Complex Plane and D.C. Polarographic Study of Different Zinc-Ethanolamine Complexes.

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D.C. Polarographic study of Zinc-Ethanolamine (Mono-, Di- & Tri-) complexes gave the formulae of the complexes and kinetic parameters; the values of kinetic parameters are compared with those obtained by complex plane polarography. The interesting results obtained by simple d.c. polarographic method are confirmed by complex plane polarographic method.

Simple systems are studied by DC and also by complex plane polarography [1,2] but metal complexes are not studied by this technique. In the present work, results have been reported of the zinc-ethanolamine (mono-, di- & tri-) complexes by complex plane polarography and compared with results of simple d.c. polarography wherever possible.

EXPERIMENTAL

DC polarographic studies are carried out with a manual setup. The complex plane polarography measurements are made with a unit fabricated locally and similar to the one described earlier [1,3].

The mono-, di- and tri- ethanolamines are distilled under vacuum before use. Experiments have been carried out with zinc sulphate (AR grade) at different concentrations alongwith the ethanolamines in the presence of ethanolamines perchlorates . All experiments are carried out at 303±0.1°K. The other details are as described earlier [2].

RESULTS AND DISCUSSION

Zinc-Monoethanolamine System

It was found necessary to add 0.05% gelatin to avoid maxima in DC polarography experiments. D.C. polarographic experiments have been carried out with both monoethnolamine and the corresponding ammonium perchlorate varying in the range 0.1 - 1.0 M. Results show that the electroreduction is quasi-reversible in nature. The reversible $E_{1/2}$ values have been calculated using extrapolation method [4]. At a constant concentration (1 M) of monoethanolamine, the pH changes from 9.8 to 10.86 with concentration of the amine perchlorate (0.1 M - 1.0 M). The corresponding shift in $E_{1/2}$ is 19 mV. At constant concentration (0.1 M) of $MEAClO_4$, the pH changes from 9.605 - 10.55 for a change in the concentration of MEA from 0.1 - 1.0 M. The reversible $E_{1/2}$ shifted by 98 mV indicating complex formation. The data have been analysed using Lingane's equation for a case of two ligands [5]. The results show that Zn is present as a complex ion of

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composition $Zn(OH)M_2^{++}$ (M = Monoethanolamine). The stability constant of this complex in 0.1M $MEAClO_4$ solution containing 1M monoethanolamine is found to be $10^{12.6}$.

Matsuda and Ayabe [6] have discussed the case of a complex solution where a complex of a lower coordination number actually participates in the electrode reaction. They have given the method of calculating k_c^* - the kinetic parameter of the electrode process and $(k_{sh})_D$ - the rate constant of the overall reaction. These calculations have been carried out. Typical results are given in Table 1.

Table 1

Rate constants by D.C. Polarography

[Zn^{++}] = 3 mM; [$MEAClO_4$] = 0.1 M; [MEA] varying; [gelatin] = 0.05 %; Drop time = 4 secs.

[Amine] M	$E_{1/2}$ (V)	$E_{1/2}^{rev}$ (V)	k_c^*	$(k_{sh})_D \times 10^3$ cm.sec^{-1}
0.2	-1.236	-1.212	1.7021	0.086
0.3	-1.246	-1.226	0.2070	0.571
0.5	-1.259	-1.244	0.2544	1.01
1.0	-1.285	-1.272	0.2885	1.44
5.0	-1.302	-1.294	0.3487	7.86

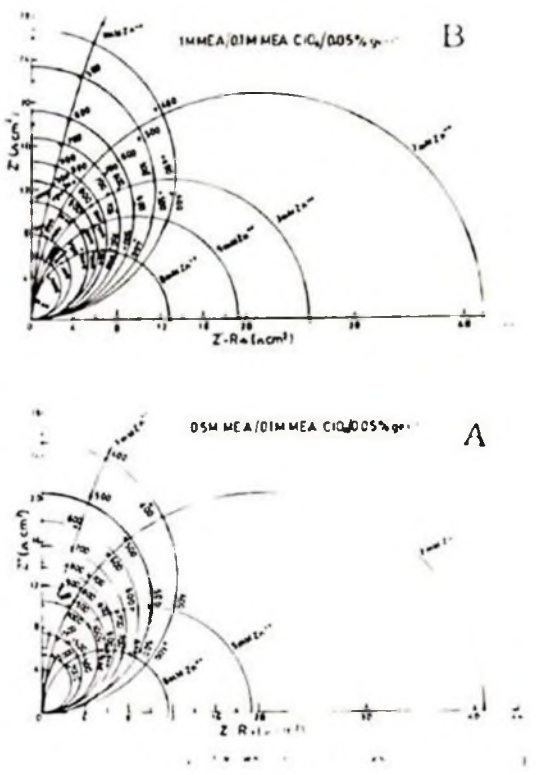
The standard potential (E_{ii}°) of the overall reaction

$$Zn(OH)M_2^{++} + 2\,e \longrightarrow Zn + OH^- + 2M$$

is calculated to be -1.1361 V.

Complex Plane Polarography

The Z'-Z" plots at different frequency are made. The points are practically on a semi circle. A few typical plots are given in Fig.1A & B. The value of θ is read directly from Z' vs Z" plot. The value of rate constants are calculated using all the 3 equations (eqn.6 of ref 7, eqn. 4a of ref.8 and eqn.2 of ref.1). The E° values are obtained from $E_{1/2}$ using the experimentally calculated values of diffusion coefficients. The agreement between k_{sh} calculated from different equations by complex plane polarography and that obtained by d.c. polarography are quite satisfactory.



Zinc with Other Ethanolamines

Due to solubility problem, experiments on both d.c. polarography and complex plane polarography are carried out at 1mM Zn^{++} ion only.

Table 2

Calculation of $k_{s,h}$ by Complex Plane Polarographic Method

Conc. of gelatin = 0.05 % Conc. of $MEAClO_4$ = 0.1 M

[MEA]	$[Zn^{2+}]$	$\theta(\Omega cm^2)$	α	E-E° V	eq.6[7]	$k_{s,h}$ (cm.sec^{-1} x 10^3 by eq.2[1]	eq.4a[8]	polarog
0.2	3	54.4	0.4		1.02	2.02		0.086
0.3	3	38	0.34		1.45	3.0		0.52
0.5	2	40.6	0.25	0.013	1.94	5.2	2.6	-
	5	19.3	0.32	0.0085	1.7	3.6	1.8	-
	8	11.7	0.27	0.0045	1.7	4.3	1.6	-
Mean					**1.78**	**4.4**	**2.0**	**1.01**
1.0	2	41.5	0.27	0.031	1.91	4.7	5.35	
	3	25.8	0.33	0.031	2.12	4.18	5.08	
	5	19.4	0.28	0.24	1.66	4.08	3.28	
Mean					**1.83**	**4.14**	**4.03**	**1.4**
5.0	3	28.4	0.28	0.059	1.8	5.73	28.5	
	8	16.2	0.2	0.049	1.67	4.45	11.0	
Mean					**1.74**	**5.09**	**19.8**	**7.86**

Table 3

Calculation of rate constants

Conc. of Zn^{++} = 1 mM

[Amine] M	[AmineClO_4] M	θm (cm^2)	E-E_o (V)	$k_{s,h}$x 10^4 by eq.4a [7] (cm.sec^{-1}
Diethanolamine System				
0.1	0.5	81	-0.071	17.7
0.1	1.0	115	-0.047	1.49
0.3	1.0	92	-0.047	2.95
0.5	1.0	105	-0.033	7.03
Triethanolamine System				
0.1	0.3	140	-0.058	1.86
0.3	0.3	120	-0.057	1.02
0.5	0.3	200	-0.051	0.7
0.1	1.0	280	-0.033	4.85
0.3	1.0	190	-0.041	3.16
0.5	1.0	140	-0.043	3.87

From the d.c. polarographic study of the systems, the composition of the complex formed with diethanolamine under the conditions of the experiment is ZnD_2^{++} (where D=Diethanolamine) and stability constant is found to be $10^{5.56}$. In case of triethanolamine, the composition of the complex is ZnT_2^{++} (T-Triethanolamine).

The rate constants are calculated by complex plane polarography by using the general equation of θ and by approximating q_m as equal to θ_m. The standard potential to be used at each concentration of the complexing agent is calculated from the reversible half-wave potential after correcting for the diffusion coefficients.

The results are given in Table 3.

GENERAL CONLUSIONS

The reduction in monoethanolamine system is found to be quasireversible, in diethanolamine system and it is more irreversible in triethanolamine system. In mono- and di- ethanolamine system it is noticed that with increase in the concentration of amine, reversiblity slightly increases.

The composition of the complexs formed in mono-, di- and tri- ethanolamine systems are $Zn(OH)M_2^+$, ZnD_2^{++} and ZnT_2^{++} respectively.

The rate constants determined for monoethanolamine system by d.c. polarographic method agree well with those obtained by complex plane polarographic method. In di- and tri- ethanolamine sytems, the rate constants are determined by complex plane polarographic method only.

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