STABILITY CONSTANTS OF SOME LANTHANIDE IONS WITH DIETHYLENETRIAMINEPENTA ACETIC ACID (DTPA), TRIETHYLENETETRAAMINEHEXA ACETIC ACID (TTHA) AND PYROGALLOL

Poonam Mor*

Dr. K.C. Gupta**

ABSTRACT

Lanthanides form mixed complexes with diethylenetriaminepenta acetic acid (DTPA) and triethylenetertraaminehexa acetic acid (TTHA) (primary ligands) and pyrogallol (pyr.) (secondary ligand). Stability constants ($\log K_{MAB}^{MA}$) were calculated by using the modified method of Irving and Rossotti at three different temperatures and μ=0.2M HNO_3. The thermodynamic parameters have also been determined. All the calculations were computerized by using the basic programme on PC computer.

*Research Scholar, Singhania University, Singhania, Pacheri Bari, Jhunjhunu Rajasthan.

**Supervisor, Professor & HOD, Department of Chemistry, S.I.E.M, Mathura

In the present work the stability constant and thermodynamic parameters of the lanthanide mixed complexes of the type M:A:B in the ratio 1:1:1 in aqueous medium, where M = Sm^{+3}, Gd^{+3}, Dy^{+3} and Yb^{+3}, A = DTPA and TTHA and B = pyrogallol, have been calculated. The modified method of Irving and Rossotti[1,2] was applied to evaluate $\log K_{MAB}^{MA}$ at 30, 40 and 50 (±1 °C) and at μ = 0.2M HNO_3 to the reaction MA + B → MAB. The thermodynamic parameters viz. change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were also evaluated by using the temperature coefficient and Gibbs-Helmholtz equation[3]. The stability constant of the metal ions follow the order $Sm^{+3}<Gd^{+3}<Dy^{+3}<Yb^{+3}$

DTPA and TTHA (Fluka) and other chemicals used were of BDH (AR) and E. Merck make. The stock solutions of metal ions were prepared by dissolving the oxides of metals in AR-HNO_3. The metal contents were estimated by standard method[4]. The solution of DTPA and TTHA were prepared by dissolving in NaOH (disodium salt). The solution of Pyrogallol was prepared by dissolving directly in conductivity water. The solutions of NaOH and perchloric acid were prepared in distilled water and estimated by titration technique.

The titrations were carried out with a digital Systronics pH meter model 335 with the accuracy range ±0.01 pH digits. The magnetic stirrer for the continuous stirring of the solution during the titration, and a thermostat were used to maintain the temperature constant.

Four mixtures of solutions were prepared and the total volume was kept 50ml by adding the required amount of conductivity water.

The final concentration of each component in the mixture was as follows –

(A) 2 X 10^{-2}M HNO_3

(B) 2 X 10^{-2}M HNO_3 + 2 X 10^{-3}M secondary ligand

(C) 2 X 10^{-2}M HNO_3 + 2 X 10^{-3}M metal nitrate +2 X 10^{-3}M primary ligand

(D) 2 X 10^{-2}M HNO_3 + 2 X 10^{-3}M metal nitrate +2 X 10^{-3}M primary ligand + 2 X 10^{-3}M secondary ligand

The ionic strength was maintained by adding requisite amount of neutral solution of KNO_3 and the ration of M:A:B was kept 1:1:1. After mixing the solutions, they were allowed to equilibrate by keeping them for one hour. Each of the mixture was titrated against 0.2M KOH solutions and titrations were repeated for the sake of accuracy.

The PK value of pyrogallol were calculating by using the Martell and Cheberk method[5] at 30, 40 and 50° C(±1 °C) (Table 1.)

Table 1- Dissociation constant

	Temperature (°C)	pK_1	K_2
Pyrogallol	30	9.19 (0.06)	12.76 (0.06)
	40	8.97 (0.06)	12.54 (0.06)
	50	8.86 (0.06)	12.42 (0.06)

The formation constants have been determined by plotting a graph between n and pL value which were calculated between the pH from 5.70 to 8.20. the values of $\log K_{MAB}^{MA}$ have been evaluated at n = 0.5 and are summarized in Table 2. The error limits are 0.06 log unit.

The value of ΔG^0, ΔH^0 and ΔS^0 have been calculated at three deferent temperatures and at μ = 0.2M (HNO_3) by using the temperatures coefficient and Gibbs-Helmholtz equation and are reported in Table -2.

The order of the stability constants of the metal ions follow the order of the ionic radii of the metals viz. $Sm^{+3} < Gd^{+3} < Dy^{+3} < Yb^{+3}$. The above trend is further confirmed by the obtained values of ΔG^0.

Table-2 Stability constant and thermodynamic parameters of mixed ligand complexes at different temperatures-

System	Temp. (°C)	$\log K_{MAB}^{MA}$	ΔG^0 (Kcal mol^{-1})	ΔH^0 (Kcal mol^{-1})	ΔS^0 (Kcal mol^{-1})
Sm-DTPA-Pyr	30	9.90	-13.72		
	40	9.37	-13.42	-17.01	-11.46
	50	9.14	-13.50		
Gd-DTPA-Pyr	30	10.01	-13.87		
	40	9.57	-13.70	-15.22	-4.85
	50	9.33	-13.79		
Dy-DTPA-Pyr	30	10.21	-14.15		
	40	9.76	-13.97	-14.33	-1.15
	50	9.57	-14.14		
Yb-DTPA-	30	10.43	-14.46		
	40	9.99	-14.30	-15.22	-2.93
	50	9.75	-14.41		

Pyr	30	9.82	-13.61		
	40	9.39	-13.44	-12.53	-2.90
	50	9.26	-13.68		
Sm-TTHA-	30	9.91	-13.74		
Pyr	40	9.56	-13.69	-12.98	2.26
	50	9.53	-13.79		
	30	10.11	-14.01		
Gd-TTHA-	40	9.76	-13.97	-12.31	5.30
Pyr	50	9.56	-14.13		
	30	10.21	-14.15		
	40	9.97	-14.28	-10.74	11.30
Dy-TTHA-	50	9.73	-14.38		
Pyr					
Yb-TTPA-Pyr					

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