Mixed Ligand Complexes of Mn(II) with Reactive Methylene Compounds of Malonamic and Succinic acids - Polarographic Study

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Mn(II) formed a single mixed complex with Succinate and DCM or MM, the value of β_{11} for Mn -(DCM) -(Suc) being 7.70 and for Mn(Suc)(MM) being 8.86. Both indicate that the mixed complex is more stable than the simple complex.

A survey of literature shows that simple and mixed complexes of Mn(II) with a number of carboxylate ions and organic ligands have been studied polarographically [1-3]. Reactive methylene compounds appear as excellent starting materials for the synthesis of various types of chemotherapeutic agents and analytical reagents. The present authors have studied complexation of these methylene compounds as ligands [4-6]. But so far, no polarographic study of mixed complexes of Mn(II) -succinate with DCM and MM have been made. Hence the present investigation was undertaken.

MATERIALS AND METHODS

All chemicals used were of analytical reagent grade; their solutions were prepared in conductivity water. The concentration of Mn(II) was maintained at $1x10^{-3}$M ion in each case. $NaNO_3$ was used to maintain constant ionic strength (2.0M) and as the supporting electrolyte. All measurements were made at 25±0.1°C and pH = 6.0. Polarograms were obtained using a manual polarograph (Toshniwal CLO2A) in conjunction with polyflex galvanometer (PL50). The solution was deaerated with nitrogen gas.

RESULTS AND DISCUSSION

The formation constants of the complexes of Mn(II) with Suc^{2-}, DCM and MM were measured separately under identical conditions. The plots of $[\log i/(i_d - i)]$ *vs* $E_{d.e}$ were linear with a slope of 75±6 mV which showed that the reductions were irreversible for a value of n = 2. Gelling's method is used to determine the $E^r_{1/2}$ value. Deford and Hume's method was applied for the determination of composition and stability constants. The plots of $\Delta E^r_{1/2}$ *vs* log [Suc^{2-}] and [DCM] are straight lines showing the formation of a single complex. Analysis of the data by Lingane's method gave a value of number of ligands as 2 and formation constant of complex [log β_2] = 5.24 and 5.57 respectively. However, in the case of Mn(II) - MM system, the plot of $\Delta E^r_{1/2}$ *vs* log [MM] is a smooth curve indicating the formation of more than one complex. Analysis of the data showed the presence of two complexes

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$[Mn(MM)]^{+}$ and $[Mn(MM)_2]$ with stability constants log β_1 = 3.30 and log β_2 = 6.74.

Mixed System

Mixed ligand complexes were studied in Mn-DCM-Suc and Mn-Suc-MM systems. In the former case, $[Suc^{2-}]$ was kept constant at 0.0005 M and [DCM] was varied from 0 to 0.008M. In the latter case, [MM] was kept constant & $[Suc^{2-}]$ was varied from 0 to 0.005 M. The $E_{1/2}$ values were more negative in presence of the constant ligand concentration than without it, indicating formation of mixed ligand complexes. Method of Schaap and McMaster [9] was used to determine composition and stability of the complex. The polarographic characteristics and $F_{ij}[x,y]$ functions [x = DCM^{-}, y = Suc^{2-}] of the systems is presented in Table 1.

In both cases, a single mixed complex was indicated . The calculated values are included in Table 1.

The mixing constant K_m for the reaction is defined as [10]

Table 1

Polarographic Characteristics, Kinetic Parameters and $F_{ij}[X,Y]$ Functions for Mn(II)-DCM-Suc and Mn(II)-Suc-MM Systems

$[Mn^{2+}]$ = 1x10^{-3}M : μ = 2.0 M $NaNO_3$: pH = 6.0: Temp =25±0.1°C
m = 2.404 mg.sec^{-1}; t = 3.4 sec in 2.0 M $NaNO_3$, open circuit at h_{corr} = 55.6 cm
$[-E_{1/2}]_s$ = 1.410 V (SCE), $[-E'_{1/2}]_s$ = 1.396 V (SCE)

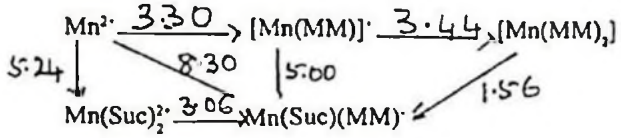
Conc M	i_d μA	$-E_{1/2}$V (SCE)	slope mV	$-E'_{1/2}$V (SCE)	α	k_{sh}x10^5 cm/sec	$F_{00}[X,Y]$	$F_{10}[X,Y]$ x 10^{-4}	$F_{20}[X,Y]$ x10^{-6}
[DCM] =									
0.001	4.76	1.455	69	1.453	0.478	6.05	110.05	7.00	-
0.002	4.62	1.474	72	1.468	0.471	6.00	429.73	19.48	72.4
0.004	4.41	1.488	73	1.484	0.467	5.88	1368.98	33.20	70.5
0.006	4.35	1.504	73	1.493	0.465	5.78	2888.01	47.46	70.7
0.008	4.21	1.512	74	1.500	0.459	5.61	4888.77	60.67	69.5
log A = 1.60;		**log B = 4.47**		**log C = 7.84**					
A single mixed complex Mn(DCM)(Suc)$^{-}$ with log β_{11} = 7.70									
$[Suc^{2-}]$ =									
0.0005	4.87	1.456	81	1.453	0.480	6.43	110.45	-	-
0.001	4.48	1.485	80	1.483	0.465	5.96	1240.50	114.05	-
0.002	4.35	1.502	80	1.498	0.455	5.78	3800.14	185.00	8.7
0.003	4.21	1.511	81	1.508	0.440	5.61	8956.18	265.20	8.5
0.004	4.08	1.518	81	1.514	0.429	5.40	13329.46	330.72	8.2
log A = 2.00;		**log B = 5.30;**		**log C = 8.86**					
A single mixed complex [Mn(Suc)(MM)]$^{-}$ with log β_{11} = 8.3									

$$\log K_M = \log \beta_{11} - 1/2[\log \beta_{01} + \log \beta_{20}]$$

The value for Mn -(DCM) -(Suc) case is + 2.30 and for Mn(Suc)(MM) is +2.31. Both indicate that the mixed complex is more stable than the simple complex.

The results of the present study have been summerised in the following scheme:

Scheme Mn(II). MM. Suc System



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