ELECTROCHEMICAL BEHAVIOUR OF ZN (II) IN ORGANIC DIBASIC ANIONS AT DME

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Zn^{2+} forms complexes with a number of ligands but its reduction is not reversible at dropping mercury electrode and hence the formation constants could not be calculated from observed half-wave potentials ($E_{1/2}$). With the development of Matsuda [1] and Gellings [2] treatment for quasi-reversible reductions, reversible current voltage curve and thus the formation constants can be calculated. The electrode kinetics and formation constants of complexes formed by Zn (II) with formate, salicylate and benozoate ions [3,4] have been reported earlier.

The present paper deals with the determination of kinetic parameters and formation constants of the complexes formed by Zn(II) with malonate, and succinate ions.

EXPERIMENTAL

The current voltage curves were obtained with a manual set up with a galvanometer having the sensitivity of 0.0556 uA/div. The dropping mercury electrode characteristics were m = 2.267 mg/sec and t = 4.4 sec (at -1.0 V vs SCE in 1 M KNO_3). The H-type cell with an agar-agar plug saturated with potassium chloride was employed. Purified nitrogen gas was bubbled through the solution for about 20 minutes for deaeration. All the measurements were performed at 30 $\pm$ 0.1 $^{\circ}$ C which was maintained with Haake type ultrathermostat. Sodium malonate and sodium succinate, were used as complexing agents. Solutions containing 1 mM Zn(II) and varying concentrations of complexing ions were prepared in 10 ml volumetric flasks. The ionic strength was kept constant at unity by addition of requisite amount of potassium nitrate solution. The pH of the solutions were maintained at 6.6 $\pm$ 0.1.

RESULT AND DISCUSSION

Single well defined reduction wave appeared in each case. The plots of i_d vs $\sqrt{h}$ (h = effective mercury pressure after applying back pressure correction) were linear and passed through origin. The plots of log $[i/i_d - i]$ vs E_{de} for all the solutions were linear upto half-wave potential but the plots were curved at more negative potential. The slope of the plots in linear region were of the order of 40 $\pm$ 2 mV, which becomes larger in curved region. The above results show that the electrode process are diffusion controlled and quasi-reversible. The half-wave potential determined using log plot has shown that $E_{1/2}$ shifted towards more negative value and diffusion current decreases with increasing ligand concentration. This suggests the complex formation by Zn(II) with these complexing agents.

The formation constants could not be evaluated from observed half wave potential as reduction were not reversible. The reversible half wave potential is calculated by Gellings treatment [2] for quasi-reversible electrode process.

According to this treatment

$$\lim_{i \to o} \left[E + \frac{2.303\ RT}{nF} \log \frac{i}{(i_d - i)} \right] = E^{r}_{1/2} \quad (1)$$

The plot of $E + 2.303\ RT/nF \log [i/(i_d - i)]$ vs i were found to be curved. The extrapolation of these curves to zero current values results in $E^{r}_{1/2}$. The plots of $E^{r}_{1/2}$ vs - log C (C = complexing agent concentration, in moles) were smooth curves for these systems suggesting the formation of two or more complex species which are in equilibrium. Thus the classical method due to Lingane [5] could not be applied to calculate the coordination number and formation constants. For this purpose, DeFord and Hume's method [6] for stepwise complex formation has been used.

The experimentally determined value of $E^{*}_{1/2}$ together with calculated F_j [X] values are given in Table (1). Assuming that the several activity coefficients probably changed very little at the constant ionic strength, over all formation constants were obtained by graphical extrapolation of the F_j [X] function to zero ligand concentration. As expected, the complexes formed by Malonate ions are stronger than that formed with succinate ions. The kinetic parameters, (the standard rate constant k_s and transfer coefficient) have been calculated by Gellings Method [2].

The plots of log (Z-1) vs $(E - E^{r}_{1/2})$ for both the system were linear. The slope and intercept of the line gave the values α & λ which ultimately gave the value of k_s. The results have been summarised in the Table 2. It is evident that the values of k_s are of the order

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TABLE 1

Analysis of $F_3[X]$ Functions

Ligand concentration Mol/l	Zn(II)-Malonate System $E^r_{1/2}$ (-V vs SCE)	i_d (division)	$F_o[X]$	Zn(II)-Succinate System $E^r_{1/2}$ (-V vs SCE)	i_d (division)	$F_o[X]$
0.0	0.9995	60.0	-	0.9995	60.0	-
0.02	1.0340	55.5	10.15	1.0075	53.5	2.01
0.04	1.0390	54.5	25.57	1.0105	51.5	3.57
0.06	1.0455	53.5	50.48	1.0155	50.0	4.53
0.08	1.0505	52.5	80.48	1.0195	49.5	6.54
0.10	1.0560	51.5	120.17	1.0240	48.0	8.44
0.12	1.0600	50.0	165.00	1.0275	47.5	10.05
0.14	1.0655	49.0	225.20	1.0305	47.0	12.76
0.16	1.0675	46.5	281.50	1.0330	46.0	16.10
0.20	1.7350	45.0	435.40	1.0380	44.0	26.37

of 10^3 cm/sec confirming that the reductions are quasi-reversible.

Zn(II) forms complexes with both the ligands. The values of β_1 and β_2 for malonate ions are 275 and 9200 whereas for succinate they are 57 and 107. Thus the complexes formed by succinate ions are much weaker than those with malonate ion.

TABLE 2

KINETIC PARAMETERS

Ligand concentration (Mol/l)	Zn(II)-Malonate α	Zn(II)-Malonate $k_s \times 10^3$ (cm/sec)	Zn(II)-Succinate α	Zn(II)-Succinate $k_s \times 10^3$ (cm/sec)
0.0	0.98	2.55	0.98	2.59
0.10	0.98	1.26	0.97	2.98
0.14	0.98	1.09	0.97	2.44
0.20	0.98	0.85	0.97	2.41

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