5-Nitro salicylaldehyde
Mn^{++}	15.7	23.1	6.8	-	3.828	3.882
Fe^{++}	16.2	24.0	7.6	-	-	-
Co^{++}	17.1	25.1	8.3	5.6	-	-
Ni^{++}	18.2	25.8	9.2	6.5	-	3.966
Cu^{++}	20.2	27.9	13.3	9.2	4.570	4.724
Zn^{++}	17.9	27.2	8.1	5.4	4.4	-

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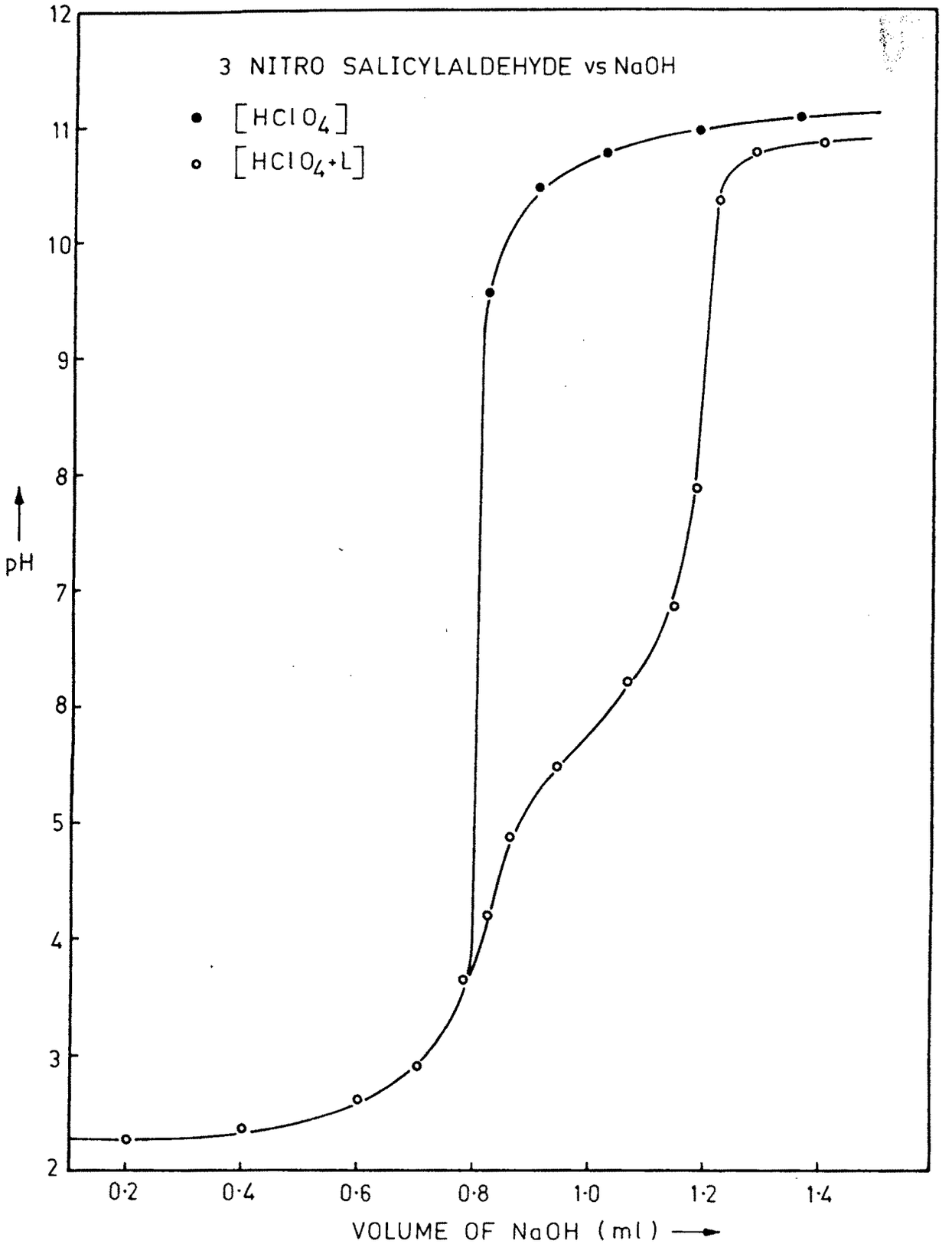

Fig. 3·1·1 a : TITRATION CURVES

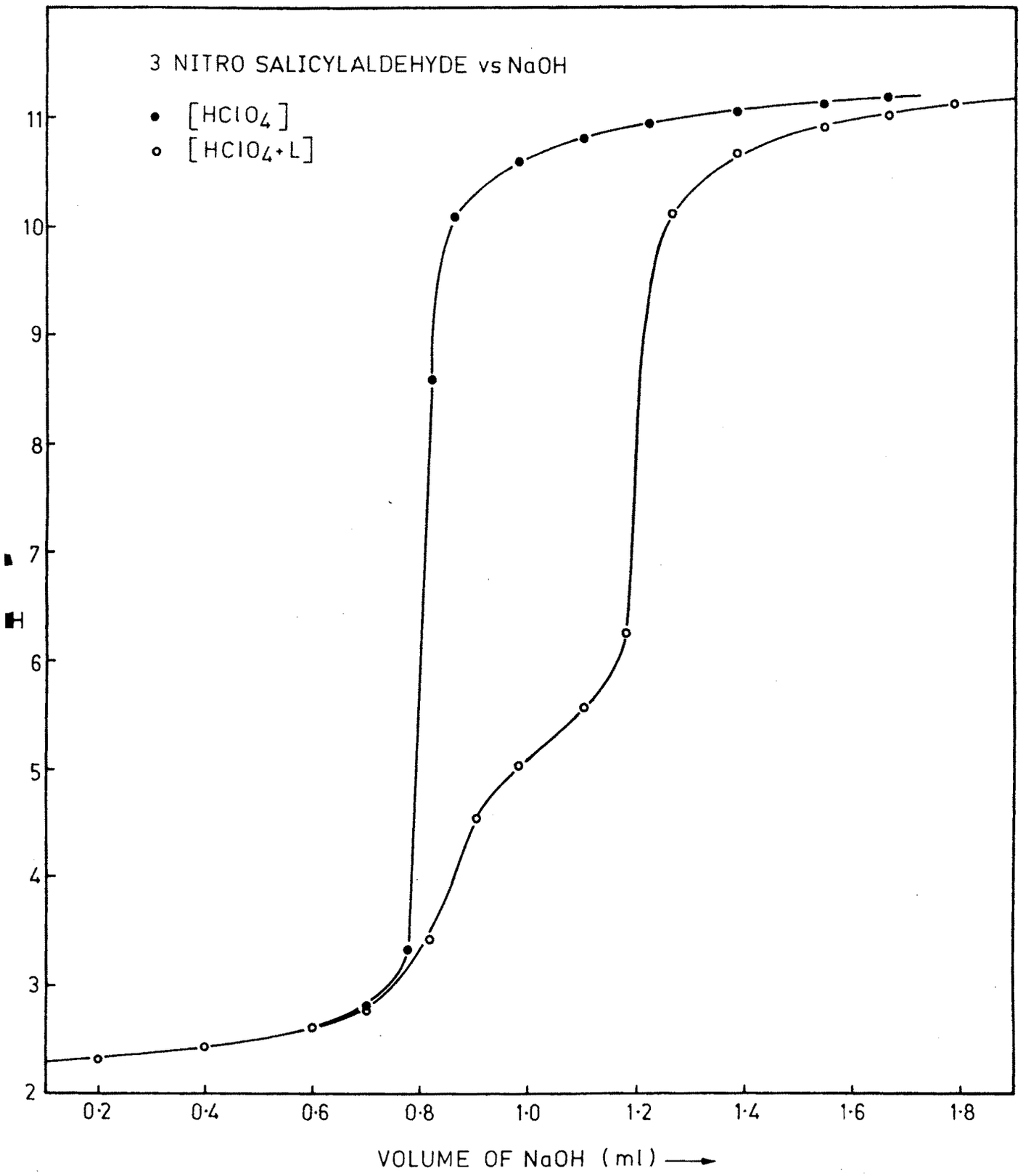

Fig. 3·1·1 a : TITRATION CURVES.

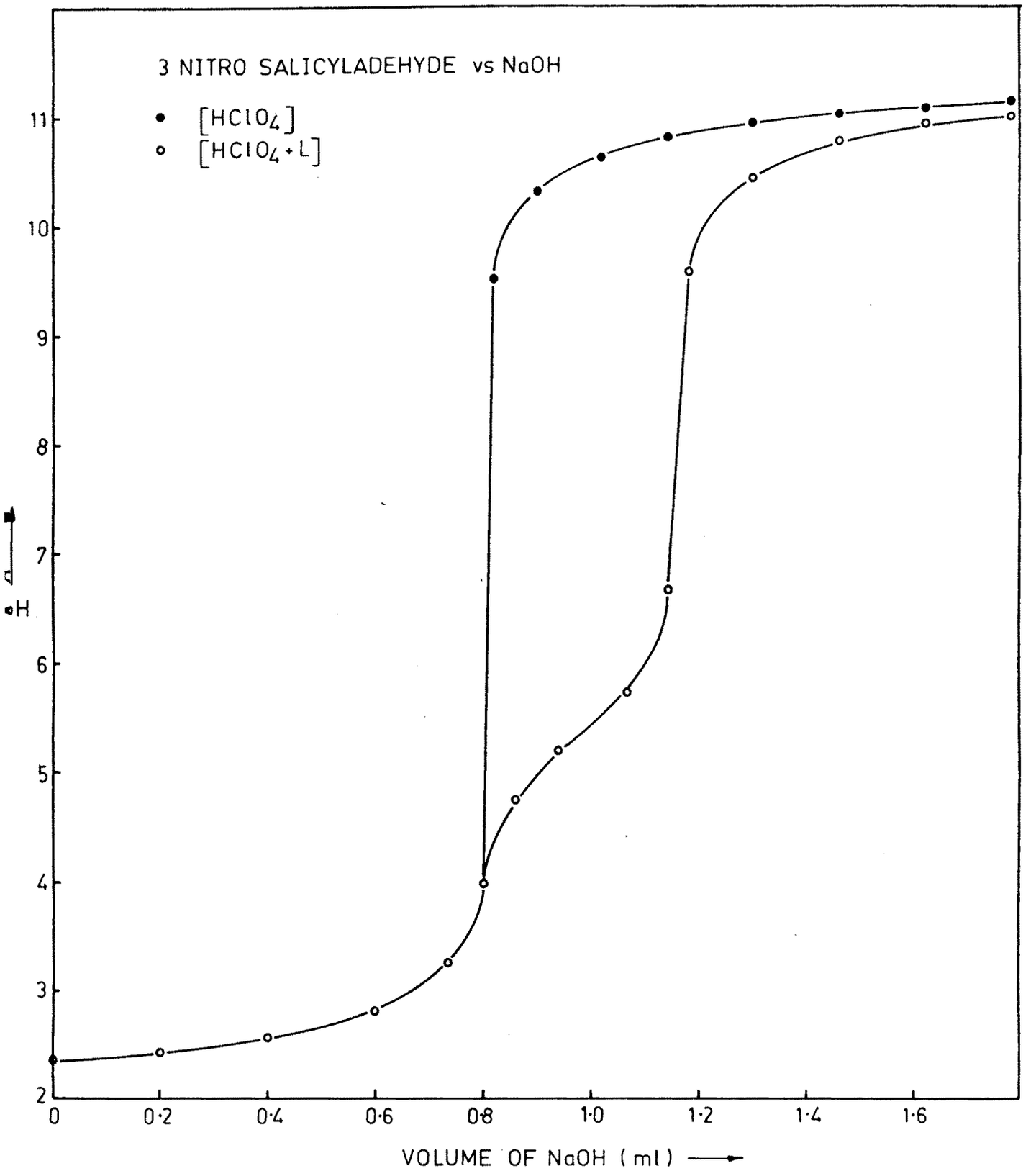

Fig. 3·1·1″a : TITRATION CURVES

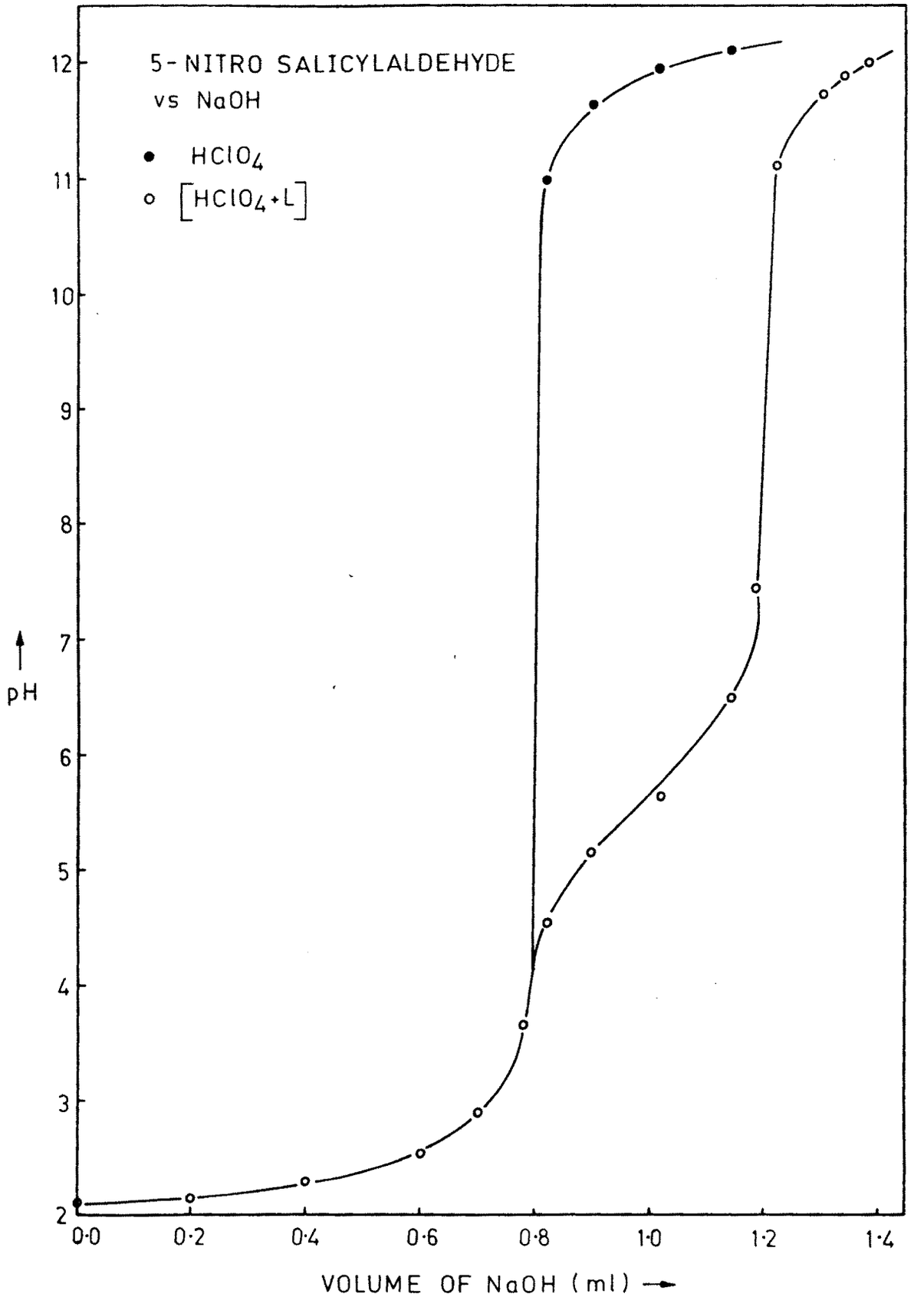

Fig. 3·2·1a: TITRATION CURVES

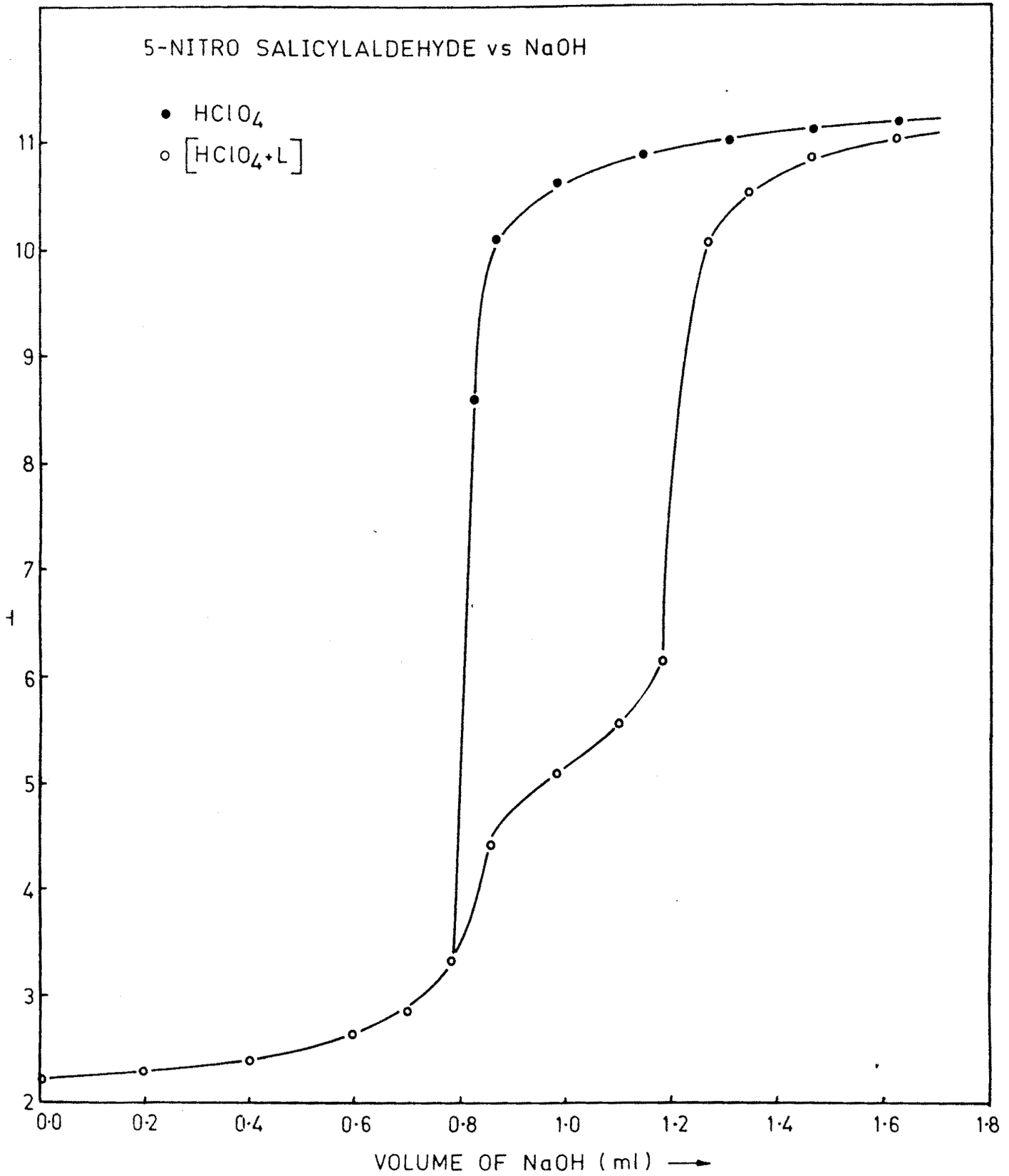

Fig. 3·2·1'a : TITRATION CURVES

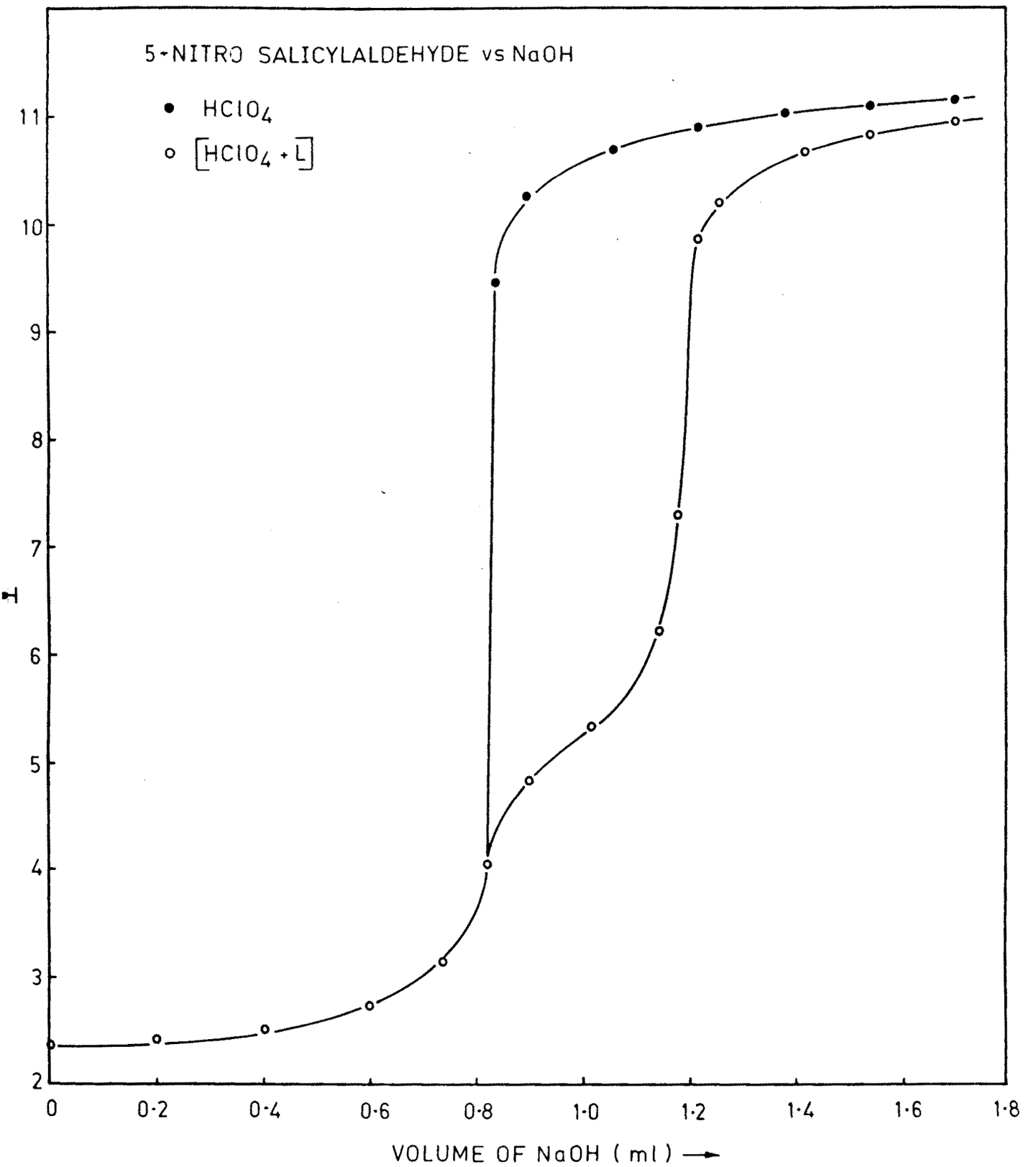

Fig. 3·2·1″a : TITRATION CURVES

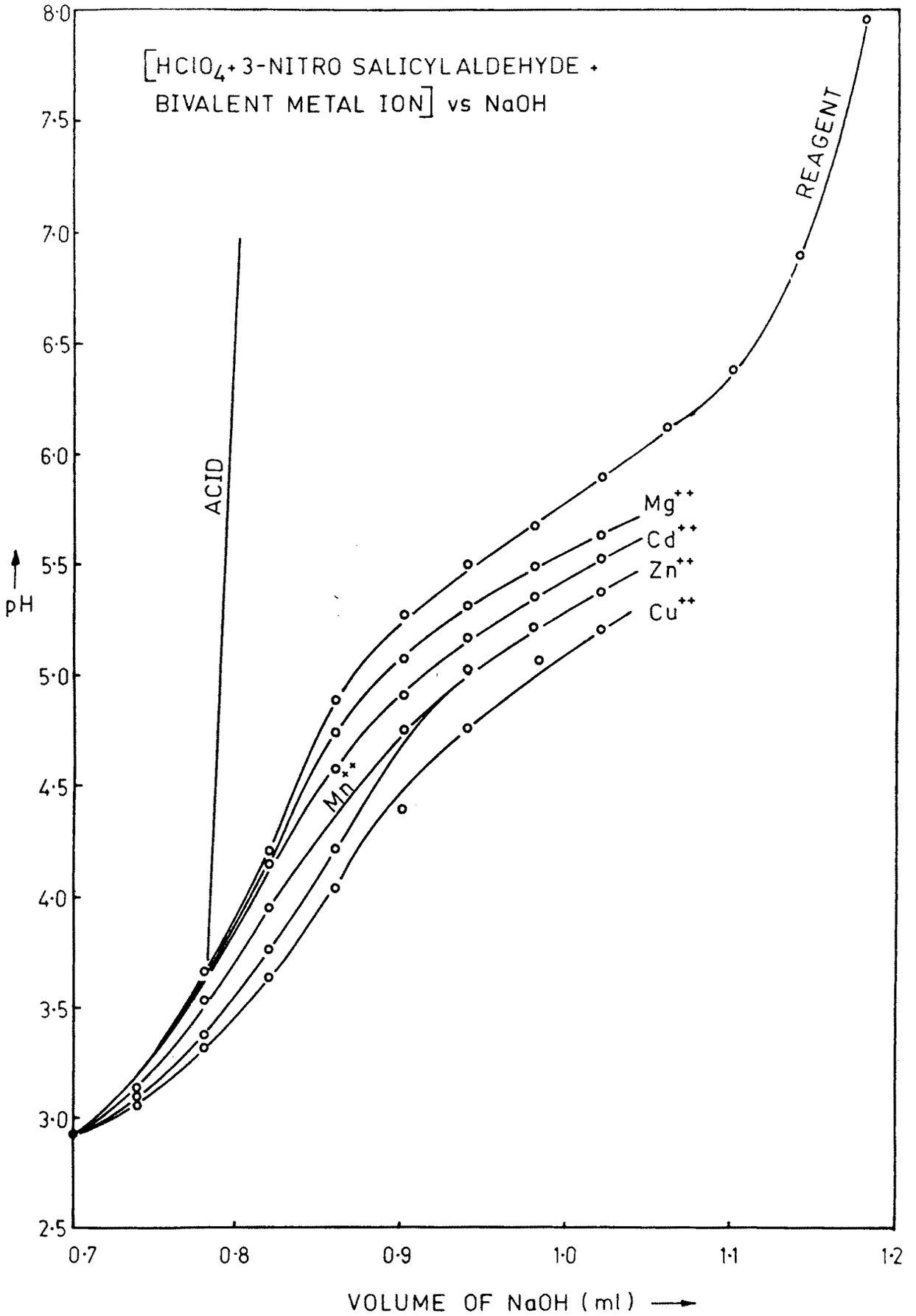

Fig. 3·1·1 b : TITRATION CURVES

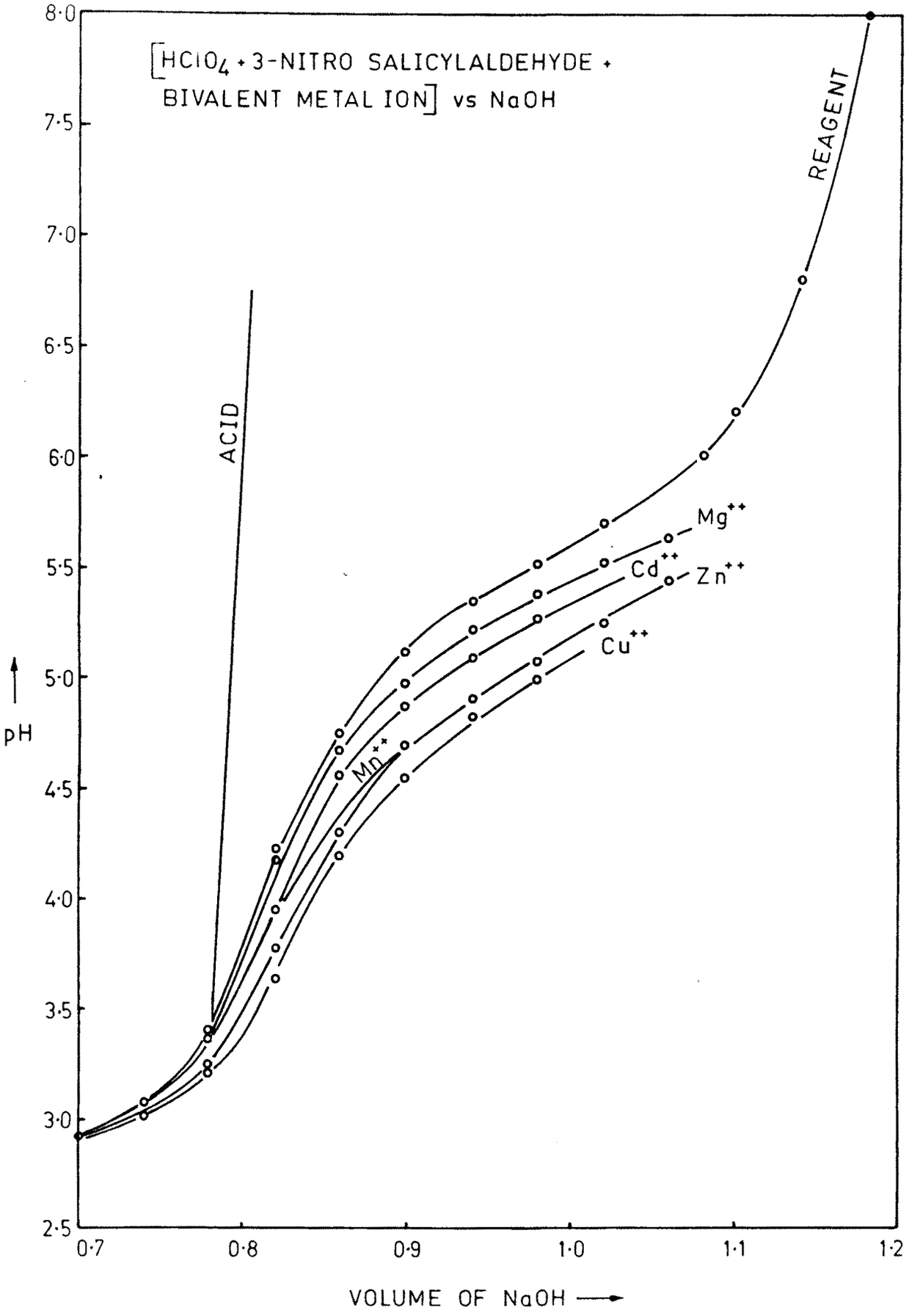

Fig. 3·1·1'b : TITRATION CURVES

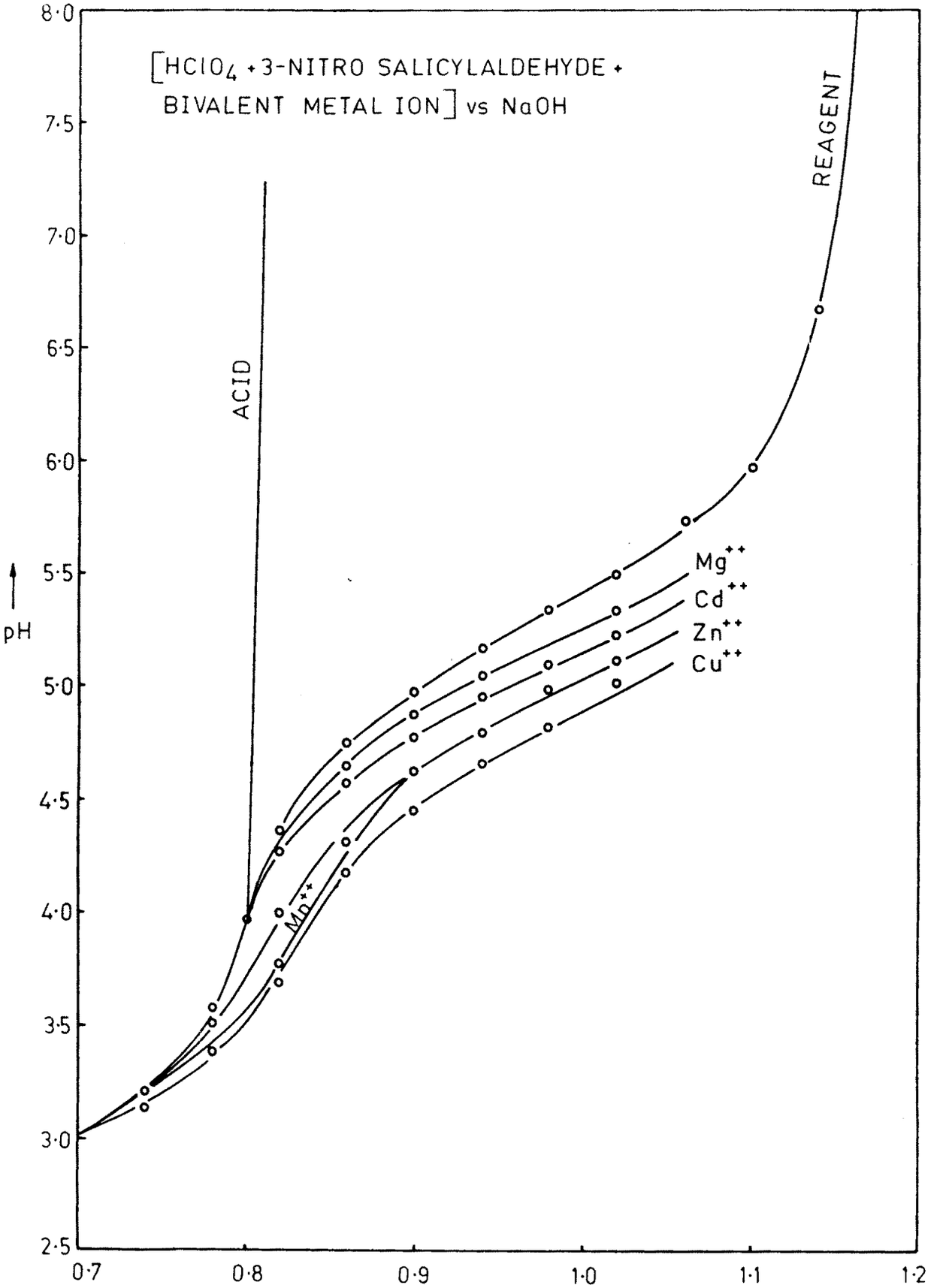

Fig. 3·1·1″b : TITRATION CURVES

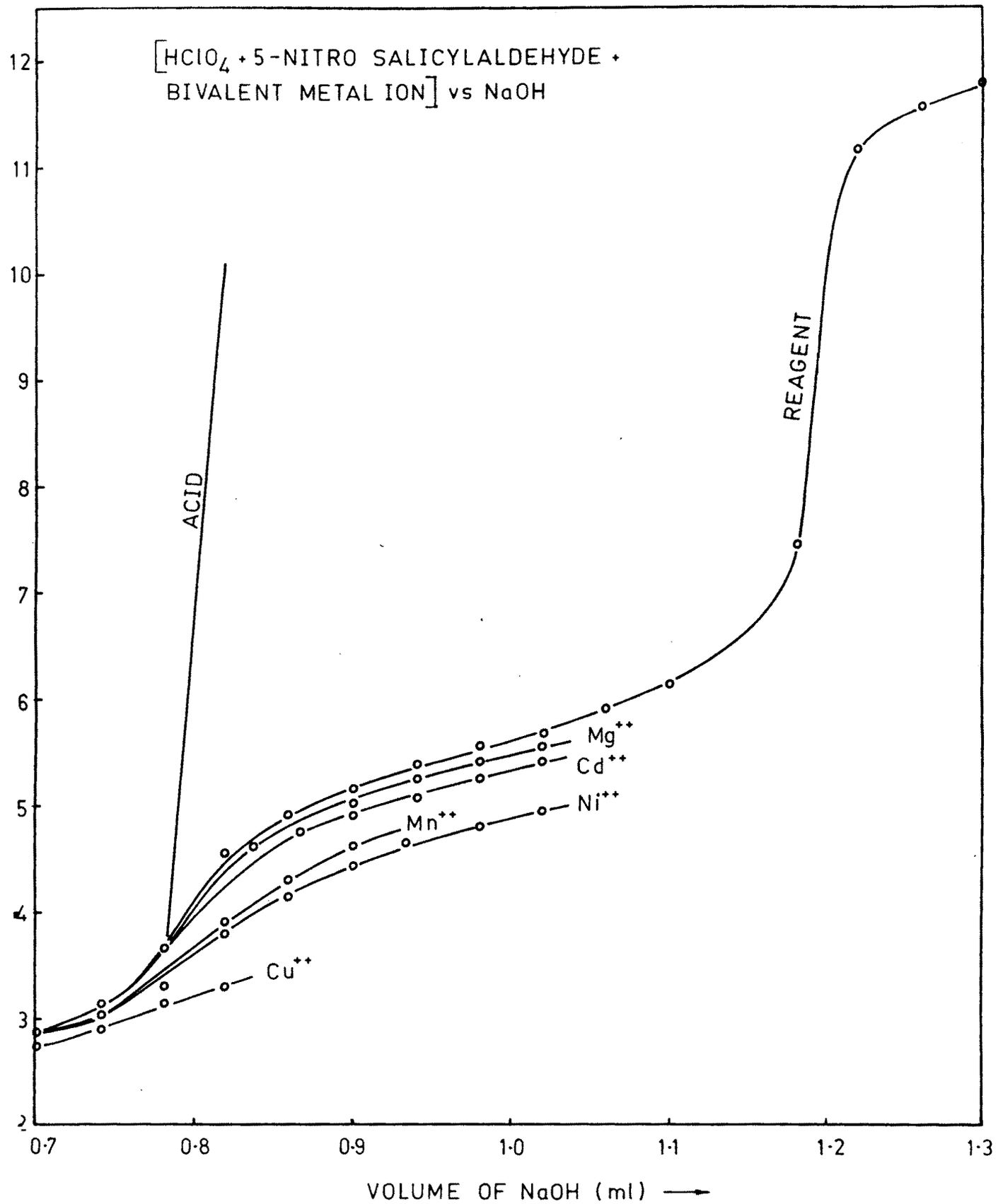

Fig. 3·2·1 b : TITRATION CURVES

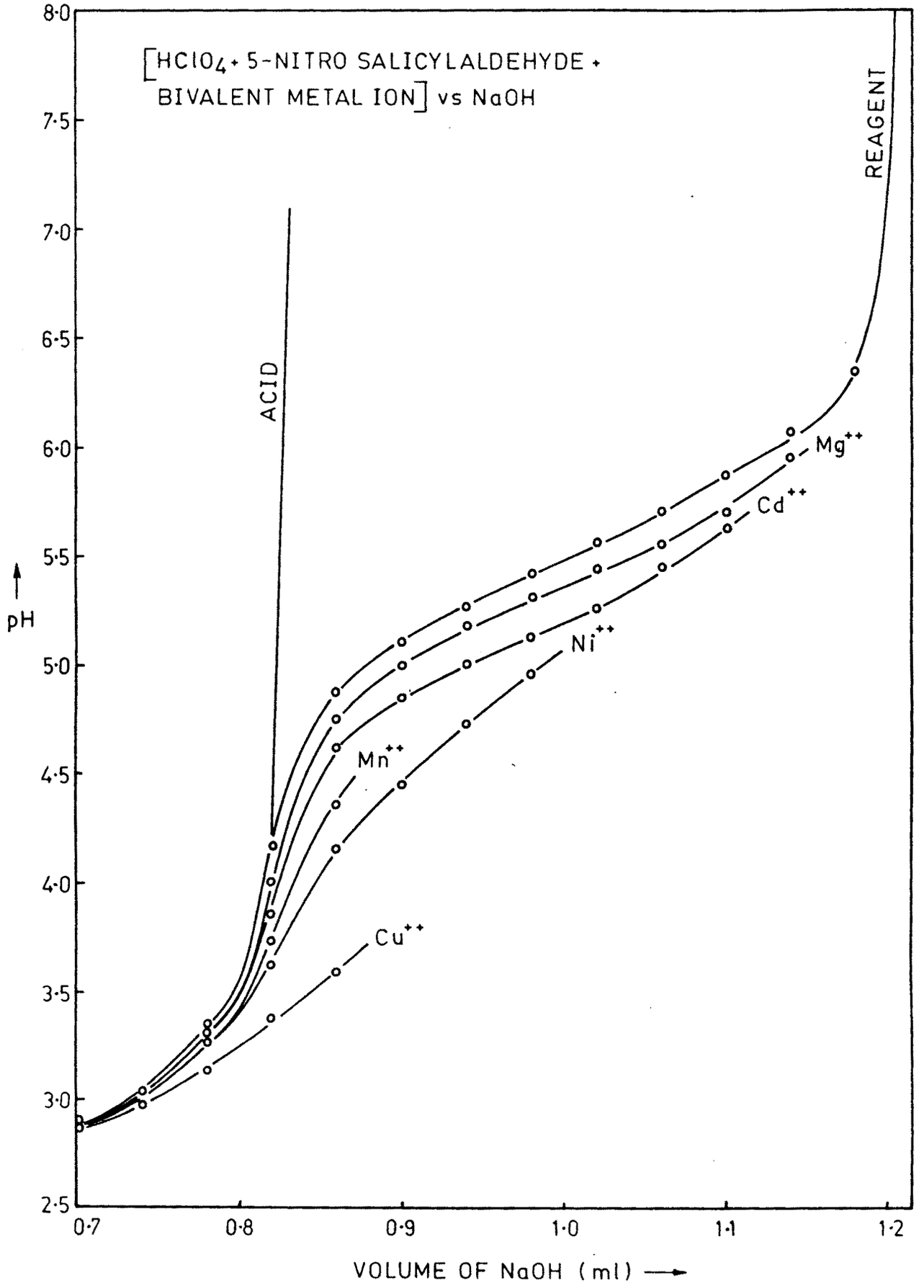

Fig. 3·2·1b: TITRATION CURVES

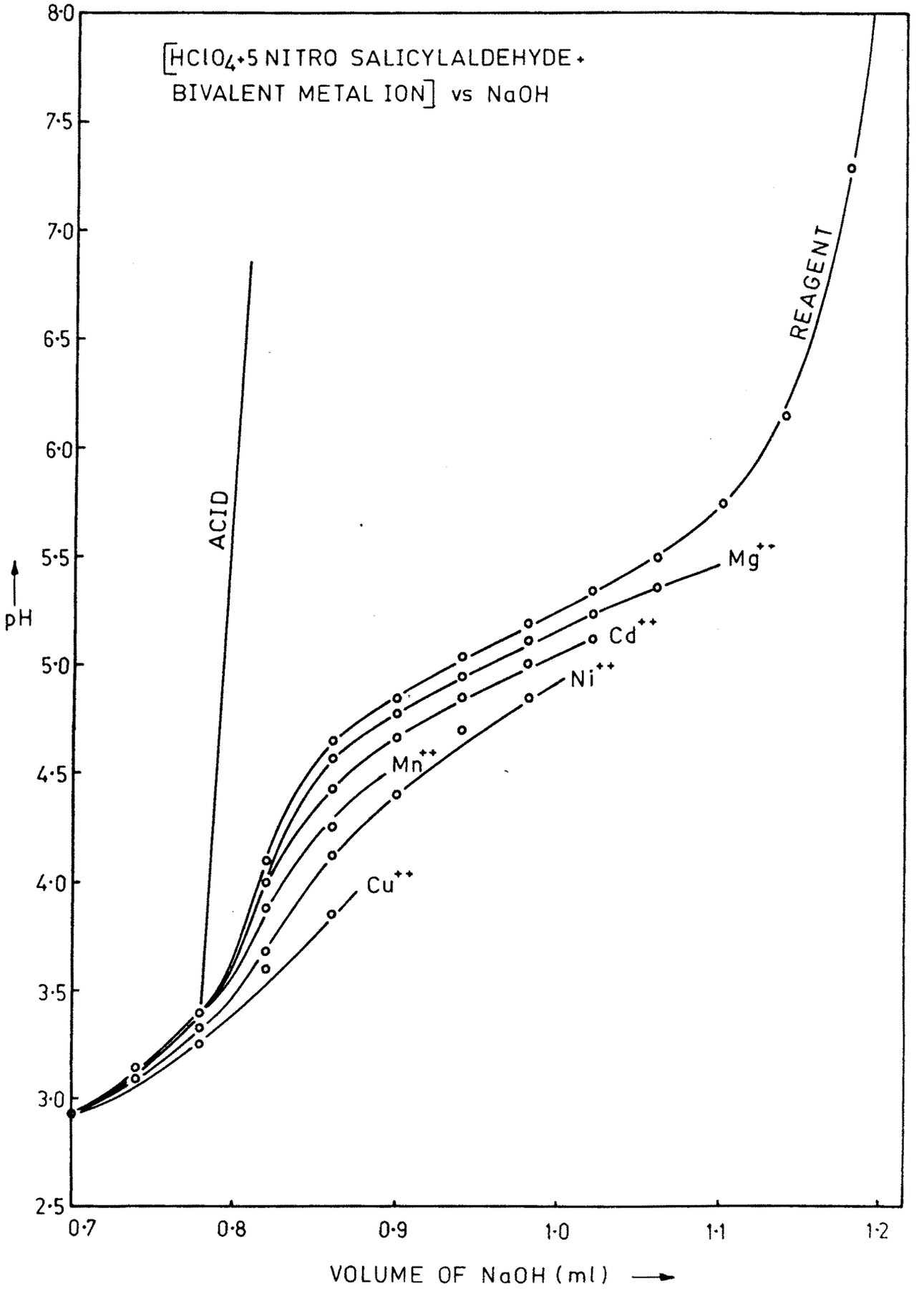

Fig. 3·2·1″b: TITRATION CURVES

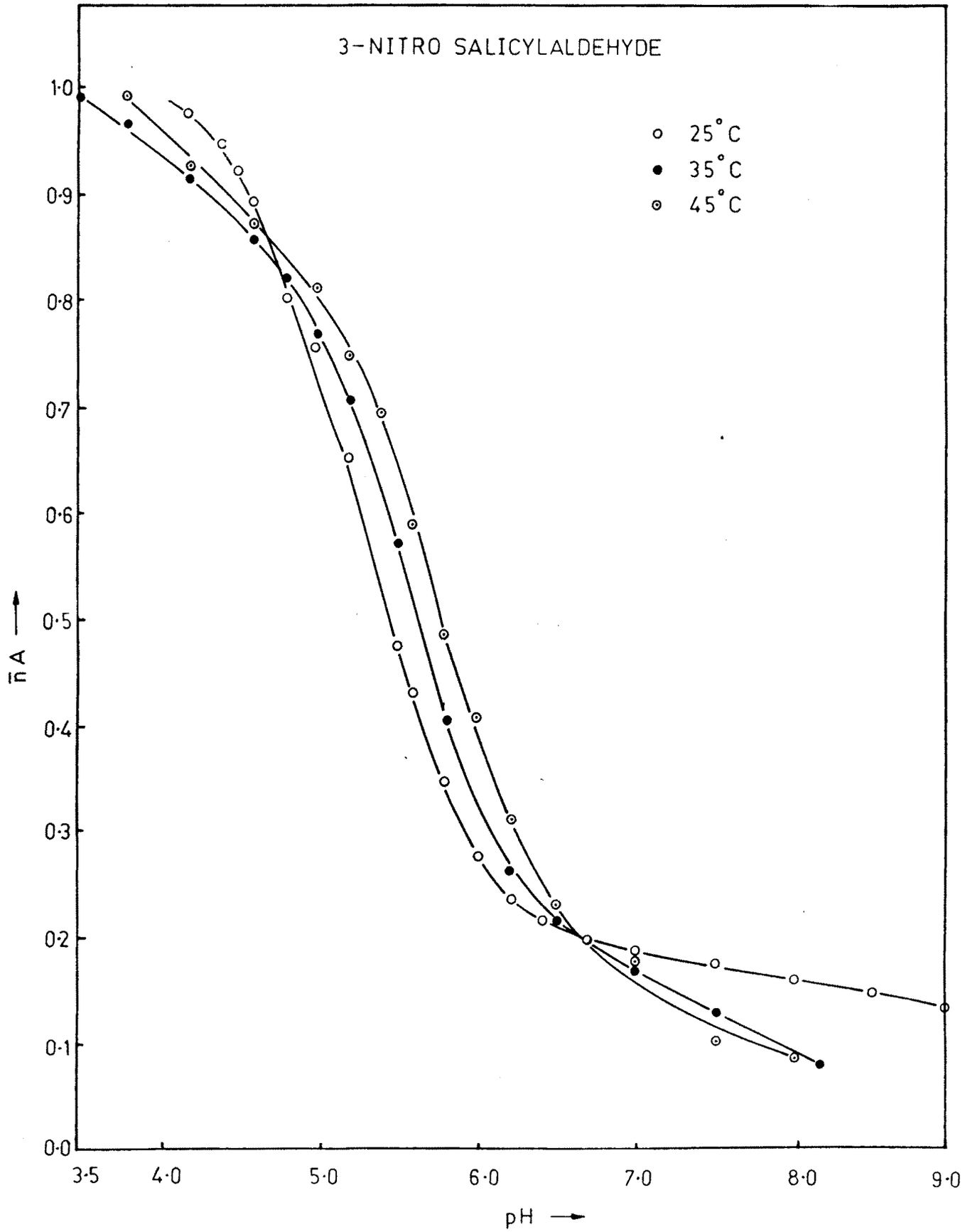

Fig. 3·1·2 : FORMATION CURVES FOR PROTON LIGAND SYSTEMS

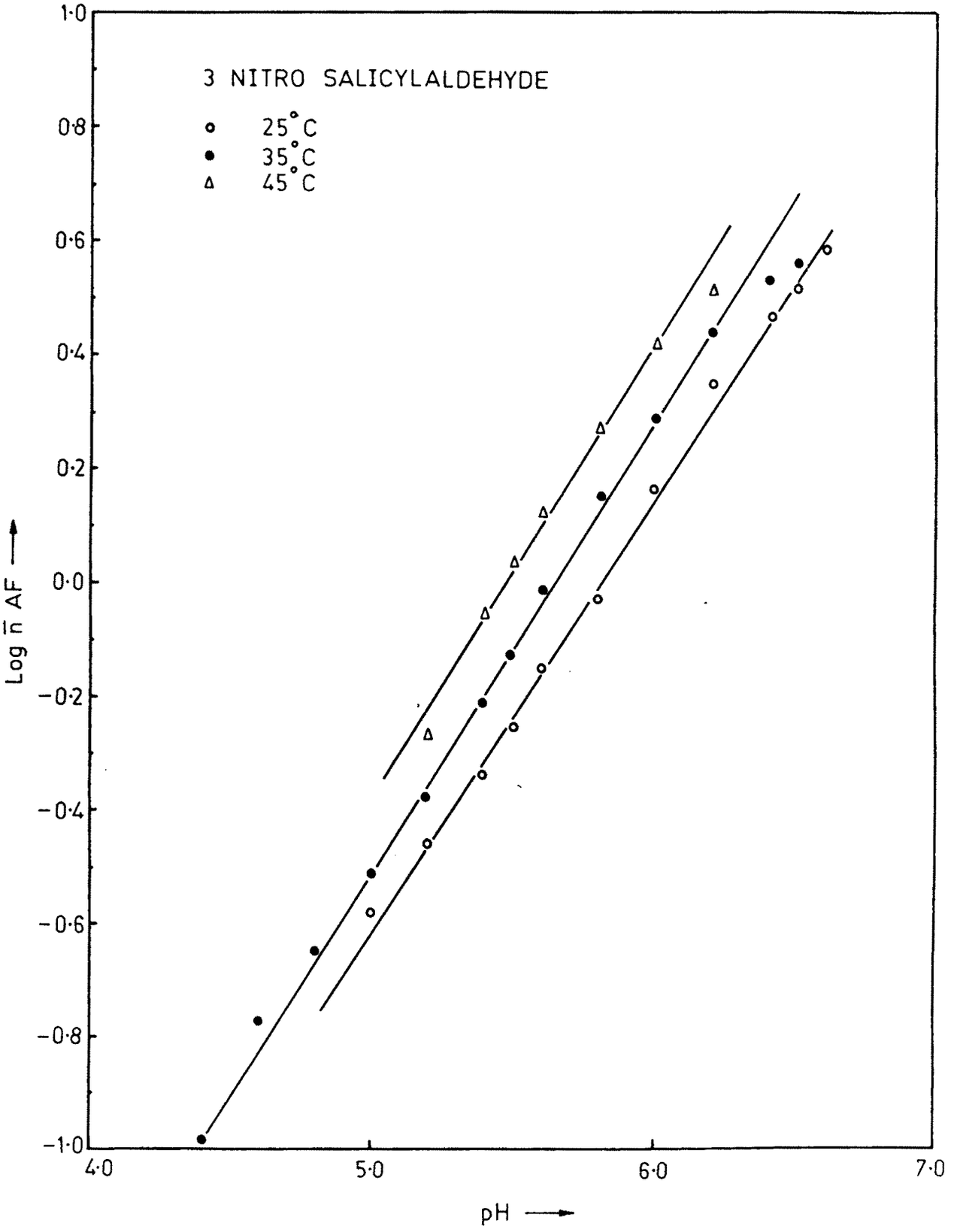

Fig. 3·1·3 : FORMATION CURVES FOR PROTON-LIGAND SYSTEMS.

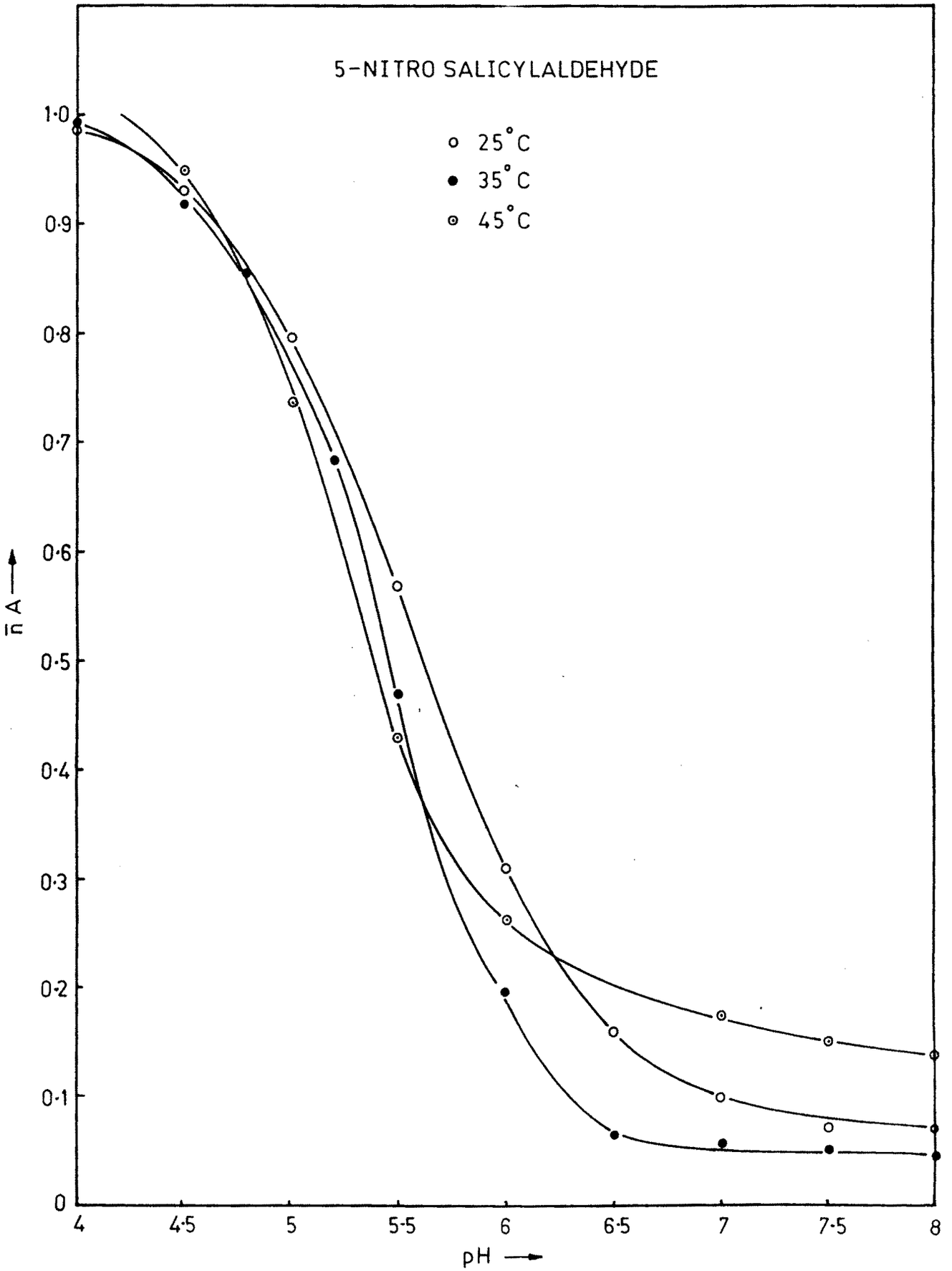

Fig. 3·2·2 : FORMATION CURVES FOR PROTON LIGAND SYSTEMS

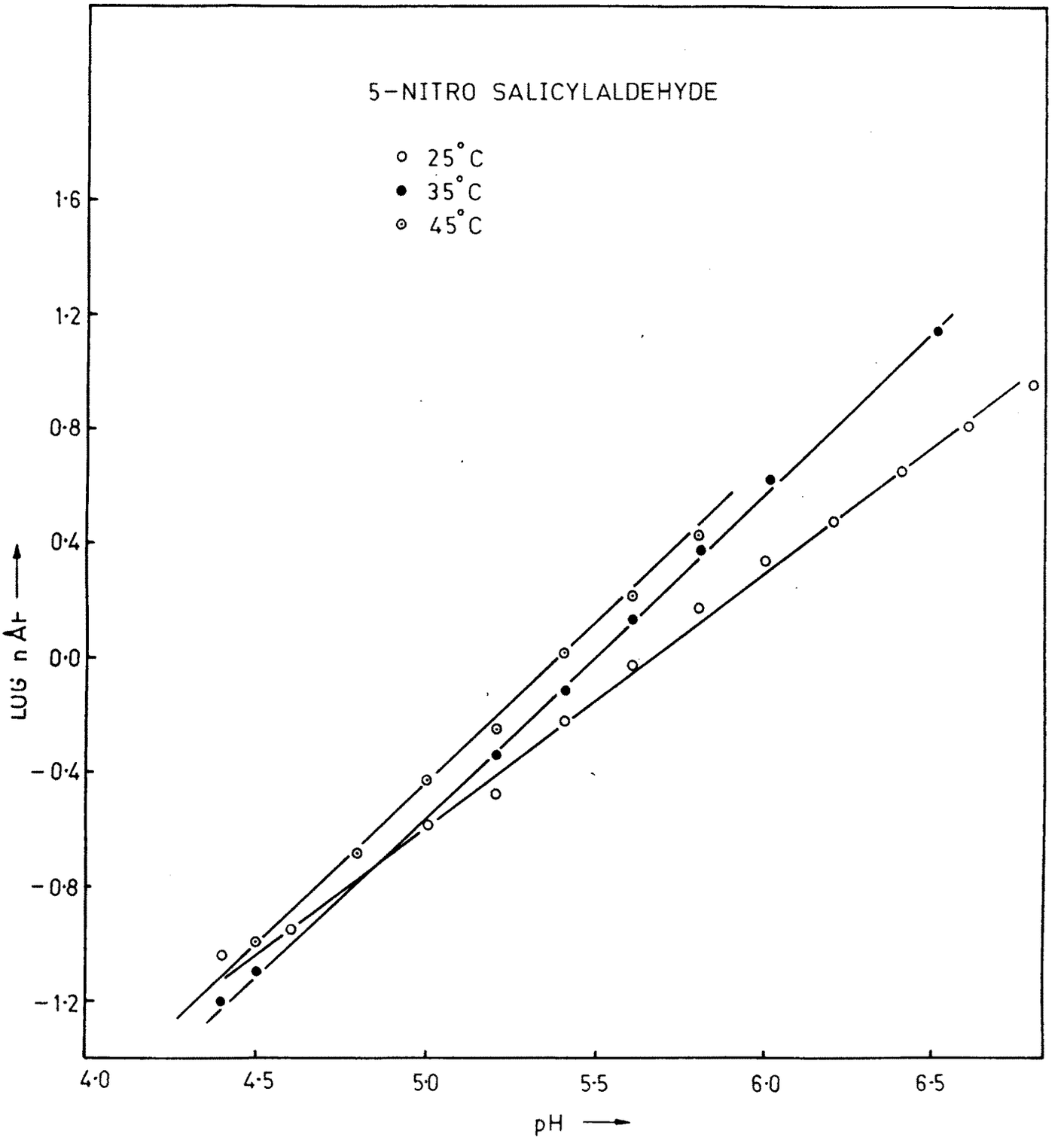

Fig. 3·2·3 : FORMATION CURVES FOR PROTON LIGAND

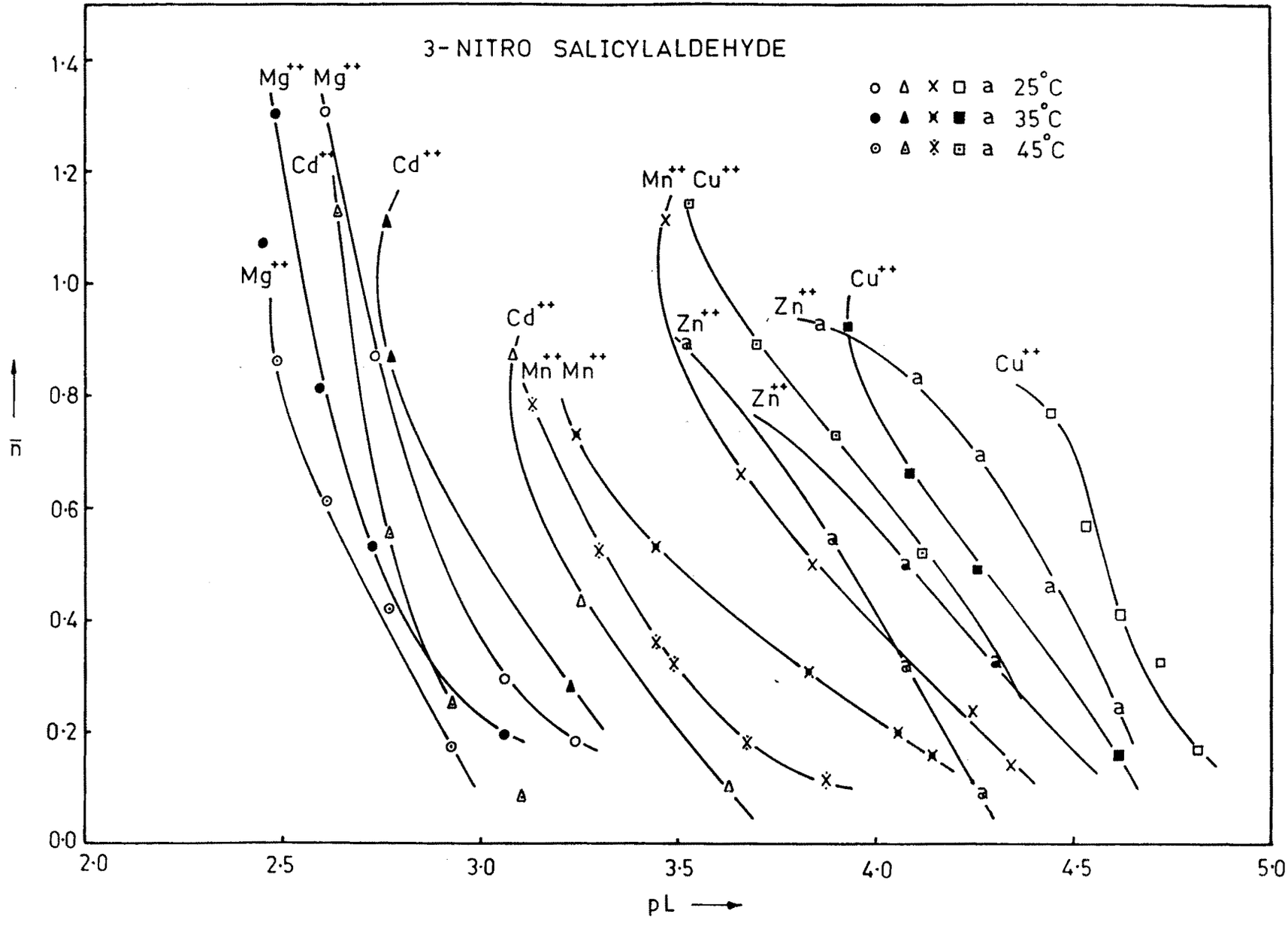

Fig.3·1·4 : FORMATION CURVES FOR METAL LIGAND SYSTEMS

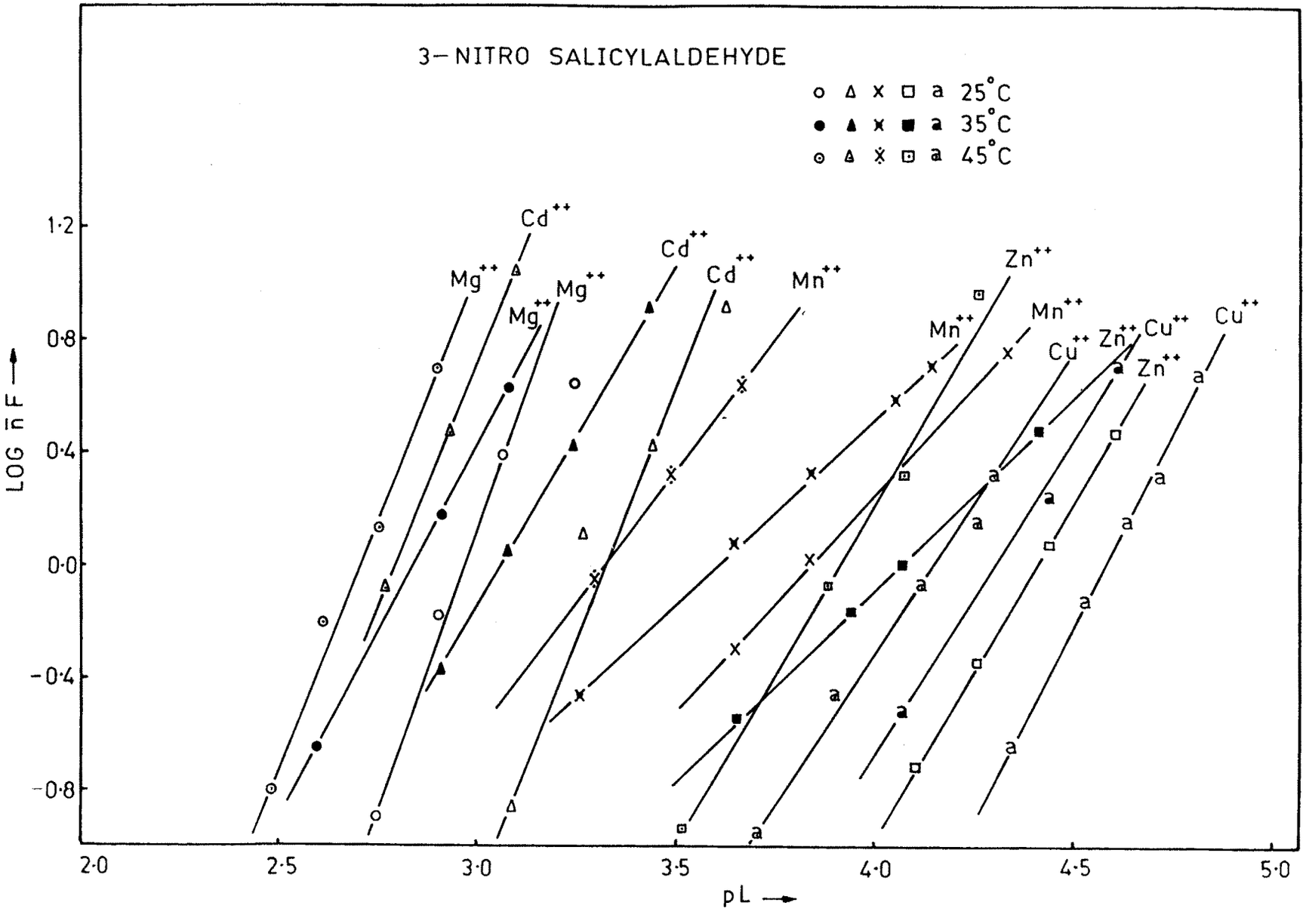

Fig. 3·1·5 : FORMATION CURVES FOR METAL-LIGAND SYSTEMS

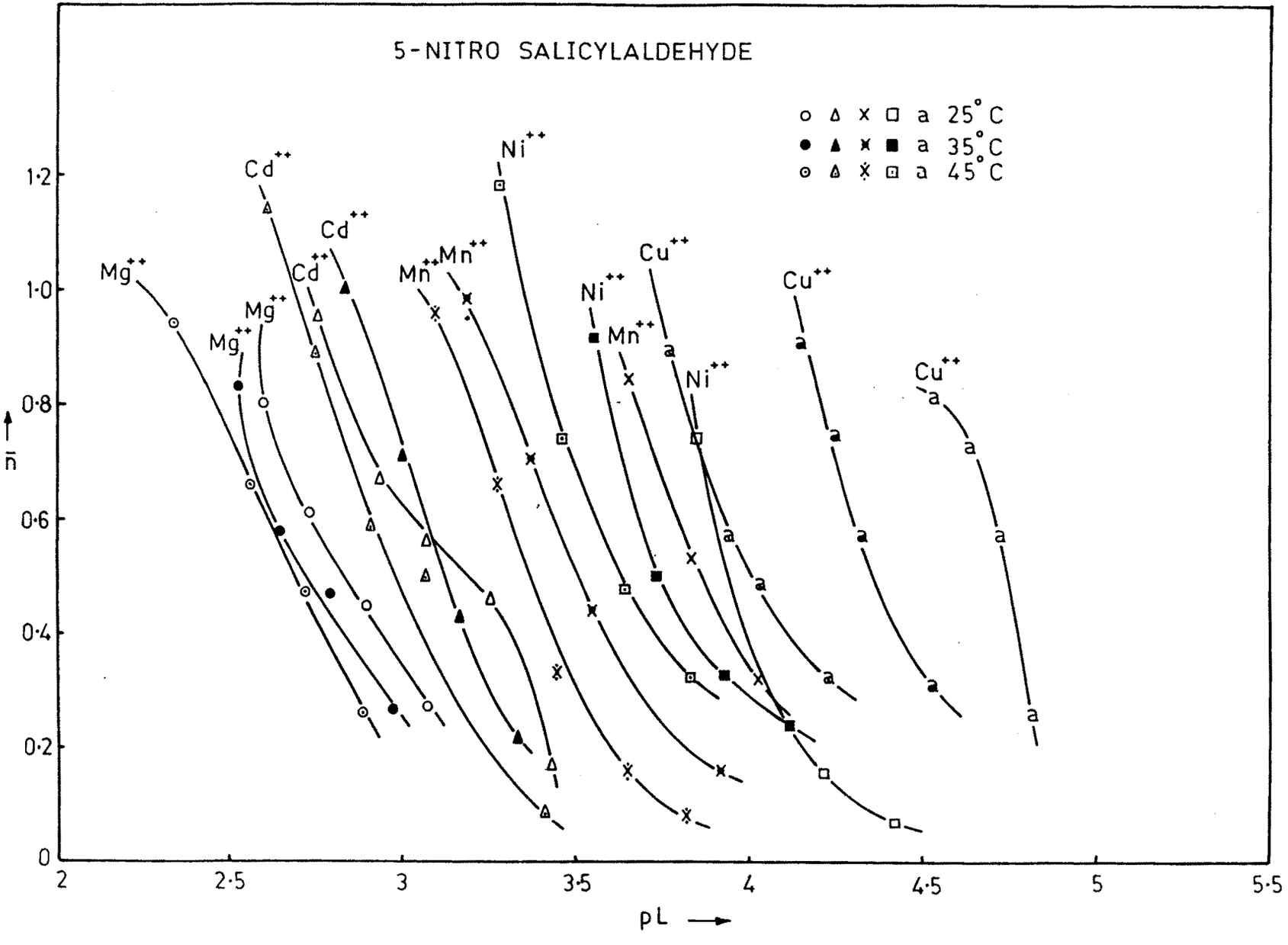

Fig. 3·2·4 : FORMATION CURVES FOR METAL LIGAND SYSTEMS

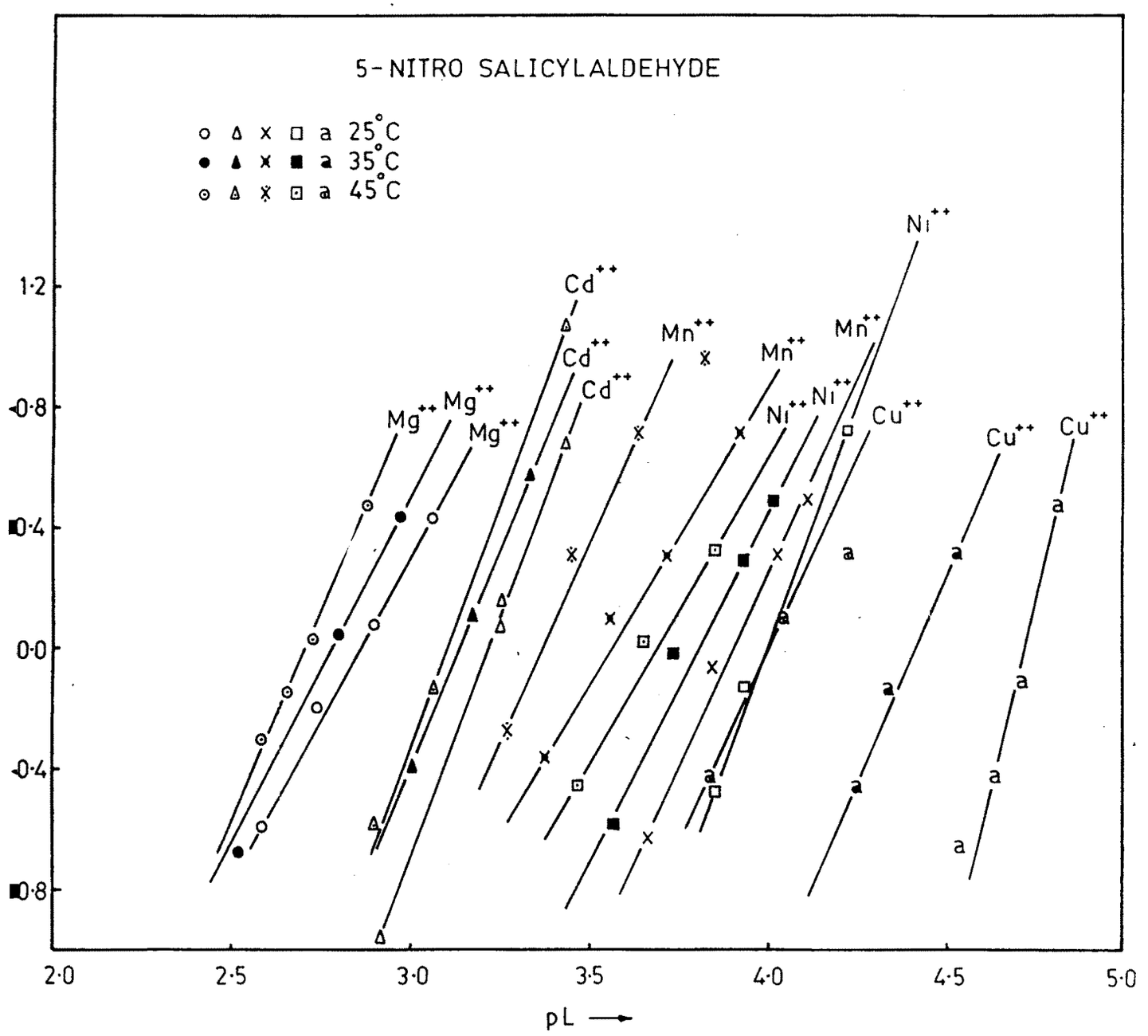

Fig. 3·2·5 : FORMATION CURVES FOR METAL-LIGAND SYSTEMS

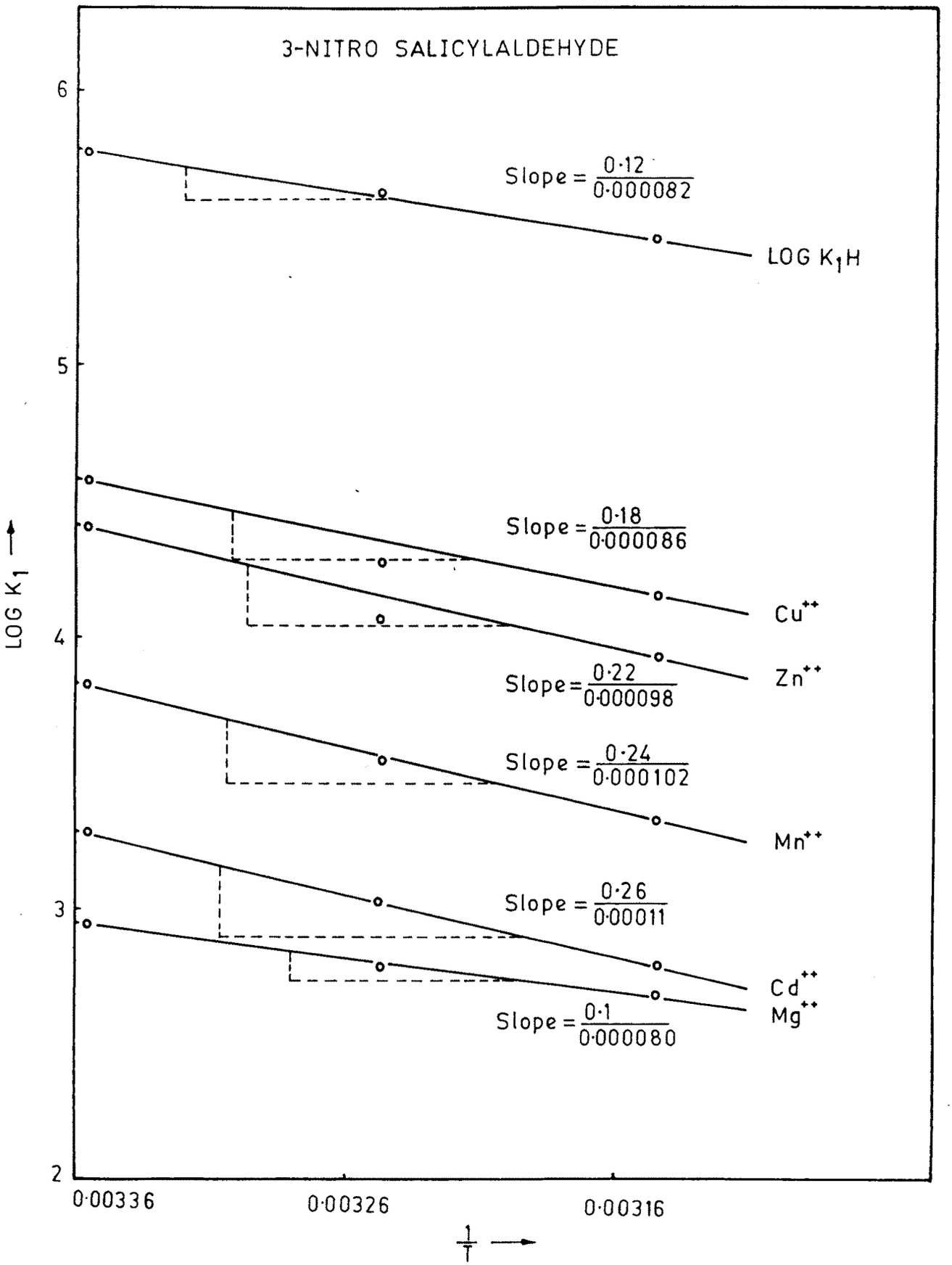

Fig. 3·1·6 : ΔH BY ISOBAR EQUATION

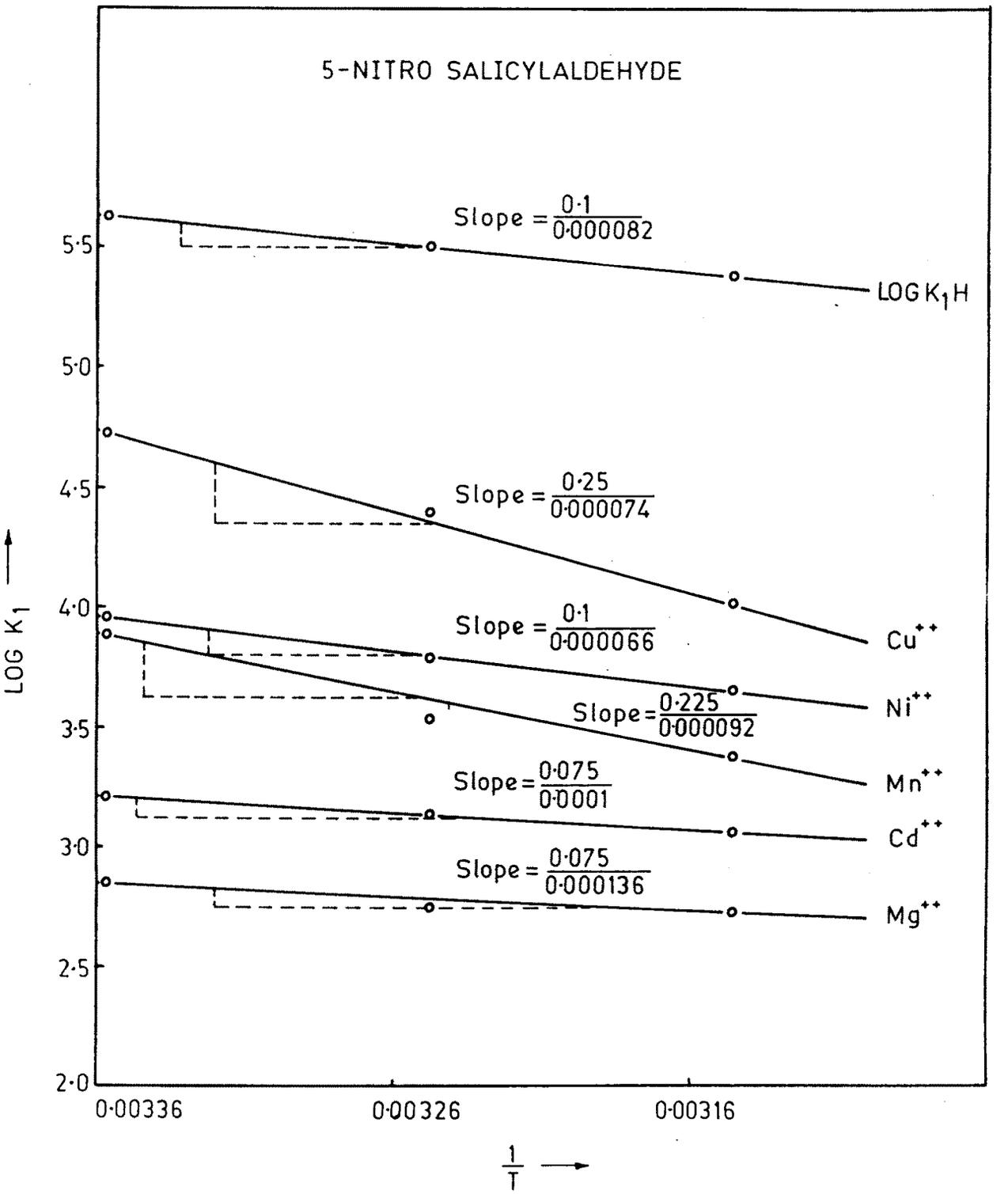

Fig. 3·2·6 : ΔH BY ISOBAR EQUATION