Electroanalytical Studies of Zn^{2+} and Co^{2+} Complexes with N-Methylpiperazine at DME

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The heterocyclic compounds are specific and selective complex forming agents [1]. The reduction of the complex compounds of Zn^{2+} and Co^{2+} at DME has been studied to calculate stability constants [2]. In most of the cases, mixed electrolyte and maximum supressor are used. Thus, sensitivity and accuracy in the measurement of diffusion current tend to decrease. With N-methylpiperazine, there is, however, no need of mixed electrolyte and maximum supressor. Many metals are not reduced under these conditions, thus the sensitivity of the method is increased. This prompted the authors to conduct this investigation for the determination of zinc and cobalt in presence of each other and also in standard reference materials.

EXPERIMENTAL

All the metal chloride or sulphate solutions were prepared from anlytical grade materials. A 1.0 M N-methylpiperazine was prepared from the freshly distilled reagent.

Test solutions were prepared by mixing 0.2 ml of 0.1 M metal salt, 0.2 ml of 0.1 M ligand and required BR buffer solution and making up to 20 ml. The pH was measured using a Century pH meter. Purified nitrogen gas was passed through the solution in the cell for deaeration. Current - potential measurements in all instances were recorded with a manual adopt polarograph using DME - SCE electrode system. Polarograms were constructed. The I_d values of this wave was used to get a calibration graph and the concentration of metal in the solution could be determined.

RESULTS AND DISCUSSION

The shape of wave remains the same in the concentration range of 0.1 to 0.5 M N-methylpiperazine but the half-wave potential becomes more negative with increasing concentration of ligand indicating complex formation. The various criteria for irreversibility [3,4] indicate that the electrode reactions for both metal ions are irreversible. Coulometry showed the n value to be 2. The electrode reaction may be represented as

$$M^{2+} + 2e^- \longrightarrow M\ (Hg),$$

where M = Zn^{2+} or Co^{2+}.

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Effect of Metal-ion Concentration

Polarograms over the concentration ranges 0.50-6.00 mM for Zn^{2+} and 0.50-8.00 mM for Co^{2+}, were recorded in the presence of 0.1 M N-methylpiperazine at pH 6.5±0.1. The values of diffusion current constant (I) was calculated using equation: $I=i_d /(C\ m^{2/3}\ t^{1/6})$

This was found to be a constant with change in ligand concentration (Table 1).

Table 1

Polarographic Characteristics of Zn^{2+} and Co^{2+}

Zi^{2+} / Co^{2+} conc. = 1.0 x 10^{-3} M;
N-methylpiperazine = 0.1 M;
μ = 0.1 M KNO_3; pH = 6.5± 0.1;
$m^{2/3}t^{1/6}$ = 2.9 $mg^{2/3}\,sec^{-1/2}$ at h_{corr} = 20.5 cm
Waves are irreversible in both cases; n = 2

Metal	-E V	Id μA	I*	slope (mV)	Relative Std. Deviation(%)#
Zinc	1.25	11.8	4.07	82	1.85
Cobalt	0.94	8.17	3.0	104	0.95

* μA $sec^{1/2}/mg^{2/3}$ mM # 5 replicate analysis

General procedure for the determination of Zn^{2+} and Co^{2+}

A calibration graph (i_d *vs* concentration) was prepared for each of the metals by recording the polarograms of the metal at various concentrations in a 0.1 M N-methylpiperazine medium at pH 6.5±0.1. It was found to be linear. The polarograms of solution containing the metal in unknown concentration was also recorded under identical conditions. The i_d values obtained from this wave were referred to the calibration graph and the concentration of metal ion could then be determined. The results are given in Table 2.

Table 2

Polarographic Determination of Zn^{2+} and Co^{2+} with N-methylpiperazine System

Metal ion conc. = 1.0 x 10-3 M;
N-methylpiperazine = 0.1 M;
μ = 0.1M KNO_3; pH = 6.5 ± 0.1; n = 2

Amount of the metal /(mg) Taken	Found*	Error %
Zinc		
1.96	1.98	+1.02
3.27	3.21	-1.83
4.57	4.65	+1.75
5.88	5.81	-1.19
Coblat		
1.77	1.80	+1.70
2.95	2.90	-1.70
4.13	4.20	+1.69
5.31	5.23	-1.51

* Average of five replicate analysis.

Effect of Foreign Ions

The effect of acetate, nitrate, salicylate, citrate, thiosulphate, tartrate and formate on the polarograms of 1 mM zinc / cobalt with 0.1 M N-methyl piperazine was

studied. In all instances the $E_{1/2}$ values remained constant. Tl(IV), W(VI), Se(IV), Pt(IV), Ba(II), Cr(III), Al(III) do not undergo reduction and can be tolerated in a ten fold excess. U(VI), Cd(II), Cu(II) and Pb(II) undergo reduction at low potentials and can be tolerated upto three- to five- fold excess. Only Ni(II) and Mn(II), in the case of Co(II) and Te(IV) in the case of Zn(II) interfered. Interference of Ni(II) can be masked with the addition of 5 ml of 10% solution of sodium cyanide while interference of Mn(II) can be masked by pre adsorption at pH 4.0. The Te(IV) usually does not occur with zinc.

Mixed Polarogram of Zinc-Cobalt

From the individual polarogram of zinc and cobalt, it is apparent that it is possible to defferentiate between the two metals when they are complexed with N-methylpiperazine as their $E_{1/2}$ values differ by 0.3 V. Consequently, a series of polarograms recorded for mixed, synthetic solution of the two metals and the I_d values obtained for each metal were referred to its calibration graph. Table 3, shows concentration of metals determined in the mixed solution. The results obtained are accurate and reproducible.

Analysis of Standard Reference Materials

A 0.1-0.5 g sample of each of the standard reference materials was dissolved with 50-60 ml of hydrochloric acid and 10-20 ml of conc. nitric acid.

Table 3

Simultaneous Determination of Zi^{2+} and Co^{2+} in Binary Mixtures.

N-methylpiperazine = 0.1M; pH = 6.5 ± 0.1

Zinc			Cobalt		
Taken	Found	Error	Taken	Found	Error
2.84	2.86	+0.70	1.89	1.85	-2.11
3.94	3.89	-1.27	2.65	2.67	+0.75
4.06	4.00	-1.47	3.64	3.68	+1.10

Table 4

Analysis of standard Reference Materials for Co and Zn

	Amount (mg)		%
Metal	Taken	Found	Error
JSS 651 Stainless Steel of % composition 0.04 C; 1.72 Mn; 0.082 Cu; 0.249 Ni#; 0.002 Al; 0.22 Co; 0.028 P; 0.063 S; 0.087 N; 0.72 Si			
Co	2.55	2.53	-0.78
High Speed Steel of % composition 0.40 Mn; 18.50 W; 9.25 Co; 0.05 P; 0.05 S; 0.75 Si; 4.15 Cr; 5.50 Mo			
Co	3.85	3.83	-0.52
Brass No 412 of % composition 58.18 Cu; 2.56 Pb; 38.99 Zn; 0.09 Fe; 0.12 Sn			
Zn	2.95	2.93	0.15
NBS SRM 171 Mg Alloy of % composition 0.65 Mn; 0.003 Pb; 1.05 Zn; 0.001 Fe; 0.011 Si; 2.98 Al; 0.011 Cu; 0.009 Ni#			
Zn	2.10	2.13	1.04

* Average of five replicate analysis;
# Ni masked by addition of 5 ml of 10 % NaCN solution

A 3-5 ml volume of 30% hydrogen peroxide was then added and the solution heated on a hot plate until the sample dissolved completely and the volume reduced to about 5 ml. After cooling, 10 ml of distilled water were added to dilute the solution. The solution was filtered and the filtrate diluted to 50 ml. An aliquot of this solution was taken and the metals determined by the described procedure. The interference of Ni(II) in the analysis of JSS 651 stainless steel was masked by addition of 5 ml of 10% NaCN solution. The results obtained are given in Table 4.

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