

Spectrophotometric Studies on the Composition,
Stability and Analytical Applications of Lanthanum(III)

1, 2, 5, 8 Tetra Hydroxy Anthraquinone (Quinalizarin) Chelate in Solution

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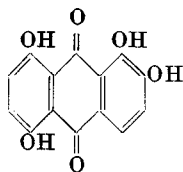
With 12 Figures

Summary

The formation of a violet colour produced by the interaction of 1, 2, 5, 8 Tetrahydroxy anthraquinone (quinalizarin) and Lanthanum has been studied to determine the composition, stability and other characteristics of the chelate formed. The absorbance curves of the complex show maxima at 530 m μ . The composition of the chelate has been determined by three methods. The molar ratio of the metal to chelating agent is 1:2. The chelate is soluble in aqueous ethanol and is stable between pH 6.5–7.2. The maximum colour formation is attained at pH 6.8, when the mixture contains greater than five fold excess of the reagent with respect to the metal solution and the colour intensity remains unaltered even after keeping the mixture for three hours at room temperature. The stability constant of the chelate has been calculated by three different methods (a–c). The values of log K in 50% ethanolic medium at 30° are respectively a) 10.1 ± 0.1 , b) 10.2 ± 0.1 , c) 10.1 ± 0.1 and the free energies of formation at the same temperature are a) -14.0 ± 0.1 , b) -14.1 ± 0.1 , c) -14.0 ± 0.1 K.cal. The range of concentration for adherence to BEER'S Law and value of optimum concentration range are 1.26 to 6.32 ppm and 1.4 to 3.5 ppm. Studies have also been made to establish optimum conditions for the spectrophotometric determination of Lanthanum.

Introduction

1, 2, 5, 8 Tetrahydroxy anthraquinone (Quinalizarin)



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forms coloured complexes in solution with many metal ions and has widely been used in analytical chemistry¹⁻¹⁵), though detailed data on the nature of complexes produced are not available. SRIVASTAVA and BANERJI¹⁶) investigated the composition and stability of lead chelate of Quinalizarin. It has now been observed that Quinalizarin also forms coloured chelate with lanthanum.

In the present communication the formation of lanthanum Quinalizarin chelate is reported for the first time along with the composition, nature and stability of the chelate. The beautiful violet coloured chelate of lanthanum (III) with Quinalizarin has been studied in 50% ethanolic medium by the spectrophotometric method. Suitable conditions for the micro determination have been worked out, and described.

Experimental

Reagents

Quinalizarin: A 0.001 M solution was prepared by dissolving Quinalizarin (B.D.H. reagent grade) in redistilled ethyl alcohol. Suitable working solutions were prepared from this solution by dilution with ethanol.

Lanthanum Acetate: A 0.001 M solution of lanthanum acetate (Johnson and Matthey) was prepared by dilution of 0.0125 M solution after standardising by EDTA titration using xylenol orange as indicator¹⁷).

Buffer Solution: A pH value 6.8 buffer solution was prepared in the usual manner with Ammonium Acetate. For spectrophotometric study, the pH was adjusted by buffering the mixed solution with 2.5 ml. of 1 M ammonium acetate.

- 1) H. A. LEIBHAFFSKY and E. H. WINSLOW, *J. Amer. chem. Soc.* **60**, 1776 (1938).
- 2) H. A. LEIBHAFFSKY and E. H. WINSLOW, *J. Amer. chem. Soc.* **69**, 1130 (1947).
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- 15) F. BURRIEL and S. BOLLE TACHEO, *An. R. Soc. esp. Fis. Quim.* **50B**, 957 (1954).
- 16) K. C. SRIVASTAVA and S. K. BANERJI, *Aust. J. Chem.* **20**, 1385 (1967).
- 17) K. UENO, *Chelate Titration*, Nankodo, Tokyo, 1960, p. 328.

Ionic Strength: During spectrophotometric measurements, the ionic strength was kept relatively constant by maintaining a concentration of 0.10 M sodium perchlorate and low concentration of ligand and metal ion.

The apparatus used was the same as reported on previously¹⁶). All experiments were carried out at $30 \pm 0.1^\circ\text{C}$.

Procedure: The composition of the chelate was studied by 1. the method of continuous variations^{18) 19)}, 2. mole ratio method²⁰⁾, and 3. slope ratio method²¹⁾, using absorptiometric measurements. The method of continuous variations has been very popular for the studies of composition of chelates and in spite of the criticisms of the method²²⁻²⁷⁾, it is agreed that the results are reliable when absorbance measurements are carried out.

A series of solutions is prepared for the continuous variation method, containing varying mole fractions of metal and reagent, their sum remaining constant. When the difference of absorbance is plotted against the composition of the mixture, a curve of continuous variation is obtained.

A series of mixtures is prepared for the mole ratio method containing varying amounts of one constituent with a constant amount of the other and viceversa. The absorbances of mixtures are measured and plotted against the concentration ratios, the curves rise linearly from the origin when both the interactants are colourless, and break sharply to a constant absorbance at the molar ratio of the components in the complex.

The stoichiometry is obtained in the slope ratio method, by comparing the slopes of the two straight line plots of the absorbance of solutions obtained by varying the concentration of the first one and then the other component in the presence of a large excess of the second component.

Evaluation of the Stability constant

A convenient method for the evaluation of apparent stability constant is the method of ANDERSON and coworkers^{28) 29)} based on the comparison of the composition of mixtures having identity of colour, i.e., the same absorbance value. The method has been adopted³⁰⁾ for use of a coloured ligand and a colourless cation instead of a colourless ligand and a coloured cation. This method has been found to be useful and applicable under a wider variety of conditions.

¹⁸⁾ P. JOB, *Compt. rend.* **180**, 928 (1925).

¹⁹⁾ P. JOB, *Ann. Chim.* **9** (10), 113 (1928); **6** (11), 97 (1936).

²⁰⁾ J. H. YOE and A. L. JONES, *Ind. Eng. Chem. Analyt. Ed.* **16**, 111 (1944).

²¹⁾ A. E. HARVEY and D. L. MANNING, *J. Amer. chem. Soc.* **72**, 4488 (1950).

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²⁴⁾ L. SOMMER and M. HNILČKOVÁ, *Bull. Soc. Chim. France* **1959**, 36.

²⁵⁾ M. M. JONES and K. K. INNES, *J. physic. Chem.* **62**, 1005 (1958).

²⁶⁾ E. ASMUS, *Z. analyt. Chem.* **183**, 321 (1961); **183**, 401 (1961); E. ASMUS and P. MEYER, *Z. analyt. Chem.* **190**, 390 (1962).

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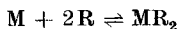
²⁸⁾ R. T. FOLEY and R. C. ANDERSON, *J. Amer. chem. Soc.* **70**, 1195 (1948); **71**, 909 (1949).

²⁹⁾ S. E. TURNER and R. C. ANDERSON, *J. Amer. chem. Soc.* **71**, 912 (1949).

³⁰⁾ A. K. MUKHERJI and A. K. DEY, *J. Inorg. Nucl. Chem.* **6**, 314 (1958); *Anal. Chim. Acta* **18**, 324 (1958); S. K. BANERJI and A. K. DEY, *Proc. Symp. Chem. Coord. Compounds Agra* 1959, **2**, 198 (1960).

In this method the results from the method of continuous variations are employed using equimolecular solutions, and the concentrations of the reactants are read from the to descending portions of the curves.

In a complex forming reaction of the type



the formation constant K is given by

$$K = \frac{x}{(a-x)(b-2x)^2}, \quad (1)$$

where x = the concentration of the chelate at equilibrium and a and b are respectively the initial concentrations of the metal ion and the chelating agent. Taking two concentrations showing the same absorbance, that is the same value of x , we have

$$K = \frac{x}{(a_1-x)(b_1-2x)^2} = \frac{x}{(a_2-x)(b_2-2x)^2} \quad (2)$$

or

$$x^2 = 4[(a_1 + b_1) - (a_2 + b_2)] + x[(b_2^2 - b_1^2) + 4(a_2 b_2 - a_1 b_1)] \\ + (a_1 b_1^2 - a_2 b_2^2) = 0. \quad (3)$$

Hence from a knowledge of two initial concentrations a and b , the value of x can be calculated, and the value of K can be obtained by substitution in (1).

The stability constant has been calculated by the method of continuous variations using non equimolar solutions using the expression

$$K = \frac{[2 - 3x](p-1)^2}{C^2 p [(p+2)x-2]^3}.$$

The stability constant has been calculated from the mole ratio curves also, through a calculation of the degree of dissociation, as proposed by HARVEY and MANNING. The stability constant K is given by equation

$$K = 1 - \alpha/4\alpha^3 C^2,$$

$$\alpha = E_m - E_s/E_m.$$

The values obtained from these methods have been found in close agreement and are recorded in Table 4. The free energy change of formation has also been calculated using the expression

$$\Delta G^\circ = -RT \ln k.$$

Results and Discussion

Quinalizarin behaves as a colloidal electrolyte and therefore very dilute solutions of the order of 10^{-4} M were used in these investigations.

Effect of pH on colour development of complex

The effect of pH on the colour development of the lanthanum complex was studied with solutions varying in pH value 5 to 7.2. Fig. 1 shows that maximum colour is obtained at pH 6.8 hence a pH of 6.8 was selected for subsequent studies.

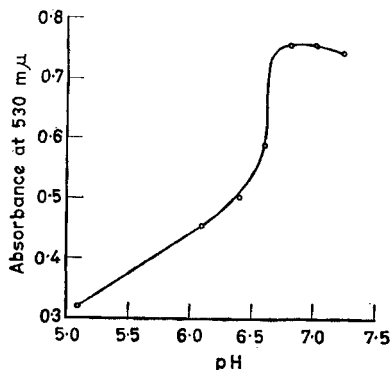


Fig. 1. Effect of pH on colour development.

La: 173 μ g, pH 6.8, μ 0.1 NaClO₄

Influence of pH on the Stability of the chelate

The absorbance of mixtures containing 2.5×10^{-4} M lanthanum acetate and 5.0×10^{-4} M Quinalizarin at different pH were measured at different wave lengths and the results have been plotted in Fig. 2. It was thought of interest to compare the influence of pH on the λ max of the complex with that of the dye. The change of λ max of Quinalizarin with pH is represented in Fig. 3. It may be seen that the chelate is stable between 6.5 and 7.2.

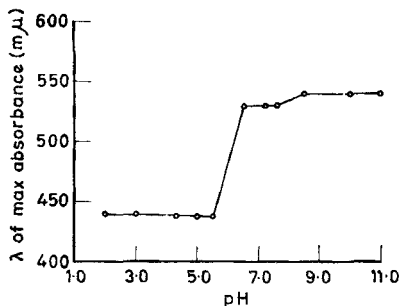


Fig. 2. Variation of λ max with pH of lanthanum quinalizarin complex C = 5.0×10^{-4} M; p = 2

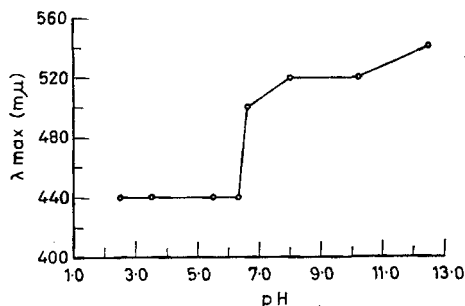


Fig. 3. Variation of λ max with pH of quinalizarin C₁ = 2.0×10^{-4} M

Effect of amount of Quinalizarin

The effect of reagent concentration was studied with solutions containing a known volume, i.e., 2 ml of 1×10^{-3} M lanthanum acetate and varying volume of a 1×10^{-3} M solutions of Quinalizarin. The total volume being kept constant at 25 ml. The pH value of the solutions were kept constant at 6.8. The results are plotted in Fig. 4. A constant absorbance is obtained when 10–12 ml of the reagent solutions is used. Therefore for purposes of determination there should be a five fold molar excess of the reagent over lanthanum concentration.

Stability of the Complex

Fig. 5 shows the stability of the coloured complex of lanthanum. The colour is stable at room temperature for at least three hours which is sufficient for the purposes of absorbance measurements.

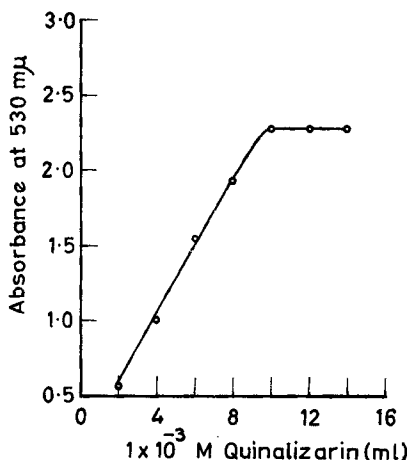


Fig. 4. Effect of amount of Quinalizarin. La: 278 μg; pH 6.8, μ 0.1 NaClO₄

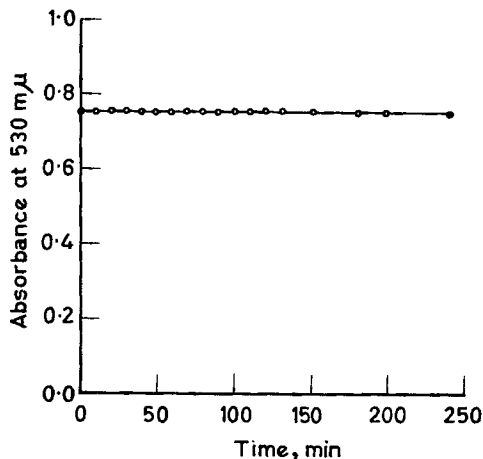


Fig. 5. Stability of Lanthanum Quinalizarin chelate. La: 173 μg; pH 6.8, μ 0.1 NaClO₄

The order of the addition of the reagent

Varying the order in which the reagents were added had no significant effect on the results. In all cases the colour was fully developed within two minutes.

BEER'S Law and optimum range

BEER'S Law is obeyed over the concentration range from 1.26 to 6.32 ppm of Lanthanum. The optimum concentration range for the determination of Lanthanum was determined by the method described by RINGBOM³¹⁾ and was found to be 1.4 to 3.5 ppm.

Standard procedure for the Lanthanum determination

Into a 25 ml volumetric flask an aliquot of the solution containing up to 85 μg of lanthanum was pipetted after which 5 ml of Ammonium Acetate buffer solution of pH 6.8 and 5 ml of 1×10^{-3} M Quinalizarin solution were added. The volume of the alcohol was kept at 12.5 ml, total volume 25 ml. After mixing the solution was allowed to stand for about 30 minutes. The absorbance of the solution was measured at 530 mμ against a reagent blank treated in a similar manner.

³¹⁾ A. RINGBOM, Z. analyt. Chem. **115**, 332 (1938/1939).

Nature of the complex formed in solution

For the determination of the nature of complex formed in solution, the method of VOSBURGH and coworkers³²⁾ was followed. Mixtures containing Lanthanum acetate and Quinalizarin in different stoichiometric ratios, viz. 0:1, 2:1, 1:1, 1:2, 1:3 and 1:4, etc., were prepared keeping volume of ethanol at 12.5 ml and total volume at 25 ml. The absorbance of each of them was measured at suitable wavelength interval. Fig. 6 shows that the reagent has its λ max at 510 μ , whereas in all the mixtures the region of maximum absorption shifts to 530 μ , indicating formation of only one chelate having λ max at 530 μ under the conditions of study.

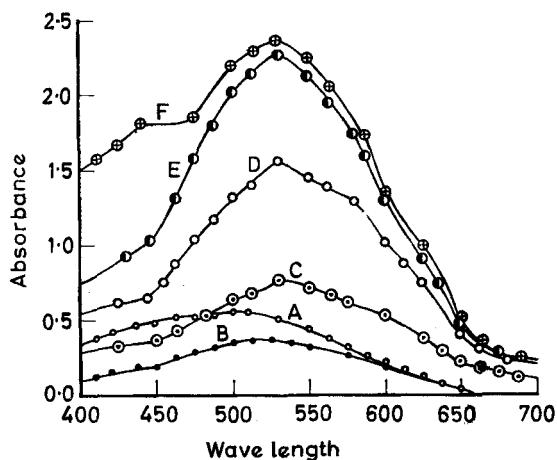


Fig. 6.

Absorption spectra of mixtures of Lanthanum acetate and quinalizarin at pH 6.8 ± 0.1 , μ 0.1 NaClO₄.
 Curve A: reagent = 1.0×10^{-4} M;
 Curve B: C = 0.5×10^{-4} M, p = 0.5;
 Curve C: C = 1.0×10^{-4} M, p = 1.0;
 Curve D: C = 2.0×10^{-4} M, p = 2.0;
 Curve E: C = 3.0×10^{-4} M, p = 3.0;
 Curve F: C = 4.0×10^{-4} M, p = 4.0

Composition of the chelate

Job's method: Job's method of continuous variation was adopted for determining the composition of the coloured complex formed. The absorbance of the mixture and chelating agent were measured at 530 and 550 μ , using both equimolecular and non equimolecular solutions, adjusting the pH at 6.8; ionic strength 0.1 in 50% ethanolic medium, keeping the volume constant at 25 ml. The absorbance data obtained was corrected for the contribution made by the ligand by usual methods. Some of the typical observations have been plotted in Figs. 7–10.

Mole ratio method: A series of solutions were prepared from 2.0×10^{-4} M of the Lanthanum Acetate and Quinalizarin at pH 6.8 and ionic strength 0.1 maintaining a 50% ethanolic medium and varying amounts of equimolar solutions of the metal were added such that the mole ratio of the

³²⁾ W. C. VOSBURGH and coworkers, J. Amer. chem. Soc. **63**, 437 (1941); **64**, 1630 (1942).

reagent to metal was from 1:0.2 to 1:4. The results plotted in Fig. 11 show a break at a ratio of one mole of the reagent to 0.5 mole of the metal.

Slope ratio method: The concentration of the variable component was 1.0×10^{-4} M. The volume of the variable component was varied from 1 to 12.5 ml in the presence of 12.5 ml of excess concentration of 2.5×10^{-4} M

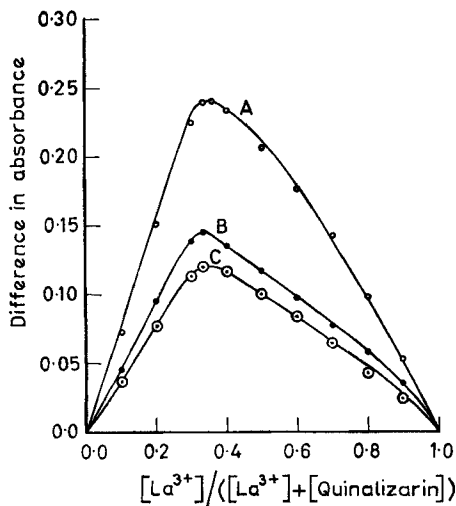


Fig. 7. Absorption of equimolecular solutions of Lanthanum acetate and quinalizarin at $530 \text{ m}\mu$ ($p = 1$, $\text{pH } 6.8 \pm 0.1$) $\mu = 0.1 \text{ NaClO}_4$. Curve A: $C = 2.0 \times 10^{-4} \text{ M}$; Curve B: $C = 1.25 \times 10^{-4} \text{ M}$; Curve C: $C = 1.0 \times 10^{-4} \text{ M}$

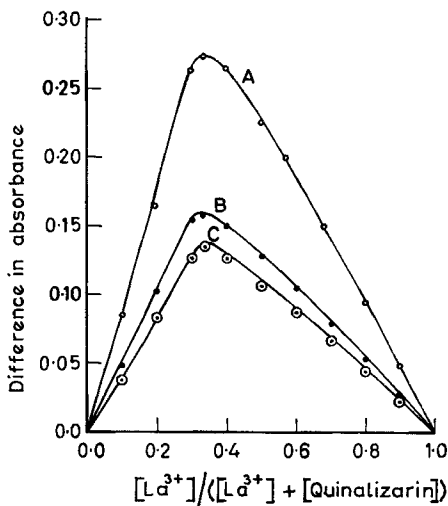


Fig. 8. Absorption of equimolecular solutions of lanthanum acetate and quinalizarin at $550 \text{ m}\mu$ ($p = 1$), $\text{pH } 6.8 \pm 0.1$) $\mu = 0.1 \text{ NaClO}_4$. Curve A: $C = 2.0 \cdot 10^{-4} \text{ M}$; Curve B: $C = 1.25 \times 10^{-4} \text{ M}$; Curve C: $C = 1.0 \times 10^{-4} \text{ M}$

of the constant component. The total volume was 25 ml and the volume of ethanol in each case was kept 12.5 ml. The pH of the solution was maintained at 6.8 and ionic strength at 0.1. Fig. 12 shows the measured absorbance at 530, 550 and 580 $\text{m}\mu$ plotted against the volume of the variable component. The slopes of the two straight line in each case gave Lanthanum Quinalizarin ratio as 1:2.

The present study has shown that the results obtained by the three different methods are in good agreement and show the utility of these methods for such studies.

Calculation of the stability constant of the chelate: The apparent stability constants of the chelate formed were calculated from the absorbance data by the three methods, viz., (a) method of DEY and co-workers (b) method of continuous variation using non equimolecular solu-

tions and (c) mole ratio method. The values of change in free energy of formation were also calculated.

For the calculation of K by method (a) concentration of the metal ions used are shown in Table I ($p = 1$). For method (b), the concentrations and the volume of the metal ion used at the peak are shown in Table 2.

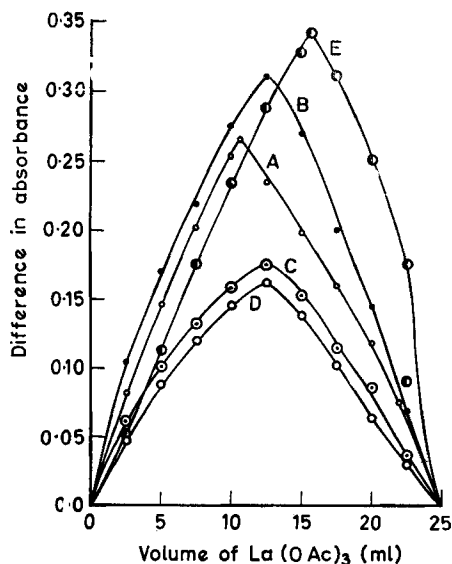


Fig. 9. Absorption of non-equimolecular solutions lanthanum acetate and quinalizarin at $530 \text{ m}\mu$; $\text{pH } 6.8 \pm 0.1$, $\mu = 0.1 \text{ NaClO}_4$.

Curve A: $C = 2.0 \times 10^{-4} \text{ M}$, $p = 1.5$; Curve B: $C = 2.5 \times 10^{-4} \text{ M}$, $p = 2.0$; Curve C: $C = 1.25 \cdot 10^{-4} \text{ M}$, $p = 2.0$; Curve D: $C = 1.0 \cdot 10^{-4} \text{ M}$, $p = 2.0$; Curve E: $C = 2.0 \times 10^{-4} \text{ M}$, $p = 4.0$

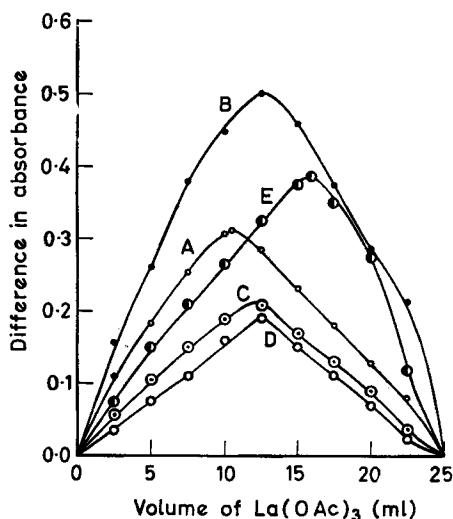


Fig. 10. Absorption of non-equimolecular solutions of lanthanum acetate and quinalizarin at $550 \text{ m}\mu$, $\text{pH } 6.8 \pm 0.1$, $\mu = 0.1 \text{ NaClO}_4$.

Curve A: $C = 2.0 \times 10^{-4} \text{ M}$, $p = 1.5$; Curve B: $C = 2.5 \cdot 10^{-4} \text{ M}$, $p_1 = 2.0$; Curve C: $C = 1.25 \times 10^{-4} \text{ M}$, $p = 2.0$; Curve D: $C = 1.0 \times 10^{-4} \text{ M}$, $p = 2.0$; Curve E; $C = 2.0 \times 10^{-4} \text{ M}$, $p = 4.0$

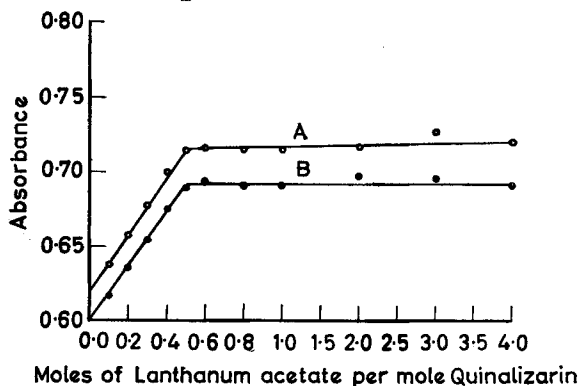


Fig. 11. Absorbance of quinalizarin lanthanum acetate solutions by the molar ratio method $\text{pH } 6.8 \pm 0.1$, $\mu = 0.1 \text{ NaClO}_4$. Conc. = $2.0 \times 10^{-4} \text{ M}$; Curve A at $530 \text{ m}\mu$; Curve B at $550 \text{ m}\mu$.

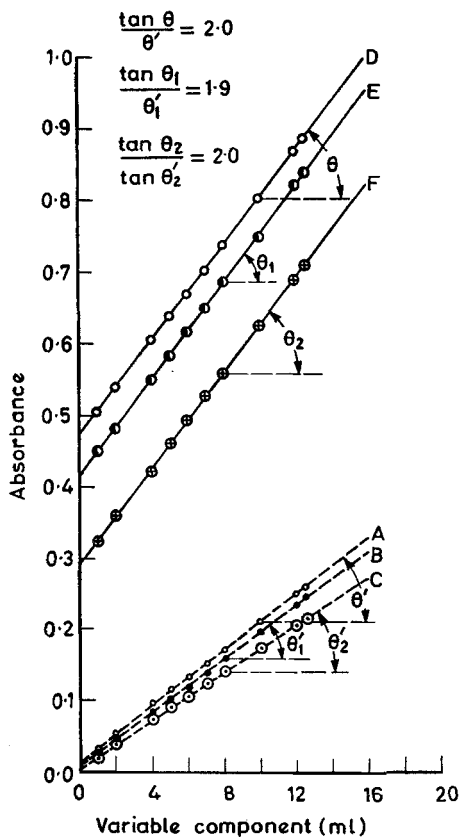


Fig. 12. The slope ratio method; pH 6.8 ± 0.1 ; $\mu = 0.1 \text{ NaClO}_4$ $2.5 \times 10^{-4} \text{ M}$ excess component (12.5 ml) + $1.0 \times 10^{-4} \text{ M}$ Variable component (x ml) + water or ethanol (12.5 - x ml). A: quinalizarin varying (530 $\mu\mu$); B: quinalizarin varying (550 $\mu\mu$); C: Quinalizarin varying (580 $\mu\mu$); D: Lanthanum acetate varying (530 $\mu\mu$); E: Lanthanum acetate varying (550 $\mu\mu$); F: Lanthanum acetate varying (580 $\mu\mu$)

Table 1

Curve	10^4 C(M)	p
B	2.00	1.0
C	1.25	1.0
D	1.00	1.0

Table 2

Fig. No.	Curve	10^4 C(M)	p	Volume of the metal ion used at the peak
9	A	2.0	1.5	10.4
	E	2.0	4.0	16.0

For calculation of K by method (c) the concentrations E_m , E_s and α are shown in Table 3.

Table 3

Fig. No.	Curve	$10^4 C(M)$	Em	Es	α
11	A	2.0	.715	.660	.0769
	B	2.0	.690	.635	.0797

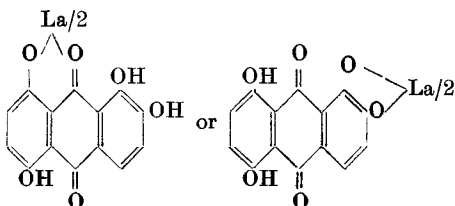
Table 4 records the values of $\log K$ at $\text{pH } 6.8 \pm 0.1$, ionic strength 0.1 at 30° determined by three different methods. The values obtained are in close conformity.

Table 4

Method	pH	Ionic Strength	$\log K$	ΔG° at 30° (K.cal)
a) Dey and coworkers	6.8 ± 0.1	0.1 M	10.1 ± 0.1	-14.0 ± 0.1
b) Continuous variation	6.8 ± 0.1	0.1 M	10.2 ± 0.1	-14.1 ± 0.1
c) Mole Ratio	6.8 ± 0.1	0.1 M	10.1 ± 0.1	-14.0 ± 0.1

Suggestions on the structure of the chelate

It is not possible to derive any definite information on the basis of the experimental results mentioned in the present communication regarding the structure of the chelate. There are evidently two alternative positions where chelation might occur.



The metal ion may be coordinated between the phenolic oxygens or between the quinoid oxygen and the adjacent oxygen of the phenolic group.

It is interesting to note that in strongly alkaline medium ($\text{pH } 10.4$ and above) where the removal of phenolic hydrogen by ionization is likely, the region of maximum absorbance of Quinalizarin is at $540 \text{ m}\mu$ whereas in the neutral or slightly alkaline medium ($\text{pH } 6.8$ to 8.1) the λ_{max} is found to be $510\text{--}520 \text{ m}\mu$ and shifts to $440 \text{ m}\mu$ in the acidic medium (below $\text{pH } 6.4$). Thus it seems possible that as a result of chelation, the phenolic hydrogen is replaced by the metal ion hence the wavelength of maximum absorbance of the chelate is 530 . This would lead to the formation of anionic complex. This has been confirmed by complete adsorption of the colour of the chelate by

ion exchange resin Amberlite IR 45 (OH) (B.D.H. AnalaR). Nothing very definite can be said from the present studies, excepting that an anionic complex gets formed, as has been confirmed by ion exchange studies.

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