POLAROGRAPHIC BEHAVIOUR OF CADMIUM, COPPER, LEAD, NICKEL, COBALT, ZINC AND IRON IN ETHANOLAMINES AND POTASSIUM SULPHATE OR NITRATE

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SUMMARY

The polarographic behaviour of ethanolamine complexes of cobalt, nickel, zinc, cadmium, iron, lead and copper has been studied in presence of potassium sulphate or nitrate. Evidence is obtained for the formation of the following complexes:—

(1) $Cd(Moen)_3^{++}$ (2) $Cd(Dien)_3^{++}$ (3) $Cd(Trien)_2^{++}$

(4) $Cu(Moen)_3^{++}$ (5) $Cu(Dien)_3^{++}$ (6) $Pb(Moen)_2^{++}$

(7) $Pb(Dien)_2^{++}$ (8) $Ni(Moen)_3^{++}$ (9) $Ni(Dien)_3^{++}$

(10) $Ni(Trien)_2^{++}$ (11) $Co(Dien)_2^{++}$ (12) $Co(Trien)_2^{++}$

(13) $Zn(Moen)_3^{++}$ (14) $Zn(Dien)_3^{++}$ (15) $Zn(Trien)_3^{++}$.

In the above formulæ Moen, Dien and Trien represent monoethanolamine, diethanolamine, and triethanolamine respectively.

INTRODUCTION

It has been shown by the present author that in the case of iron[1] and cadmium,[2] the complexes with ethanolamines are associated with radicals like OH^-, $CO_3^=$ NH_3 when the base solution contains sodium hydroxide, carbonate and ammonia. Similar results have also been noticed by the author with regard to the complexes of copper, lead, nickel, cobalt and zinc. It is generally stated that the sulphate or the nitrate does not enter the complex. In the present paper the results of the polarographic behaviour of ethanolamine complexes of cadmium, copper, lead, nickel, cobalt, zinc and iron in presence of the nitrate or sulphate radicals have been presented.

EXPERIMENTAL

The details of the apparatus and the experimental procedure have been described previously.[1] The value of 'm' of the capillary has been $1 \cdot 150$ mg. per second and the droptime 't' 5 seconds in normal potassium chloride. The polarograms have been recorded at $30°$ C. $\pm 0 \cdot 1 °$ C.

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RESULTS AND DISCUSSION

The half-wave potentials and the values of $(E_{\frac{3}{4}} - E_{\frac{1}{4}})$ of the polarographic waves obtained for cadmium, copper, lead, nickel, cobalt and zinc complexes are given in Table I. From the table it is clear that the polarographic waves of mono- and diethanolamine complexes are generally nearly reversible while the triethanol-amine complexes are irreversible in nature. The number of ethanolamine groups that enter the complex has been calculated by employing the equations for reversible and irreversible processes.[1] It can be seen from Table I that all the metals except lead and cobalt have three molecules of mono- and diethanolamines while lead and cobalt have only two molecules. The structure of these complexes can be written thus:
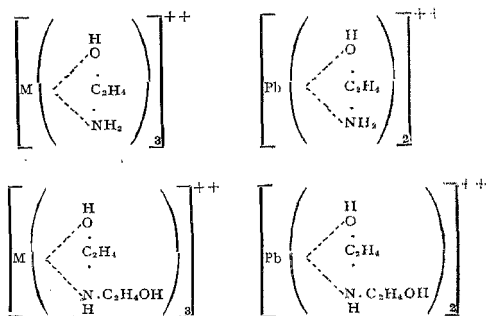
It has also been noticed that in a few cases it is not possible to get an idea from polarographic data of the number of triethanolamine groups that are attached to the metal ion, due to a wide variation in the irreversibility of the complex at different concentrations of the amine. In many cases two molecules of triethanolamine enter the complex while in the case of zinc, three molecules get into the complex. In presence of large concentrations of ammonia, $CO_3^=$, or OH^- the bond between the metal and the hydroxyl of the alcoholic group attached to the amine is broken and its place is taken by new groups. The breaking of the bond, between metal and the nitrogen of the ethanolamine, is not probable.[3] Flannery and others[4] have studied the polarographic behaviour of mono- and diethanolamine complexes of copper in base solutions containing less than $0 \cdot 1$ M amine. They state that four molecules of the amine has entered the complex and that the amine is monodentate. It has to be pointed out, however, that the authors have assumed that the reduction process is reversible even though the slope of the log plot is about $0 \cdot 040$ to $0 \cdot 045$ V. Applying the equations for irreversible waves to their data in the region where the irreversibility is a constant we get that three molecules of

TABLE I

Polarographic behaviour of cadmium, copper, lead, nickel, cobalt and zinc in ethanolamines

Concentration of potassium sulphate : 0·10 Molar

Cation used	Amine used	Concn. of amine (Molar)	$E_{\frac{1}{2}}$ vs. S.C.E. (Volt)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (Volt)	No. of ethanol-amines attached	Remarks
Cadmium	Monoethanolamine	0·30	−0·693	0·029	3	
		1·00	−0·742	0·034		
	Diethanolamine	0·30	−0·658	0·032	3	
		1·00	−0·704	0·032		
	Triethanolamine	0·30	−0·600	0·051	2(?)	Doublet and hence the values of
		1·00	−0·677	0·062		$E_{\frac{1}{2}}$ and $E_{\frac{3}{4}} - E_{\frac{1}{4}}$
Copper* ..	Monoethanolamine	0·10	−0·319	0·039	3	are only approximate
		1·00	−0·424	0·037		
	Diethanolamine	0·10	−0·296	0·040	3	
		1·00	−0·396	0·037		
	Triethanolamine	0·10	−0·291	0·063	..	No conclusion can be reached regarding the No. of ligands attached
		1·00	−0·517	0·161		
Lead ..	Monoethanolamine	0·30	−0·576	0·033	2	
		1·00	−0·610	0·029		
	Diethanolamine	0·30	−0·585	0·031	2	
		1·00	−0·620	0·036		
	Triethanolamine	0·30	−0·630	0·037	..	No conclusion can be reached regarding the No. of ligands attached
		1·00	−0·674	0·075		
Nickel† ..	Monoethanolamine	0·30	−0·926	0·037	3	
		1·00	−0·999	0·035		
	Diethanolamine	0·30	−0·994	0·060	3	
		1·00	−1·103	0·065		
	Triethanolamine	0·30	−1·185	0·083	2	
		1·00	−1·265	0·079		
Cobalt† ..	Monoethanolamine	0·30	−1·214	0·024	..	No conclusion can be reached regarding the No. of ligands attached
		1·00	−1·263	0·050		
	Diethanolamine	0·30	−1·265	0·077	2	
		1·00	−1·361	0·090		
	Triethanolamine	0·30	−1·440	0·100	2	
		1·00	−1·531	0·094		
Zinc ..	Monoethanolamine	0·30	−1·221	0·041	3	
		1·00	−1·277	0·039		
	Diethanolamine	0·30	−1·161	0·038	3	
		1·00	−1·228	0·045		
	Triethanolamine	0·30	−1·243	0·088	3	
		1·00	−1·383	0·079		

* In these experiments 0·2 M potassium nitrate has been used.

† 0·005% gelatin has been added to the base solutions.

mono- and two molecules of diethanolamines enter into the complex. The work recorded in the present paper clearly indicates that at higher concentrations of

ethanolamine where it is possible to expect only the complex with the largest number of ligands, three molecules of mono- and three molecules of diethanolamine are present in the complex. Co-ordination is through hydroxyl oxygen and amino nitrogen indicating that the complexing agent is not monodentate.

The polarographic behaviour of iron in presence of potassium sulphate does not throw much light on the constitution of the complexes. In the first place the solubility of the monoethanolamine complexes is too low to be amenable to polarographic measurements. With diethanolamine (0·3 M) the first wave of iron shows the phenomenon of split wave, while the second wave is very nearly reversible, but on increasing the concentration of the amine to 1 M, the second wave is split into two waves very close to each other. When triethanolamine is used as the complexing agent, there is a shift in the half-wave potential of the first wave (from − 0·79 to − 0·86 V) but the shift in the half-wave potential of the second wave is very small. Further, the second wave is complicated by the presence of a second species whose half-wave potential is beyond the final current rise.

In conclusion, it can be stated that ethanolamines alone form complexes with various metal cations even when other co-ordinating groups such as CO_3^-, NH_3 and OH^- are not present in the solution.

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