POLAROGRAPHIC STUDY OF MIXED COMPLEXES OF Mn(II) WITH PYRIDINE AND FORMATE

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After the significant contribution of Schaap and Mc Master [1], polarography has been used to study mixed ligand complexes. Literature reveals that there are only a few references for the polarographic behaviour of mixed ligand complexes of manganese [3,4]. In the present communication, the polarographic behaviour of manganese(II)-pyridine-formate system has been reported.

EXPERIMENTAL

All the chemicals used were of analytical reagent grade and their solutions were prepared in conductivity water. Pyridine and sodium formate were used as ligands. Triton-X-100 (0.002%) was used as the maximum supressor. The ionic strength was maintained constant at μ = 0.8 M ($NaClO_4$) and pH 7.0. All experimental details are as in ref [2].

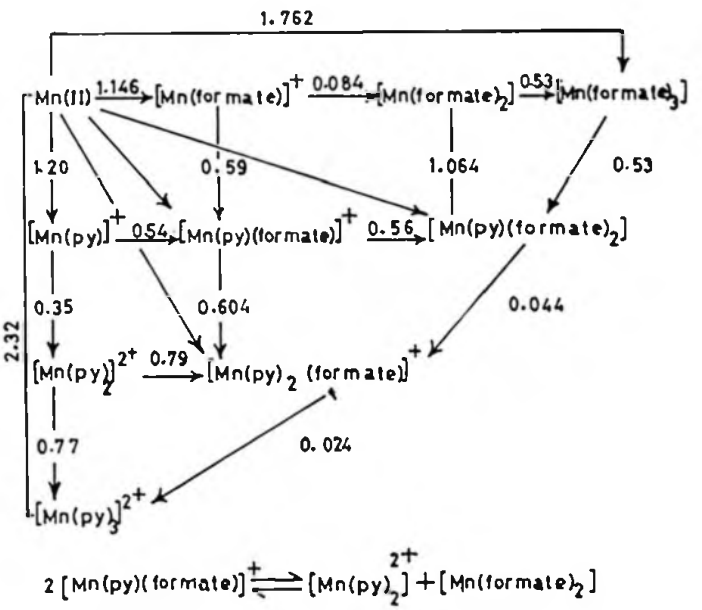
RESULTS AND DISCUSSION

The polarographic reduction of manganese(II) in 0.8 M $NaClO_4$ with and without py and formate separately was found to be reversible and diffusion controlled. The slopes of linear log plots were of the order of 30 ± 1 mV.

Stability constants of simple complexes of Mn(II) with pyridine and formate were determined separately prior to the study of mixed ligand systems. Identical conditions were maintained in both the simple and mixed systems.

A plot of $E_{1/2}$ vs log [py] or log [formate] (after correction at pH 7.0) was a smooth curve indicating the formation of successive complexes in both the cases. Deford and Hume's method [5] was applied for the determination of composition and stability constants. Three successive complexes, viz. $[Mn(py)]^{2+}$, $[Mn(py)_2]^{2+}$ and $[Mn(py)_3]^{2+}$ with stability constants log β_{10} = 1.20, log β_{20} = 1.556 and log β_{30} = 2.32 and $[Mn(formate)]^{+}$, $[Mn(formate)_2]$ and $[Mn(formate)_3]^{-}$ with stability constants, log β_{01} = 1.146, log β_{02} = 1.230 and log β_{03} = 1.762 are formed in both the cases.

Formate concentration is maintained at 0.2 M or 0.4 M and concentrations of py was varied from 0.05 to 0.25 M (after correction at pH 7.0). In each case, a single well-defined reversible and diffusion controlled wave was obtained. The $E_{1/2}$ values were found to be more negative than those obtained in the absence of formate showing the formation of mixed ligand complexes. Schaap and McMasters [1] method has been used to determine the composition and the stability constants of mixed complexes. The polarorgraphic characteristics and F(X,Y) functions (X = py and Y = formate) have been summarized in Table 1. From the plots of F(X,Y) functions vs [py], the following intercept values have been obtained; series 1: log A = 0.903, log B = 1.544, log C = 1.778 and log D = 3.419 Series 2: log A = 1.079, log B = 1.845, log C = 2.30 and log D = 3.72. Three mixed complexes viz. $[Mn(py)_2(formate)]^{+}$, $[Mn(py)(formate)_2]$ and $[Mn(py)(formate)]^{+}$ are formed with stability constants, log β_{11} = 1.740, log β_{12} = 2.300 and log β_{21} = 2.344 .



The results of the present study have been summarized in the above diagram, where the numerical values show the log K for the reactions indicated.

The values for the equilibrium constants of

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TABLE 1

VALUES OF F(X,Y) FUNCTIONS OF Mn(II)-PYRIDINE-FORMATE, $[Mn^{2+}]$ = 0.5 mM, μ = 0.8 M $NaClO_4$ Temperature = 30 ± 0.1°C.

Py M	$\Delta E_{1/2}$ V vs SCE	Log I_s/I_c	$F_{00}(X,Y)$	$F_{10}(X,Y)$ x 10^{-1}	$F_{20}(X,Y)$ x 10^{-2}	$F_{30}(X,Y)$ x 10^{-3}
Series 1 Formate = 0.2 M (fixed)						
0.05	0.020	0.3309	9.92	3.84	-	-
0.10	0.025	0.3189	14.17	6.17	2.67	2.07
0.15	0.032	0.3068	23.57	10.38	4.58	2.65
0.20	0.038	0.3219	38.66	15.33	5.91	2.65
0.25	0.045	0.3315	67.60	23.84	8.13	3.01
Series 2 Formate = 0.4 M (fixed)						
0.05	0.0280	0.2952	1.68	9.70	5.40	-
0.10	0.0320	0.3425	2.56	13.65	6.65	4.60
0.15	0.0400	0.3187	4.47	21.82	9.88	5.20
0.20	0.0480	0.3165	8.22	25.10	14.65	6.02
0.25	0.0525	0.3435	12.35	44.60	15.05	5.21

Series 1, log A = 0.9030, log B = 1.5440, log C = 1.778, log D = 3.419
Series 2, log A = 1.079, log B = 1.845, log C = 2.301, log D = 3.720

the disproportionation reactions indicated that the mixed complexes are more stable than the simple complexes.

The tedency of formate anion to add as the second ligand to $[Mn(formate)]^+$ and $[Mn(py)]^{2+}$ can be compared. The log K values are 0.084 and 0.54. The difference is more than the statistical factor of 2, therefore the charge naturalization will be there. Addition of uncharged pyridine ligand to above complexes gives rise to log K values of 0.35 and 0.59 respectively, a difference equal to that predicted by statistical factor.

Rather startling results are obtained upon comparison of the equilibrium constants for the addition of formate anion or pyridine molecule to the various bis ligand complexes. Addition of either a pyridine molecule or a formate anion to $Mn(py)_2^{2+}$ would be hindered, despite the opposite charges of the latter two species, while addition of either ligand to $Mn(formate)_2$ would proceed more readily. It is possible to explain the observed trends on the assumption that the negatively charged formate anions, each with two oxygen atoms, repel and loosen the coordinated water molecule to a greater extent than do pyridine molecule. As such $[Mn(formate)]_2$ would be weakly solvated, whereas the bispyridine complex would be strongly solvated, and can be represented as $[Mn(py)_2(H_2O)_4]^{2+}$. Addition of a third ligand to the latter would require elemination of solvent molecule at the cost of appreciable energy.

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