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Note

STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF Gd(III), Tb(III), Dy(III), Ho(III) and Y(III) CHELATES WITH GLUTAMIC ACID

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Amino acids are very good chelating agents due to the presence of active —NH_2 and —COOH groups, and are of great biological importance as many of them are essential for human life. Due to the presence of active groups the complexes of several amino acids with transition metal ions of *d*-subshell and *f*-subshell are reported in the literature. Agarwal et al. [1,2] have studied the interaction of La(III), Ce(III), Pr(III), Nd(III), and Sm(III) with glutamic acid by potentiometric titration technique. In continuation of the above studies the authors are now studying the interaction of Gd(III), Tb(III), Dy(III), Ho(III) and Y(III) with glutamic acid by the same technique. In this paper the stability constants, overall change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of Gd(III), Tb(III), Dy(III), Ho(III) and Y(III) with glutamic acid at two different temperatures (30 ± 0.1 and 40 ± 0.1°C) are reported.

EXPERIMENTAL

The nitrate salts of the rare earth metals were dissolved in conductivity water. The metal content of each solution was estimated gravimetrically by precipitating the metal as metal oxalate and then ignited as metal oxide [3,4]. Standard carbonate-free NaOH was used for potentiometric titrations. Since glutamic acid as such is not soluble in water, its monosodium salt was used. All the chemicals used were AnalaR (B.D.H. or equivalent).

The experimental procedure involved a series of pH titrations of glutamic acid with standard NaOH solution in the absence and presence of metal ions at 30 and 40°C in a constant temperature water-bath where the temperature was electrically controlled within 0.1°C. In all the titrations, volume (50 ml) and ionic strength (0.1 M KCl) were kept constant. Other experimental details have been described previously [3,4].

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TABLE 1

Metal—ligand stability constants and thermodynamic functions of the complexes at μ = 0.1 M KCl

	log k		ΔG (kcal mole^{-1})		ΔH for temp. difference of 10°C	ΔS (cal deg^{-1} mole^{-1})	
	30°C	40°C	30°C	40°C		30°C	40°C
Gd(III)	4.192	4.045	−5.815	−5.797	−6.381	−1.868	−1.864
Tb(III)	4.306	4.160	−5.973	−5.961	−6.339	−1.521	−1.527
Dy(III)	4.445	4.285	−6.166	−6.139	−6.948	−2.581	−2.584
Ho(III)	4.603	4.432	−6.386	−6.351	−7.423	−3.423	−3.425
Y(III)	4.721	4.547	−6.548	−6.501	−7.553	−3.321	−3.361

RESULTS AND DISCUSSION

At different pH, the horizontal distances between the curves in the absence and presence of metal ions measure quite accurately the additional base consumed due to complex formation. Therefore, at various pH, the different $\bar{n}$ and log (1/A), i.e. (log k) values were obtained for each metal at 30 ± 0.1 and 40 ± 0.1°C by the integral method of Calvin and Bjerrum [5—7] as adopted by Irving and Rossotti [8]. The different $\bar{n}$ values so obtained were plotted and metal—ligand stability constants for 1 : 1 metal—ligand ratio were determined. The ratio of metal—ligand was also determined by conductometric titration as adopted by Job [9]. The metal—ligand stability constant of rare earth metal ions with glutamic acid and thermodynamic functions are reported in Table 1.

On going through the values of different constants for La(III), Ce(III), Pr(III), Nd(III) and Sm(III) from previous publications [1,2], and Gd(III), Tb(III), Dy(III), Ho(III) and Y(III) from the present study, it is evident that the order of stability constants follows the well-established order: La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III) < Tb(III) < Dy(III) < Ho(III) < Y(III).

In the present investigation it is also evident that if we plot change in enthalpy (ΔH) of the complexes against inverse of the ionic radii the Gd(III) divides the rare earth metals into two groups and therefore acts as a bridge element [10,11].

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REFERENCES

1 R.C. Agarwal, R.P. Khandelwal and P.C. Singhal, J. Indian Chem. Soc., 53 (1976) 977.
2 R.C. Agarwal, J. Indian Chem. Soc., 55 (1978) 220.
3 R.C. Agarwal, J. Indian Chem. Soc., 51, (1974) 772.

4 R.C. Agarwal, J. Indian Chem. Soc., 55 (1978) 984.
5 M. Calvin and K.W. Wilson, J. Am. Chem. Soc., 67 (1954) 2003.
6 M. Calvin and N.C. Melchior, J. Am. Chem. Soc., 70 (1948) 3270.
7 J. Bjerrum, Metal Amine Formation in Aqueous Solution, P. Hasse and Son, Copenhagen, 1941.
8 H. Irving and H.S. Rossotti, J. Chem. Soc., (1953) 3397; (1954) 2904.
9 P. Job, C.R., 176 (1923) 422; 180 (1925) 928; 184 (1927) 204.
10 T. Moeller, The Chemistry of Lanthanides, Pergamon Press, Oxford, 1973.
11 B.C. Bhuyan and S.N. Dubey, J. Indian Chem. Soc., 57 (1980) 289.