

Spectrophotometric studies of formation constant of lanthanide complexes

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ABSTRACT

The formation constant of Tm(III)-systems with different sulphonanilide ligand namely 3-carboxy-4-hydroxy-2'-chloro benzene sulphonanilide, 3-carbomethoxy-4-hydroxy-2'-chloro benzene sulphonanilide and 3-carbomethoxy-4-hydroxy-2'-chloro benzene sulphonanilide have been determined with the help of spectrophotometric method. Results shows that the stability of lanthanide complexes is found similar to $[\text{Ag}(\text{NH}_3)_2]^+$ type of complex

Key words: Formation constant, Tm(III)-sulphonanilide complex.

INTRODUCTION

Lanthanides are known to form complexes less readily due to deeply buried f-orbitals and the shielding of 4f-orbital by 5d, 6s, 6p-orbitals are responsible for difference in properties of transition metal and lanthanide metal¹⁻³.

These deeply buried 4f-orbitals are not much affected by ligand environment and give rise to narrow f-f transition, but their bonding tendency with various types of ligands is also found in literature⁴⁻⁵.

Formation constant (K) shows the stability of complex⁽⁶⁻¹⁰⁾, although lanthanide complexes are thermodynamically and kinetically less stable as compared to transition metal complexes and actinide complexes.

EXPERIMENTAL

Spectrophotometric method¹¹⁻¹³ is based on the fact that most of the complexes absorb light differently than the metal ions from which they are

formed. The relationship between the absorbance or optical density at particular wavelength and concentration is expressed by Beer's law¹⁴⁻¹⁵.

In this method, standard grade chemicals-TmCl₃.6H₂O (molecular weight-275.29) has been used for studies. Three sulphonanilide ligands (prepared in this lab.) have been used for preparation of systems with Tm(III) and the solution spectra of these systems have been recorded by using a standard spectrophotometer (at 790 nm).

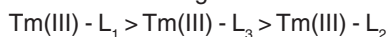
Three representative ligands (L₁, L₂ & L₃) have been used for this study.

- L₁ = 3-carboxy-4-hydroxy-2'-chloro benzene sulphonanilide
L₂ = 3-carbomethoxy-4-hydroxy-2'-chloro benzene sulphonanilide
L₃ = 3-carbomethoxy-4-hydroxy-2'-chloro benzene sulphonanilide

Results have been given in table 1.01 to table 1-3 & the computed values of the formation constant from the spectroscopic data have been tabulated in table 1-3.

RESULTS AND DISCUSSION

The values of formation constant have been found to be from 2.9118 to 3.6532 (table-1.03) which shows the following order-



The formation constant data show that the stability of lanthanide complexes is similar to Pr(III) and Nd(III) and $[\text{Ag}(\text{NH}_3)_2]^+$ type of complexes, which have been reported by earlier workers¹⁶⁻¹⁷ at room temperature.

Table 1: observed values of absorbance at various concentration of tm(iii) with sulphonanilides

Metal ion concentration (in %) with sulphonanilides	Values of absorbance in mixed solutions with different sulphonanilide		
	With L ₁	With L ₂	With L ₃
10	0.001	0.001	0.002
20	0.004	0.007	0.006
30	0.005	0.008	0.011
40	0.010	0.013	0.013
50	0.021	0.016	0.019
60	0.014	0.012	0.009
70	0.012	0.010	0.007
80	0.009	0.007	0.006
90	0.004	0.005	0.003

Table 2: Values of absorbance in different mixed solutions

Concentration of Tm(III)	Concentration of sulphonanilide	Absorbance in mixed solutions of Tm(III) with sulphonanilide		
		L ₁	L ₂	L ₃
M/40	M/40	0.023	0.021	0.019
M/50	M/40	0.019	0.020	0.016
M/60	M/40	0.017	0.017	0.014
M/70	M/40	0.015	0.015	0.011
M/80	M/40	0.014	0.012	0.010

Table 3: Computed values of formation constant from observed data

Ligand No	Initial conc. of Tm (III) in moles/lit a	Initial conc. of ligand in moles/lit a	Equilibrium conc. of complex in moles/lit x	Equilibrium conc. of Tm (III) in moles/lit a-x	Equilibrium conc. of ligand in moles/lit a-x	$K = \frac{x}{(a-x)(a-x)}$	log K
1	M/50	M/50	M/45	M/50 - M/45	M/50 - M/45	4500	3.6532
2	M/50	M/50	M/64	M/50 - M/64	M/50 - M/64	816.32	2.9118
3	M/50	M/50	M/40	M/50 - M/40	M/50 - M/40	1000	3.0000

[Ag(NH₃)₂]⁺ type of complex (logK =3.24 -3.81)

1:1 Pr(III)-oxy diacetic acid (logK=2.53)

1:1 Nd(III)-oxy diacetic acid(logK=2.67)

1:1 Pr(III)-sulphonanilide ligand (logK=2.9118-3.3551)

Low stability constant makes the isolation of these complexes in solid state difficult.

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