

STUDIES ON ELECTRODE KINETICS OF MIXED LEGAND COMPLEXES OF MN (II) IN
DIOXAN AT DME

Preeti Jain, R. Pandey and P.S. Verma

Department of Chemistry, University of Rajasthan, Jaipur-302055. India.

Email: jaindrpreeti28@gmail.com Mobile no. 7877365395

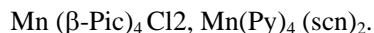
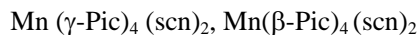
ABSTRACT:- Mixed ligand complexes of Mn (II) with pyridines and halides and pseudohalides have been synthesised. The reduction of synthesised complexes at dropping mercury electrode in various percentage of dioxan have been studied. The reductions are diffusion controlled. Slope values indicate reduction to be irreversible. Kinetic parameters [K_m^0 , αn & ϵ] have been calculated by Meites Isreal and Gaur Bhargava Methods. The effects of various compositions of dioxan have been investigated.

Key words: Electrode, kinetics, Ligand, Dioxan

INTRODUCTION

A detailed study about the reduction of Mn (II) with various aminoacids (Kumar, Suresh, Meena and O.D. Gupta, 2010). Zn (II) with erythromycin (Susmita Sharma, et.al., 2010). Ga (III) with L-glutamine (Vinita Sharma & K.D. Gupta, 2011). In (III) & Tl (I) with DL-a-alanine (Vinita Sharma & K.D. Gupta, 2009). and Cu (II) with oxoglutarate (O.D. Gupta, et. al., 2010). are available. Some reduction studies of In (III) & Ga (III) in the presence of pyridine (Vinita Sharma & K.D. Gupta, 2010, 2003). and Cd (II) with glycine (Suresh Kumar, et. al., 2009). in aqueous and aqueous-nonaqueous media have been done. Mixed ligand complexes of transition metals with hetero cyclic amines, halides and pseudohalides have been known for many years (G.B. Kauffman, et. al., 1973). Complexes of Mn (II) and Cd (II) with mixed ligand have been studied polarographically and reported (Anju Varshney, 1981) (J.N. Gaur and N.K. Goswami, 1967).

The Present study deals with the study of electrode kinetics of the following synthesized complexes at the dropping mercury electrode in aqueous dioxan mixtures.



These complexes have been synthesised by the Method suggested by Kauffman (G.B. Kauffman, et. al., 1973). Identified by elemental analysis and IR spectral studies. The reduction in all cases is found to be irreversible and as such the Kinetic parameters have been calculated by the Meites Isreal (L. Meites & Y. Isreal, 1961). and Gaur Bhargava (J.N. Gaur and S.K. Bhargava, 1973) Methods.

EXPERIMENTAL

A conventional type manual polarograph was used for obtaining current -voltage curves. The dropping mercury electrode had the following characteristics. $m=3.0$ mg / sec, $t = 2.2$ s. triton x-100 (0.001 %) was used to suppress the maxima. Solution of Mn(II) complexes were prepared in various percentage (20-60 %) of purified dioxan dissolved. Oxygen was removed by bubbling purified nitrogen through the solution, which was presaturated with a solution having the same composition as that of the experimental mixture. Sodium per chlorate was used as base electrolyte. Solutions containing [1.0 mM] of the compound in different percentages of the solvent [by vol] were prepared at constant ionic strength [$\mu = 0.1$].

RESULTS AND DISCUSSION

A single well defined wave was obtained during the reduction of all such complexes at the dropping mercury electrode. The reduction was found to be diffusion controlled for all these complexes as confirmed from the plots of i_d vs \sqrt{h} and i_d vs concentration which were linear and passed through the origin. The kinetic parameters have been evaluated by Meites - Israel Method [s] and its Modification by Gaur and Bhargava (J.N. Gaur and S.K. Bhargava, 1973). Meites and Israel have extended the Koutecky graphical method into a comparatively more precise mathematical form. According to them, the equation for a totally irreversible wave becomes.

$$E_d.e = \frac{0.05915}{\alpha n} \log \frac{1.34K^{\circ} f_{\text{th}} c^{\circ}}{D^{1/2}} - \frac{0.0542}{\alpha n} \log \left\{ \frac{i}{i_d - i} \right\} - [1]$$

which may be written as

$$E_d.e = E_{1/2} - \frac{0.0542}{\alpha n} \log \left\{ \frac{i}{i_d - i} \right\} - [2]$$

$$\text{with } E_{1/2} = \frac{0.05915}{\alpha n} \log \frac{1.34K^{\circ} f_{\text{th}} c^{\circ}}{D^{1/2}} - [3]$$

where K°_{th} is formal rate constant for the forward reaction, D is the diffusion coefficient, α is transfer coefficient and other terms have their usual significance. Thus the values of αn is obtained from slope $\frac{0.0542}{n}$ of straight line of $E_d.e$ vs $\log \frac{i}{i_d - i}$. The intercept of the same plot the value of $E_{1/2}$ which is used to calculate K°_{th} after having the value of D from the ilkovic equation.

Gaur and Bhargava (J.N. Gaur and S.K. Bhargava, 1973) have extended the Koutecky's treatment for irreversible wave. They considered that the diffusion to the electrode surface is spherical and not a linear process as assumed earlier. According to them :

$$E_d.e = E_{1/2} - \frac{0.05690}{\alpha n} \log \left\{ \frac{i}{i_d - i} \right\} - [4]$$

$$\text{with } E_{1/2} = \frac{0.05915}{\alpha n} \log \frac{K^{\circ} f_{\text{th}} c^{\circ}}{1.128D^{1/2}}$$

In Eq.[3] and [5], the potentials are referred to N.H.E.

The polarographic characteristic and Kinetic parameters K° [The rate constant for the electron transfer reaction at zero volts] and α [transfer coefficient] are calculated by meites and Isereal and also Gaur and Bhargava Methods. The polarographic characteristics and Kinetic parameters have been summarized in tables 1 and table 2.

The half - wave potential is shifted towards more cathodic direction as the percentage of dioxan is increased from 20-60% in both these complexes. The behaviour of simple Mn(II) has been studied under similar conditions by Gaur and Goswami (N.K. Goswami, 1976). who found a regular shift in half-wave potential (More cathodic) with increase in percentage of dioxan. The more cathodic behaviour of half wave potential may be concluded to be due to the physical properties (viscosity, low dielectric constant) of dioxan as described earlier.

Table-1. Polarographic characteristics of Mn (II) complexes in aqueous - dioxan mixtures.

Complex	%Dioxan [by vol]	i_d (uA)	$E_{1/2}$ (-Vvs sce)	Slope (mV)	$D^{1/2} \times 10^3$ (cm ² -sec ⁻¹)
Mn (γ pic) ₄ (scn) ₂	20	7.77	1.512	80	2.698
Mn (γ pic) ₄ (scn) ₂	40	7.70	1.524	84	2.674
Mn (γ pic) ₄ (scn) ₂	60	7.64	1.530	87	2.653
Mn (β pic) ₄ (scn) ₂	20	7.82	1.515	77	2.715
Mn (β pic) ₄ (scn) ₂	40	7.79	1.520	80	2.705
Mn (β pic) ₄ (scn) ₂	60	7.70	1.536	82	2.674
Mn (β pic) ₄ Cl ₂	20	7.90	1.567	79	2.743
Mn (β pic) ₄ Cl ₂	40	7.82	1.572	83	2.715
Mn (β pic) ₄ Cl ₂	60	7.80	1.575	85	2.708
Mn (Py) ₄ (scn) ₂	20	7.93	1.582	82	2.754
Mn (Py) ₄ (scn) ₂	40	7.90	1.585	85	2.743
Mn (Py) ₄ (scn) ₂	60	7.82	1.587	88	2.715

The slope of the log plots indicate irreversible reduction of the complexes. The K_f values indicate that the electrode process for the reduction of these complexes becomes more irreversible when the percentage of dioxan is increased and also the nature of electrode process is not uniform. The variation in polarographic characteristics of the complexes and the irreversibility of the electrode process with change in solvent composition may be attributed solely to the physical properties of the solvent. The structure of the double layer also plays the significant role in the electrode kinetics.

In presence of dioxan the electrical layer is changed as suggested by Minc et al (S. Minc, et. al., 1961). Adsorption of a dioxan solvent hinders the approach of electroactive species at dme. Hence increase in percentage of dioxan may be due to change in structure of double layer. If only physical properties would have been considered, as the criterion.

Table - 2. Kinetic parameters for Mn(II) complexes in aqueous - dioxan mixtures.

Complex	%Dioxan [by vol]	ϵ	α	K_f [cm.s ⁻¹] Meites Israel Method	K_f [cm.s ⁻¹] Gaur - Bhargava Method
Mn(γ pic) ₄ (scn) ₂	20	0.108	0.67	6.47x10 ⁻¹⁹	9.8x10 ⁻¹⁹
Mn(γ pic) ₄ (scn) ₂	40	0.107	0.64	3.17x10 ⁻²⁰	4.8x10 ⁻²⁰
Mn(γ pic) ₄ (scn) ₂	60	0.106	0.62	1.01x10 ⁻²¹	1.5x10 ⁻²¹
Mn(β pic) ₄ (scn) ₂	20	0.108	0.70	1.27x10 ⁻¹⁹	1.93x10 ⁻¹⁹
Mn(β pic) ₄ (scn) ₂	40	0.107	0.67	5.25x10 ⁻²⁰	8.00x10 ⁻²⁰
Mn(β pic) ₄ (scn) ₂	60	0.106	0.66	9.15x10 ⁻²¹	1.39x10 ⁻²⁰
Mn(β pic) ₄ cl ₂	20	0.109	0.68	9.15x10 ⁻²⁰	1.39x10 ⁻²⁰
Mn(β pic) ₄ cl ₂	40	0.108	0.65	5.99x10 ⁻²¹	9.12x10 ⁻²¹
Mn(β pic) ₄ cl ₂	60	0.107	0.63	1.42x10 ⁻²²	2.16x10 ⁻²¹
Mn(Py) ₄ (scn) ₂	20	0.110	0.66	2.88x10 ⁻²⁰	4.39x10 ⁻²⁰
Mn(Py) ₄ (scn) ₂	40	0.109	0.63	1.12x10 ⁻²⁰	1.70x10 ⁻²⁰
Mn(Py) ₄ (scn) ₂	60	0.108	0.61	4.05x10 ⁻²¹	6.16x10 ⁻²¹

The half - wave potential shift would have been more anodic which is actually not the case.

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