Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry
2016, 5 (6): 1298-1301
(International Peer Reviewed Journal)

Electrode Kinetics of Mixed Ligand Complexes of Zn (II) in Aqueous-Tetrahydrofuran Mixtures at D.M.E.

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

*Department of chemistry, University of Rajasthan, Jaipur-302055, **INDIA**

Email: jaindrpreeti28@gmail.com

Accepted on 16th November 2016, Published online on 27th November 2016

ABSTRACT

Mixed ligand complexes of Zn (II) with pyridines, β-and γ-picoline as organic bases and its isothiocynate and chloride complexes have been synthesized. The reduction studies of synthesized complexes at dropping mercury electrode in various percentage of tetrahydrofuran have been studied. The reductions are diffusion controlled. Slope values indicate reduction to be irreversible. Kinetic parameters [$K^0_{fh,}$ αn & ε] have been calculated by Meites Isreal and Gaur Bhargava Methods. The effects of various compositions of tetrahydrofuran have been investigated.

Keywords: Electrode, kinetics, Ligand, Tetrahydrofuran.

INTRODUCTION

Electrochemical behaviour of Zn (II) with erythromycin [1], Ga (III) with L-glutamine [2], In (III) & Tl (I) with DL-a-alamine [3] and Cu (II) with oxoglutarate [4] Mn (II) with various amino acids [5] at dropping mercury electrode has been reported. Some reduction studies of In (III) & Ga (III) in the presence of pyridine [6, 7] and Cd (II) with glycine [8] in aqueous and aqueous-nonaqueous media have been done. Mixed ligand complexes of transition metals with hetero cyclic amines, halides and psuedohalides have been known for many years [9]. Complexes of Mn (II) and Cd (II) with mixed ligand were studied polarographically and reported [10, 11].

The Present study deals with the study of electrode kinetics of the following synthesized complexes at the dropping mercury electrode in aqueous tetrahydrofuran mixtures.
$Zn(\beta\text{-Pic})_2(NCS)_2$, $Zn(Py)_2(NCS)_2$,
$Zn(\beta\text{-Pic})_2Cl_2$, $Zn(\gamma\text{-Pic})_2(NCS)_2$

These complexes have been synthesized by the Method suggested by Kauffman [9] and 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 [12] and Gaur Bhargava [13] methods.

MATERIALS AND METHODS

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^{-1}, t = 2.2 s. triton x-100 (0.001 %) was used to suppress the maxima. Solution of Zn (II) complexes were prepared in various percentage (20-60 %) of purified tetrahydrofuran 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 (u= 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 id vs ✓h and id vs concentration which were liner and passed through the origin. The kinetic parameters have been evaluated by Meites - Israel Method [12] and its Modification by Gaur and Bhargava [13]. 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.

$$\text{Ed.e} = \frac{0.05915}{\alpha n}\ \log \frac{1.34K^{\circ}{}_{fh}t½}{D½}\ -\ \frac{0.0542}{\alpha n}\ \log \left\{ \frac{i}{id-i} \right\} – (1)$$

which may be written as

$$\text{Ed.e} = \text{E } ½ - \frac{0.0542}{\alpha n}\ \log \left\{ \frac{i}{id-i} \right\} – (2)$$

$$\text{with E}½ = \frac{0.05915}{\alpha n}\ \log \frac{1.349K^{\circ}{}_{fh}t½}{D½}\ \text{-(3)}$$

where K$^{o}{}_{fh}$ is formal rate constant for the forward reaction, D is the diffusion coefficeint, 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 Ed.e vs log $\frac{i}{id-i}$. The intercept of the same plot the value of E½ which is used to calculate k$^{o}{}_{fh}$ after having the value of D from the ilkovic equation.

Gaur and Bhargava [13] 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:

$$\text{Ed.e} = \text{E } ½ - \frac{0.05690}{\alpha n}\ \log \left\{ \frac{i}{id-i} \right\} – (4)$$

$$\text{with E}½ = \frac{0.05915}{\alpha n}\ \log \frac{K^{\circ}{}_{fh}t½}{1.128D½}$$

In Eq. (3) and (5) , the potentials are referred to N.H.E.

The Polarographic characteristic and Kinetic parameters K^{o}f [The rate constant for the electron transfer reaction at zero volts] and α [transfer coefficient] are calculated by meites and Isereal [12] and also Gaur and Bhargava [13] Methods. The Polarographic characteristics and Kinetic parameters have been summarized in tables 1 and table 2.

Table 1: Polarographic characteristics of Zn(11) complexes in aqueous - tetrahydrofuran mixtures.

S.No.	Complex	%Tetrahydrofuran [by vol]	id (uA)	E½ (-Vvs sce)	Slope (mV)	D½x10^{3} (cm^{2}-sec^{-1})
1	Zn (γ-pic)$_2$ (NCS)$_2$	20	5.62	1.056	73	1.951
2	Zn (γ-pic)$_2$ (NCS)$_2$	40	5.60	1.060	74	1.944
3	Zn (γ-pic)$_2$ (NCS)$_2$	60	5.55	1.063	77	1.927
4	Zn (β-pic)$_2$ (NCS)$_2$	20	5.64	1.052	71	1.958

5	Zn (β-pic)$_2$ (NCS)$_2$	40	5.61	1.055	73	1.948
6	Zn (β-pic)$_2$ (NCS)$_2$	60	5.58	1.058	75	1.937
7	Zn (β-pic)$_2$ Cl$_2$	20	5.60	1.055	75	1.944
8	Zn (β-pic)$_2$ Cl$_2$	40	5.57	1.058	77	1.934
9	Zn (β-pic)$_2$ Cl$_2$	60	5.52	1.060	80	1.916
10	Zn (Py)$_2$ (NCS)$_2$	20	5.58	1.060	74	1.937
11	Zn (Py)$_2$ (NCS)$_2$	40	5.53	1.064	75	1.920
12	Zn (Py)$_2$ (NCS)$_2$	60	5.50	1.067	78	1.909

Table-2: Kinetic parameters for Zn(II) complexes in aqueous-tetrahydrofuran mixtures.

S.No.	**Complex**	**%Tetrahydrofuran [by vol]**	ε	α	**K^o_f [cm.s^{-1}] Meites Israel Method**	**K^o_f [cm.s^{-1}] Gaur - Bhargava Method**
1	Zn(γ-Pic)$_2$(NCS)$_2$	20	0.078	0.74	$5.41x10^{-17}$	$8.24x10^{-17}$
2	Zn(γ-Pic)$_2$(NCS)$_2$	40	0.077	0.73	$7.27x10^{-17}$	$1.10x10^{-16}$
3	Zn(γ-Pic)$_2$(NCS)$_2$	60	0.077	0.70	$2.15x10^{-16}$	$3.28x10^{-16}$
4	Zn(β-Pic)$_2$(NCS)$_2$	20	0.078	0.76	$2.59x10^{-17}$	$3.94x10^{-17}$
5	Zn(β-Pic)$_2$(NCS)$_2$	40	0.077	0.74	$5.56x10^{-17}$	$8.47x10^{-17}$
6	Zn(β-Pic)$_2$(NCS)$_2$	60	0.077	0.72	$1.14x10^{-16}$	$1.74x10^{-16}$
7	Zn(β-Pic)$_2$ Cl $_2$	20	0.077	0.72	$1.25x10^{-16}$	$1.90x10^{-16}$
8	Zn(β-Pic)$_2$ Cl $_2$	40	0.077	0.70	$2.48x10^{-16}$	$3.77x10^{-16}$
9	Zn(β-Pic)$_2$ Cl $_2$	60	0.076	0.67	$6.92x10^{-16}$	$1.05x10^{-15}$
10	Zn(Py)$_2$(NCS)$_2$	20	0.077	0.73	$7.25x10^{-17}$	$1.10x10^{-16}$
11	Zn(Py)$_2$(NCS)$_2$	40	0.076	0.72	$9.60x10^{-17}$	$1.46x10^{-16}$
12	Zn(Py)$_2$(NCS)$_2$	60	0.076	0.69	$2.78x10^{-16}$	$4.24x10^{-16}$

The half - wave potential is shifted towards more cathodic direction as the percentage of tetrahydrofuran is increased from 20-60% in these complexes. The behaviour of simple Zn (II) has been studied under similar conditions by Gaur and Goswami [14], who found a regular shift in half-wave potential (More cathodic) with increase in percentage of tetrahydrofuran. The more cathodic behaviour of half wave potential may be concluded to be due to the different physical properties (viscosity, low dielectric constant) of tetrahydrofuran as that of water. The slope of the log plots indicates irreversible reduction of the complexes. The K^o_f values indicate that the electrode process for the reduction of these complexes becomes more irreversible when the percentage of tetrahydrofuran 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 tetrahydrofuran the electrical layer is changed as suggested by Minc [15]. Adsorption of a tetrahydrofuran solvent hinders the approach of electro active species at DME. Hence increase in percentage of tetrahydrofuran may be due to change in structure of double layer. If only physical properties were considered, as the criterion. The half - wave potential shift would have been more anodic which is actually not the case.

APPLICATIONS

The more cathodic behaviour of half-wave potential due to the different physical properties (i.e. viscosity and dielectric constant) of tetrahydrofuran as that of water. Values of K^0_{fh} increase as the percentage of THF is increased in mixture. It means that irreversibility of the electrode reaction increases with increasing the percentage of the organic solvent.

CONCLUSIONS

Increase in the percentage of THF in the solvent mixture has greater effect on $E_{½}$ Values i.e. half wave potential becomes more cathodic. The K^{0}_{fh} values which are in order of $10^{-16\pm1}$ further confirm that the reduction of metal complexes studied is completely irreversible.

ACKNOWLEDGEMENTS

The author is thankful to the Head, Department of Chemistry, University of Rajasthan, Jaipur to provide research facilities.

REFERENCES

[1] S. Sharma, A. Garg and R. Pandey, *Journal Indian chem. soc*, **2010**, 87, 1205-1209.
[2] V. Sharma, K.D. Gupta, *Monatsh Chem*, **2011**, 142, 481- 485.
[3] V. Sharma, K.D. Gupta, *Asian Journal of Chemistry,* **2009,** 21, 6.
[4] O.D. Gupta, M. Singh, J. Singh, *Asian Journal of Chemistry*, **2010**, 22, 2043 - 2050.
[5] S. Kumar, M. Gupta, O.D. Gupt,a *Asian Journal of chemistry*, **2010,** 22, 5019 - 5024.
[6] V. Sharma, K.D. Gupta, *Collect. Czech. Chem. Commun,* **2010** 75, 653-663.
[7] V. Sharma, K.D. Gupta, *J. of electrochemical society of India*, **2003,** 52.
[8] S. Kumar, Meena, A. K. Barjatya, O.D. Gupta, *Rasian Journal of chemistry*, **2009,** 2 (2), 371 - 374.
[9] G.B. Kauffman, R.A. Albers, F.L. Haron, *J. Chem, Educ,* **1973,** 50 (1), 70.
[10] A.Varshney, K. Singh, M. Singh, *Journal of Inorganic and Nuclear Chemistry*, **1981,** 43, 2075 - 2078.
[11] J.N.Gaur, N.K.Goswami, *Electrochim Act.*, **1967,** 12, 1483.
[12] L. Meites, Y Isreal, *J. Amerchem Soc,* **1961,** 83, 4903.
[13] J.N. Gaur, S.C. Bhargava, *Bull Chem. Soc. Japan*, **1973,** 46, 3314.
[14] N.K. Goswami, *Ph.D Thesis, Rajasthan University,* Jaipur, **1976.**
[15] S. Minc, J. Jastrazebska, M. Brozostowska, *J. electrochem, Soc,* **1961**, 108, 1160.

AUTHORS' ADDRESSES

1. **Dr. Preeti Kala Jain**
Lecturer, Department of Chemistry,
Agarwal P.G. College, Jaipur, India
Email: jaindrpreeti28@gmail.com, Mob: 7877365395
2. **Dr. Rajayashree Pandey (Retd.)**
Associate Professor, Department of Chemistry
University of Rajasthan, Jaipur, India
Email: rajayashree@yahoo.com, Mob: 9414323183
3. **Dr. Prem Singh Verma (Retd.)**
Professor, Department of Chemistry,
University of Rajasthan, Jaipur, India
Email: psvermajaipur@gmail.com, Mob: 9414073672