TECHNICAL REPORT

THERMODYNAMICS AND STABILITY OF THE Cd(II) SUCCINATE—PROPYLENEDIAMINE-MIXED COMPLEXES

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Polarographic measurements have been used to determine the overall formation constants of simple and mixed complexes of Cd (II) with succinate and propylenediamine. DeFord and Hume's treatment suggests that both the ligands form 1 : 3 high complexes separately in aqueous medium and the Schaap and McMasters treatment reveals the presence of three mixed complexes with stoichiometery 1 : 1 : 1; 1 : 1 : 2 and 1 : 2 : 1 in the same medium as for the simple complexes. Thermodynamic parameters of the mixed complexes have been calculated. The equilibrium of various simple and mixed complexes involving substitution and addition of various ligands are discussed.

Mixed complexes are generally formed when metal ion is present in a mixture of two or more ligands in solution. The DeFord and Hume's method[1] for simple complexes was extended to study the formation constants of mixed complexes by Schaap and McMasters[2], which has been extensively used by several workers[3—6]. The mixed complexes of various metal ions with organic ligands particularly dicarboxylic acids have been studied using polarographic measurements[7,8].

Experimental

All the solutions contained 5×10^{-4} M Cd^{2+}. All the chemicals used were of reagent grade purity. The solutions were prepared in double distilled water. KNO_3 was used as the base electrolyte to maintain the ionic strength constant at 2.0M. For mixed complexation, the two concentrations of succinate being kept constant were 0.10M and 0.25M. The solutions were deaerated by passing purified nitrogen. Temperatures were maintained at 293 ± 0.1 and 303 ± 0.1°K. The capillary of d.m.e. had the following characteristics m = 2mg Sec^{-1} and t = 4.6 sec. at the height 65.5 cm of mercury head and the polarograms were obtained manually.

Result

The reduction of Cd^{2+} in the medium of succinate and propylenediamine separately was found reversible and diffusion controlled. The slopes of straight line plot of log $i/(i_d-i)$ vs. E. were 30 ± 2mV. and the plots of i_d vs. $h^{\frac{1}{2}}$ of mercury column was a straight line passing through the origin.

Overall formation constants of simple complexes were determined by DeFord and Hume's method using polarographic measurements. The results are summarised below :-

Complex species	Overall formation constant	
	293°K	303°K
[Cd (Succ)] $\log\beta_{01}$	1.653	1.580
$[Cd (Succ)_2]^{2-}$; $\log \beta_{02}$	2.763	2.699
$[Cd (Succ)_3]^{4-}$; $\log \beta_{03}$	3 045	2.977
$[Cd (PDA)]^{2+}$; $\log \beta_{10}$	8.000	7.903
$[Cd (PDA)_2]^{2+}$; $\log \beta_{20}$	9.000	8.602
$[Cd (PDA)_3]^{2+}$; $\log \beta_{30}$	12.477	11.340

It was observed that the addition of propylenediamine to a solution of Cd(II) and succinate shifts the $E_{\frac{1}{2}}^{r}$ to more negative side, showing that mixed complexes are formed in the solution.

The overall formation constants of mixed complexes at two temperatures are recorded in table I. The thermodynamic characteristics of the mixed complexes are recorded in table II.

Table - I : Overall formation constants of mixed complexes

Complex Species	Overall formation constant	
	293°K	303°K
[Cd(PDA)(Succ)] ; $\log \beta_{11}$	9.204	9.083
[Cd(PDA)(Succ)] ; $\log \beta_{12}$	10.380	9.991
$[Cd(PDA)_2(Succ)]$; $\log \beta_{21}$	11.380	10.415

Table – II : Thermodynamic Parameters

Complex species	Theromodynamic Parameters		
	ΔH^O Kcal deg^{-1} mole	ΔF^O Kcal deg^{-1} mole^{-1}	ΔS^O Cal deg^{-1} mole^{-1}
[Cd(PDA) (Succ)]	–4.960	– 12.421	+25.464
[Cd(PDA) $(Succ)_2]^{2-}$	– 15.907	– 14.008	– 6.481
$[Cd(PDA)_2(Succ)]$	– 39.468	– 15.358	– 82.286

Discussion

Cd(II) is hexa co-ordinated (the ligand being bidentate) in the present case. Three mixed complexes thus existing in solution have the following equilibrium. The equilibrium constants (log value) have been calculated and written against each equilibrium :-

		log K (293°K)
1.	$Cd^{2+} + PDA + Succ.^{2-} \rightleftarrows$ [Cd(PDA) (Succ)]	9 204
2.	$Cd^{2+} + (PDA) + 2Succ^{2-} \rightleftarrows$ $[Cd (PDA) (Succ)]^{2-}$	10.380
3.	$Cd^{2+} + 2 (PDA) + Succ^{2-} \rightleftarrows$ $[Cd (PDA)_2 (Succ)]$	11 380
4.	$[Cd(PDA) (Succ)] + (PDA) \rightleftarrows$ $[Cd (PDA)_2 (Succ)]$	2.176
5.	$[Cd(PDA) (Succ)] + Succ^{2-} \rightleftarrows$ $[Cd (PDA) (Succ)_2]^{2-}$	1.176
6.	$[Cd(PDA) (Succ)_2]^{2-} + (PDA) \rightleftarrows$ $[Cd(PDA)_2(Succ)] + Succ^{2-}$	1.000
7.	$[Cd(PDA)]^{2+} + Succ^{2-} \rightleftarrows$ [Cd(PDA) (Succ)]	1.204
8.	$[Cd (PDA)_2]^{2+} + Succ \rightleftarrows$ $[Cd(PDA)_2 (Succ)]$	2.380
9.	[Cd(Succ)] + (PDA) $\rightleftarrows$ [Cd (PDA) (Succ)]	7.551
10.	$[Cd (Succ)_2]^{2-} + (PDA) \rightleftarrows$ $[Cd(PDA) (Succ_2]^{2-} + Succ^{-2}$	7 717
11.	$[Cd (Succ)_3]^{4-} + (PDA) \rightleftarrows$ $[Cd(PDA) (Succ)_2]^{2-} + Succ^{2-}$	7.235
12.	$[Cd(PDA)_2 (Succ)] + (PDA) \rightleftarrows$ $[Cd(PDA)_3]^{2+} + Succ^{2-}$	1.097

From the above equilibrium constant values the tendency of a ligand to add to a complex and to substitute another ligand may be compared. It is seen that (PDA) adds to [Cd(PDA)(Succ)] complex more easily than $succ^{2-}$. The relative tendencies are seen from the equilibrium constant values (equilibrium 4 and 5). The saturated mixed complex [Cd(PDA) $(Succ)_2$] can accommodate (PDA) in place of $(Succ)^{2-}$ i.e. (PDA) can replace $succ^{2-}$. (PDA) has tendency to replace $Succ^{2-}$ from $[Cd(PDA)_2(Succ)]$ mixed complex. Thus the complexing tendency of (PDA) is much more than $succ^{2-}$. The same conclusion may be drawn from the substitution of (PDA) in place of $Succ^{2-}$ in the complex $Cd(Succ)_3^{4-}$. Equilibrium 11 favours mixed complexation over the simple. In the same way there are many other reactions which favour mixed complex formation, over the simple complex formation.

The stability of three mixed complexes as seen from their overall formation constant values follows the order $[Cd(PDA,(Succ)] < [Cd(PDA)(Succ)_2]^{2-} < [Cd(PDA)_2 (Succ)]$

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