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Electrochemical study and electrode kinetics of complexes of Ga(III) with various amino acids

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ABSTRACT

The electroreduction of Ga(III) in the aqueous medium has been investigated at DME. The stability constants of Ga(III)-Amino acids have been evaluated by the method of DeFord and Hume's method and Kinetic parameters have been calculated by Koutecky's method. The reduction of complexes has been found to be irreversible and diffusion controlled involving three electrons in each case. Ga(III) formed 1:1 1:2 and 1:3 complexes with these ligands. The change in thermodynamic parameters DG°, DH° and DS° have been evaluated. The mathematical Mihailov's method has also been applied for the comparison of stability constant values obtained by graphical method.

Key words: Alanine, asparagine, serine, D.C. polarography.

INTRODUCTION

Amino acids play an important role in our body. Alanine is an a-amino acid. The a-carbon atom of Alanine is bound with methyl group ($-CH_3$) making it one of the simplest a-amino acid. Deamination can be induced in solid or aqueous Alanine[1-2] by radiation. Serine is important in metabolism in that it participates in the biosynthesis of purines and pyrimidines. D-Serine, synthesized by Serine racemase from L-Serine, serves as a neuronal signal by activating NMDA receptors in the brain[3]. Asparagine has carboxamide as the side chain functional group. Asparagine also provides key sites for N-linked glycosylation.

The binary and ternary Pd(II) complex of the N-sulfonyl derivative[4] of asparagine and glutamate were studied by polarography.

Interaction between Cd(II)[5-6] with L-Lysine, L-ornithine L-serine and L-aspartic acid has been studied by simple D.C. polarography. Polarographic studies of Histidine[7-8] with some P-block elements like Ga(III), In (III), Tl(I) have been carried out separately at ionic strength kept constant (m=1) by using KCl and 308K temp.

Electrode kinetics of Zn(II) and Ni(II)[9-10] with a-amino acids have been studied by Verma *et al.* The aim of the present paper is to determine the stability constants, thermodynamic parameters and kinetic parameters of Ga(III)complexes with amino acids (Ala, Ser, Asp.)

EXPERIMENTAL

All chemicals used were of analytical reagent grade purity and their solutions were prepared in double distilled water. The C.V. data for the test solutions were recorded after passing the pure nitrogen gas in test solution and Triton X-100 was used as a maxima suppressor. The current-voltage measurement was performed with two electrode assembly, a dropping mercury electrode as working electrode, calomel as reference electrode. A C.L. 362 polarographic analyzer was used to record the current-voltage data. The capillary with the following characteristics m = 4.62 mg/s t = 2 sec. was used.

RESULTS AND DISCUSSION

Ga(III) complexes have been studied with amino acids (Ala, Ser, Asp.) and current-voltage curves were obtained. The concentration of amino-acids was varied from 0.001M to 0.007M and stability constants have been determined at two different temps (298K and 308K).

The reduction of Ga(III) with Ala., ser. and Asp. was found ir-reversible. The values of stability constants for Ga(III)Ala, Ga(III)Ser and Ga(III)Asp. complexes are recorded in Tables I to III. Ga(III) formed 1:3 the highest complexes with L-alanine, L-serine and L-aspargine. Ga(III) formed stronger complexes with Ala. than Ser. because –OH group present in the structure of Ser. which reduces the charge density on the negatively charged oxygen atom of –COOH group. Ga(III) formed more stable complex with Ser. than Asp. due to presence of bulky group – $CONH_2$

The overall changes in thermodynamic parameters DG°, DH° and DS° on complex formation have been determined and thermodynamic parameters for Ga(III)complexes with these amino acids are summarized in Tables IV to VI.

Table 1: Stability constants of Ga(III)-Alanine Complex in aqueous medium

Metal ion	Temp.	$\log\beta_j$	DeFord and Hume Method	Mihailov Method
Ga(III)	298K	$\log \beta_1$	5.250	5.254
		$\log \beta_2$	6.990	6.992
		$\log \beta_3$	7.624	7.620
	308K	$\log \beta_1$	5.215	5.210
		$\log \beta_2$	6.949	6.978
		$\log \beta_3$	7.609	7.615

Table 2: Stability constants of Ga(III)-Serine Complex in aqueous medium

Metal ion	Temp.	$\log\beta_j$	DeFord and Hume Method	Mihailov Method
Ga(III)	298K	$\log \beta_1$	3.170	3.168
		$\log \beta_2$	4.189	4.185
		$\log \beta_3$	5.568	5.570
	308K	$\log \beta_1$	3.110	3.112
		$\log \beta_2$	4.121	4.119
		$\log \beta_3$	5.485	5.489

Table 3: Stability constants of Ga(III)-Asparagine Complex in aqueous medium

Metal ion	Temp.	$\log\beta_j$	DeFord and Hume Method	Mihailov Method
Ga(III)	298K	$\log \beta_1$	2.892	2.890
		$\log \beta_2$	3.482	3.485
		$\log \beta_3$	4.822	4.820
	308K	$\log \beta_1$	2.750	2.748
		$\log \beta_2$	3.390	3.392
		$\log \beta_3$	4.790	4.792

Table 4: Thermodynamic parameters of Ga(III)-Alanine at 298K in aqueous medium

Metal Complex Species	1og β_j 298K	308K	ΔG(-) (KCal mole^{-1})	ΔH(-) (K.Cal. Mole^{-1})	ΔS (K.Caldeg^{-1} mole^{-1})
MX_1	5.250	5.215	7.200	1.4700	0.01922
MX_2	6.990	6.949	9.5943	1.7220	0.026
MX_3	7.624	7.609	10.359	6.300	0.013

M = Ga(III), X = Alanine

Table 5: Thermodynamic parameters of Ga(III)-Serine at 298K in aqueous medium

Metal Complex Species	1og β_j 298K	308K	ΔG(-) (KCal mole^{-1})	ΔH(-) (K.Cal. Mole^{-1})	ΔS (K.Caldeg^{-1} mole^{-1})
MX_1	3.170	3.110	4.3075	2.520	0.069
MX_2	4.189	4.121	5.6922	2.856	00095
MX_3	5.568	5.485	7.566	3.486	0.01369

M = Ga(III), X = Serine

Table 6: Thermodynamic parameters of Ga(III)-Asparagine at 298K in aqueous medium

Metal Complex Species	1og β_j 298K	308K	ΔG(-) (KCal mole^{-1})	ΔH(-) (K.Cal. Mole^{-1})	ΔS (K.Caldeg^{-1} mole^{-1})
MX_1	2.892	2.750	4.7315	5.964	0.0068
MX_2	3.482	3.390	6.5524	3.864	0.0029
MX_3	4.822	4.790	10.359	1.344	0.0174

M = Ga(III), X = Asparagine

Table 7: Kinetic parameters for Ga(III)-Alanine at 298K in aqueous Solution

C_x (moles lit^{-1})	$E^r_{1/2}$ (Volt vs S.C.E.)	$D^{1/2}$ (cm^2 s^{-1})	αn	K^o_{fh} (cm s^{-1})
0.001	1.12	1.324	0.4962	1.41×10^{-10}
0.002	1.132	0.6309	0.4863	8.9×10^{-11}
0.003	1.37	0.3885	0.4820	6.4×10^{-11}
0.004	1.140	0.285	0.4701	7.9×10^{-11}
0.005	1.144	0.1812	0.4620	2.29×10^{-11}
0.006	1.152	0.129	0.4620	2.08×10^{-11}
0.007	1.158	0.113	0.4539	1.98×10^{-11}

C_x = Ga(III) concentration, moles lit^{-1}

Table 8: Kinetic parameters for Ga(III)-Serine at 298K in aqueous Solution

C_x (moles lit^{-1})	$E^r{}_{1/2}$ (Volt vs S.C.E.)	$D^{1/2}$ ($cm^2\ s^{-1}$)	αn	$K^o{}_{fh}$ ($cm\ s^{-1}$)
0.001	1.134	1.3047	0.5175	2.818×10^{-11}
0.002	1.139	0.6451	0.4962	5.6×10^{-11}
0.003	1.42	0.3859	0.486	4.8×10^{-11}
0.004	1.152	0.2849	0.4812	3.39×10^{-11}
0.005	1.159	0.1884	0.4735	3.5×10^{-11}
0.006	1.168	0.1208	0.4716	2.9×10^{-11}
0.007	1.173	0.1193	0.4693	2.2×10^{-11}

Cx = Ga(III) concentration, moles lit^{-1}

Table 9: Kinetic parameters for Ga(III)-Asparagine at 298K in aqueous Solution

C_x (moles lit^{-1})	$E^r{}_{1/2}$ (Volt vs S.C.E.)	$D^{1/2}$ ($cm^2\ s^{-1}$)	αn	$K^o{}_{fh}$ ($cm\ s^{-1}$)
0.001	1.114	0.8714	0.5536	3.5×10^{-11}
0.002	1.120	0.40707	0.5366	2.45×10^{-11}
0.003	1.135	0.2356	0.5262	1.65×10^{-11}
0.004	1.145	0.163	0.5176	1.28×10^{-11}
0.005	1.160	0.126	0.5108	1.0×10^{-11}
0.006	1.168	0.105	0.5089	0.8×10^{-11}
0.007	1.175	0.0902	0.5012	0.23×10^{-11}

Cx = Ga(III) concentration, moles lit^{-1}

Kinetic parameters have been calculated by Ilkovic equation and Koutecky's method. The value of formal rate constants of Ga(III) complexes with Ala, Ser, and Asp. are in the order Ala > Ser > Asp. Kinetic parameters have been recorded in Tables VII-IX.

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