

Spectrophotometric analysis of formation constant of some rare earth metal complexes

Gourav Chawla, Seema Gakhar

Rare Earth Research Laboratory, P. G. Department of Chemistry, Govt. Dungar College, Bikaner, Rajasthan, India

Abstract

The formation constant of Tm (III)-systems with different sulphonanilide ligand namely 3-carboxy-4-hydroxy-4'-nitro benzene sulphonanilide, 3-carbomethoxy-4-hydroxy-4'-nitro benzene sulphonanilide and 3-carbomethoxy-4-hydroxy-4'-nitro benzene sulphonanilide in DMF media have been determined with the help of spectrophotometric method. Results shows that the stability of lanthanide complexes is found similar to $[Ag(NH_3)_2]^+$ type of complex.

Keywords: Tm (III), formation constant, sulphonanilide complex

Introduction

Lanthanides show comparatively little tendencies to form complexes with a variety of coordinating agents 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 metal [1, 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 literature [4, 5]. After the publication of Judd-Ofelt theory [6, 7] for lanthanide intensities, a great deal of work has been reported on the measurement of f-f transitions of free & complexed ion of lanthanide in different chemical environment by several workers [8, 20].

Formation constant (K) shows the stability of complex [21, 25], although lanthanide complexes are thermodynamically and kinetically less stable as compared to transition metal complexes and actinide complexes.

Experimental

Spectrophotometric method [26, 28] 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 law [29, 30].

In this method, standard grade chemicals- $TmCl_3 \cdot 6H_2O$ (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 (L_1, L_2 & L_3) have been used for this study.

L_1 = 3-carboxy-4-hydroxy-4'-nitro benzene sulphonanilide

L_2 = 3-carbomethoxy-4-hydroxy-4'-nitro benzene sulphonanilide

L_3 = 3-carbomethoxy-4-hydroxy-4'-nitro benzene sulphonanilide

Results have been given in table 1.01 to table 1.02 & the computed values of the formation constant from the spectroscopic data have been tabulated in table – 1.03.

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

Metal ion concentration (in %) with sulphonanilide	Values of absorbance in mixed solutions with different sulphonanilides		
	With L_1	With L_2	With L_3
10	0.002	0.004	0.005
20	0.010	0.008	0.006
30	0.015	0.009	0.008
40	0.016	0.010	0.011
50	0.018	0.017	0.021
60	0.010	0.012	0.016
70	0.007	0.011	0.015
80	0.006	0.009	0.010
90	0.003	0.008	0.008

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	0.020	0.021	0.027
M/50	M/40	0.019	0.020	0.025
M/60	M/40	0.018	0.019	0.022
M/70	M/40	0.016	0.018	0.021
M/80	M/40	0.014	0.016	0.014

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	X K = (a-x) (a-x)	log K
1	M/50	M/50	M/60	M/50 -M/60	M/50 -M/60	1500	3.1761
2	M/50	M/50	M/75	M/50 -M/75	M/50 -M/75	300	2.4771
3	M/50	M/50	M/70	M/50 -M/70	M/50 -M/70	437.5	2.6410

Results and discussion

The values of formation constant have been found to be from 2.4771 to 3.1761 (table-1.03) which shows the following order-

Tm (III) - L₁ > Tm (III) - L₃ > Tm (III) - L₂

The formation constant data show that the stability of lanthanide complexes is similar to Pr (III), Nd (III), Sm (III) and [Ag(NH₃)₂]⁺ type of complexes, which have been reported by earlier workers^[31, 32] at room temperature.

[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)

1:1 Sm (III)-sulphonanilide ligand (logK=2.48-2.91)

Low stability constant makes the isolation of these complexes in solid state difficult, so modify doped model technique has been taken in the electronic spectral study.

Acknowledgement

The authors are grateful to Principal Dungar College, Bikaner for providing necessary facilities and to Dr H K Pandey for fruitful discussion.

References

- Lee JD. Concise inorganic chemistry, Chapman & Hall; edition, (1992).
- Huchen JE. Inorganic Chemistry, Harper International S I Edition, edition, (1983).
- Malik WU, Tuli GS, Madan RD. Selected topics in inorganic chemistry, S Chand publication, edition, (1993).
- Grenthe I, Fernelius VC, J Am. Chem. Soc,1960:82:6285.
- Whelwright EJ, Spedding FK, Schwarzenbech GJ, Am Chem. Soc., 1953:75:4196.
- Judd BR. Phys. Rev., 1962:127:750.
- Ofelt GS, J Chem. Phys,1962:37:511.
- Carnall WT, J. Chem. Phys,1965:42:3797.
- Tandon SP, J. Chem. Phys,1987:66(12):7243.
- Mishra SN, Joshi GK, Indian J, Pure & Applied Phys,1981:19:279.
- Surana SSL, Singh M, Misra SN, Inorg J, Nud Chem.,1980:42:61.
- Peacock RD, Chem J. Soc. (A),1971, 2028.
- Gupta BK, Joshi GK, Bhati PR. Indian Journal of Pure and Applied Physics,1990:28:525.
- Bhati PR, Soni KP, Joshi GK, Swami SN, Asian J. Chem.,1992:4(4):1992:828.
- Nagar R, Driwedi PC, Sharma RC, Indian J. Chem,1989:28A:722.
- Vyas M, Int J. Chem. Sci.,2012:10(2):829.
- Paswan S, Jaiswal N, Modanawala VK, Patel MK, Rana MK, Singh KP. Inorganic Chimica Acta,2020:513:119955.
- Meena ML, Sudipta S, Singh RK, Lu CH. Polyhedron,2020:177:114322.
- Thomas S, George R, Qamhie N, Gopchandran KG, Saleh TM, Quatela A. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,2021:248:119187.
- Shaobo Y, Shaozhen L, Zhuohong F. Journal of Luminescence, 2021:238:11821.
- Chiarizia R, Danesi PR, Scibona G, Magon L. Journal of Inorganic and Nuclear Chemistry,1973:35(10):3595.
- Bandopdhyay AK, Chaudhary AK, J Ind. Chem,1987:26A:853.
- Shetyl SS, Mayadeo MS, Samyak J. Chem,1998:2:30.
- Gadpayle MR, Meshram YK. Acta ciencia Indica,2006:32(3):175.
- Murhekar GH, Raut AR, Wadekar MP, Banewar VW, Raut VM, Oriental J. of Chem,2009:25(4):1093.
- Robert VF, Ball RD, Harrington P, Harry WR, John JJ Chien MW. The Journal of Supercritical Fluids,2004:31(3):273.
- Brittain HG, Mantha S, Michael FT. Journal of the Less Common Metals,1986:126:339.
- Brucher E, Laurency G. Journal of Inorganic and Nuclear Chemistry,1981:43(9):2089.
- Herbert BS, Gaizer F, Thang P, Max S. Journal of the Less Common Metals,1986:126:315.
- Soykan C, Coskun R, Kirbag S, European Polymer Journal,2007:43(9):4028.
- Gameiro P, Rodrigues C, Teresa Baptista, Isabel Sousa, Baltazar De Castro. International Journal of Pharmaceutics,2007:334(1-2):129.
- Kumar N, Pandey HK, International Journal of Engineering Science Invention,2013:2(8):16.