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Electrode Kinetic Study of Complexes of Ga (III) with Some Amino Acids Polarographically

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Abstract: *Electrode kinetics and complex formation of Ga(III) with some amino acids (L-Threonine, Glycine) have been studied in 1 mM KNO_3which was used as supporting electrolyte. The reduction of Ga(III) has been found to be irreversible and diffusion controlled and involved three electrons transfer process. The complexes of Ga(III) have been investigated and their kinetic parameters viz. transfer coefficient (α), degree of irreversibility (λ) and rate constant (k) have been determined in aqueous medium at 308K by applying Koutecky's method.*

Keywords: Gallium(III), Electrode kinetics, L-Threonine, Glycine, Koutecky's method

I. INTRODUCTION

Gallium is blue-gray metal with orthorhombic crystalline structure having atomic number 31. Gallium nitride and arsenide are semiconductors and appear in compounds used in light emitting diodes. It is issued in metal in glass high temperature thermometers. A low temperature liquid eutectic alloy of Ga, In, Sn is widely used in medical thermometers, replacing problematic mercury. Gallium nitrate and citrate are used as radiopharmaceutical agents. Gallium is used to create brilliantmirror as gallium wets glass or porcelain. Gallium is also used as a dopant for the production of solid state devices such as transistors. It can be used to fight bacterial infection in people with cystic fibrosis

The equation for the polarographic current-potential curve corresponding to a totally irreversible process whose rate governed by a single electron transfer step has been obtained by several workers[1-2]. Polarography is one of the popular technique considered for the study of complexes and electrode kinetics of irreversible reactions[3]. An extensive work has been carried out on the electrochemical behaviour of amino acids and their complexes with several metal ions by many workers[4-5]. Complexation of Gallium(III) with L-serine, L-methionine has been investigated potentiometrically by Bianco et al[6]. The researchers have also worked extensively on extraction and synthesis of variety of complexes of Gallium[7-8].

Amino acids have wide variety of applications varying from biological, pharmaceutical and other chemical uses and have been reported to form complexes with some metals and hence the importance of this class of compounds have grown. Number of electrochemical studies on the behaviour of amino acids and their complexes[9-14] have been already carried out, which have been found useful applications in biochemistry and medicine". Amino acids are well known for formingspecific ring compounds with several metal ions as these contain side chains donar atoms and potentially capable of forming chelate rings with metal-ion bound at the α-amino nitrogen.

Vinita Sharma [16-18] carried out the electrode kinetic study of Ga(III) with DL- α-alanine, N-glycyl-glycine and pyridine in aqueous and aqueous-ethanol medium. V.N. Spiridonov et al.[19] studied the kinetics of alanine at a DME with Pd(II). Sreechar[20] investigated the electrode kinetics of anticancer drug Zileutron using D.M.E. Sindhu and coworkers[21] have investigated the polarographicbehaviour of complexes of Ga(III) with disubstituted pyridine. Indu and Singh[22] have studied the effect of surfactants on the polarographic maxima of Ga(III). Sarkar and Cruck[23] have reported the isolation of a mixed complex from human serium and have prepared mixed Cu(II) complexes of amino acids at the physiological pH.Saxena and coworkers [24-26] carried out polarographic studies on Cd(II) and Pb(II) complexes of L-Tyrosine and L-Threonine. Polarographic studies of histidine with some p-block elements like Ga(III), In(III), TI(I) have been carried out separately at constant ionic strength (μ = 1.0M) using KCI at 298K and 308K[27] temperatures. The electrode kinetic

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study of Ga(III)-complexes with citrulline and Tyrosine at different temperature by polarographic[28-29] method has been carried out.

The present paper deals with the complexation of Ga(III) with some amino acids (Glycine and L-Threonine) and determination of kinetic parameters by applying the Koutecky's method.

Experimental

A CL-362 polarographicanalyser was used to record the polarograms using saturated calomel electrode as the reference electrode and dropping mercury electrode was used as microelectrode. A.R. grade purity chemicals were used and their solutions were prepared in doubly distilled water. Amino acids were purchased from Samir-tech Chem Pvt. Ltd. and Hi media laboratories limited and Gallium nitrate from Across and used as such without further purification.

The test solutions contain 0.1 mM of Ga(III) KNO_3 of 1M concentration, different concentration of different ligands and 0.002% Triton X-100 as maxima suppressor. Precaution was taken to avoid possible contamination by traces of surface active metal. The temperature was kept constant (308K,318K) using Haake-type ultra thermostat. Before polarographic measurement, purified N_2gas was passed for 10-15 minutes to remove dissolved oxygen. The capillary has the following characteristics m=4.6 mg/s, t=2 sec and height of mercury column h_{eff} =43 cm

II. RESULTS AND DISCUSSION

The current-voltage curve was obtained. Ga(III) and its complexes gave well defined three electron irreversible reduction wave and process is diffusion controlled. This is indicated by the slope of log plot of E_{dme}vs log i/i_d-i and from direct proportionality between $i_d$and h_{eff} .When the concentration of ligand was varied (0.001M to 0.007M), the half-wave potential exhibits cathodic shift which was coupled with decrease in diffusion current due to larger size of complex ion than aqua ion. This shows the complexation between Gallium(III) and ligands (Glycine and L-Threonine) Gelling methods was used to $E^r_{1/2}$values.

By knowing the value of 'n' the diffusion coefficient ($D^{1/2}$) ofthe depolarizer was calculated by using Ilkovic equation at different concentration of the ligand.

$i_d = 607ncD^{1/2}m^{2/3}t^{1/6}$

$D^{1/2} = i_d/607\ ncm^{2/3}t^{1/6}$

Where

i_d= diffusion current

n= number of electron involved in reaction

c= concentration

m= mass of mercury drop

t= drop time

DeFord and Hume's method has been used to determine the stability constant, which were further verified by using Mihailov's method. The overall stability constants determined by both the methods are recorded in Table 1-4 at 308K and 318K temperatures, respectively.

Table-1. Stability constants of Ga(III) -Threonine system at 308K

Methods	$\log\beta_1$	$\log\beta_1$	$\log\beta_1$
DeFord& Hume	3.30	5.95	8.70
Mihailov	2.96	5.80	8.46

Table-2. Stability constants of Ga(III)-L-Threonine system at 318K

Methods	$\log\beta_1$	$\log\beta_1$	$\log\beta_1$
DeFord& Hume	3.15	5.60	8.60
Mihailov	2.20	6.23	9.09

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Table-3. Stability constants of Ga(III) -L-Glycine system at 308K

Methods	$\log\beta_1$	$\log\beta_1$	$\log\beta_1$
DeFord& Hume	3.70	6.04	8.88
Mihailov	3.10	5.93	8.59

Table-4. Stability constants of Ga(III)-L-Glycine system at 318K

Methods	$\log\beta_1$	$\log\beta_1$	$\log\beta_1$
DeFord& Hume	3.60	6.0	8.84
Mihailov	2.64	5.82	9.60

Table - 5 .Kinetic parameters of Ga(III) in various concentration of L-Threonine at 308K in aqueous media
[Ga(III)] = 0.1mM; Ionic Strength (μ) = 1.0 M (KNO_3)

C_x mole/litre	$D^{1/2}$ Cm^2sec^{-1}	α	$E^r_{1/2}$ -V vs S.C.E	$LogK^o_{fh}x10^1$
0	-	-	1.075	
0.001	1.447	0.8089	1.081	1.810
0.002	0.7101	0.8603	1.089	1.905
0.003	0.4639	0.9033	1.096	1.993
0.004	0.3430	0.9509	1.105	2.104
0.005	0.2683	1.204	1.111	2.683
0.006	0.2209	1.355	1.117	3.036
0.007	0.1845	1.869	1.22	4.225

C_x = L-Threonine concentration (moles $litre^{-1}$)

Table - 6 . Kinetic parameters of Ga(III) in various concentration of L-Threonine at 318K in aqueous media
[Ga(III)] = 0.1 mM; Ionic Strength (μ) = 1.0 M (KNO_3)

C_X mole/litre	$D^{1/2}$ Cm^2sec^{-1}	α	$E^r_{1/2}$ -V vs S.C.E	Log $K^o_{fh}x10^1$
0	-	-	1.075	-
0.001	1.440	0.20	1.084	5.985
0.002	0.7029	0.140	1.095	8.355
0.003	0.4603	0.092	1.104	1.993
0.004	0.3394	0.068	1.112	2.104
0.005	0.266	0.050	1.118	2.683
0.006	0.2195	0.048	1.122	3.036
0.007	0.1840	1.042	1.125	4.225

C_x = L -Threonine concentration (moles $litre^{-1}$)

The effect of increasing concentration of ligands on polarographic characteristics and kinetic parameters are
The decrease in the values of a with the increase in concentration of the ligand, implies that the transfer of electron is getting increasingly difficult and the reduction of Ga(III) can also be noticed from the decreasing trends of K^o_{fh}.
The thermodynamic parameters have also been determined and the values of enthalpy (ΔH°), free energy (ΔG°), and entropy (ΔS°), have been recorded in Table-7.

Table-7. Thermodynamic parameters of Complexes of Ga(III) with L- Threonine and Glycine

Metal	ligand	complex	ΔG°(-) Kcal/mol	ΔH°(-) Kcal/mol	ΔS°(-) Kcal/mol/deg
Ga(III)		MX_1	4.6138	6.723	6.632
	L-Threonine	MX_2	8.202	15.687	23.536
		MX_3	12.597	4.482	25.517

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		MX_1	5.273	4.482	2.487
	Glycine	MX_2	8.788	1.793	21.998
		MX_3	12.948	1.614	35.643

M=Ga(III), X=L-Threonine/Glycine

The results show that there is a regularity in the variation of the values of standard rate constant K°_{fh}. As the concentration of the ligand increases, the value of formal rate constant increases.

By knowing the thermodynamic functions, the effect of temperature on stability of complexes will be defined. It is concluded that more negative value of ΔG°shows that the driving tendency of complexation reaction is from left to right and reaction tends to proceed spontaneously and negative value of ΔH°show that the formation of these complexes is an exothermic process.

The complexes of Ga(III) with Glycine are more stable than the L- Threonine due to the effect of 'R' group.

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