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Evaluation of stability constants of 1-(3-bromo-4-hydroxy-5-methoxy benzylidene) thiosemicarbazide(TRM-1) with copper (II), cobalt (II) and nickel (II) complexes by pH metric method

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ABSTRACT

This study was taken out for determine the stability constants of the complexes of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene) thiosemicarbazide (TRM-1) in Dioxane: Water ratio 60: 40 (V/V) mixture by pH-Meter. The proton-ligand and metal-ligand stability constants of Cu(II), Ni(II) and Co(II) metal ions with TRM-1 have been performed pH metric method at 0.1 M ionic strength at 30℃ ± 0.2℃ temperature. The Proton-ligand stability constants $\log pK_1^{\,H}$, $\log pK_2^{\,H}$ *and* $\log \beta^H$ *is 10.66, 3.11 and 13.77 respectively and the Metal ligand stability constants is determine different Computational Methods.*

Keywords: Proton-ligand stability constants and Metal ligand stability constants, 1-(3-bromo-4-hydroxy-5-methoxybenzylidene) thiosemicarbazide, pH metric

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INTRODUCTION

Recently, the high stability of the complexes prepared with *vic*-dioxime ligands have been extensively used for various purposes including model compounds for vitamin B12 analytical and medicinal chemistry, pigments [1, 2]. Schnauzer has found that this kind of complexes exhibits semiconductor property [3]. An investigation4 has been done about spectrometric and potentiometric characterizations of these kinds of compounds and stability constants with divalent metal ions.

Stability constants of metals complexes have been determined by many different methods such as spectroscopy [4] and potentiometry [5]. It is well-known that the simplest electroanalytical technique for determination of stability constants is potentiometric titration system used for the glass electrode. SUPERQUAD [6], a powerful computer program, was used in the evaluation of data obtained from this technique. In the literature, the synthesis of *vic*-dioximes and their various derivatives have been a subject of study for a long period of time [7]. The determination of the metal – ligand stability constant requires the knowledge of reliable and accurate values of proton-ligand stability constants. Thus, proton-ligand and metal-ligand stability constants are correlated with each other.

The present work describes the interaction between Cu (II), Ni (II) and Co (II) with 1-(3-bromo-4-hydroxy-5-methoxybenzylidene) thiosemicarbazide (TRM-1) as ligand in Dioxane: Water ratio 60: 40 (V/V) mixture has been determined by pH-Meter. The ligand are insoluble in water hence, 60% dioxane-aqueous medium was used as solvent. The proton ligand stability constants and metal ligand stability constants at 30° ± 0.2°C temperatures for synthesized ligands and metal complexes by the Calvin Bjerrum titration technique adopted by Irvin and Rossetti. the Metal ligand stability constants is determine different Computational Methods like Half integral method [8]/ Interpolation at half $\bar{n}$ values [10], Least square method [9], Linear plot method [8] and Point wise calculation method [11].

MATERIALS AND METHODS

Chemicals and Reagents
All the chemicals used in the present study were Analar grade. The glassware's used in the present experiment were borosil glass quality and standardized as per standard procedure.

Preparation of the sample solution
The solutions of reagents were prepared in double glass distilled water having 6.80-6.90 pH. The NaOH solution was prepared in double distilled water and fresh solution was used as a titrant for pH titrations. It is standardized with 0.05 M succinic acid. The 1.0 M $NaNo_3$ solutions were prepared to maintain the 0.1 M ionic strength of the titration solutions by taking requisite amount of Sodium nitrate. The metal solutions were standardized by usual procedure [12].

Digital pH meter
pH of solutions to calculate the proton ligand stability constants and metal ligand stability constants were measured with a EQUIP-TRONICS instrument (Model EQ-614) equipped with a combined electrode and magnetic stirrer pH-meter (accuracy ± 0.005 units) with a combined glass electrode assembly of pH range 0 to 14. This instrument has been built in an internal electronic voltage supply with a temperature compensator covering the range from 0 to 100°C. The instrument was calibrated with buffer solution of known pH before starting the pH titrations. All the necessary precautions were taken for smooth working of electrode [13].

Calvin Bjerrum pH titration
The following sets of solutions were prepared for pH titration.

Set 1 : 0.8 mL 0.1 M HNO_3 + 11.2 mL distilled water + 24.0 mL dioxane + 4.0 mL 1 M $NaNO_3$.

Set 2 : 0.8 mL 0.1 M HNO_3 + 11.2 mL distilled water + 22.0 mL dioxane + 2.0 mL 0.1 M ligand solution + 4.0 mL 1 M $NaNO_3$.

Set 3 : 0.8 mL 0.1 M HNO_3 + 10.8 mL distilled water + 22.0 mL dioxane + 2.0 mL 0.1 M ligand solution + 4.0 mL 1 M $NaNO_3$ + 0.4 mL 0.1 M metal solution.

The total volume (V°) of the every set is 40 mL. The ligand solutions were prepared in Dioxane : Water ratio 60 : 40 (V/V).

Solutions mentioned above sets were allowed to stand at a 30°C ± 0.2°C temperature for few minutes then titrated against standard alkali solution (NaOH 0.5 N) under an inert atmosphere of nitrogen. The change in the pH of the solution with each addition of alkali was recorded are given in TABLE 3.

RESULTS AND DISCUSSION

The proton-ligand stability constant and metal-ligand stability constants(Log K) of TRM-1and their complexes with Cu(II), Ni(II) and Co(II) metal ions determined in 60% dioxane-water mixture at 30°C ± 0.2°C.

We have studied the proton ligand stability constants and metal ligand stability constants at 30° ± 0.2°C temperatures for synthesized ligands and metal complexes by the Calvin Bjerrum titration technique adopted by Irvin and Rossotti.

Table 1: Proton-ligand stability constants of the ligands at 30° ± 0.2°C

Ligand	$\log pK_1^H$	$\log pK_2^H$	$\log \beta^H$
TRM – 1	10.66	3.11	13.77

Table 2: Metal ligand stability constant of M(TRM - 1)₂ at 30° ± 0.2°C

Chelates	Stability Constant	Computational Methods			
		a	b	c	d
Cu(TRM-1)$_2$	$\log K_1$	8.62	8.63	8.60	8.64
	$\log K_2$	4.73	4.71	4.76	4.72
	$\log \beta_2$	13.35	13.34	13.36	13.36
Ni(TRM-1)$_2$	$\log K_1$	9.02	8.98	8.99	8.96
	$\log K_2$	5.61	5.62	5.62	5.66
	$\log \beta_2$	14.63	14.63	14.61	14.62
Co(TRM-1)$_2$	$\log K_1$	8.61	8.60	8.61	8.63
	$\log K_2$	5.35	5.36	5.37	5.36
	$\log \beta_2$	13.95	13.96	13.98	13.99

(a) Interpolation at half $\bar{n}$ values , (b) Least square method, (c) Linear plot method , (d)Point wise calculation method

Calvin and Wilson have demonstrated that pH measurements made during titrations with alkali solution of ligand in the presence and absence of metal ion could be employed to calculate the formation functions $\bar{n}_A$, $\bar{n}$ and pL and stability constants can be computed. Irving and Rossotti [14], titrated following solutions against standard sodium hydroxide solution N° keeping total volume V° constant.

The formation functions $\bar{n}_A$, $\bar{n}$ and pL can be computed from the following eqations:

$$\bar{n}_A = Y - \frac{(V_1 - V_2)(N^\circ - E^\circ)}{(V^\circ + V_1)T_{CL^\circ}} \quad (1)$$

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_1)(\bar{n}_A)(T_{CM^\circ})} \quad (2)$$

$$pL = \log_{10} \frac{1 + K_1^H[H] + K_1^H K_2^H [H]^2 + ...}{T_{CL^\circ} - \bar{n}T_{CM^\circ}} \times \frac{V^\circ + V_3}{V^\circ}$$

$$pL = \log_{10} \frac{\sum_{n=0}^{n} \beta_n^H \cdot \frac{1}{(anti \log B)^n}}{T_{CL^\circ} - \bar{n}T_{CM^\circ}} \times \frac{V^\circ + V_3}{V^\circ} \quad (3)$$

Where,
Y = number of dissociable protons
V_1, V_2 and V_3 = volume of alkali employed bring the solution 1, 2 and 3 to same pH value
T_{CL° = total concentration of the ligand
T_{CM° = total concentration of metal ion

By the knowledge of $\bar{n}_A$, $\bar{n}$, pH and pL protonation and stepwise stability constants can be computed by different methods such as Half integral method/Interplotation at half $\bar{n}$ values, Least square method, Linear plot method and Point wise calculation method.

Table 3: The pH titration reading of acid, acid + ligand (TRM - 1) and acid + ligand(TRM - 1) + metal ions.

Vol. of alkali added	Acid	Acid + ligand	Acid + ligand + metal ions		
			Cu^{+2}	Ni^{+2}	Co^{+2}
0.00	1.70	1.70	1.70	1.70	1.70
0.50	1.80	1.85	1.85	1.85	1.85
1.00	2.00	2.35	2.45	2.32	2.40
1.20	2.30	2.71	2.62	2.70	2.60
1.30	2.35	2.90	2.85	2.88	2.81
1.40	2.50	3.25	3.20	3.23	3.21
1.50	2.75	3.75	3.75	3.55	3.65
1.52	2.82	3.90	3.85	3.95	3.77
1.54	2.90	4.00	3.96	4.10	3.83
1.56	3.01	4.19	4.07	4.16	4.00
1.58	3.10	4.40	4.20	4.21	4.25
1.60	3.20	4.52	4.25	4.25	4.50
1.62	3.55	4.61	4.50	4.52	4.62
1.64	4.35	4.75	4.52	4.65	4.80
1.66	8.40	5.00	5.02	4.77	4.98
1.68	10.25	8.50	5.24	5.00	5.25
1.70	11.20	8.98	5.72	5.25	5.74
1.75	11.75	9.70	6.26	6.01	6.59
1.80	12.10	10.30	7.78	6.56	7.60
1.85	12.25	10.76	8.69	8.56	8.48
1.90	12.30	11.00			8.95
1.95	12.41	11.18	9.04	9.24	9.39
2.00	12.50	11.40	9.50		

$N° = 0.5$, $E° = 0.02$ M, $V° = 40.0$ ml, $T_{CL}° = 5 \times 10^{-3}$ M, $T_{CM}° = 1 \times 10^{-3}$ M, $t = 30 \pm 0.2$ ℃, $u° = 0.1$ M
Solvent = Dioxane : water 60 : 40 (v/v).

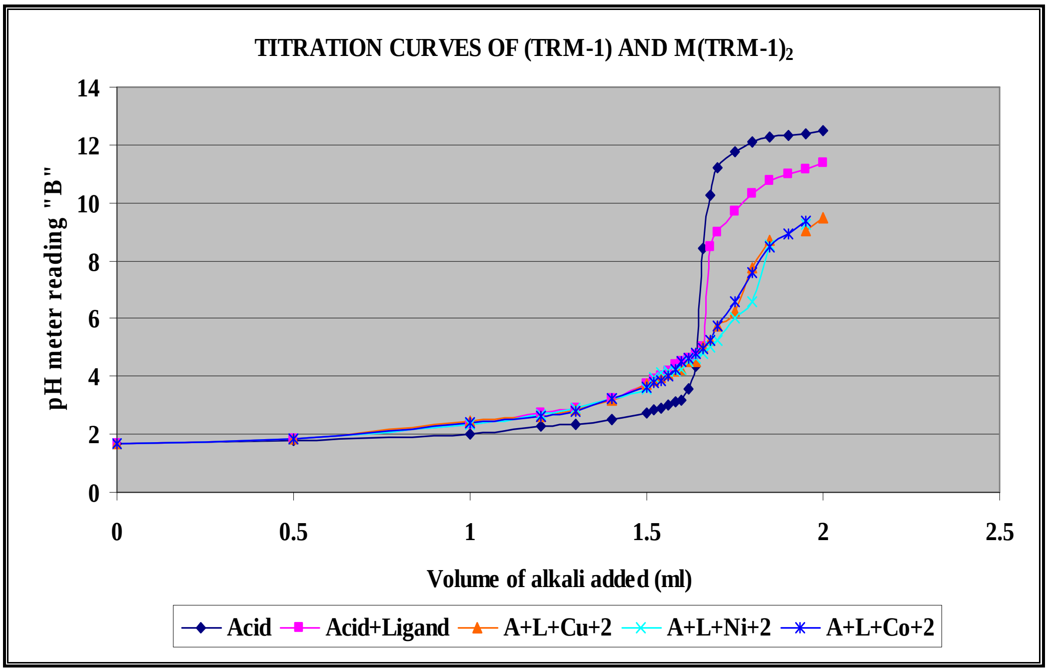

Figure 1: Graph of pH v/s volume of added NaOH of HNO_3 acid, ligand(TRM-1) and Cu(II), Ni(II) and Co(II) ions

The maximum values of in all cases were found to be ≥ 2, indicating that ML and ML2 type complexes are formed in solution [15]. The precipitate was formed during the titration its indicating that the possibility of formation of metal hydroxide can be included [16]. The stability of all complexes are higher than those of corresponding ligands because thiosemicarbazone compounds are good complexing agents.

Table 4: 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide(TRM- 1) at 30° ± 0.2°C

B	$V_1 - V_2$	$\bar{n}_A$	$\log \frac{2-\bar{n}_A}{\bar{n}_A - 1}$	$\log PK_2^H$
2.50	0.321	1.8042	-0.6135	3.1135
2.75	0.279	1.6967	-0.3613	3.1113
3.00	0.226	1.5640	-0.1118	3.1118
3.25	0.171	1.4252	0.1311	3.1188
3.50	0.116	1.2901	0.3887	3.1113
3.75	0.075	1.1876	0.6366	3.1134
4.00	0.046	1.1149	0.8865	3.1135
4.25	0.027	1.0680	1.1339	3.1161
4.50	0.016	1.0394	1.3877	3.1123
4.75	0.009	1.0226	1.6377	3.1152
5.00	0.005	1.0128	1.8845	3.1155

Average $\log PK_2^H$ = 3.1138

B	$V_2 - V_1$	$\bar{n}_A$	$\log \frac{\bar{n}_A}{1-\bar{n}_A}$	$\log PK_1^H$
9.25	0.015	0.9626	1.4122	10.6612
9.50	0.026	0.9355	1.1613	10.6013
9.75	0.044	0.8908	0.9111	10.6611
10.00	0.072	0.8208	0.612	10.6612
10.25	0.112	0.7204	0.4114	10.6614
10.50	0.163	0.5920	0.1615	10.6615
10.75	0.221	0.4493	-0.0883	10.6617
11.00	0.275	0.3142	-0.3398	10.6610
11.25	0.318	0.2049	-0.5889	10.6611
11.50	0.350	0.1267	-0.8384	10.6616

Average $\log PK_1^H$ = 10.6613

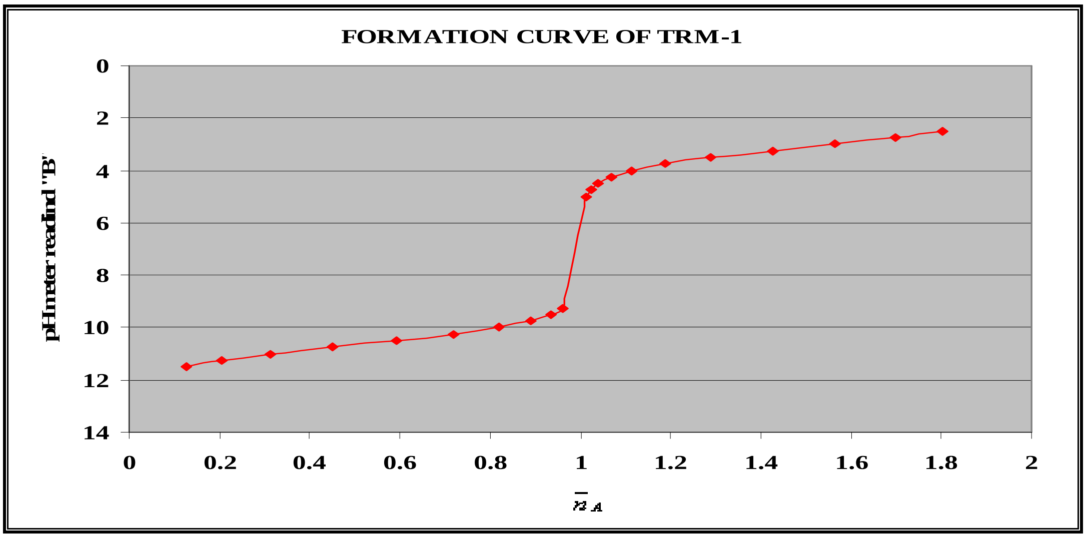

Figure 2: Graph of pH v/s $\bar{n}_A$

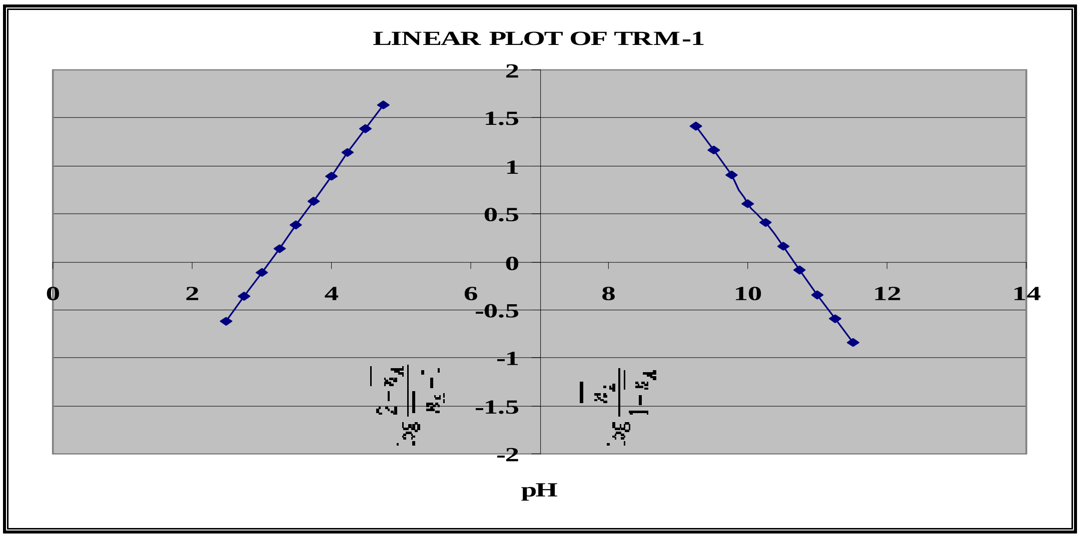

Figure 3: Graph of pH v/s $\log \frac{2-\overline{n_A}}{\overline{n_A}-1}$ **and** $\log \frac{\overline{n_A}}{1-\overline{n_A}}$

Table 5: Copper + 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide(TRM- 1) at 30° ± 0.2°C

B	V_3	V_2	V_3-V_2	$\bar{n}$	pL
4.50	1.602	1.593	0.009	0.0958	11.7559
4.75	1.614	1.600	0.014	0.1749	11.0227
5.00	1.636	1.618	0.018	0.1957	10.2819
5.25	1.665	1.637	0.028	0.3183	9.5419
5.50	1.678	1.640	0.038	0.4745	8.8043
5.75	1.698	1.643	0.055	0.6868	8.0651
6.00	1.711	1.647	0.064	0.7992	7.3253
6.25	1.730	1.650	0.080	0.9985	6.5865
6.50	1.751	1.654	0.097	1.2107	5.8486
6.75	1.765	1.660	0.105	1.3106	5.1863
7.00	1.778	1.663	0.115	1.4352	4.7307
7.25	1.789	1.666	0.123	1.5351	3.6388
7.50	1.800	1.670	0.130	1.6225	2.8988
7.75	1.810	1.673	0.137	1.7096	2.1617
8.00	1.820	1.682	0.138	1.8145	1.8094
8.25	1.838	1.688	0.150	1.8832	0.4843

Table 6: Nickel + 1-(3-bromo-4-hydroxy-5- ethoxybenzylidene)thiosemicarbazide(TRM- 1) at 30° ± 0.2°C

B	V_3	V_2	V_3-V_2	$\bar{n}$	pL
4.25	1.595	1.588	0.007	0.0784	12.4071
4.50	1.611	1.593	0.018	0.1830	11.7650
4.75	1.627	1.600	0.027	0.2859	11.0228
5.00	1.651	1.618	0.033	0.3784	10.3881
5.25	1.675	1.637	0.038	0.4683	9.5508
5.50	1.696	1.640	0.056	0.6591	8.8150
5.75	1.721	1.643	0.078	0.8995	8.0785
6.00	1.745	1.647	0.098	1.1481	7.3414
6.25	1.765	1.650	0.115	1.3477	6.6034
6.50	1.778	1.654	0.124	1.4725	5.8648
6.75	1.789	1.660	0.129	1.5723	5.1298
7.00	1.801	1.663	0.138	1.6846	4.3914
7.25	1.813	1.666	0.147	1.7845	3.6541
7.50	1.823	1.670	0.153	1.8460	2.9206

Table 7: Cobalt + 1-(3-bromo-4-hydroxy-5- ethoxybenzylidene)thiosemicarbazide(TRM- 1) at 30° ± 0.2°C

B	V_3	V_2	V_3-V_2	$\bar{n}$	pL
4.50	1.601	1.593	0.008	0.0903	12.0930
4.75	1.613	1.600	0.013	0.1499	11.3530
5.00	1.637	1.618	0.019	0.1968	10.6161
5.25	1.664	1.637	0.027	0.3205	9.8789
5.50	1.677	1.640	0.037	0.4623	9.1416
5.75	1.688	1.643	0.045	0.5744	8.4010
6.00	1.709	1.647	0.062	0.7866	7.6630
6.25	1.724	1.650	0.074	0.9989	6.9238
6.50	1.755	1.654	0.101	1.3081	6.1850
6.75	1.771	1.660	0.111	1.4105	5.4498
7.00	1.781	1.663	0.118	1.5110	4.7095
7.25	1.793	1.666	0.127	1.6226	3.9700
7.50	1.803	1.670	0.133	1.7096	3.2321
7.75	1.815	1.673	0.142	1.8090	2.4984
8.00	1.833	1.682	0.151	1.8828	1.7600

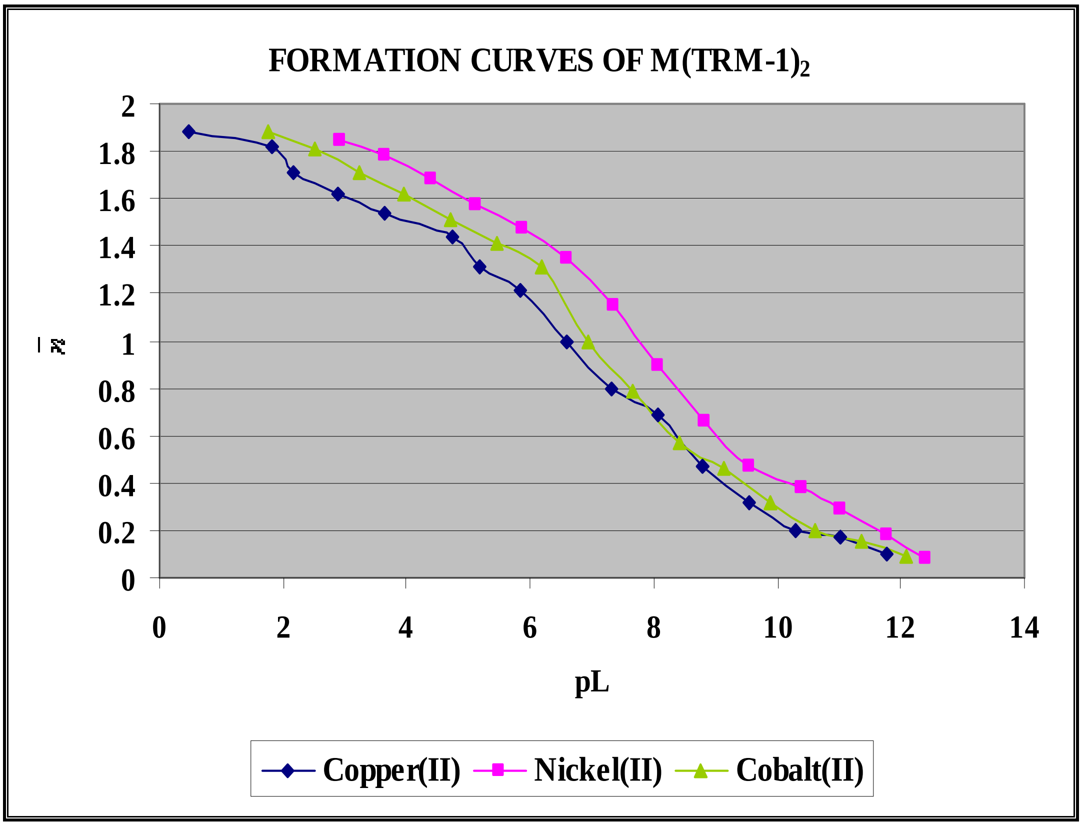

Figure 4: Graph of $\bar{n}$ v/s pL for Cu(II), Ni(II) and Co(II) ions

CONCLUSION

In the present study, the stability constants of complexes of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene) thiosemicarbazide(TRM- 1) with metals Cu (II), Ni (II) and Co (II) that concluded the difference between log K_1 and log K_2 values is greater. This shows the stepwise complex formation. The difference between log K_1 and log K_2 complexes was indicating the simultaneous formation of 1:1 and 1:2 complexes. The stability constants of thiosemicarbazone metal complexes are higher than that of ligands, from the data reveal in Table 1 and 2 the metal complexes are stable than the ligand because higher the stability constant more stable the compound. Nickel(II) and cobalt(II) complexes are more stable than the copper(II) complexe.

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