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Studies of stability constants values of Ln (III)-dithiocarbamic acid

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Abstract
The stability constant for the complexes formed by Yb (III) with dithiocarbamic acid has been investigated. The effects of temperature and standard thermodynamic functions on the complexation have been studied. The decrease in standard change in enthalpy and effect of temperature indicate that lower temperature favours the formation stable complexes. The reduction of Ln (III) metal ion with dithiocarbamic acid has been investigated.

Keywords: Dithiocarbamic acid, polarographic studies, standard thermodynamic functions

Introduction
The lanthanide (III) metal complexes have been great importance in the pharmacological applications. Lanthanide metal complexes have also been found some antifungal activities but the preparations of metal complexes in initial age were very difficult such as carbazic acid, dithiocarbamic acid. The labile metal complexes have specific role in carrier transportation in permeation liquid membranes. This permeation liquid membrane may serve as bioanalogical devices that help to elucidate the environmental and physicochemical processes occurring at the surface of biological membranes. According to survey of pesticide action Network North America, the complexes of dithiocarbamic 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 dithiocarbamic acid at different temperatures. The reduction of complexe of Yb (III) with dithiocarbamic acid was studied by polarographic method [1] the stability of constant of complexes were calculated by the known methods [2, 3].
Polarographic studies of dithiocarbamic acid with Yb (III) have been carried out.
Stability constant of mixed-ligand complexes have been evaluated by the Schaap and McMasters method [4].

Experimental
In this paper we discuss with the determination of stability constants by the graphical method [5] and mathematical method [3] of complexes formed by Tl (I) with dithiocarbamic acid.
A CL-362 polarographic analyzer was used to record polarograms. Using saturated calomel electrode as the reference electrode and D.M.E. used microelectrode. All chemicals were of reagent grade. Dithiocarbamic acid was used as ligand and all solution were prepared in distilled water. To maintain the constancy of constant ionic strength potassium nitrate was used as a supporting 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 = 2s and height of the mercury column h_{eff} = 100cm. purified N_2 was used for deaeration.
Current-voltage relationship was obtained. The concentration of dithiocarbamic acid was varied from 0.001 to 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 was reversible and diffusion controlled. The polarographic method was applied to determine the values of stability constants of successive complexes. The polarographic measurements have been recorded in table-2and table-3 and Mihailov's

mathematical approach was applied to evaluate stability constants from F_0 [(X)] functions values.

Effect of temperature

Successive stability constants for complexes of Yb (III) metal ion with dithiocarbamic acid are in Table-1.

Table 1: Successive Stability constants for Complexes of Yb(III)- dithiocarbamic acid

System		Stability constants	
	Methods	$\log\beta_1$	$\log\beta_2$
Yb(III) dithiocarbamic acid at 35 °C	DeFord	3.4770	6.5051
	Mihailov`s	3.6315	6.0474
Yb(III) dithiocarbamic acid at 45 °C	DeFord	3.0791	5.8226
	Mihailov`s	3.0593	5.9332

The table explains that stability constants gradually decrease with rise in temperature showing that lower temperature favours the formation of stable complexes. The reduction of 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 $\log\beta_1$ values were determined at different temperature 308 and 313 K, which is summarized in Table-1 and Table-2, respectively.

Table 2: Polarographic measurements of F_i[(X)] values for Complex Yb(III)-dithiocarbamic acid.

Yb(III)0.1 mM, μ(KNO$_3$), Temperature = 35 °C					
dithiocarbamic acid (mol/lit)	**I_d**	**$\Delta E_{1/2}$**	**F_0 [(X)]**	**F_1 [(X)]×10^3**	**F_2 [(X)]×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	0.00002
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	6388

Table 3: Polarographic measurements of F_i[(X)] values for Complex Yb(III)-dithiocarbamic acid

Yb(III)0.1 mM, (KNO$_3$), Temperature = 45 °C					
dithiocarbamic acid (mol/lit)	**I_d**	**$\Delta E_{1/2}$**	**F_0 [(X)]**	**F_1 [(X)]×10^3**	**F_2 [(X)]×10^7**
0.000	7.68	....	....	....	....
0.001	7.00	0.004	1.7108	0.710	....
0.002	6.92	0.015	3.372	1.186	....
0.003	6.84	0.021	11.59	3.53	0.776
0.004	6.82	0.025	18.30	4.370	0.792
0.005	6.76	0.030	25.60	4.904	0.740
0.006	6.72	0.038	40.43	6.498	0.880
0.007	6.65	0.042	120.64	17.110	2.272

Table 4: Thermodynamic functions for Yb(III)-dithiocarbamic acid system at 35 °C

Complex species	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (KJ/mol)
MX_1	-20.50	-35.106	– 0.04740
MX_2	-38.36	-53.590	– 0.04947
M = Yb (III), dithiocarbamic acid			

Thermodynamic parameters

Standard Thermodynamic functions such as standard change in free energy (ΔG^0), standard change in entropy (ΔS^0) and standard change in enthalpy (ΔH^0) of complexation have been evaluated at 308 K with the help of corresponding standard equation and are recorded in Table-4.

The negative value of standard change in free energy show that the reaction tends to proceed spontaneously. The negative values of standard change in enthalpy indicates 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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