

A Physico-Chemical and Analytical Study of Chelation Between Thallous Ion and β -Resorcylic Acid

Abstract

The chelation between Thallous ion and β -Resorcylic acid has been studied by conductometric and potentiometric methods. The structure and configuration suggested have been confirmed by magnetic studies. The complex ion has been isolated and analysed. The stability constant of the chelate in solution has been determined by Bjerrum's method and found to be 1.3978×10^8 . The free energy of the chelate was calculated and found to be $\Delta F = -4.821 \times 10^{-3}$ Cal. / mole.

Keywords: Thallous Ion, β -Resorcylic Acid, Chelate, Isolation, Stability Constant.

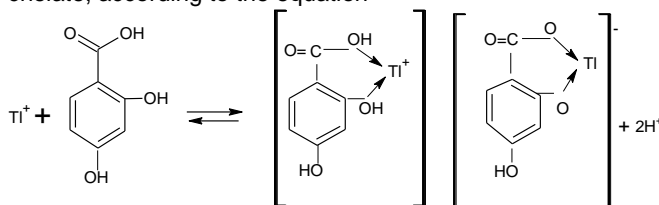
Introduction

β -Resorcylic acid is known to be a considerably strong polydentate chelating molecule.¹⁻⁶ It has been reported to form complexes with a number of metals. It has been used in the detection and quantitative determination of elements⁷⁻¹³. No information regarding the reaction between Thallous salts and β -Resorcylic acid is, however available in literature. The study of Thallous compounds is interesting due to the presence of the 'inert pair' in it, and hence the reaction between Thallous sulphate and β -Resorcylic acid has been studied extensively.

Experimental

Analysed samples of Thallous sulphate, Thallous acetate and β -Resorcylic acid were used. Solutions were made in conductivity water. Systronics conductivity meter, pH meter, Guoy's magnetic balance were used for the study.

Potentiometric titrations of Thallous acetate with β -Resorcylic acid show a break at 1:1, indicating the formation of a mono- β -Resorcylyate chelate, according to the equation



Equation : 1

The nature of the curve 2 (fig.2) are almost similar to that of curve 1(fig.1), although the fall in pH is more. This shows that the tendency for chelation in the alkaline medium is much more.

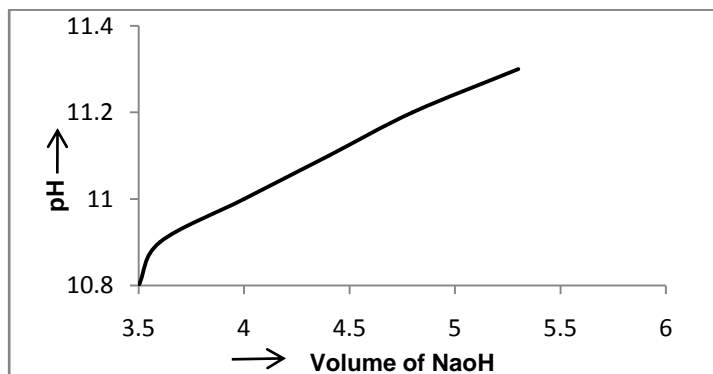


FIG. 1 : Volume of NaOH Vs pH : Curve



Rajesh Chourasia
Professor & Head,
Deptt. of Chemistry,
R.D.Govt. P.G. College,
Mandla (M.P.)

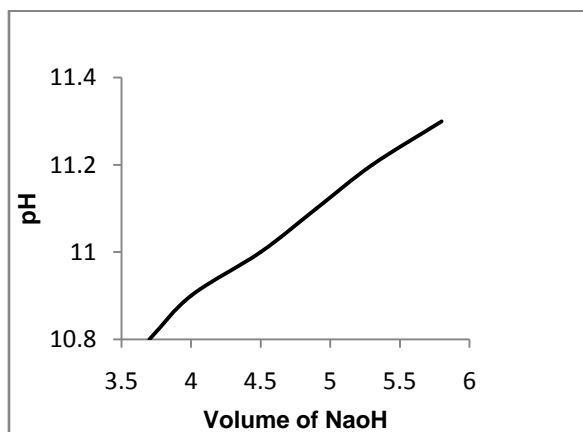


FIG.2 : Volume of NaOH Vs pH : Curve 2

Addition of alkali to the reaction mixture will neutralize the H⁺ ions produced by chelation, the number of equivalence of alkali required being equal to the number of H⁺ ions liberated. The potentiometric and conductometric titrations of Thallous acetate with caustic soda in the presence of one mole of β-Resorcylic acid show sharp inflexion at m=2 (where m represents moles of base added per mole of the metal ion), indicating formation of the mono- β-Resorcylyate derivative with liberation of the two H ions. Formation of the mono-β -Resorcylyate only is indicated irrespective of the amount of β – Resorcylic acid and pH.

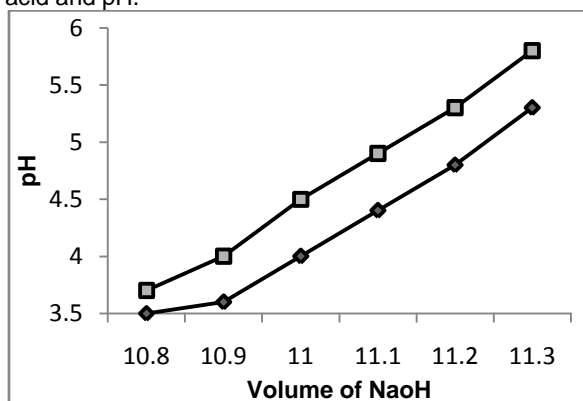
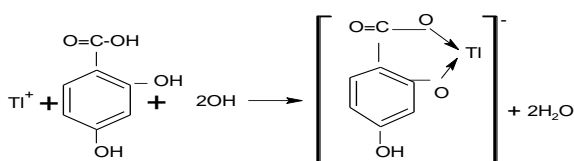


FIG.3 : Volume of NaOH Vs pH : Curve 1-2

In order to confirm the stoichiometry further, potentiometric titration of β – Resorcylic acid alone and in presence of small amount of Thallous acetate (curve 1,2 fig.3) were carried out with caustic soda. At a particular pH, the difference in the values of m (m= equivalence of alkali per mole of metal ion) on curves 1 & 2 (table 1) would indicate the amount of Resorcylic acid chelated with TI⁺.



Equation : 2

Table -1 Volume of NaOH at a particular pH

pH	0.5 M NaOH consumed in		Volume of 0.5 NaOH required in curve 2 compared to curve 1(in moles) in ml.	
	Curve 1(in ml)	Curve 2(in ml)		
10.8	3.50	3.70	0.20	0.80
10.9	3.60	4.00	0.40	1.00
11.0	4.00	4.50	0.50	2.00
11.1	4.40	4.90	0.50	2.00
11.2	4.80	5.30	0.50	2.00
11.3	5.30	5.30	0.50	2.00

The excess alkali consumed in curve 2 compared with curve 1 is always found to be 2 ml. or 2 moles.

Thalious ion has however, been reported to be four coordinate, bonding occurring through p³d hybridization¹⁴. The rest two positions around thalious ion could be occupied by the sulphate ion or the water molecules. The amount of sulphate estimated in the mixture of thalious sulphate and β – Resorcylic acid in 1:1 ratio corresponds exactly with the theoretical value, showing thereby that the sulphate ions are not involved in complexation. As a result of p³d hybridization most probable positions of the four coordinate groups will be at the corners of the base of tetragonal pyramid. Such a compound should be diamagnetic, and this has been confirmed by magnetic study.

Isolation of the Complex

The complex was isolated by refluxing the mixture of M/2 solutions of thalious sulphate and β – Resorcylic acid for eight hours and subsequent crystallization. The thalious content estimated (56.99%) as thalious chromate¹⁵ in the complex agreed well with the theoretical value (57.34%), in accordance with the above structure. The carbon and hydrogen contents determined in the complex by combustion studies (C=23.9%, H=1.18%) agreed well with the molecular formula of the complex.

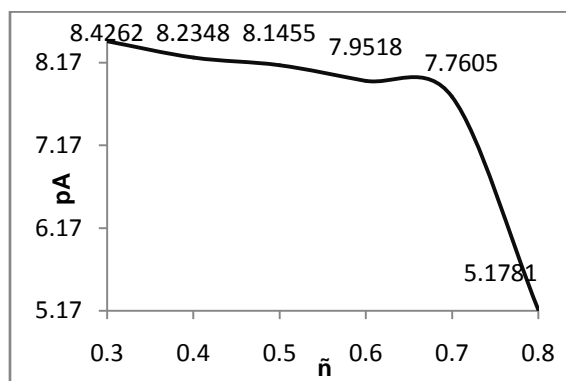
Stability Constant

The stability constant of the chelate in solution was found out by Bjerrum's method. Since only 1:1 complex was formed the stability constant was determined only at n 0.5 on the formation curve.

The pH titration of the ligand with standard alkali in absence and presence of metal ion were carried out by using pH meter. In 10 ml. of 0.04 molar ligand solution was added sufficient amount of 0.02 molar nitric acid to bring down the pH to 2.0. The ionic strength was maintained at 0.1 M by varying amounts of 2 M KCl. When titrating in presence of metal ions 5 ml of 2 X 10⁻³ M thalious sulphate solution was added at this stage. The total volume was maintained at 50 ml in both the cases.

Table – 2 Calculated values of free ligand at a particular pH

pH	Concentration of ligand $\times 10^{-4}$			(A)	1/(A)	log 1/(A) or pA	
	\bar{n}	metal-bound	Total				Free
2.65	0.3	1.174168	78.277878	77.10371	37.4819×10^{-10}	2.6679×10^8	8.4262
2.75	0.4	1.541426	77.071286	75.52986	58.2250×10^{-10}	1.7175×10^8	8.2348
2.80	0.5	1.897530	75.911330	74.00380	71.5390×10^{-10}	1.3978×10^8	8.1455
2.90	0.6	2.247192	74.906362	72.65917	111.711×10^{-10}	8.1617×10^7	7.9518
3.00	0.7	2.583025	73.800735	71.21771	173.557×10^{-10}	5.7618×10^7	7.7605
3.20	0.8	2.867383	71.684583	68.81720	663.379×10^{-8}	1.5074×10^5	5.1781

Fig. 4 : \bar{n} vs pA

From the horizontal distance between curve 1 and 2 (fig.3) \bar{n} was calculated (Table 2). The extra alkali consumed was double of the metal-bound ligand. The total metal-bound ligand, divided by the total metal-ion concentration provides \bar{n} at different values of pH. The value of free ligand (A) was calculated from the total ligand concentration and its dissociation constant (2.4370×10^{-12}). The formation curve for the metal chelate was obtained by plotting the values of \bar{n} against pA (fig. 4). The values of pA at $\bar{n} = 0.5$ corresponds to log K. Since the values of \bar{n} are only up to 0.8, this also confirms the formation of the 1:1 chelate only. The value of the stability constant works out to be 1.3978×10^8 and $\Delta F = -4.831$ calories per mole.

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