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NOTE

Polarographic Determination of Stability Constant Values of Complexes of Levulinic Acid with Ga(III) and Tl(I) by DeFord and Hume's and Mihailov's Methods

SUMAN MEENA, SMITA AGRAWAL and O.D. GUPTA*

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

*Corresponding author: E-mail: gupta_od@yahoo.co.in

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The reduction of Ga(III) and Tl(I) with levulinic acid has been investigated electrochemically in aqueous medium and the stability constants of complexes have been evaluated. The metal complexes of levulinic acid with ratio as 1:1, 1:2, 1:3 for Ga(III) and 1:1, 1:2 for Tl(I) have been reported. The values of stability constants of complexes of levulinic acid with Ga(III) have log β_1 = 2.92, log β_2 = 5.74, log β_3 = 8.39 and complex of levulinic acid with Tl(I) have log β_1 = 2.62, log β_2 = 5.58 at 308 K, which have been calculated by DeFord and Hume's method. The mathematical Mihailov's method was also used.

Key Words: Levulinic acid, Gallium(III), Thallium(I), D.M.E. Polarographic study.

Levulinic acid is a potential precursor to nylon-like polymers, synthetic rubbers and plastics. It is a versatile synthetic intermediate. Levulinic acid and feed stock for producing a wide range of industrially important products like methyltetrahydrofuran, valerolactone and ethyl levulinate.

A systematic survey of literature reveals that no references is available regarding the electrode kinetics of complexes of levulinic acid with *p*-block elements. The present paper deals with the determination of stability constants graphically by the method of DeFord and Hume's[1]. The overall formation constants of complexes have also been calculated using mathematical method of Mihailov[2]. The thermodynamic parameters ΔGº, ΔHº, ΔSº have been also determined to study the electrode process between dropping mercury electrode and electro active species.

A CL-362 polarographic analyser was used to record polarograms using saturated calomal electrode as reference electrode and dropping mercury electrode (DME) was used as microelectrode. All reagent grade chemicals were used. Potassium nitrate was used as supporting electrolyte to maintain the ionic strength constant at 1.0 M, Triton X-100 was used in all the solutions to suppress the observed maxima. The capillary had the following characteristics m = 4.62 mg/s, t = 2 sec and the height of mercury column h = 43 cm. The test solution of Ga(III) and Tl(I) contain 0.1 M concentration. All the polarograms were recorded after deaeration with purified nitrogen gas. The temperature was kept constant by using Haake type water circulation thermostat.

Current-voltage relationship were obtained. The concentration of levulinic acid was varied from 0.001 to 0.007 M. The values of half-wave potential for metal ions and their complexes shifted to more negative values with the increasing of the concentration of ligand. The complex ion formed is of much larger size as compared to aqua-metal ion, hence the low values of diffusion current were observed with the increase of ligand concentration. The reduction was found to be reversible in case of Tl(I) and irreversible for Ga(III) system. Direct proportionality of the diffusion current to the square root of effective height of mercury column indicates that the nature of all the waves were diffusion controlled. The method of DeFord & Hume's was applied to determine the value of stability constants of successive complexes.

Polarographic measurements have been recorded in Table-1 and Mihailov's mathematical approach was applied to evaluate stability constants from $F_0(X)$ function values for the Ga(III)-Levulinic acid and Tl(I)-Levulinic acid systems at 308 K in aqueous media are recorded in Tables 2 and 3.

From the above data thallium(I) shows 1:1, 1:2 complexation. On the other hand Ga(III), show 1:1, 1:2, 1:3 complexation. The greater stability of Ga(III)-levulinic acid complexes is due to the smaller size of Ga(III) metal ions and the large electron accepting tendency of Ga(III) metal ions.

Thermodynamic parameters have been evaluated and recorded in Tables 4 and 5.

The negative values of ΔHº ensure that the reactions are exothermic in nature. Thermodynamic parameters *viz.* free

TABLE-2
POLAROGRAPHIC MEASUREMENTS AND F_i (X) FUNCTION VALUES FOR THE Ga(III)-LEVULINIC ACID SYSTEM AT 308K [Ga(III)] = 0.5 mM, μ =1 (KNO_3)

C_X (mol/L)	i_d (μA)	$E^r_{1/2}$ (-V *vs* SCE)	F_0 (X)	F_1 (X) × 10^3	F_2 (X) ×10^5	F_3 (X) × 10^8
0.000	8.17	1.066	-	-	-	-
0.001	7.88	1.069	1.455	0.45	-	-
0.002	7.74	1.083	7.209	3.100	11.50	4.25
0.003	7.67	1.087	11.43	3.47	6.67	1.22
0.004	7.58	1.093	22.79	5.44	11.60	2.15
0.005	7.15	1.102	66.85	13.17	24.74	4.34
0.006	6.93	1.106	108.39	17.89	28.48	4.24
0.007	6.86	1.110	172.10	24.44	33.77	4.39

C_x = levulinic acid concentration, mol/L

TABLE-3
POLAROGRAPHIC MEASUREMENTS AND F_i(X) FUNCTION VALUES FOR THE Tl(I)-LEVULINIC ACID SYSTEM AT 308 K [Tl(I) = 0.5 mM, μ =1 (KNO_3)]

C_X (mol/L)	i_d (μA)	$E_{1/2}$ (-V vs SCE)	F_0(X)	F_1(X) × 10^2	F_2(X) × 10^5
0.000	7.68	0.450	-	-	-
0.001	6.98	0.462	1.725	7.25	3.05
0.002	6.88	0.473	2.64	8.25	2.023
0.003	6.81	0.483	3.89	9.63	1.810
0.004	6.79	0.496	6.38	13.45	2.312
0.005	6.72	0.508	10.11	22.77	3.371
0.006	6.64	0.519	15.24	23.73	3.255
0.007	6.60	0.529	22.79	31.12	3.845

C_x = levulinic acid concentration, mol/L

TABLE-1
DeFORD AND HUME'S AND MIHAILOV'S STABILITY CONSTANTS OF LEVULINIC ACID WITH Ga(III) AND Tl(I) SYSTEM

Solvent	Temperature (K)	log β_j	DeFord and Hume	Mihailov
Gallium(III)	308	log β_1	2.90	2.93
		log β_2	5.47	5.74
		log β_3	8.60	8.39
	313	log β_1	2.30	2.96
		log β_2	5.30	5.68
		log β_3	8.36	8.23
Thallium(I)	308	log β_1	2.62	2.80
		log β_2	5.58	5.33
	313	log β_1	2.30	3.35
		log β_2	5.56	5.148

TABLE-4
STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF Ga(III) LEVULINIC ACID SYSTEM IN AQUEOUS MEDIA AT 308 K

Metal complex species	log β_j		ΔGº (–)	ΔHº (–)	ΔSº (–)
	308 K	313 K	Kcal/mol	Kcal/mol	Kcal/mol/deg
MX_1	2.9030	2.30	4.11	53.11	0.1590
MX_2	5.47	5.30	7.77	15.53	0.0025
MX_3	8.602	8.36	12.20	21.20	-0.02921

M = Ga(III), X = Levulinic acid

TABLE-5
STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF Tl(I) LEVULINIC ACID SYSTEM IN AQUEOUS MEDIA AT 308 K

Metal complex species	log β_j		ΔGº (–)	ΔHº (–)	ΔSº (–)
	308 K	313 K	Kcal/mol	Kcal/mol	Kcal/mol/deg
MX_1	2.62	2.30	3.7168	28.14	0.0793
MX_2	5.58	5.56	8.2848	22.29	0.0194

M = Tl(I), X = Levulinic acid

energy ΔGº, enthalpy charge ΔHº and entropy change ΔSº, were determined. The more negative values of ΔGº for 1:3 complex show that the driving tendency of the complexation reaction is from left to right and the reaction tends to proceed spontaneously.

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