NOTE

Determination of Stability Constants of Thallium(I) Complexes with Diglycolic Acid

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The reduction of Tl(I) with diglycolic acid has been investigated electrochemically in aqueous medium and the stability constants of complexes formed by Tl(I) with diglycolic acid have been evaluated. The values of stability constants of complexes of Tl(I) with diglycolic acid are log β_1 = 3.477, log β_2 = 6.5051 at temperature 308 K and log β_1 = 3.0791, log β_2 = 5.8976 at temperature 313 K which have been calculated by DeFord and Hume's method. The mathematical Mihailov's method was also used.

Key Words: Thallium (I), Diglycolic acid, D.M.E.

Diglycolic acid and its labile metal complexes having specific role in carrier-transporation in permeation liquid membranes (PLM). This permeation liquid membranes may serve as bioanalogical devices that help to elucidate the environmental physicochemical processes occurring at the surface of biological membranes. According to survey of Pesticide Action Network North America (PANNA) the complex of diglycolic acid contain toxicity to humans including carcinogenicity.

From the literature survey, it has been found that there are few references in literature regarding polarographic studies of the complexes of diglycolic acid at different temperatures. The reduction of complexes of Cu(II) and Pb(II) with diglycolic acid such as Pb(II) diglycolate and Cu(II) diglycolate was studied by polarographic method[1]. The stability constant of complexes were calculated by the methods of DeFord and Hume's and Mihailov's[2,3].

Polarographic studies of diglycolic acid with some metals like, plutonium, tungsten, molybdenum have been carried out. Stability constant of mixed-ligand complexes have been evaluated by the Schaap and McMasters method[4].

The present paper deals with the determination of stability constants by the graphical DeFord and Hume[5] and mathematical Mihailov[3] methods of complexes formed by Tl(I) with diglycolic acid.

A CL-362 polarographic analyzer was used to record polarograms. Using saturated calomel electrode as the reference electrode and d.m.e. used as microelectrode. Reagent grade chemicals were used. Diglycolic acid was used as complexing agents and all solution were prepared in double distilled water.

Potassium nitrate was used as a supporting electrolyte to maintain constant ionic strength.

Triton X-100 was used in the final solution to suppress the maxima observed. The d.m.e. had the following characteristics, m = 4.62 mg/s, t = 2 s and height of the mercury column h_{eff} = 100 cm. Purified N_2 was used for deaeration.

Current-voltage relationship was obtained. The concentration of diglycolic acid was varied from 0.001-0.007 M. The values of half-wave potentials for metal ions and their complexes shifted to more negative value on increasing the concentration of the ligand. The nature of all the waves were reversible and diffusion controlled. The method of DeFord Hume[1] was applied to determine the values of stability constants of successive complexes. The polarographic measurements have been recorded in Tables 2 and 3 and Mihailov's mathematical approach was applied to evaluate stability constants from $F_0[(X)]$ functions values.

Effect of temperature: It is seen from Table-1 that stability constants gradually decreases with rise in temperature showing that lower temperature favours the formation of stable complexes. The reduction of Tl(I) ligand complexes gives well defined cathodic wave (diffusion controlled) and reversible in each case. $E_{1/2}$ *versus* -log C_x was smooth curve indicating successive complexation. The log β_j values were determined at different temperature 308 and 313 K which are summarized in Tables 1 and 2, respectively.

Thermodynamic parameters: Thermodynamic functions such as free energy ($\Delta G°$), entropy ($\Delta S°$) and enthalpy ($\Delta H°$) of complexation have been evaluated at 308 K with the help of standard equation and are recorded in Table-4.

TABLE-1
SUCCESSIVE STABILITY CONSTANTS FOR
COMPLEXES OF Tl(I)-DIGLYCOLIC ACID

System	Stability constant		
	Methods	$\log \beta_1$	$\log \beta_2$
Tl(I) diglycolic acid at 308 K	DeFord	3.4770	6.5051
	Mihailov's	3.6315	6.0474
Tl(I) diglycolic acid at 313 K	DeFord's	3.0791	5.8226
	Mihailov's	3.0591	5.9332

TABLE-2
POLAROGRAPHIC MEASUREMENTS OF $F_i[(X)]$
VALUES FOR THE Tl(I)-DIGLYCOLIC SYSTEM
Tl(I) = 0.1 mM, μ = 1 M (KNO$_3$), temperature = 308 K

C_x (Diglycolic acid) (mol L^{-1})	I_d	$\Delta E_{1/2}$	$F_0[(X)]$	$F_1[(X)] \times 10^3$	$F_2[(X)] \times 10^7$
0.000	7.68	–	–	–	–
0.001	7.33	0.003	1.4705	0.470	–
0.002	7.38	0.018	7.948	3.47	0.0000235
0.003	7.25	0.033	44.05	14.35	0.3783
0.004	7.13	0.035	56.27	15.91	0.3225
0.005	7.03	0.043	140.95	19.88	0.3360
0.006	6.98	0.048	249.91	41.33	0.6388
0.007	6.65	0.062	1276.4	181.2	2.5457

C_x = Diglycolic acid concentration (mol L^{-1}). $\log \beta_1$ = 3.477, $\log \beta_2$ = 6.5051.

TABLE-3
POLAROGRAPHIC MEASUREMENTS OF $F_i[(X)]$
VALUES FOR THE Tl(I)-DIGLYCOLIC SYSTEM
Tl(I) = 0.1 mM, μ = 1 M (KNO$_3$), temperature = 313 K

C_x (Diglycolic acid) (mol L^{-1})	I_d	$\Delta E_{1/2}$	$F_0[(X)]$	$F_1[(X)] \times 10^3$	$F_2[(X)] \times 10^6$
0.000	7.68	–	–	–	–
0.001	7.00	0.004	1.7108	0.710	–
0.002	6.92	0.010	3.372	1.186	–
0.003	6.84	0.021	11.59	3.53	0.776
0.004	6.82	0.025	18.48	4.370	0.792
0.005	6.76	0.028	25.52	4.904	0.740
0.006	6.72	0.032	39.99	6.498	0.880
0.007	6.65	0.042	120.78	17.111	2.272

C_x = Diglycolic acid concentration (mol L^{-1}), $\log \beta_1$ = 3.0791, $\log \beta_2$ = 5.8976.

TABLE-4
THERMODYNAMIC FUNCTIONS ($\Delta G°$, $\Delta H°$, $\Delta S°$)
FOR Tl(I)-DIGLYCOLIC SYSTEM AT 308 K

Complex species	$\Delta G°$ (KJ/mol)	$\Delta H°$ (KJ/mol)	$\Delta S°$ (KJ/°/mol)
MX$_1$	-20.50	-35.106	-0.04740
MX$_2$	-38.36	-53.590	-0.04947

M = Tl(I), X = Diglycolic acid.

The negative values of ($\Delta G°$) show that the reaction tends to proceed spontaneously. The negative values of ($\Delta H°$) indicate the exothermic nature of reaction process in fair agreement with increasing stability constants suggesting lower temperature favours the chelation process. The entropy values indicate that complexation is favoured by enthalpy and entropy factors.

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