



The Electrode Kinetic Study of Ga(III) Complexes with Citrulline at Different Temperatures by Polarographic Technique

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(Received: June 01, 2010; Accepted: July 10, 2010)

ABSTRACT

Polarographic behaviour of Ga(III) has been investigated in the presence of Citrulline at dropping mercury electrode and the reduction of Ga(III) has been found to be irreversible in the supporting electrolyte with or without complexing agent. The complexes of Ga(III) have been investigated and their kinetic parameters have been evaluated. Transfer coefficient (α) and formal rate constant (K_m^0) have been determined in aqueous medium at 300K and 308K by applying Koutecky's method.

Key words: Gallium(III), Citrulline, Dropping mercury electrode, Kinetic parameters, Koutecky's method.

INTRODUCTION

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 authors^{1,2}.

A plot of E_{de} Vs $\log i/(i_d-i)$ employing average current in the logarithmic term should be linear and should have slope of 0.0591/an at 25°C. Complexation of Gallium(III) with L-serine, L-methionine has been investigated potentiometrically by Bianco et al.³. The researchers have also worked extensively on extraction and synthesis of variety of complexes of Gallium^{4,5}. Polarography is one of

the popular technique considered for the study of complexes and electrode kinetics of irreversible reactions⁶. An extensive work has been carried out on the electrochemical behaviour of amino acids and their complexes with several metal ions by many workers^{7,8}. Vinita Sharma⁹⁻¹¹ carried out the electrode kinetic study of Ga(III) with DL- α -alanine, N-glycyl-glycine and pyridine in aqueous and aqueous ethanol medium. The kinetics of alanine at a DME was studied in solution with the Palladium by V.N. Spiridonov et al.¹². The electrode kinetics of anticancer drug Zileuton was investigated DCP and DPP using DME by N.Y. Sreedhar et al.¹³. Kinetic parameters and stability constants of complexes of Mn with doxycycline, chlortetra cycline, oxytetra cycline, tetra cycline monocycline, amoxicillin

reported polarographically by Farid Khan and Rakhi Agrawal¹⁴. The literature search reveals that Polarographic study of Gallium(III) complexes with Citrulline has not been attempted so far. This fact inspired us to investigate polarographic behaviour of Ga(III) in presence of citrulline.

EXPERIMENTAL

Polarograms were obtained with a carefully calibrated polarograph. The test solutions were prepared using conductivity water. The solutions contain 0.1mM of Ga(III) and different concentrations of ligand. The solution of KNO_3 of 1M concentration was used as supporting electrolyte to maintain the ionic strength constant of the solution and 0.002% Triton-X-100 was used as maximum suppressor. Before examining the solutions polarographically, purified nitrogen gas was passed through each solution for 10-15 min. to remove dissolved oxygen. The bridge compartment of the H-cell was thoroughly cleaned and refilled with fresh saturated solution of potassium chloride just before each polarogram was recorded.

RESULTS

The value of half-wave potential ($E_{1/2}$) exhibits cathodic shifts and diffusion current shows descending behaviour with the increase in the concentration of Citrulline. This indicates complexation between Gallium(III) and Citrulline and variation in the size of Ga(III) and Citrulline on the formation of complex. The number of electrons involved in the reduction process of Gallium(III) found to be three. By knowing the value of 'n', the diffusion coefficient ($D^{1/2}$) of the depolarizer was calculated by using Ilkovic equation at different concentration of the ligand.

The effect of increasing concentration of Citrulline on polarographic characteristics and kinetic parameters are recorded in Table 1 at 300K and 308K, respectively. The decrease in the values of ' α ' with increase in concentration of the ligand, implies that the transfer of electrons is getting increasingly difficult and the reduction of Ga(III) can also be noticed from the decreasing trends of K^0_{th} .

The effect of temperature on different

Table 1: Electrode kinetic parameters of Ga(III) in various concentration of Citrulline at 300K and 308K

Cx mM	at 300K				at 308K			
	$D^{1/2}$ $\text{cm}^2 \text{sec}^{-1}$	α	$E_{1/2}$ -V vs Sec-1	$\log K^0_{th}$ cm sec^{-1}	$D^{1/2}$ $\text{cm}^2 \text{sec}^{-1}$	α	$E_{1/2}$ -V vs Sec-1	$\log K^0_{th}$ cm sec^{-1}
0	-	0.2855	1.2245	-	-	0.3364	1.1912	-
0.001	13.2325	0.2849	1.2256	-3.9964	13.5633	0.3349	1.1921	-4.6284
0.002	6.4508	0.2842	1.2264	-4.2998	6.6162	0.3335	1.1929	-4.9214
0.003	4.2454	0.233	1.2279	-4.4739	4.3556	0.3321	1.1938	-5.0850
0.004	3.1840	0.2825	1.2291	-4.5922	3.2667	0.3302	1.1949	-5.1868
0.005	2.4810	0.2818	1.2302	-4.6935	2.5472	0.3286	1.1962	-5.2762
0.006	2.0400	0.2809	1.2311	-4.7682	2.0675	0.3274	1.1975	-5.3548
0.007	1.7249	0.2796	1.2319	-4.8230	1.7485	0.3263	1.1988	-5.4156

Cx = Citrulline concentration in mM, D = Diffusion coefficient, α = transfer coefficient

$E_{1/2}$ = Reversible half-wave potential, K^0_{th} = Standard rate constant.

parameters can also be measured. The results show that $E_{1/2}^r$ values shifts to more positive values as the temperature increased which indicates the easier reduction of Ga(III)-L-Citrulline system at d.m.e. The values of ' α ' and K_{th}^0 show an increase with the temperature shows that the electrode reduction of Ga(III)-L-Citrulline system tends to become less irreversible as the temperature is increased.

DISCUSSION

The results show, that there is a regularity in the variation of the values of standard rate constant K_{th}^0 . As the concentration of the ligand increases, the values of formal rate constant decreases on increasing the temperature.

The reason of decreases of formal rate constant at higher temperature may be due to the breaking of chelating rings. At higher temperature

the rings may be broken down and the complexes. At higher temperature the bidentate chelated ligand may become more energetic to collide which might be causing faster reaction.

CONCLUSION

We conclude that the values of diffusion coefficient ($D^{1/2}$) and transfer coefficient (α) are higher at 308K than 300K, and the values of formal rate constant (K_{th}^0) are lower at higher temperature.

ACKNOWLEDGEMENTS

The authors are thankful to the Head, Department of Chemistry, University of Rajasthan, Jaipur for providing facilities to carry out this research. One of the authors (Santosh Kumar) is thankful to UGC for awarding Rajeev Gandhi Research Fellowship.

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