RESEARCH ARTICLE

Potentiometric Study of some Ternary Complexes of Gallium(III)

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ABSTRACT	KEYWORDS
Modified form of Irving Rossotti's pH titration technique has been employed to investigate mixed ligand complex formation tendency of Ga (III) with Thioglycolic acid as a primary ligand and Malonic acid ,Fumaric acid, Itaconic acid, Malic acid and Tartaric acid as secondary ligands. The study was carried out at three different temperatures, 25^0C, 35^0C and 45^0C.The thermodynamic parameters viz. ΔG, ΔH and ΔS have been evaluated. The ΔG and ΔH values have been further separated into their electrostatic components ΔGe, ΔHe and cratic components ΔGc and ΔHc. Effect of change in dielectric constant and change in ionic strength have been studied on these systems. The results were correlated on the basis of steric and structural characteristics of the chelate formed.	Gallium, Dielectric Constant, Ionic strength, Chelate formation.
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INTRODUCTION

Development in the field of coordination chemistry is closely related to the study of mixed ligand complexes. The study of mixed ligand complexes is of extreme importance because it helps to predict general and probable form of existence of element in solution, makes it possible to understand the mechanism and kinetics in analytical reactions and open new prospects for development of selective and sensitive method for determination and separation. It also enables to determine composition and stability constant of mixed ligand complex. In recent past there has been considerable interest in the study of mixed ligand complex by pH metric method of heavier metals, however such study of Ga (III) is less reported (Akari and Hiroshita, 2007; Clausan *et al*., 2003; Fadeeve *et al*., 2004; Hittoshi *et al*., 1988; Munshi *et al*., 1984; Wood and Jain, 2006).

The present paper deals with mixed ligand complexes of Ga (III) using Thioglycolic acid (TMA) as a primary ligand and Malonic acid (MLA), Fumaric acid (FA), Itaconic acid (ITCA), Malic acid (MA) and Tartaric acid (TA) as secondary ligands. The study was carried out using Irving and Rossotti's pH titration technique at three different temperatures, 25^0C, 35^0C and45^0C at constant ionic strength of 0.2 M KNO₃. Thermodynamic parameters namely change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) have been evaluated. The values of ΔG and ΔH have been separated into their cratic components ΔGc and ΔHc and electrostatic components ΔGe and ΔHe by method of Nancollas (Nancollas,1960) to know the extent of covalent and ionic bonding in the complexes. The effect of change in dielectric constant of the medium on complexation equilibria has been studied using three solvents dioxane, ethanol and methanol. The effect of variation of ionic strength has also been studied.

MATERIALS AND METHODS

A standard solution of 0.02 M Ga $(NO_3)_3$. XH_2O was prepared by dissolving the requisite amount in the calculated quantity of nitric acid to prevent hydrolysis of metal ion. The metal content was estimated gravimetrically by precipitating as 8-hydroxyquinolinate (Eredy, 1965).

The fresh solution of thioglycolic acid (S. D. Fine Chemicals Limited). malonic acid (John Baker Inc Colorado USA), fumaric acid (BDH), itaconic acid (BDH), malic acid (E. Merck, A. G.) and tartaric acid (Anala R Glaxo Labortories) were prepared by dissolving requisite quantities in double distilled water and were standardised potentiometrically against standard NaOH (Vogel, 1972l). Dioxane, methanol and ethanol were purified by standard methods (Vogel, 1972). All experiments were carried out in nitrogen atmosphere. An ECIL expanded scale pH meter (accuracy ± 0.02pH units) with glass calomel electrode assembly was used for pH measurements. Temperature was maintained constant with an accuracy of ± 0.02^{0}C by dipping the assembly in ultra cryostat MK-70.

The experimental procedure involved potentiometric titration of the following four mixtures (total volume 100 ml) against standard carbonate free sodium hydroxide solution at constant ionic strength maintained by adding KNO_3 solution:
a) 2.0x10^{-2} M nitric acid
b) 2.0x10^{-2} M nitric acid + 1x10^{-3} M secondary ligand solution.
c) 2.0x10^{-2} M nitric acid + 1.0x10^{-3} M Ga (III) nitrate solution + 1.0x10^{-3} M TGA and
d) 2.0x10^{-2} M nitric acid + 1.0x10^{-3} M Ga (III) nitrate solution + 1.0x10^{-3} MTGA +1.0x10^{-3} M secondary ligand solution.

The ratio of metal - primary ligand – secondary ligand was maintained at 1:1:1 in each system.

Irving Rossotti's pH titration techniques as modified by Bhattacharya et al., (1969) were used for calculating stability constants.
The four plots obtained were:
(A) Acid Curve
(B) Secondary Ligand Curve
(C) Primary complexation Curve
(D) Mixed Ligand Complexation Curve.

RESULTS

Proton ligand stability constants of secondary ligand:

The values of ñA at various pH values have been calculated from curves A and B. The proton ligand stability constants have been evaluated by interpolation at various ñA values. The values of proton ligand stability constants at different temperatures have been presented in Table1. The values of proton ligand stability constants at different compositions viz. 15%, 30%, 45% and 60% of dioxane , ethanol and methanol for MLA are tabulated in *Table* 2, while the values at different ionic strengths viz. 0.1M, 0.2M and 0.3M of KNO_3 are Tabulated for secondary ligands in Table3. The error limit for $\log K_2^H$ was ± 0.04 and that for $\log K_1^H$ is ± 0.06. These values were taken into consideration while calculating the formation constants.

Metal ligands stability constants:

The mixed ligand formation constants $\log K_{MAL}^{MA}$ have been evaluated from horizontal difference $(V_4–V_3) – (V_2–V_1)$ where V_1, V_2, V_3 and V_4 are volumes of NaOH required to reach the same pH on curves A, B, C and D respectively. The formation constants were evaluated by interpolation at various ñ values. The formation constants obtained at different temperatures and at constant ionic strength of 0.2M in aqueous medium are presented in *Table 1*. While calculating formation constants at different dielectric constants, appropriate correction factors were applied (van Utert, 1953). The values of $\log K_{MAL}^{MA}$ at different dielectric constants and at different ionic strengths have been given is *Table* 2 and 3 respectively. The error limits for $\log K_{MAL}^{TGA}$ is ± 0.08. Ga (III)-TGA complex was very s*table* and was formed at lower pH. The formation of the complex started at pH ≈ 1.7 and was completed at pH≈2.2. The stability constant of the complex was 11.52 at 35^{0}C which was in good agreement with values stated earlier Sarinand Munshi, 1972). The primary complex was s*table* up to pH≈4.1 after which the complex got hydrolysed.

The mixed ligand complex curve D diverged from primary complex curve C at pH≈ 2.1 for TA as secondary ligand, at pH≈2.2with MA and MLA and

ITCA as secondary ligand, at pH≈ 2.3 with FA as secondary ligand. This signifies that mixed ligand complex formation did not take place during formation of primary complex. The mixed ligand complex formation of [Ga (III)-TGA] with MLA took place at pH≈2.3, with FA at pH≈ 2.6 and with ITCA, MA and TA at pH≈2.4. The n values reached up to ≈ 0.7 where pL values systematically decreased and the pH of hydrolysis increased up to ≈ 4.6 indicating suppression of hydrolysis due to secondary ligand.

Since the primary complex [Ga (III)–TGA] was very *stable* and was formed at lower pH, there was no possibility of any replacement reaction. MLA forms most *stable* complex due to formation of *stable* 6 member ring. MA complex was *stable* due to presence of –OH group which has electron withdrawing tendency. Lower stability of FA is due to *trans* nature of the ligand. MA, ITCA FA and TA form 7 member ring and hence have slightly lower stability.

Table **1:** Proton ligand and Metal Ligand Stability Constants (μ=0.2M KNO_3).

Systems	Constants	Temperature ^{0}C		
		25^0	35^0	45^0
MLA	$\log K_1^H$	5.22	5.08	5.02
	$\log K_2^H$	2.72	2.68	2.65
FA	$\log K_1^H$	4.16	4.10	4.06
	$\log K_2^H$	3.04	3.00	2.95
ITCA	$\log K_1^H$	5.56	5.50	5.40
	$\log K_2^H$	3.48	3.46	3.40
MA	$\log K_1^H$	4.56	4.54	4.48
	$\log K_2^H$	3.00	2.98	2.92
TA	$\log K_1^H$	4.36	4.25	4.12
	$\log K_2^H$	3.00	2.95	2.88
[Ga (III) – TGA – MLA]	$\log K_{MAL}$	6.92	6.56	6.30
[Ga (III) – TGA – FA]	$\log K_{MAL}$	5.71	5.44	5.22
[Ga (III) – TGA – ITCA]	$\log K_{MAL}$	6.24	5.95	5.69
[Ga (III) – TGA – MA]	$\log K_{MAL}$	6.53	6.15	5.83
[Ga (III) – TGA – TA]	$\log K_{MAL}$	6.36	5.97	5.45

Table **2 :** Proton ligand and Metal Ligand Stability Constants in different composition of Dioxane– Water, Ethanol – Water and Methanol – Water mixture at fixed Ionic Strength μ=0.2M KNO_3 and at 35^oC.

Solvent (System)	Constants	Percentage			
		15%	30%	45%	60%
Dioxane (MLA)	$\log K_1^H$	5.32	5.41	5.46	5.60
	$\log K_2^H$	3.12	3.16	3.22	3.36
Ethanol(MLA)	$\log K_1^H$	5.18	5.30	5.40	5.58
	$\log K_2^H$	2.92	3.02	3.06	3.20
Methanol(MLA)	$\log K_1^H$	5.12	5.18	5.24	5.34
	$\log K_2^H$	2.94	2.97	3.05	3.11
Dioxane [Ga(III) - TGA–MLA]	$\log K_{MAL}$	7.14	7.35	7.63	8.10
Ethanol [Ga(III) - TGA–MLA]	$\log K_{MAL}$	6.61	6.75	6.93	7.16
Methanol Ga(III)TGA– MLA	$\log K_{MAL}$	6.72	6.78	6.86	6.96

Table 3: Proton ligand Stability Constants and Metal Ligand Stability Constants at different values of ionic Strengths.

Ligand/Systems	Constants	Ionic Strengths(M)		
		0.1	0.2	0.3
MLA	$\log K_1^H$	5.12	5.08	5.05
	$\log K_2^H$	2.70	2.68	2.64
FA	$\log K_1^H$	4.16	4.10	4.06
	$\log K_2^H$	3.07	3.04	3.01
ITCA	$\log K_1^H$	5.50	5.46	5.43
	$\log K_2^H$	3.59	3.55	3.51
MA	$\log K_1^H$	4.57	4.54	4.51
	$\log K_2^H$	3.00	2.98	2.96
TA	$\log K_1^H$	4.31	4.25	4.21
	$\log K_2^H$	2.97	2.95	2.93
[Ga (III) – TGA – MLA]	$\log K_{MAL}$	6.66	6.56	6.45
[Ga (III) – TGA – FA]	$\log K_{MAL}$	5.50	5.44	5.38
[Ga (III) – TGA – ITCA]	$\log K_{MAL}$	6.21	5.95	5.60
[Ga (III) – TGA – MA]	$\log K_{MAL}$	6.34	6.15	6.01
[Ga (III) – TGA – TA]	$\log K_{MAL}$	6.16	5.97	5.87

Table 4 : Thermodynamic parameters of Mixed ligand complexes of Galium (III) μ=0.2M KNO_3 t=35°C.

Systems	$-\Delta G$ Kcals mole^{-1}	$-\Delta H$ Kcals mole^{-1}	$-\Delta S$ Kcals/degree/mole	$+\Delta Ge$ Kcals/mole^{-1}	$-\Delta He$ Kcals mole^{-1}	$-\Delta Gc$ Kcals mole^{-1}	$-\Delta Hc$ Kcals mole^{-1}
[Ga (III)-TGA-MLA]	9.24	13.71	0.014	1.31	0.53	8.04	13.17
[Ga (III)-TGA-FA]	7.66	10.15	0.008	0.80	0.04	5.15	10.15
[Ga (III)-TGA-ITCA]	8.38	13.71	0.017	1.97	0.801	8.92	12.91
[Ga (III)-TGA-MA]	8.66	15.23	0.021	2.84	1.15	8.33	14.08
[Ga (III)-TGA-TA]	8.41	19.80	0.036	6.1	2.49	4.81	17.45

Table 5: Thermodynamic stability constants ($\log K^o$)

System	Thermodynamic stability constants ($\log K^0$)	$-\Delta G$ Kcals mole^{-1}
[Ga (III)-TGA-MLA]	6.93	9.61
[Ga (III)-TGA-FA]	6.66	9.38
[Ga (III)-TGA-ITCA]	6.96	9.80
[Ga (III)-TGA-MA]	6.78	9.55
[Ga (III)-TGA-TA]	6.60	9.95

The thermodynamic stability constantsΔG, ΔH and ΔS were calculated at 35^0C. The positive value of ΔS indicates that formation of mixed ligand complex was favoured. The negative values of ΔG indicated that the reactions were spontaneous in all the cases. The negative values of enthalpy change suggest the exothermic nature of reaction.

The ΔG and ΔH values were separated into temperature dependent cratic component and temperature independent electrostatic components. Comparison of electrostatic and cratic components of ΔH and ΔG (*Table* 4) shows that the values of cratic components were more negative than those of electrostatic components indicating participation of covalent bonding in mixed ligand complexes formed. This was in agreement with observation of Sacconi and Giannoni (1954); Sarin and Munshi (1972).

Effect of change in dielectric constant of the medium

The proton ligand stability constants of MLA with change in dielectric constants at 35^0C and at $\mu= 0.2$M , calculated by method of extrapolation at various ñ values are given in *Table* 2. The proton ligand stability constants increased with increase is percentage of Dioxane, Ethanol and Methanol. This observation is in agreement with observation of Bhattacharya*et al*., (1954); Steger and Corisini (1969); Nakamure and Sekido (1910). The plots of log K_1^H and log K_2^H, in different organic solvent-water media followed the nature of the dielectric constants of the media. Dioxane was in top position as it has large proton solvation capacity and as it decreases hydrogen bonding in water to the maximum extent.

The stability constant of mixed ligand complex [Ga(III)–TGA –MLA] in different organic solvent –Water. Media (*Table* 2) show that values of log K_{MAL} increase with decrease in dielectric constant of the medium. A lowering of dielectric constant would increase the electrostatic attraction between metal ion and negatively charged ligand leading to more *stable* complex formation. The sequence of stability was as follows:

Dioxane-Water> Ethanol-Water > Methanol- Water

The plots between log K vs mole fractions were linear. From this study it may be concluded that the ion – ion interaction including metal ion and anionic oxygen donor of ligand, increase to a greater extent as compared to ion dipole interaction between metal and solvent molecules as the dipole moment of the medium decrease.

Effects of change in ionic Strength

The proton ligand and metal ligand constants were also found to decrease with increase in ionic strength of the medium. Plots of $\sqrt{\mu}$ vs proton ligand and metal ligand stability constants were linear proving the validity of Bronsted equation. The thermodynamic stability constants are obtained by extrapolating the straight line to zero ionic strength. The values are tabulated in *Table* 5.

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