CHAPTER - VIII

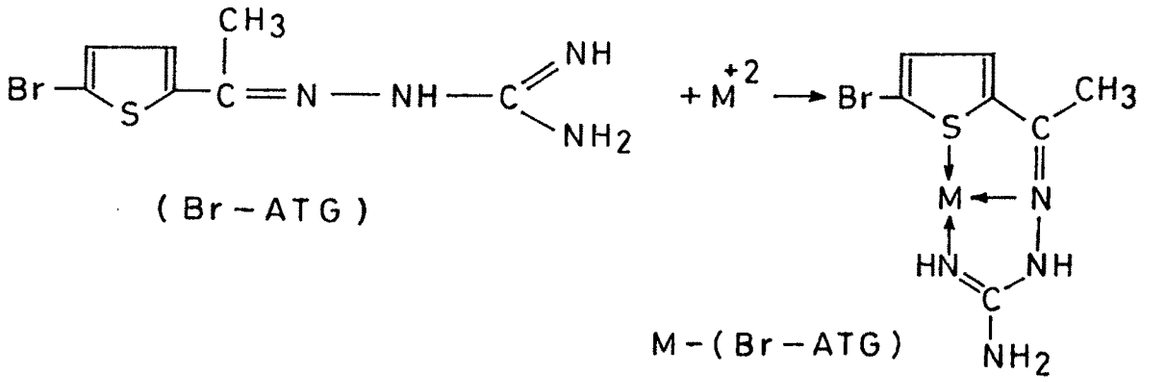
STABILITY CONSTANTS OF 5-BROMO-2-ACETYL THIOPHENE GUANYLHYDRAZONE COMPLEXES WITH SOME METAL IONS

8.1 INTRODUCTION

5-Bromo-2-acetyl thiophene guanylhydrazone (Br-ATG) forms a stable five membered ring with metal ions. This chapter deals with the study of solution equilibria in metal-(Br-ATG) system in 50% ethanol-water medium at 25°C by using pH-metric Calvin-Bjerrum technique.

The formation constants of Cu(II), Ni(II), Co(II), Mn(II) and Cd(II) with (Br-ATG) have been determined.

The reaction is



(Br-ATG)

M-(Br-ATG)

8.2 EXPERIMENTAL RESULTS

The reagent, (Br-ATG) has been used to study the formation constants with Cu, Ni, Co, Mn and Cd. In acidic medium, the ligand solution is colourless, but acquires yellow colour on addition of sodium hydroxide. All the coloured metal ions give coloured complex species. In case of Ni and Co, the initial colours of the solution change to pale blue on addition of alkali. While initially the colour of the Cu solution is pale blue, but changes to pale green by addition of sodium hydroxide.

The experimental results of pH titration are given in table 8.1 (Figure 8.1).

Table 8.1 : 5-Bromo-2-acetyl thiophene guanylhydrazone (Br-ATG) used as a ligand [L]

N^* = 0.98 M E^* = 0.02 M T^*_L = 0.0025 M μ = 0.1 M

V^* = 40.0 ml T^*_M = 0.0005 M t = 25°C A = $[HClO_4]$

Medium = 50% V/V Ethanol-water

Volume of NaOH, ml	pH						
	A	A+L	A+L+Cu^{++}	A+L+Ni^{++}	A+L+Co^{++}	A+L+Mn^{++}	A+L+Cd^{++}
0.00	1.78 CL	1.76 CL	1.76 PB	1.76 PG	1.78 PP	1.78 CL	1.76 CL
0.20	1.86	1.83	1.83	1.83	1.86	1.86	1.83
0.40	1.97	1.95	1.95	1.95	1.94	1.97	1.95
0.60	2.19	2.17	2.17	2.17	2.19	2.19	2.17
0.62	2.24	2.23	2.23	2.23	2.25	2.25	2.22
0.64	2.28	2.27	2.27	2.27	2.27	2.27	2.27
0.66	2.34	2.32	2.32	2.32	2.32	2.32	2.31
0.68	2.39	2.38	2.38	2.38	2.38	2.39	2.37
0.70	2.51	2.49	2.49	2.49	2.49	2.49	2.50
0.72	2.65	2.62	2.62	2.62	2.62	2.62	2.61
0.74	2.79	2.76	2.76	2.76	2.76	2.76	2.77
0.76	2.94	2.89	2.89	2.89	2.89	2.89	2.90
0.78	3.20	3.04	3.03	3.05	3.06	3.06	3.06
0.80	3.58	3.21	3.16	3.11	3.21	3.21	3.36
0.82	6.50	3.72	3.58	3.38	3.42	3.72	3.74
0.84	9.53	5.20	4.26	3.94	4.05	4.52	4.71
0.86	10.40	7.02	5.15	4.65	5.00	5.60	6.35
0.88	10.92	8.52 PY	5.85 PG	5.31	6.13	6.71	7.41
0.90	11.03	9.20	6.40	5.91 PB	6.82	7.83	8.14
0.92	11.14	9.60	6.90	6.55	7.36	8.39	ppt
0.94	11.22	9.91	ppt	7.06	7.80	ppt	
0.96	11.30	10.37		ppt	ppt		
0.98	11.38	10.75					
1.00	11.46	10.99					
1.02	11.55	11.16					
1.04	11.63	11.32					
1.06	11.70	11.39					

CL = Colourless PY = Pale Yellow
PG = Pale Green PB = Pale Blue
PP = Pale Pink

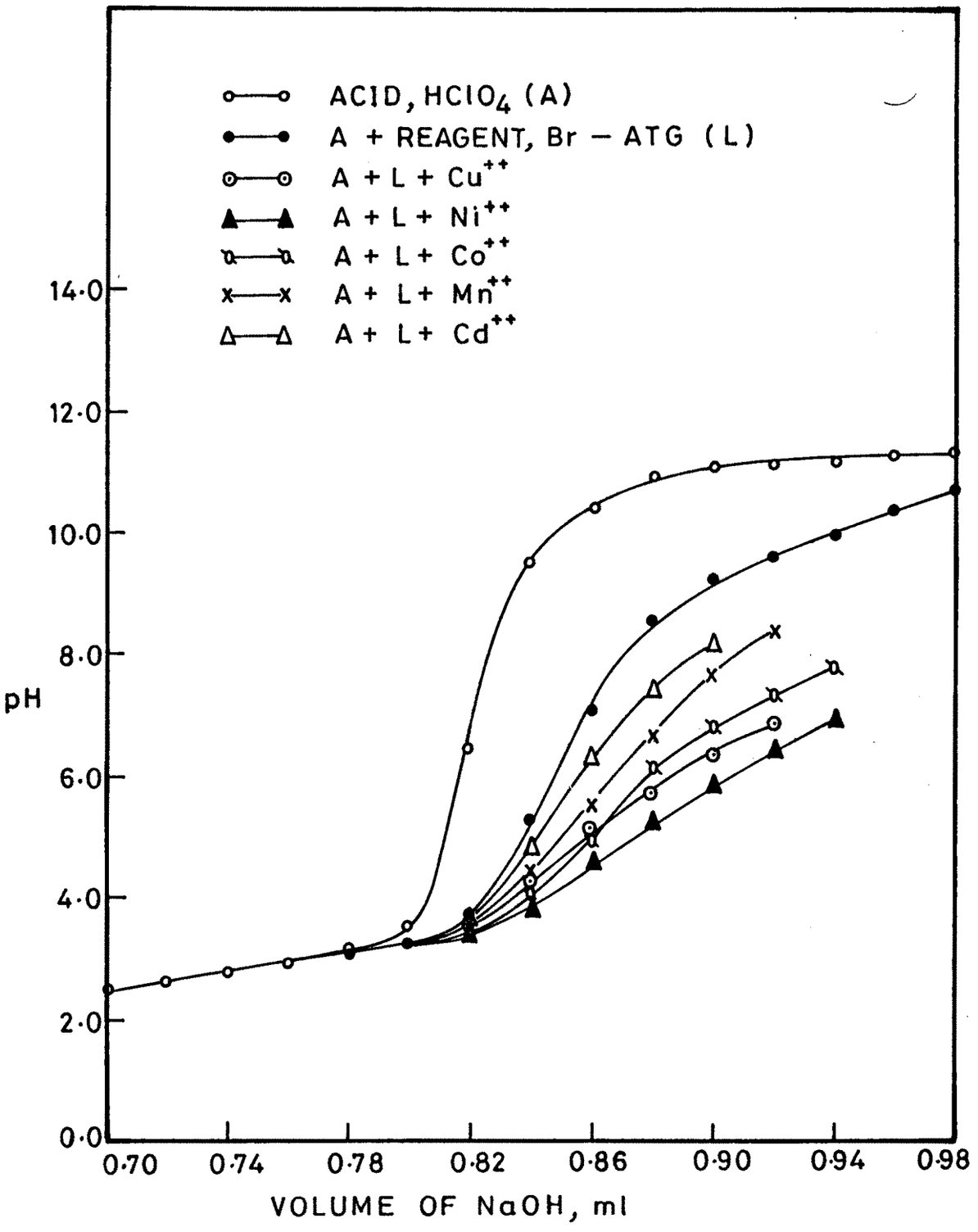


FIG. 8·1 – TITRATION CURVES
[$HClO_4$ + 5-BROMO-2-ACETYL THIOPHENE GUANYLHYDRAZONE + BIVALENT METAL ION VS NaOH].

8.3 PROTON-LIGAND STABILITY CONSTANT

The proton-ligand stability constant of the ligand, (Br-ATG) is determined. The formation constants are calculated by the data given in table 8.1.

Proton-ligand stability constant was found to be as $\log K_1^H = 8.64$ by half integral method which is in good agreement with graphical method ($\log K_1^H = 8.65$).

Table 8.2 : Proton-ligand stability constant 5-Bromo-2-acetyl thiophene guanylhydrazone (Br-ATG) used as a ligand [L]

$N^* = 0.98$ M $E^* = 0.02$ M $TL^* = 0.0025$ M $\mu = 0.1$ M

$V^* = 40.0$ ml Medium = 50% V/V Ethanol-water t = 25°C

pH	V'	V"	$\bar{n}A$	$\log \bar{n}AF$
3.00	0.768	0.777	0.9116	- 1.0138
3.50	0.793	0.813	0.8333	- 0.6989
4.00	0.806	0.824	0.8235	- 0.6690
4.50	0.811	0.831	0.8039	- 0.6129
5.00	0.813	0.838	0.7549	- 0.4887
5.50	0.815	0.843	0.7255	- 0.4222
6.00	0.817	0.848	0.6962	- 0.3601
6.50	0.820	0.853	0.6766	- 0.3206
7.00	0.823	0.860	0.6374	- 0.2451
7.50	0.826	0.866	0.6080	- 0.1907
8.00	0.831	0.872	0.5787	- 0.1379
8.50	0.832	0.880	0.5297	- 0.0517
8.75	0.834	0.888	0.4710	+ 0.0503
9.00	0.836	0.896	0.4122	+ 0.1539
9.50	0.840	0.915	0.2654	+ 0.4421

Proton-ligand stability constant

Method	$\log K_1^H$
(a) Half integral (Fig. 8.2)	= 8.64
(b) Graphical (Fig. 8.3)	= 8.65

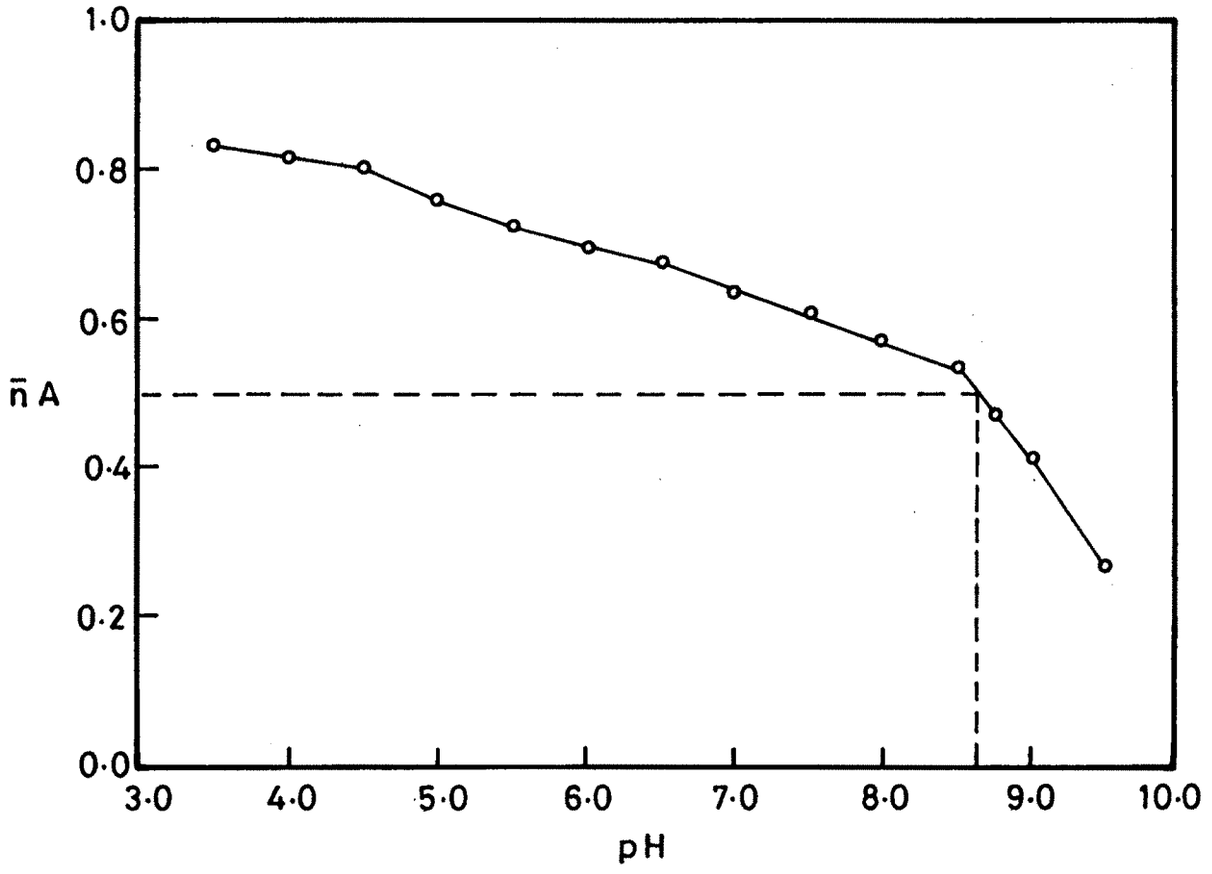


FIG. 8·2 – FORMATION CURVE FOR PROTON-LIGAND SYSTEM OF (Br-ATG).

$\log K_1^H = 8{\cdot}64$

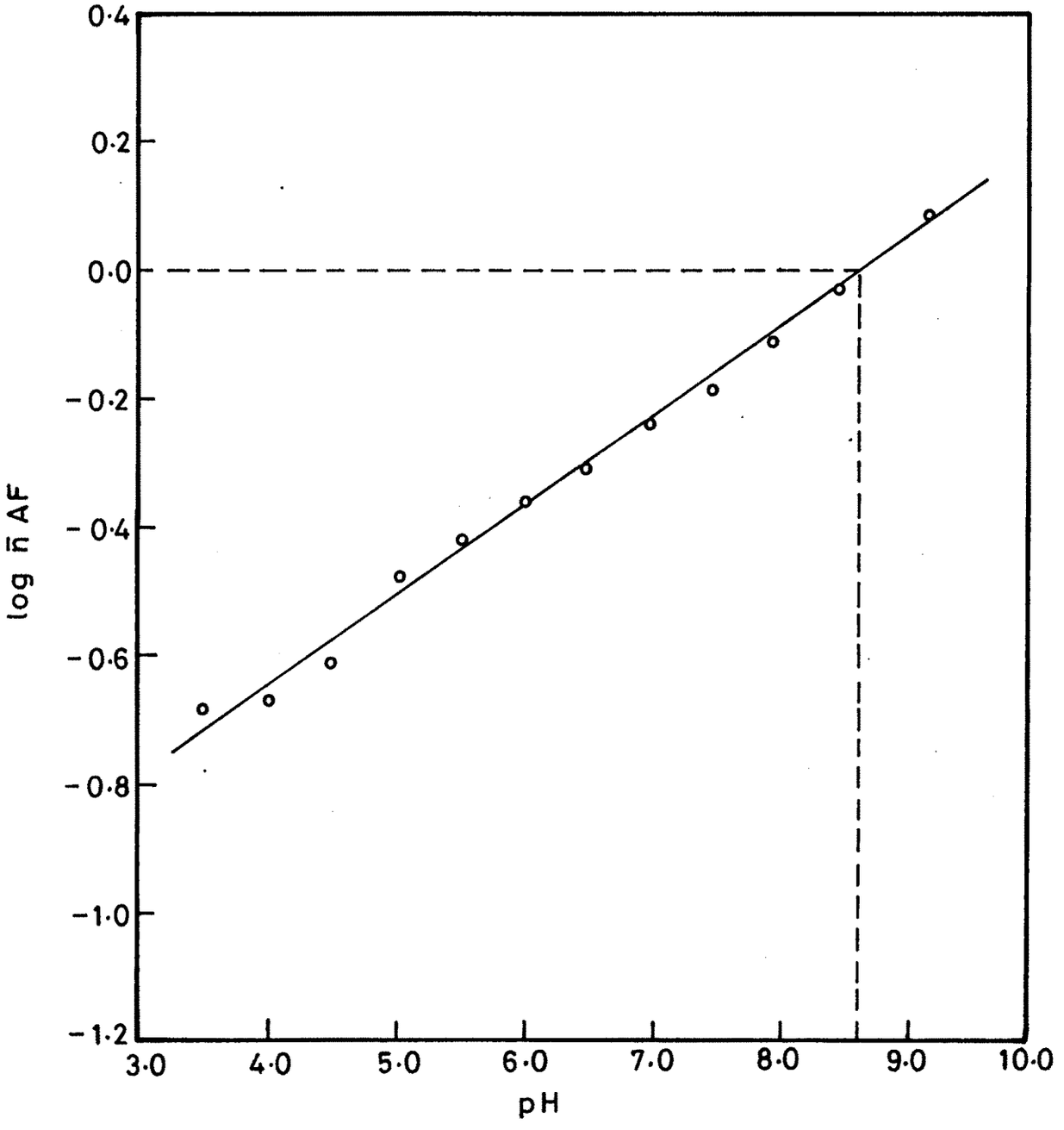


FIG.8·3 - FORMATION CURVE FOR PROTON-LIGAND SYSTEM OF (Br-ATG).

$\log K_1^H = 8{\cdot}64$

8.4 METAL-LIGAND STABILITY CONSTANTS

Metal-ligand stability constants of Cu-(Br-ATG), Ni-(Br-ATG), Co-(Br-ATG), Mn-(Br-ATG) and Cd-(Br-ATG) have been calculated by using the data available in tables from 8.3 to 8.7.

Table 8.3 : Stability constant of Cu-(Br-ATG) system

N^{*} = 0.98 M E^{*} = 0.02 M TL^{*} = 0.0025 M

μ = 0.1 M V^{*} = 40.0 ml $T^{*}Cu^{++}$ = 0.0005 M

t = 25°C Medium = 50% V/V Ethanol-water

pH	V'	V"	V"'	$\bar{n}$	pL	$\log \bar{n}F$
3.20	0.780	0.800	0.802	0.1518	9.0740	+ 0.7469
3.40	0.789	0.809	0.813	0.2747	7.8852	+ 0.4236
3.60	0.800	0.818	0.822	0.2642	7.6844	+ 0.4447
3.80	0.803	0.822	0.828	0.3893	7.4961	+ 0.1955
4.00	0.805	0.825	0.834	0.5783	7.3144	- 0.1372
4.20	0.807	0.828	0.839	0.7103	7.1276	- 0.3895
4.40	0.808	0.830	0.843	0.8455	6.9416	- 0.7385
4.60	0.809	0.833	0.847	0.9343	6.7510	- 1.1535

Metal-ligand stability constant

Method	$\log k_1$
(a) Half integral (Fig.8.4)	= 7.37
(b) Graphical (Fig.8.5)	= 7.36

Table 8.4 : Stability constant of Ni-(Br-ATG) system

N' = 0.98 M E° = 0.02 M TL° = 0.0025 M
μ = 0.1 M V° = 40.0 ml $T°Ni^{++}$ = 0.0005 M
t = 25°C Medium = 50% V/V Ethanol-water

pH	V'	V"	V"'	$\bar{n}$	pL	$\log \bar{nF}$
2.90	0.760	0.760	0.766	0.2944	8.3866	+ 0.3796
3.00	0.764	0.775	0.780	0.2897	8.2863	+ 0.3894
3.10	0.775	0.795	0.798	0.2128	8.1795	+ 0.5681
3.20	0.780	0.800	0.809	0.5787	8.1141	- 0.1378
3.30	0.784	0.805	0.815	0.6490	8.0212	- 0.2669
3.40	0.789	0.809	0.821	0.7615	7.9326	- 0.5041
3.50	0.795	0.814	0.824	0.6302	7.8194	- 0.2316
3.60	0.800	0.818	0.829	0.6807	7.7245	- 0.3287
3.70	0.802	0.820	0.832	0.7402	7.6305	- 0.4547
3.80	0.803	0.822	0.835	0.8107	7.5378	- 0.6319

Metal-ligand stability constant

Method	**$\log k_1$**
(a) Half integral (Fig.8.4)	= 8.04
(b) Graphical (Fig.8.5)	= 8.03

Table 8.5 : Stability constant of Co-(Br-ATG) system

N' = 0.98 M E° = 0.02 M TL° = 0.0025 M
μ = 0.1 M V° = 40.0 ml $T°Co^{++}$ = 0.0005 M
t = 25°C Medium = 50% V/V Ethanol-water

pH	V'	V"	V"'	$\bar{n}$	pL	$\log \bar{nF}$
3.20	0.782	0.798	0.802	0.2510	8.1500	+ 0.4746
3.40	0.794	0.811	0.817	0.3773	7.8949	+ 0.2174
3.60	0.800	0.817	0.825	0.4949	7.7061	+ 0.0088
3.80	0.804	0.821	0.833	0.7300	7.5295	- 0.4320
4.00	0.807	0.824	0.837	0.7887	7.3356	- 0.5722
4.20	0.809	0.827	0.842	0.9185	7.1492	- 1.0522

Metal-ligand stability constant

Method	**$\log k_1$**
(a) Half integral (Fig. 8.4)	= 7.73
(b) Graphical (Fig. 8.5)	= 7.72

Table 8.6 : Stability constant of Mn-(Br-ATG) system

N' = 0.98 M E° = 0.02 M TL° = 0.0025 M
μ = 0.1 M V° = 40.0 ml $T°Mn^{++}$ = 0.0005 M
t = 25°C Medium = 50% V/V Ethanol-water

pH	V'	V"	V"'	$\bar{n}$	pL	$\log \frac{\bar{n}}{nF}$
3.80	0.804	0.821	0.824	0.2008	7.4787	+ 0.5996
4.00	0.807	0.824	0.829	0.3184	7.2895	+ 0.3304
4.20	0.809	0.827	0.834	0.4426	7.1012	+ 0.1000
4.40	0.811	0.829	0.838	0.5616	6.9128	- 0.1075
4.60	0.812	0.832	0.842	0.6391	6.7205	- 0.2483
4.80	0.813	0.835	0.845	0.6581	6.5229	- 0.2844
5.00	0.813	0.838	0.849	0.7532	6.3325	- 0.4847
5.20	0.814	0.840	0.851	0.7648	6.1334	- 0.5122
5.40	0.814	0.842	0.855	0.9237	5.9501	- 1.0835

Metal-ligand stability constant

Method	$\log k_1$
(a) Half integral (Fig. 8.4)	= 6.90
(b) Graphical (Fig. 8.5)	= 6.91

Table 8.7 : Stability constant of Cd-(Br-ATG) system

N' = 0.98 M E° = 0.02 M TL° = 0.0025 M
μ = 0.1 M V° = 40.0 ml $T°Cd^{++}$ = 0.0005 M
t = 25°C Medium = 50% V/V Ethanol-water

pH	V'	V"	V"'	$\bar{n}$	pL	$\log \frac{\bar{n}}{nF}$
3.80	0.803	0.822	0.823	0.0882	7.4686	+ 1.0141
3.90	0.804	0.823	0.826	0.2086	7.3794	+ 0.5789
4.00	0.805	0.825	0.828	0.2126	7.2798	+ 0.5683
4.20	0.807	0.828	0.832	0.2785	7.0854	+ 0.4134
4.40	0.808	0.830	0.835	0.3459	6.8921	+ 0.2765
4.60	0.809	0.833	0.839	0.4219	6.6994	+ 0.1366
4.80	0.810	0.835	0.842	0.4939	6.5063	+ 0.0105
5.00	0.812	0.838	0.846	0.5677	6.3135	- 0.1183
5.20	0.813	0.840	0.849	0.6434	6.1211	- 0.2564
5.40	0.814	0.842	0.852	0.7212	5.9291	- 0.4127
5.60	0.815	0.844	0.855	0.8011	5.7374	- 0.6050

Metal-ligand stability constant

Method	$\log k_1$
(a) Half integral (Fig. 8.4)	= 6.50
(b) Graphical (Fig. 8.5)	= 6.50

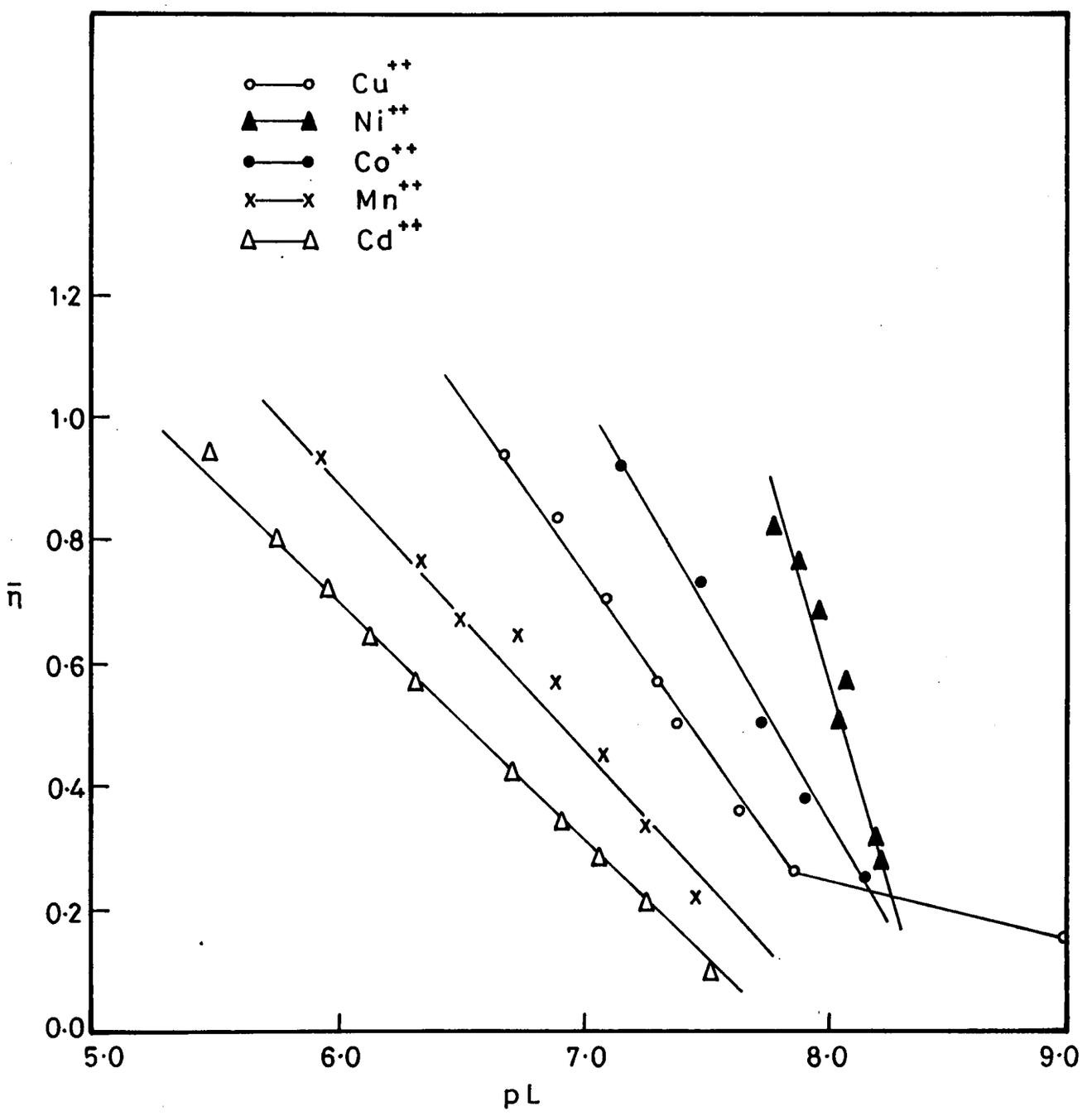


FIG.8·4 - FORMATION CURVES FOR METAL-LIGAND SYSTEMS OF (Br – ATG).

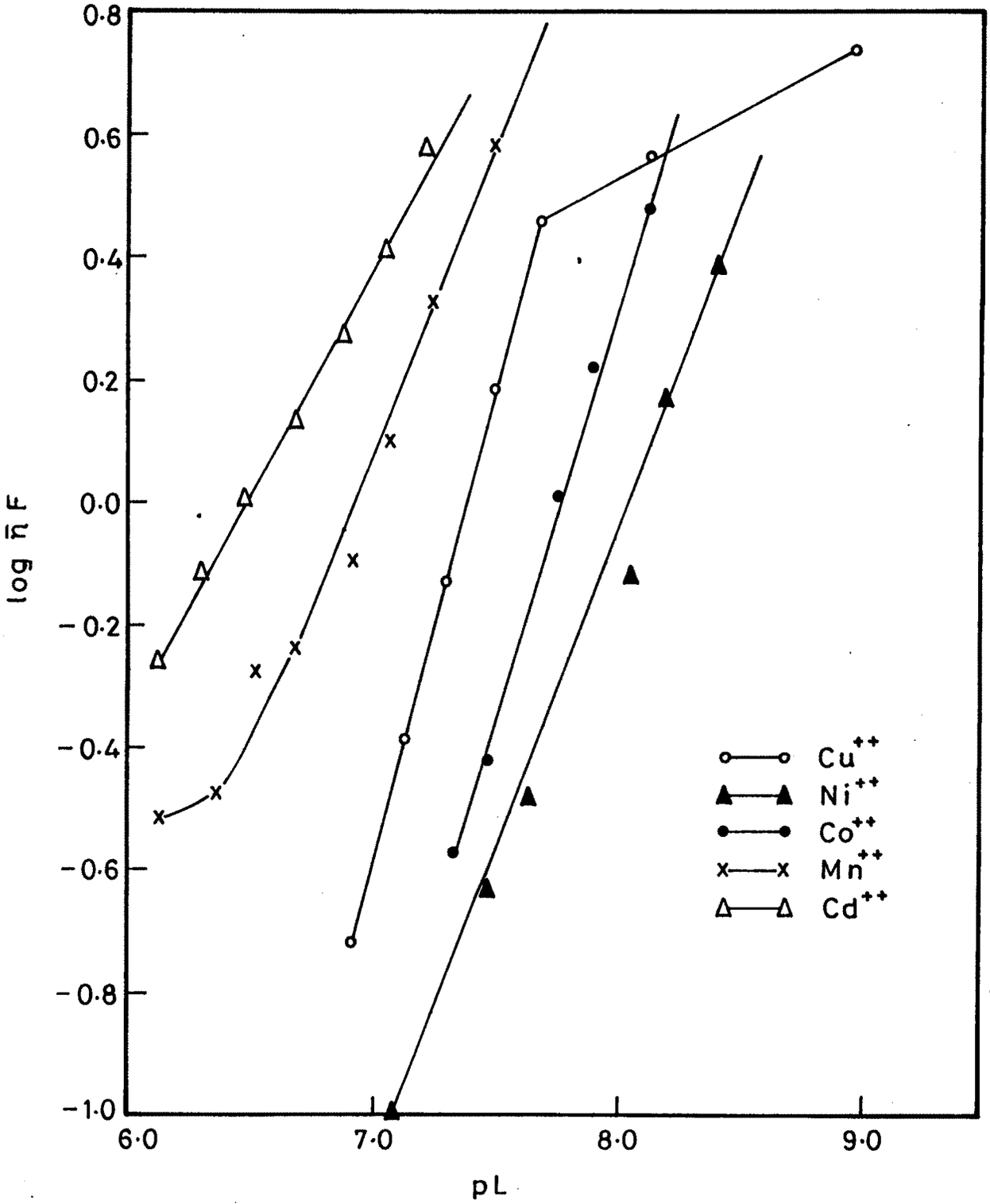


FIG.8·5 – FORMATION CURVES FOR METAL–LIGAND SYSTEMS OF (Br–ATG).

Metal-ligand stability constants of the complexes with Br-ATG are given in table 8.8.

Table 8.8 : Metal-ligand stability constants

a - Half integral
b - Graphical
c - Mean

Metal ion	log K_1		
	a	b	c
Cu^{++}	7.37	7.36	7.365
Ni^{++}	8.04	8.03	8.035
Co^{++}	7.73	7.72	7.725
Mn^{++}	6.90	6.91	6.905
Cd^{++}	6.50	6.50	6.500

8.4.1 Order of log K Values:

In the present work, the stability constant order of metal complexes with (Br-ATG) is Ni > Co > Cu > Mn > Cd.