



THE KINETIC STUDY OF Ga (III) COMPLEXES WITH HIPPURIC ACID AT DIFFERENT TEMPERATURES BY POLAROGRAPHIC TECHNIQUE

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ABSTRACT

Polarographic behaviour of Ga (III) has been investigated in the presence of Hippuric acid at dropping mercury electrode and the reduction of Ga (III) has been found to be irreversible in the presence of 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 300 K and 308 K by applying Koutecky's method.

Key words: Gallium (III), Hippuric acid, 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 $0.0591/\alpha n$ 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-

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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, chlorotetracycline, oxytetracycline, tetracycline monocyline, amoxicillin reported polarographically by Farid Khan and Rakhi Agrawal¹⁴. The literature search reveals that polarographic study of Gallium (III) complexes with Hippuric acid has not been attempted so far. This fact inspired us to investigate polarographic behaviour of Ga (III) in presence of Hippuric acid.

EXPERIMENTAL

Polarograms were obtained with a carefully calibrated polarograph. The test solutions were prepared using conductivity water. The solutions contain 0.1 mM of Ga (III) and different concentrations of ligand. The solution of KNO₃ 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 AND DISCUSSION

The value of half-wave potential ($E_{1/2}^r$) exhibits cathodic shifts and diffusion current shows descending behaviour with the increase in the concentration of Hippuric acid. This indicates complexation between Gallium (III) and Hippuric acid and variation in the size of Ga (III) and Hippuric acid 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 Hippuric acid on polarographic characteristics and kinetic parameters are recorded in Table 1 at 300 K and 308 K, 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_{fh}^0 .

The effect of temperature on different parameters can also be measured. The results show that $E_{1/2}^r$ values shifts to less negative values as the temperature increased which

indicates the easier reduction of Ga (III)-L-Hippuric acid system at d.m.e. The increase of values of ' α ' and K_{fh}^0 with the temperature shows that the electrode reduction of Ga (III)-L-Hippuric acid system tends to become less irreversible as the temperature is increased.

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

C_x mM	at 300 K				at 308 K			
	$D^{1/2}$ cm ² sec ⁻¹	α	$E_{1/2}^r$ -V vs Sec ⁻¹	$\log K_{\text{fh}}^0$ cm sec ⁻¹	$D^{1/2}$ cm ² sec ⁻¹	α	$E_{1/2}^r$ -V vs Sec ⁻¹	$\log K_{\text{fh}}^0$ cm sec ⁻¹
0	-	0.3714	1.2044	-	-	0.4597	1.1818	-
0.001	11.7438	0.3679	1.2061	-5.3081	12.0746	0.4535	1.1839	-6.5222
0.002	5.7065	0.3642	1.2079	-5.5721	5.8719	0.4457	1.1861	-6.7271
0.003	3.5838	0.3615	1.2096	-5.7409	3.8043	0.4388	1.1877	-6.8179
0.004	2.6051	0.3575	1.2121	-5.8281	2.7705	0.4315	1.1894	-6.8506
0.005	2.0179	0.3540	1.2142	-5.8941	2.1502	0.4250	1.1915	-6.8727
0.006	1.6540	0.3501	1.2166	-5.9307	1.7643	0.4175	1.1933	-6.8503
0.007	1.3705	0.3463	1.2188	-5.9626	1.4650	0.4127	1.1949	-6.8654

C_x = Hippuric acid concentration in mM; D = Diffusion coefficient; α = transfer coefficient\
 $E_{1/2}^r$ = Reversible half-wave potential; K_{fh}^0 = Standard rate constant

The results show, that there is a regularity in the variation of the values of standard rate constant K_{fh}^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_{fh}^0) are lower at higher temperature.

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