TABLE 2 — STABILITY CONSTANTS OF THE MIXED COMPLEXES AND DIFFERENCES OF OVERALL STABILITY CONSTANTS OF THE BINARY AND TERNARY COMPLEXES AT 30° AND $\mu = 0.2M$ (NaClO$_4$)

Metal	$\log K^{M.EDTA}_{M.EDTA.tiron}$	$\log \beta^{M}_{M.tiron}$ $-\log K^{M.EDTA}_{M.EDTA.tiron}$
Sc (III)	8·44	18·66
Y(III)	7·90	15·05
Ia(III)	6·38	10·67
Pr(III)	7·14	11·21
Nd(III)	7·22	11·26
Sm(III)	7·68	12·37

The mixed complex curve and the composite curve overlap in the lower pH range, which shows that in the lower pH range where 1 : 1 (rare earth-EDTA) complex is formed. Tiron does not combine with the rare earth or rare earth-EDTA complex. This also proves that there is no exchange of ligand because of very high stability of M(EDTA) as compared to that of M(Tiron). The mixed ligand curve deviates from the composite curve at higher pH values (5·5 to 6·0) which proves the formation of mixed complex in that pH region.

The values of $\bar{n}$ in the plot of $\bar{n}$ against pL never exceeded 1·0, which reveals the formation of only 1 : 1 : 1 mixed complex. The values of stability constants of mixed complexes were obtained by half $\bar{n}$ value method. The values of stability constants of the mixed complex, along with the differences in the overall stability constants of the binary and ternary complexes are given in Table 2.

From Tables 1 and 2 it can be seen that for all the rare earth ions under investigation, the stability of the ternary mixed complex (1 : 1 : 1) is less than that of the corresponding binary (1 : 1) complex.

This may be due to the fact that for binary complex formation, all the coordination sites around the metal ion can be occupied by the incoming ligand while in the ternary system, six of the coordination sites are already occupied by the hexadentate ligand EDTA, and only remaining one or two positions are left for the second incoming ligand. Secondly, there will be electrostatic repulsion between the ion M(EDTA) and the incoming negatively charged secondary ligand.

From Tables 1 and 2, it can be seen that the stability constants for the binary as well as ternary complexes increase with decrease in ionic radii and the order of stability constants is the same for both the type of complexes, being Sc(III) > Y(III) > Sm(III) > Nd(III) > Pr(III) > La(III).

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Complexation of Cu(II), Co(II) & Ni(II) with Hexamethylenetetramine : A Polarographic Study

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Polarographic reductions of hexamethylenetetramine (HMTA) complexes with Cu^{2+}, Co^{2+} and Ni^{2+} are diffusion-controlled. In the case of Cu-HMTA complex, the reduction is reversible and hence the stability constants have been calculated by De Ford and Hume's method. The reduction of cobalt and nickel complexes are highly irreversible and therefore, the stability constants cannot be calculated. The diffusion coefficients (D') for Co-HMTA and Ni-HMTA systems have been calculated using Ilkovic equation. The kinetic parameters $(\alpha n, K^{\circ}_{f,h})$ have also been calculated for both Co^{2+} and Ni^{2+} systems employing Koutecky's theoretical treatment as extended by Meites and Israel. Since the reduction of Cu^{2+}, Co^{2+} and Ni^{2+} complexes are diffusion-controlled, these ions in HMTA can be determined polarographically.

A NUMBER of workers[1-16] have qualitatively studied the complexes of hexamethylenetetramine (HMTA) with Cu(II), Co(II) and Ni(II) by various methods. However, a polarographic study of these complexes has not been undertaken so far. In continuation of our earlier work[17,18] on metal-HMTA complexes, we report here the results of polarographic investigations on the complexation reactions of Cu^{2+}, Co^{2+} and Ni^{2+} with HMTA. In the case of reversible reduction of Cu-HMTA complexes, the stability constants have been evaluated. Co(II) and Ni(II) complexes are reduced irreversibly at d.m.e. in HMTA medium. Since the stability constants cannot be calculated, the kinetic parameters $(\alpha n, K^{\circ}_{f,h})$ and diffusion coefficient (D) have been calculated for different concentrations of the ligand.

HMTA (Reidel), NiCl$_2$ (Scientific & Industrial Suppliers, Bombay), KNO$_3$, K$_2$SO$_4$, CoCl$_2$, CuSO$_4$ (all of BDH, AR) and KOAc (BDH) were used as such. Experimental solutions were prepared in air-free conductivity water. Stock solutions of

the metal ions were standardized by standard methods. Cu(II), Co(II) and Ni(II) solutions in $1.0M$ KOAc, $0.1M$ K_2SO_4 and $0.1M$ KNO_3 respectively as the supporting electrolytes were used with varying [ligand] for the polarographic measurements. In the case of Cu-HMTA system, no maxima was observed. But in Co-HMTA system, methyl red (0.0004%) and in Ni-HMTA system gelatin (0.01%) were employed as maxima suppressors.

Polarographic measurements were performed at $25^\circ \pm 1^\circ$ with a manual Toshniwal polarograph (type CLO2A) in conjunction with the Multiflex galvanometer (type MG 2). An external SCE was used as the reference electrode. Solutions were deoxygenated by passing purified H_2. The Sargent capillairy used had the following characteristics: $m = 3.033$ mg/sec, $t = 3$ sec/drop (at 28 cm of mercury pressure in $1.0M$ supporting electrolyte in open circuit). The IR drop correction was not made since the resistance was less than 1000 ohms.

Copper-HMTA system — The polarographic reduction of Cu-HMTA complexes in $1.0M$ KOAc supporting electrolyte gave two waves. It was possible to obtain reliable data only on the second (Cu$^+$ $\longrightarrow$ Cu) wave, since the early part of the cupric $\longrightarrow$ cuprous reduction wave coincides with the anodic mercury dissolution curve. The well-defined second wave was obtained only in the presence of the complexing agent in the concentration range 0.5-$2.0M$. The $E_{\frac{1}{2}}$ shifted towards negative values and decreased in i_d with increasing [HMTA], indicating the complex formation between Cu and HMTA. Better separation was obtained between the first and second wave at higher [HMTA]. The wave is diffusion-controlled and reversible as indicated by constant values of i_d vs $\sqrt{h}$ and the slopes (60 ± 2 mV) of the log plots respectively. De Ford and Hume method[19] of calculations were applied to the $\Delta E_{\frac{1}{2}}$ data for the evaluation of formation constants and the results are presented in Table 1. Analysis of the data in the concentration range 0.5-$2.0M$ of the amine indicated the formation of $1:1$, $1:2$ and $1:4$ (metal-ligand) complexes. Stability constants of complexes were calculated to be (log β values) 3.70, 3.82 and 3.60 respectively for the above complexes.

The percentage distribution of copper present in various forms as a function of [ligand] concentration was calculated and the results are presented in Fig. 1.

Cobalt, nickel-HMTA systems — In these systems well-defined single waves were found to be irreversible. The slope values of log plots were in the range of 40 to 60 mV. Since the reduction was irreversible, it was not possible to determine the composition of the complexes. The present investigation therefore, was confined to the kinetics of the electrode reactions. The $E_{\frac{1}{2}}$ of the complexes shifted to more positive values as compared to that of the simple ion and remained constant. This is in agreement with the observation of Willis et al.[20] on the behaviour of Co(II) and Ni(II) complexes of amines. With varying [ligand] the $E_{\frac{1}{2}}$ remained constant at 1.21 ± 0.01 V and $0.87 + 0.01$ V respectively within the experimental error, but i_d decreased (Table 2). The decrease in i_d directly corresponds to the decrease in D thereby indicating that Co(II)
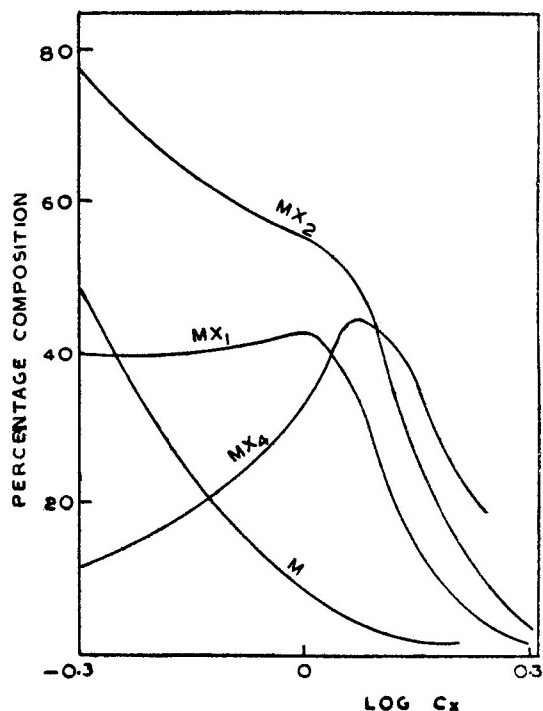

Fig. 1 — Distribution (%) of various species in Cu(II)-HMTA system in potassium acetate ($1M$) as the supporting electrolyte

TABLE 1 — POLAROGRAPHIC DATA FOR THE Cu-HMTA SYSTEM IN POTASSIUM ACETATE

[HMTA] M	$-E_{1/2}$ (V vs SCE)	I_M/I_C log	$F_0(X)$ $\times 10^{-3}$	$F_1(F)$ $\times 10^{-3}$	$F_2(X)$ $\times 10^{-3}$	$F_3(X)$ $\times 10^{-3}$	$F_4(X)$ $\times 10^{-3}$
0.0	0.000	—	1.00	—	—	—	—
0.5	0.089	0.3720	2.08	4.16	—	—	—
1.0	0.111	0.3928	11.69	11.69	6.69	—	—
1.2	0.117	0.4024	18.88	15.73	.46	2.05	39.21
1.4	0.128	0.4287	46.31	33.09	14.30	9.66	39.03
1.6	0.138	0.4812	112.00	70.00	25.39	21.33	42.70
1.8	0.149	0.4938	267.20	148.50	44.28	40.70	53.21
2.0	0.158	0.5704	633.00	316.50	77.68	74.38	59.64

Cu^{2+}. $= 1$ mM; $\mu = 1.0M$ KOAc; temp. $= 30^\circ \pm 2^\circ$; $\beta_1 = 5 \times 10^3$; $\beta_2 = 6.5 \times 10^3$; $\beta_3 = -45 \times 10^3$; $\beta_4 = 40 \times 10^3$.

TABLE 2 — POLAROGRAPHIC DATA FOR Co-HMTA AND Ni-HMTA SYSTEMS AT $25° \pm 1°$ IN K_2SO_4 AND KNO_3 RESPECTIVELY AS THE SUPPORTING ELECTROLYTES

[Ligand] M	i_d (μA)	$-E_{1/2}$ (V vs SCE)	Slope (mV)	αn	$D_0^{\frac{1}{2}} \times 10^{-3}$ cm^2/sec	$K_{f,h}^0$ cm/sec
			Co^{2+}=1 mM; $\mu(K_2SO_4)$=0·1M			
0·4	6·878	1·216	63	0·9024	2·252	$4·706 \times 10^{-22}$
1·0	5·862	1·214	60	0·9399	1·920	$7·300 \times 10^{-23}$
1·4	5·560	1·210	50	1·1280	1·821	$1·203 \times 10^{-26}$
2·0	5·267	1·206	50	1·1280	1·725	$1·308 \times 10^{-26}$
2·4	5·267	1·202	50	1·1280	1·725	$1·538 \times 10^{-26}$
			Ni^{2+}=1 mM; $\mu(KNO_3)$=0·1M			
0·8	7·127	0·880	50	1·1280	2·333	$5·728 \times 10^{-20}$
1·4	5·386	0·870	50	1·1280	1·764	$3·361 \times 10^{-20}$
2·0	4·217	0·863	46	1·2410	1·653	$4·348 \times 10^{-20}$
2·4	3·503	0·864	50	1·1280	1·140	$2·735 \times 10^{-20}$

and Ni(II)-HMTA complexes exist in the solution and their size increase up to 2·0M and completed at and above 2·0M HMTA. Potassium sulphate (0·1M) was selected as the supporting electrolyte for Co(II) as in this case the polarographic maximum could be suppressed with methyl red which is not the case with other supporting electrolytes.

The kinetic parameters (αn and $K_{f,h}^0$) have been evaluated by Koutecky's theoretical treatment extended by Meites and Isreal[21]. The experimental data and results are presentd in Table 2. The forward rate constant ($K_{f,h}^0$) of Co-HMTA complexes in K_2SO_4 is of the order 10^{-26} cm/sec whereas for Ni-HMTA in 0·1M KNO_3 it is of the order of 10^{-20} cm/sec.

The rates of reduction of the three metal ions in HMTA at d.m.e. follow the order: $Cu^{2+} >> Ni^{2+} >> Co^{2+}$. Since the reduction of all the three systems in the respective supporting electrolytes are diffusion-controlled, Cu^{2+}, Co^{2+} and Ni^{2+} ions in HMTA can be determined polarographically.

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