Polarographic Studies on Ternary Complexes of Zinc with Phenylenediamine and Succinate

Nirupma and Greesh Saxena

Chemical Research Laboratories, Raja Balwant Singh College,
Agra-282002 (INDIA)

The cathodic reduction of mixed Zinc-phenylenediamine-succinate at the dme has been found to be diffusion controlled and reversible involving two electrons. DeFord and Hume's treatment suggests that both the ligands form 1:2 high complexes separately in aqueous medium and Schaap and Mc Master's treatment reveals the presence of only one mixed complex with stiochiometry 1:1:1 in the same experimental conditions as for the simple complexes. The stability constants of the complexes have been evaluated.

The complexes of zinc with various ligands have been studied(1-6) polarographically. The determination of the nature of mixed ligand complex formation has been receiving considerable attention in recent times(7-9). Study of the polarographic behaviour of zinc in phenylenediamine and succinate, has been reported here.

EXPERIMENTAL

Solutions were prepared in doubly distilled conductivity water and all the chemicals used were of analytical reagent grade. The depolarizer concentration was kept at 5×10^{-4} M in each solution. Potassium chloride was used as a supporting electrolyte to maintain the ionic strength. Triton X-100 (2×10^{-3} %) has been used as maximum suppressor. The temperature was maintained constant at 303° K, by using a thermostatic control. Purified nitrogen was used to exclude the dissolved oxygen. All the potentials were measured against a saturated calomel electrode. A manual polarograph in conjunction with a polyflex galvanometer was used to record the current-potential curves. Pure distilled mercury was used in dropping electrode. The capillary characteristic was $m^{2/3}\ t^{1/6} = 3.1086\ mg^{2/3}\ Sec^{-1/2}$ at a mercury height of 30 cm. in KCl solution in open circuit.

RESULTS AND DISCUSSION

Zn(II) produces a well developed wave in presence of varying concentrations of phenylenediamine or succinate ions. The plots of log $i/(i_d - i)$ vs. $E_{d.e}$ were linear with slope value 30 ± 2 mV, suggesting the reversible reduction involving two electrons. Further, the plots of i_d vs $\sqrt{h}$ (h = effective height of mercury column, were found to be straight lines passing through the origin indicating the process as diffusion controlled. However, on increasing the ligand concentration, the half-wave potential shifts towards more negative values and the diffusion current decreases. The formation constants of binary complexes were evaluated by DeFord and Hume's (10) treatment. Polarographic data obtained in the binary systems are used for the study of ternary systems. Therefore, binary complexes of Zn(II) with the ligands-phenylenediamine and succinate, have been investigated first under the same experimental conditions as those used for the study of ternary system. The stability constants of the complexes $[Zn(phn)]^{2+}$, $[Zn(phn)_2]^{2+}$ formed in Zn(II)-phenylenediamine system, are: log β_1 = 2.40 , log β_2 = 4.58 and of the complexes [Zn (Succ)] , $[Zn(Succ)_2]^{2-}$ formed in Zn(II) succinate system are log β_1 = 3.40, log β_2 = 3.89.

The solutions containing 5×10^{-4} M Zn (II), 2×10^{-3} % Triton x-100, a constant concentration of succinate ions and requisite amount of supporting electrolyte, KCl (to maintain the ionic-strength, 0.6 M) were taken for polarographic investigations at various concentrations of stronger ligand (phenylenediamine). The nature of the plot, $E_{d.e}$ vs log $[i/(i_d - i)]$ and its slope indicates the reversible reduction of the mixed complex also, at dme. The diffusion current was directly proportional to the square root of the effective height of mercury column, showing the diffusion controlled nature of the reduction. Since, the reduction of the ternary complex is reversible, the method of Schaap and Mc Masters is applied in order to evaluate the formation constant of the mixed species.

Zn(II)-PHENYLENEDIAMINE-SUCCINATE SYSTEM:

The system has been studied in two sets of experiments each with constant concentration of succinate ion (0.1 M and 0.2 M). The phenylenediamine concentration was varied from 0.02 M to 0.10 M. A cathodic shift in $E_{1/2}$ with the increase in phenylenediamine concentration was observed. The formation of mixed ligand complex

was indicated by the fact that the shift in $E_{1/2}$ in the presence of both the ligands is greater than that in the presence of phenylenediamine or succinate alone. The relationship between $\Delta E_{1/2}$ and -log C_x was linear thus showing the existence of one mixed species only.

The polarographic measurements are summerized in table 1.

TABLE 1

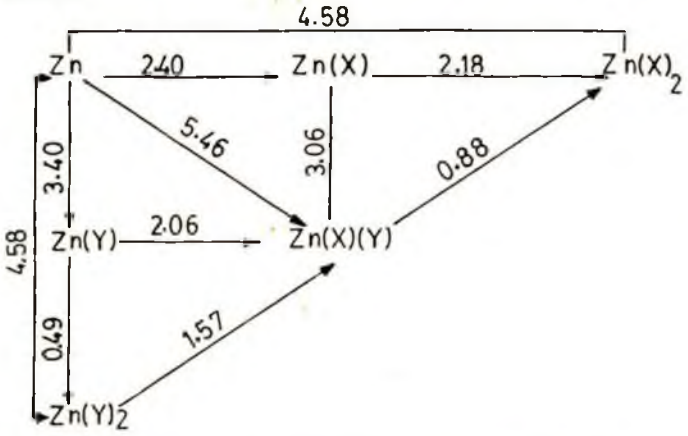
POLAROGRAPHIC MEASUREMENTS FOR TERNARY SYSTEM

$[Zn^{2+}] = 5\times10^{-4}$ M, μ = 0.6M (KCl), Temp. = 303°K

Ligand concn(M)	$\Delta E_{1/2}$	log IM/IC
(I) $[Succ]^{2-}$ = 0.10 M		
0.02	0.080	0.16
0.04	0.093	0.25
0.06	0.101	0.23
0.08	0.108	0.30
0.10	0.115	0.28
(II) $[Succ]^{2-}$ = 0.20 M		
0.02	0.092	0.20
0.04	0.102	0.26
0.06	0.110	0.25
0.08	0.117	0.29
0.10	0.124	0.30

The analysis of the data gave the formation constant of the ternary complex [Zn (phn) (Succ)] was evaluated as log β_{11} = 5.46.

The scheme showing different complexes is given below:



Consideration of the relative tendencies for the addition of a ligand to different complexes and also the value of the mixing constant K_M suggests that the formation of ternary complex [Zn (phn) (succ)] is favoured. The positive value of stabilization constant indicates that ternary species is more stable than the binary ones. The positive values of stabilization constants have also been observed by some workers(13-14).

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