METAL COMPLEXES OF CHROMOTROPE 2R
and
BROMOPYROGALLOL RED

THESIS SUBMITTED IN
PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
CHEMISTRY

by

SUBHASH CHANDER DHUPAR
BIRLA INSTITUTE OF TECHNOLOGY & SCIENCE
PILANI, RAJASTHAN, INDIA

1972

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE,
PILANI (RAJASTHAN), INDIA.

December 12, 1972.

SUPERVISOR'S CERTIFICATE

Certified that the research work described in this thesis entitled "Metal Complexes of Chromotrope 2R and Bromopyrogallol Red", is original and was carried out by Shri Subhash Chander Dhupar, under my guidance and supervision during the period, September 1969 to December 1972, in the Department of Chemistry.

(Samir K. Banerji)
M.Sc., D.Phil., F.N.A.Sc.,
Professor and Head,
Department of Chemistry.

LIST OF PUBLICATIONS

1. Spectrophotometric study of chelate formation of tetravalent Hafnium with Chromotrope 2R.

   J. Indian Chem. Soc., 48(10), 421 (1971).

2. The spectrophotometric determination of Ytterbium (III) with Chromotrope 2R.

   J. Indian Chem. Soc., 49(4), 425 (1972).

3. A spectrophotometric study on the complex formation of Nickel (II) and Cobalt (II) with Bromopyrogallol Red.

   J. Chinese Chem. Soc., 20, 55 (1972).

4. Spectrophotometric study of Aluminium (III) - Chromotrope 2R chelate.

   Institution of Chemists (India), (in press).

5. The spectrophotometric determination of Gallium (III) with Chromotrope 2R.

   J. Indian Chem. Soc., 49(10), 935 (1972).

6. Complex formation between Tungsten (VI) and Bromopyrogallol Red.

   Academia Sinica (Taiwan), (in press).

7. Thermodynamics of Cu(II) - Chromotrope 2R chelate.

   J. Indian Chem. Soc., (in press).

8. Spectrophotometric studies on chelate formation between Zirconium (IV) and Chromotrope 2R.

   J. Indian Chem. Soc., (communicated).

9. Spectrophotometric studies of the rare earths Ytterbium (III) and Praseodymium (III) by Bromopyrogallol Red.

   J. Less Common Metals. , (communicated).

10. Complex formation of Lead (II) with Bromopyrogallol Red - A spectrophotometric study.

    Academica Sinica (Taiwan) , (communicated).

11. Potentiometric studies on some bivalent metal chelates of Chromotrope 2R.

    Indian J. Chem. , (communicated).

12. Stepwise stability constants of Pb(II), [redacted]), Cu(II), Hg(II) and Zn(II) chelates of phenylazo-chromotropic acid.

    J. Inorg. Nucl. Chem. , (communicated).

GLOSSARY OF SYMBOLS AND ABBREVIATIONS

M = Metal

L = Ligand

ML_n = Complex

a_M, a_L and a_{ML} = Activity of metal, ligand and complex, respectively.

$[M]$, $[L]$ and $[ML]$ = Concentration of metal, ligand and complex respectively.

K_n, K_n^H = nth metal-ligand and proton-ligand stoichiometric step stability constant respectively.

β_n, β_n^H = Stoichiometric gross or overall stability constant of ML_n and H_nL respectively.

n, N = Maximum number of ligands associated with a metal in a complex.

Y = Number of dissociable protons attached to the ligand molecule.

N^o = Normality of the alkali used for titration.

E^o = Initial concentration of the mineral acid.

π, Σ = Product and summation of all the terms.

T_L = Total concentration of the ligand.

T_M = Total concentration of the metal ion.

p = T_L/T_M

v = Volume of alkali required at a particular interval.

V^o = Initial total volume of the solution.

$\bar{n}$, $\bar{n}_A$ = Average number of ligands and protons bound to one central group and free ligand molecule respectively.

pL = Free ligand exponent.

H = Proton or hydrogen ion.

J = Number of protons attached to the free ligand molecule in a complex system.

B = pH of the solution.

A = Absorbance or optical density.

α = The degree of dissociation.

c, C = Equilibrium concentration.

R = Universal gas constant.

T = Temperature in degrees kelvin.

CTR = Chromotrope 2R

CBT = Chromotrope 2B

SPANDS = 2-(p-sulphophenylazo)-1, 8-dihydroxy-naphthalene 3,6-disulphonic acid.

BPR = Bromopyrogallol Red.

HMT = Hexomethylenetetramine or Hexamine

PAR = 4-(2-pyridylazo)-resorcinal.

PAN = 1-(2-pyridylazo)-naphthol.

ACKNOWLEDGEMENTS

It is my privilege to express indebtedness and appreciation to Professor Samir K. Banerji, M.Sc., D.Phil., F.N.A.Sc., Head, Department of Chemistry, B.I.T.S., Pilani, for his inspiring guidance, lively discussions and the personal interest he has taken in supervising the present work at every step.

I would like to place on record my thanks to Dr. K.C. Srivastava for his constant encouragement, suggestions and help which he gave ungrudgingly in full measure during the entire period of my research work. I would also like to acknowledge the very stimulating and useful discussions with my colleagues, which took place during these studies, and like to mention particularly Dr. A.D. Taneja, Mr. C.S.G. Prasad and Mr. P.K. Govil.

I would be failing in my duty if I do not thank the faculty members of Chemistry department for their assistance in certain discussions. I am also thankful to Dr. B.K. Avinashi, Dr. (Miss) Sunita Rani, Dr. A.N. Pant, Mr. B.C. Kashyap, Mr. N.K. Agarwal, Mr. S.C. Taneja, Mr. S.K. Khanna, Mr. J.S. Gill, Mr. Viney Seth and Mr. T.K. Kaul for their whole hearted cooperation, timely help and making my stay at Pilani a pleasant experience.

I wish to record here my gratitude to Mr. Raju of the Information Processing Centre for the assistance

rendered and to Mr. S.K. Marwaha of the EEE Department for checking the electronic instruments and Shri P.L. Mehta for typing the thesis with diligent care.

It is my pleasant duty to thank Dr. C.R. Mitra, Director, B.I.T.S., and Dr. A.K. Dattagupta, Dean, Faculty of Science, for providing the necessary laboratory facilities.

I want especially to acknowledge the financial assistance from the authorities of B.I.T.S. and the University Grants Commission for the period of my work.

I express my deep sense of gratitude to my respected father and other members of my family for their blessings, inspiration, co-operation and encouragement at every step. It is also pleasant duty to express my indebtedness to my wife, for her assistance, encouragement and forbearance, without whose co-operation this work would not have been completed.

At last I would like to thank, all those who albeit, anonymously, helped me during the course of these studies.

Subhash Chander Dhupar

(Subhash Chander Dhupar)

CONTENTS

CHAPTER I

INTRODUCTION

The development of inorganic complex chemistry has been one full of ups and downs. It received a great impetus from the pioneering work of A. Werner and S.M. Jørgensen, but then fell into oblivion, because at that time it just did not pose the challenges allied fields did. With the development of modern theories of bonding, however, it has shaken itself up from its enforced hibernation and of late has developed into an active field of research with manifold applications in practically every field of human activity. Biology, Biochemistry, Agriculture and Technology are all indebted to this branch of chemistry in one way or the other. Moreover, with the development of newer techniques of physical methods, the activity in the field of co-ordination chemistry has increased considerably within the last two decades, as evidenced in the journals. Frequent symposia and discussions are being organised and an international conference on the subject has now become a regular feature[2,9,17,18].

The formation of inorganic complexes was recognised in nineteenth century by Werner and Jørgensen. At that time the nature of these complexes was not fully understood. Werner's concept of auxiliary valences and co-ordination number[22] went a long way in systematising the facts available at that time. With the development of the theory of co-valent bond, by G.N. Lewis[5], a more realistic picture of the nature of chemical bonding was available and its full advantage was taken by N.V. Sidgwick[10] and Lowry[0] who pictured the bond between a metal ion and ligand to be made up of an electron pair donated by the ligand to the metal. Thus all the neutral molecules and ions which had a loan pair of electrons were envisaged as potential ligands and the bond formed by the donation of a loan pair of electrons by the ligand to the metal was christened, the co-ordinate bond. Sidgwick went further and generalized that every metal ion accepts only that number of electron pairs, which help it to reach the effective atomic number of the next inert gas. Though this principle worked in many cases, it failed in quite a few instances, notably in the complexes of Fe(II) and in the complexes where the metal's oxidation state was zero e.g. metal carbonyls.

The development of quantum mechanics saw a further step in the theory of bonding in metal complexes. The valence bond approximation developed by Heitler and London in 1927 was extensively applied by Pauling[10] to the metal complexes. This theory envisaged the use of hybridised metal ion orbitals to overlap with the ligand orbitals and thus form directed co-valent bonds. Although this theory succeeded in giving a pictorial view of bonding in complexes but failed to explain their spectra[4]. It could predict the magnetic moments of some complexes, but failed to do so in many cases e.g. $[CoF_6]^{3-}$.

With the introduction of the concepts of group theory in quantum mechanics, theories of bonding in complexes, which were governed by the rules of symmetry, were developed. The Crystal Field Theory (CFT), developed by H. Bethe[1], treated metal-ligand interaction as purely electrostatic. According to this theory, the d-orbitals of metal ions, in electrostatic field generated by the ligands are split e.g. their five fold degeneracy in the free state is lifted. On the basis of d-orbital splitting, the CFT was able to explain the spectra and magnetic moments of complexes, but it was at best a formalism, as there is a considerable body of evidence that metal-ligand interactions are covalent to a greater or lesser extent. The Molecular Orbital Theory (MOT) of J.H. Van Vleck[19] started with the premise that overlap will occur to some extent between metal ion and ligand orbitals. It is thus seen to be more general theory than CFT. In MOT metal ion and ligand orbitals of matching symmetries are constructed and then made to overlap to form bonding and anti-bonding molecular orbitals. The electrons are then introduced into these orbitals. The MOT is conceptually elegant, but incapable of generating easy quantitative methods which is the main feature of CFT. The synthesis of the better aspects of these two theories is called Ligand Field Theory (LFT), and in the present state of knowledge, it is in that the best approach to the elucidation of bonding in complexes is obtained.

The word 'chelate' owes its origin to Morgan[8] and may be defined as a compound possessing a cyclic structure arising from the union of a metal ion with a chelating agent (ligand) which may be neutral or ionic, and which has more than one point of attachment with the metal ion. In the usual type of complexes the ligands are unidentate and so that no ring formation takes place. In case of bidentate chelates the concerned bonds may either be (i) one covalent and one co-ordinate, (ii) both covalent, (iii) both co-ordinate. In most chelates low strain i.e. five or six membered rings are formed but macrocyclic chelates have also been reported. The ring structure of a chelate gives it added stability as compared to the stability of an ordinary complex and this phenomenon is termed as 'Chelate Effect'. Earlier, chelates were considered to be a distinct class of compounds, but now it is recognised as a special class in the domain of complex compounds.

Chelates have a prominent role in every sphere of human activity and finds application in almost every branch of science and technology. These are of immense importance in chemical analysis both qualitatively and quantitatively. Complexometric titrations[13,15], spot test[3], masking and demasking[12], Weisz Ring Oven[21], colorimetry[14] and gravimetric estimations involve in them the use of complex compounds. Organic chemists use chelates in synthetic work e.g. Friedel and Crafts reaction, Grignard reaction, Sandmeyer reaction and in the area of catalysis e.g. polymerisation of ethylene and hydrogenation of olefins. In physical chemistry, complexes have provided suitable compounds for testing and expanding the theories of bonding, electrolytic behaviour of ions, magnetic behaviour, solution thermodynamics and theories of kinetic behaviour.

In recent years, biochemists have become intensely interested in the effect of metal ions in the form of complexes in biological processes[7]. Metal chelates are widely spread in nature. Chlorophyll is a magnesium chelate, Hemin, the oxygen carrier in human blood is an iron chelate and Vitamin B_{12} is a cobalt chelate[11,20]. Enzyme catalysis is probably due to the chelating tendencies of enzymes. It is also well established that the activity of most of the drugs is due to their ability to chelate with the essential metallic ions present in the body and form the backbone of a developing discipline of inorganic biochemistry.

The usefulness of this branch of chemistry in modern technology is also felt. Rapid developments of advanced technology as atomic piles, rocket etc. made it necessary to explore the chemistry of metallic ions afresh in order to find better methods for their purification and estimation. Their formation is also used in water softening, detergents, antioxidants, dyeing and leather industry.

The development of specific sensitive chelating agents and low cost high precision spectrophotometers has revolutionized chemical analysis to such an extent that many of the analysis which were difficult in recent past, have become routine methods of detection and estimation. It is estimated that more than two-third of metals have available organic chelating agents for their accurate estimation. Thus it would seem that modern methods of chemical analysis have as one of their main features the use of chelating agents for the accurate determination of metal ions. The need to carry out a wide variety of analysis under the broad spectrum of conditions has necessiated the development of co-ordination chemistry, and this is now an active field of intensive meaningful research.

* * *

REFERENCES

1. Bethe, H. Ann. Physik, 3, 133 (1929).
2. Boltz, D.F. Annual Reviews, Anal. Chem., 44(5), 300R (1972); 42(5), 152R (1970).
3. Feigal, F. 'Spot tests in inorganic analysis', Trans. R.E. Oesper, Elsevier, Amsterdam (1958).
4. Larsen, E.M. 'Transition elements', Benjamin, New York (1965).
5. Lewis, G.N. 'Valence and the structure of atoms and molecules', Chemical Catalog Co., New York (1923).
6. Lowry, T.M. J. Chem. Soc., 433 (1941).
7. Martell, A.E. and Chaberek, S. 'Organic sequestering agents', Wiley and Sons, Inc., pp. 416 (1959).
8. Morgan, G.T. and Drew, H.D.K. J. Chem. Soc., 117, 1456 (1920).
9. Pajdowski, L. 13th International Conference on Co-ordination Chemistry, Poland (1970).
10. Pauling, L. 'The nature of chemical bond', Cornell Univ. Press (1950).
11. Pauling, L. and Coryll, C.D. Proc. Natl. Acad. Sci. (U.S.A.), 22, 159 (1963); 22, 210 (1963).
12. Perrin, D.D. 'Masking and demasking of chemical reactions', Wiley, Interscience (1970).

13. Ringbom, A. 'Complexation in analytical chemistry', Interscience Publishers, New York (1963).

14. Sandell, E.B. 'Colorimetric determination of traces of metals', Interscience Publishers, New York (1963).

15. Schwarzenbach, G. 'Die komplexometerioche titration', 2nd Ed., Euke, Stuttgart (1956).

16. Sidgwick, N.V. 'Electronic theory of valency', Oxford (1927).

17. Sillen, L.G. 'Proceedings of 9th International Conference of Co-ordination Chemistry', Stockholm, Uppsala (1962).

18. Szoke, J. 'Proceedings of Symposium on Co-ordination Compounds', Wroclaw, Pergamon Press, Oxford (1964).

19. Van Vleck, J.H. 'Theory of electric and magnetic susceptibilities', Oxford Press (1956).

20. Wallace, A. 'Metal chelate in plant nutrition', National Press, California (1956).

21. Weisz, H. 'Microanalysis by the ring oven technique', Pergamon Press (1961).

22. Werner, A. 'Neure auschanungen auf dem gebiete der anorganischem chemie', 4th Ed., F. Vieweg und Sohn, Brunswick (1920).

* * *

CHAPTER II

METHODS OF INVESTIGATION

Currently a great number of methods are used for the investigation of complex compounds. It is, however, observed that any property of the system, such as absorbance, pH, conductivity, optical activity and solubility etc., which are related directly to the concentration of one of species (Metal, Ligand or Complex), may be used to determine the formation of complex, provided the change in that property is solely due to the interaction between metal ion and the ligand. The detection of complexes and the determination of stability constants are akin to one another and most of the methods which are used to determine the composition may also be used to calculate the stability constant. Some of the techniques which are widely employed for such types of studies include absorption by ion exchange[54,55,56], polarography[15,36], optico-chemical methods[29,52], solubility[41,57], reaction kinetics[59,62] and conductance[14,34]. A number of other methods like magnetic susceptibility, dielectric polarisation, molar refraction, dialysis, electrophoresis, distribution methods, heats of mixing, cryoscopic and colorimetric methods, ir absorption spectra and nmr are used in some special cases. In the present work, spectrophotometric and potentiometric techniques have been made use of for the study of the complex systems.

Spectrophotometric Studies

The application of spectrophotometry to the determination of traces of metals[37], non-metals, alloys[26], and organic substances[28] is one of the main reasons for the continued widespread utilization of this opticometric method of analysis. Reliable low cost instruments, speed, satisfactory accuracy and precision and suitability of automation are additional factors contributing to the popularity of spectrophotometric analysis. Moreover, progress still continues in the development of new and improved light absorptive chemical systems for metals and non-metals based on the wide variety of chelating agents or dyes which have high sensitivity, selectivity and molar absorptivity.

Numerous methods based on absorptiometric data have been applied in the study of complexes. Molland[40] has worked out a method which is applicable in cases where more than one central atom takes part, in the complex formation. The method of proportional absorbances developed by Buděšinský[12] is applicable for establishing the presence of binuclear complexes. Frank and Ostwalt[17] have proposed a method for the identification of 1:1 complexes. The logarithmic method[6,7], Asmus method[4] and method of isobestic points[53] have also been applied by various teams of workers. Bjerrum[9] has pointed out that the formation of complexes always appears to occur in a stepwise fashion. Newman and Hume[46] have derived general equation by means of which successive formation constants of mixed and single ligand complexes can be determined from spectrophotometric data. Sullivan and Hindman[61] had derived general mathematical equations by means of which association constants of complex ion system can be calculated. There are available only a limited number of general methods for the calculation of stability constants, although a slight modification and specific applications of these general formulations have been made by a number of investigators[1,16,27,32,43,51]. A brief account of the methods, mostly applied in this piece of work has been described in the following lines.

Methods for Discerning the Composition of Metal Chelates

Many colorimetric analyses, particularly for metals, depend upon the formation of complex ions or molecules. Ley[35] used absorption spectra to distinguish between a metal ion and its chelates. The colour of chelate compound is very significant and the intensification or the appearance of new colour is considered as an indication that a complex is formed. It is frequently important to know the molar ratio of metal to reagent in the complex. This can be ascertained from the photometric data by the following three different procedures.

(i) Job's method of continuous variation

The Job's method of continuous variation[21] requires the preparation of a series of solutions of varying mole fractions of the two constituents wherein their sum is kept constant. The difference between the measured absorbance, and the absorbance calculated for the mixed constituents on the assumption of no reaction between them, is plotted against the mole fraction of one of the constituents. The resulting curve will show a maximum (or minimum) at the mole fraction corresponding to that of the complex.

Vosburgh and Cooper[63] modified the above method to study the composition, in cases, where more than one complex is formed by conducting studies at several wavelengths. A more general treatment in such cases is given by Katzin and Gebret[25]. To differentiate monomeric and dimeric complexes, Klausen has also described such a method. Although the method has been criticised by a number of workers[4,22,24,60-66], it is agreed that the method is capable of giving reliable results when absorbance is used as the property.

(ii) Mole ratio method

In the mole ratio method of Yoe and Jones[69], the absorbances are measured for a series of solutions which contain varying amounts of one constituent with a constant amount of the other. A plot is prepared of absorbance as a function of the ratio of moles of reagent to moles of metal ion or vice versa. This is expected to give a straight line from the origin, where both the constituents are colorless and breaks sharply to a horizontal straight line at the molar ratio of the complex, because one component is completely used up, and the addition of more of the other can produce no more of the absorbing complex.

If the constituent which is in excess itself absorbs at the same wavelength, the curve after break will show a slope which is positive but of smaller magnitude than prior to break. The sharpness of the break depends on the magnitude of the stability constant.

(iii) Slope ratio method

The composition of the complex in the slope ratio method, developed by Harvey and Manning[18], is computed by comparing the slopes of the two straight line-plots of absorbance of the solutions, obtained by varying the concentration of ligand in the presence of large excess of metal ion and vice-versa. This method is useful in studying less stable complexes and is applicable to systems conforming to Beer's law.

Determination of Stability Constant

In order to understand the relationship in co-ordinate bonding and to be able to predict unknown reactions, it is necessary to have quantitative measurements on the degree of metal-ligand association which is represented as the stability constant. In order to study the formation of complexes in solutions, two kinds of stability come into question (i) Thermodynamic stability, (ii) Kinetic stability. The former being a measure of the extent to which this species will form, from or be transferred into other species under certain set of conditions when the system has reached equilibrium. Kinetic stability may be thought of as a measure of the rate at which a complex forms or decomposes to give other products. Many examples for the existence of polynuclear complexes have been reported but it has been found that mononuclear complexes are formed in a large majority of cases.

Suppose we bring a metal ion M and some monodentate ligand L, together in solution. Assuming that no insoluble products are formed, the stability of the complex is expressed by an equilibrium of the type

$$M + nL \rightleftharpoons ML_n \qquad (2.1)$$

By applying the law of mass action, the equilibrium constant for this may be represented as

$$\beta_n^o = \frac{a_{MLn}}{a_M \cdot a_L^n} \qquad (2.2)$$

where a_M, a_L and a_{ML_n} represent the activities of the metal ion, ligand and complex respectively and β_n^o is the overall thermodynamic stability constant for the reaction. In these and the following equations the co-ordinated water molecules to the metal ion and its charge are omitted in order to simplify the equations.

Reaction (2.1) almost takes place in a stepwise manner

$$M + L \rightleftharpoons ML \tag{2.3}$$

$$ML + L \rightleftharpoons ML_2 \tag{2.4}$$

$$\vdots \quad \vdots \quad \vdots$$

$$ML_{n-1} + L \rightleftharpoons ML_n \tag{2.5}$$

The stepwise stability constant K for the last step is given by the expression

$$K_n = \frac{a_{ML_n}}{a_{ML_{n-1}} \cdot a_L} \tag{2.6}$$

The constant that is determined experimentally is usually the concentration or stoichiometric stability constant β_n in which concentration of the species replace activities. Thus

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \tag{2.7}$$

By applying law of mass action to equations (2.3), (2.4) and (2.5), the stepwise stability constants can be obtained as indicated below.

$$K_1 = \frac{[ML]}{[M][L]} \tag{2.8}$$

$$K_2 = \frac{[ML_2]}{[ML][L]} \tag{2.9}$$

$$\vdots \qquad \vdots$$

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \tag{2.10}$$

and overall stability constant can be expressed as

$$\beta_1 = \frac{[ML]}{[M][L]} \quad (2.11)$$

$$\beta_2 = \frac{[ML_2]}{[M][L]^2} \quad (2.12)$$

. . . .

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \quad (2.13)$$

The overall and stepwise stability constants are related by the equation

$$\beta_n = K_1.K_2.K_3 \ldots\ldots K_n$$

$$= \prod_{i=o}^{i=n} K_i \quad (2.14)$$

where n represents the co-ordination number of the metal ion for a particular ligand, L.

The thermodynamic stability constants which are more important from the thermodynamic and the structural point of view, can be calculated by determining the values of stoichiometric stability constants, corresponding to different ionic strengths and extrapolating it to zero ionic strength either by graphical method[30,47] or by using a least squares treatment[39,44], or using a Debye-Hückel type relation. The values of the thermodynamic stability constants obtained by extrapolation to infinite dilution are more reliable than the values calculated from a single ionic strength, for they are dependent less on the choice of parameters. It is always convenient to determine the stoichiometric stability constant at a particular ionic strength which serves for most of the purposes of the stability constant[8].

A critical description of the various methods used for the determination of stability constants have been provided in various publications of Rossotti and Rossotti[50], Martell and Calvin[38], Jones[23], Murman[42], Ringbom and Harju[49], Yatsimirskii and Vasil'ev[68], Lewis and Wilkins[33] and some of the methods available for calculating the stability constants in these studies of ours are briefly described here.

(i) Molecular Extinction Coefficient Method

The molecular extinction coefficient method has its principle based upon Beer-Lambert's law which states that 'successive increments in the number of identical absorbing molecules in the path of monochromatic radiation absorb equal fractions of the radiant energy traversing them', and can be represented mathematically as

$$A = \log I_o/I = C\epsilon l \qquad (2.15)$$

where A = Absorbance of the solution

I_o = Intensity of the incident beam

I = Intensity of the transmitted beam

C = Concentration of colored substance in moles/litre

l = Depth of solution traversed by light in cms

ϵ = Molecular extinction coefficient, the value of which depends on solvent, temperature and wavelength

The molecular extinction coefficient for a path length of one cm and at a fixed wavelength transforms the above equation into

$$\epsilon = \frac{A}{C} \qquad (2.16)$$

In a complex forming reaction of the type (2.3), the formation constant K, is given by

$$K = \frac{c}{(a - c)(b - c)} \qquad (2.17)$$

where c = concentration of the complex at equilibrium

a = initial concentration of metal ion

b = initial concentration of ligand.

Knowing the values of 'ϵ' and 'A', 'C' can be readily obtained from equation (2.16). Substituting the known values of 'a', 'b' and 'c', the formation constant 'K', is evaluated.

(ii) Mole Ratio Method

The stability constant of the complex can be calculated from the mole ratio curve by using the equation

$$K = \frac{1 - \alpha}{n^n \alpha^{n+1} C^n} \qquad (2.18)$$

where C = concentration of the complex

α = the degree of dissociation, which is expressed by the equation

$$\alpha = \frac{E_m - E_s}{E_m} \qquad (2.19)$$

In this 'E_m' is the absorbance of the complex in the presence of excess of the chelating agent, or metal ion, as the case may be, and 'E_s' is the absorbance of the complex at equilibrium.

(iii) Dey and Banerji's Method

The Dey and Banerji method[5] is a modification of the Anderson and coworker's method[2,3] for the determination of formation constants, in which one of the constituents is coloured. Usually the metal ions are colorless, as dilute solutions of 10^{-4}M or more are used in these studies. With the progressive increase of the metal ion, the concentration of the ligand decreases and it may be assumed that in this part of the Job's curves, where metal ion is in large excess as compared to ligand, almost all the chelating agent is bound to the central metal ion and absorption in this part of curve is solely due to the concentration of complex ion or molecule.

In a complex forming system of the type (2.3), the formation constant 'K' is given by

$$K = \frac{c}{(a-c)(b-c)} \qquad (2.20)$$

where 'c', 'a' and 'b' have their usual meanings as in equation (2.17). Taking two concentrations 'a_1', 'a_2' and 'b_1', 'b_2' of the metal ion and the ligand respectively, which have the same absorbance value i.e. same value of 'c', then

$$K = \frac{c}{(a_1 - c)(b_1 - c)} = \frac{c}{(a_2 - c)(b_2 - c)} \qquad (2.21)$$

or

$$c = \frac{a_1 b_1 - a_2 b_2}{(a_1 + b_1) - (a_2 + b_2)} \qquad (2.22)$$

Knowing the values of 'c', 'a', and 'b', the formation constant 'K' is ascertained from equation (2.20).

Evaluation of Thermodynamic Functions

In order to have the most accurate approach for an investigation of the nature of forces acting within the complex particles when they are formed in solution, it is necessary to know the energy changes accompanying the reactions studied. Change in free energy of formation (ΔG), heat content (ΔH) and entropy (ΔS) of the system are related to the stability constants of metal chelates. By knowing these properties, relevant information can be sought about the nature of bonding between the metal and the ligand.

The change in free energy of formation can be calculated using the van't Hoff isotherm

$$\Delta G = - RT \ln K \qquad (2.23)$$

where R = Universal gas constant

T = Temperature in ^{o}K

The change in heat content is the thermal effect of the complex forming reaction. This can be determined by direct calorimetric method or by means of the equation of an isobaric chemical reaction, from the data on equilibrium constants measured at several temperatures.

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \tag{2.24}$$

where 'T', 'R' and 'K' have their usual significance. Eq. (2.24) can also be written as

$$\frac{d \log K}{d(1/T)} = \frac{\Delta H}{4.57} \tag{2.25}$$

For the calculation of ΔH, a graph of 1/T against log K is constructed. If a comparatively narrow temperature range is chosen for investigation, the value of ΔH remains approximately constant, and the graph obtained is a straight line. The slope of this line is numerically equal to $(-\frac{\Delta H}{4.57})$, from which the value of ΔH can be readily estimated. The value of ΔH, can also be obtained by using the van't Hoff isochore

·679

$$\Delta H = \frac{2.303\ R\ [\log K_2 - \log K_1]\ T_1 T_2}{T_2 - T_1} \tag{2.26}$$

where 'K_1' and 'K_2' are the stability constants at temperatures 'T_1' and 'T_2'.

Knowing the values of the free energy of formation and heat content, the entropy change of the complex forming system is evaluated from the Gibbs-Helmholtz equation

$$\Delta G = \Delta H - T.\Delta S \tag{2.27}$$

Potentiometric Studies

Measurements of the potential of galvanic cells were used to determine the activities of metal and hydrogen ions[11,45] at the end of nineteenth century and were employed in equilibrium investigations of a number of metal ion and proton complexes[10,48,58,64]. The potentiometric method has since been used extensively and now is the most widely used and probably the most accurate method for the determination of stability of metal complexes. At present instead of potential, the pH of the solution is measured, as this is related directly to emf. This method may be used for any complex forming system, provided the complex is soluble in water or in mixed aqueous solution in which the hydrogen ion concentration may be determined potentiometrically. This is based on the fact that the formation of complex directly affects the pH of the solution as most of the chelating agents are either Brønsted acids (or bases) and the formation of complex is accompanied by the displacement of a proton i.e. the pH of the solution is decreased. The reverse is the case with ligands which are basic in character. The magnitude of the observed pH change is related to the metal-ligand binding tendency and may be used to determine the stability constants of various complexes formed in the system.

In 1941, Bjerrum[9] introduced the technique of determining the stepwise stability constant by this method. Calvin and Wilson[13] have calculated through these studies, the degree of complex formation $\bar{n}$, the free ligand exponent pL, and then the stepwise stability constants of the systems. Experimental methods developed by Leden[32], Bjerrum[9] and Fronaeus[16] have been discussed by Sullivan and Hindman[01]. Irving and Rossotti[19] have introduced a volume correction term.

Bjerrum-Calvin pH titration technique[9,13] as modified by Irving and Rossotti[19] was used because it is neither necessary to convert the pH readings to stoichiometric hydrogen ion concentrations, nor to know the stoichiometric concentration of the neutral salt added to maintain the ionic strength. Moreover, the acid dissociation constants of the reagents, which are required in calculations, are determined under the same set of conditions as the formation constants.

Titrations were carried out in aqueous media and sufficient sodium perchlorate was added to give a definite overall ionic strength. To determine the stepwise stability constant, the following mixtures were titrated against standard sodium hydroxide, added in small increments, from a micro-burette with thorough stirring, and then the change in pH was recorded.

Mixture A : 5 ml of 0.2M $HClO_4$ + x ml 2.5M $NaClO_4$ (for maintaining ionic strength)

Mixture B : Mixture A + 75 ml (M/100) ligand solution

Mixture C : Mixture B + 15 ml (M/100) metal ion solution

The mixtures were diluted with double distilled water to a constant volume of 100 ml in all the cases. The metal ligand ratio was kept 1:5, to fulfil the maximum co-ordination number of the metal. Three titration curves were obtained by plotting pH (B) against volume of alkali added.

Proton-Ligand Stability Constant

The average number of protons attached per ligand molecule, $\bar{n}_A$, was evaluated using the method of Irving and Rossotti[19], from which the following equation for '$\bar{n}_A$' is obtained.

$$\bar{n}_A = y + \frac{(V' - V'')(N^o + E^o)}{(V^o + V')\,T_L} \qquad (2.28)$$

where

V' = volume of alkali required to reach a certain pH in mixture A

V'' = volume of alkali required to reach the same pH in mixture B

T_L = total concentration of the ligand

y = total number of dissociable protohs attached per ligand molecule

N^o = normality of alkali

E^o = initial concentration of the free acid

and V^o = total initial volume of mixtures.

For calculating the acid dissociation constant of the ligand, $\bar{n}_A$ is plotted against the pH (known as formation curve of the ligand), and various computational methods, viz. interpolation at half $\bar{n}_A$ values, interpolation at various $\bar{n}_A$ values, and the mid-point slope method were applied to determine the values of protonation constants.

Metal-Ligand Stability Constant

The average number of ligands attached per metal ion is given by

$$\bar{n} = \frac{(V''' - V'')\left[N^0 + E^0 + T_L(y - \bar{n}_A)\right]}{(V^0 + V'')\ \bar{n}_A\ T_M} \qquad (2.29)$$

where T_M = total concentration of metal ion

V'' = volume of alkali required by mixture C to reach the same pH as in mixture A.

The other symbols have their usual meaning.

From the different values of $\bar{n}$, the corresponding values of pL, i.e., the free ligand exponent, were calculated from the equation:

$$pL = \log_{10}\left\{\left[\frac{\sum_{n=0}^{n=j} \beta_n^H \left[1/(\text{antilog } B)\right]^n}{(T_L - \bar{n}\ T_M)}\right] \cdot \frac{V^0 + V'''}{V^0}\right\} \qquad (2.30)$$

where β_n^H is the overall proton-ligand stability constant. Metal-ligand complex formation curves were obtained by plotting '$\bar{n}$' against 'pL' values and then the stepwise metal-ligand stability constants were obtained by the following three computational methods.

(i) Interpolation at half $\bar{n}$ values

According to Bjerrum's approach,

$$\log K_n = pL_{n-\frac{1}{2}} \tag{2.31}$$

when $n = 1$ $\quad \log K_1 = pL_{1/2}$

and $n = 2$ $\quad \log K_2 = pL_{3/2}$

and so the values of $\log K_1$ and $\log K_2$ (and hence $\log \beta_2$) can be obtained by reading the values of pL corresponding to the points, where $\bar{n} = 0.5$ and 1.5 respectively. This method is applicable in cases where $K_1/K_2 \gg 10^{2.5}$. However this method suffers from a disadvantage as only one or two points are used in the whole formation curve for calculating the stability constants.

(ii) Interpolation at various $\bar{n}$ values

In this method, use is made of the Irving and Rossotti equations

$$\log K_1 = pL_{1-d} + \log 1-d/d \tag{2.32}$$

and $$\log K_2 = pL_{1+d} - \log 1-d/d \tag{2.33}$$

In these equations, the value of 'd' varies from 0.1 to 0.9 and values of $\log K_1$ and $\log K_2$ are the average values of the values so obtained. This method is justified only when $K_1/K_2 > 10^4$. The calculated values of stability constants show a drift from the true value when $K_1/K_2 < 10^4$.

(iii) Mid-point slope method

At the mid point of the formation curve where $\bar{n} = 1$

$$K_1K_2 [L_1]^2 = 1 \qquad (2.34)$$

$$\text{or} \quad \log K_1K_2 = 2\ pL_1 \qquad (2.35)$$

pL_1 = free ligand exponent at a point where $\bar{n} = 1$.

Also the slope of the formation curve at a point where $n = 1$ is given by the equation

$$D = -\frac{4.606}{2+\sqrt{\frac{K_1}{K_2}}} \qquad (2.36)$$

'D' being the slope of the formation curve at $\bar{n} = 1$.

The value of $\log K_1$ and $\log K_2$ can then be evaluated by using the equations (2.35) and (2.36) simultaneously.

This method has a limitation as it is applicable only when K_1/K_2 lies between 10^3 and 10^{-2}.

The Present Work

A thorough survey of literature on Chromotrope 2R and Bromopyrogallol Red, reveals the need for the study of some complex forming systems not reported earlier. In spite of the large amount of work recorded, regarding their use as analytical reagents, attempts have not been made as yet to study the nature, composition and stability of these systems. The aim of present work is to study systematically, the composition, stability and thermodynamic functions related to these systems. In the course of our studies, it was observed that in some cases the molecular extinction coefficient was very high, and this enabled the spectrophotometric determination of these metals in trace amounts. Attempts have also been made to study the interference of certain foreign ions in determination. Moreover, stepwise stability constants of chromotrope 2R chelates of some bivalent metals have been ascertained by using the Bjerrum-Calvin pH titration technique as modified by Irving and Rossotti(19).

The following systems have been investigated in detail and are described in the succeeding chapters.

(1) Chromotrope 2R chelates of Copper (II), Ytterbium (III), Aluminium (III), Gallium (III), Zirconium (IV) and Hafnium (IV).

(2) Bromopyrogallol Red chelates of Lead (II), Nickel (II), Cobalt (II), Ytterbium (III), Praseodymium (III) and Tungsten (VI).

(3) Potentiometric study of chromotrope 2R chelates of Uranyl (II), Beryllium (II), Copper (II), Lead (II), Cobalt (II), Nickel (II), Zinc (II), Cadmium (II) and Mercury (II).

* * *

REFERENCES

1. Ahrland, S. Acta Chem. Scand., 3, 347 (1949).

2. Anderson, R.C. and Foley, R.T. J. Am. Chem. Soc., 70, 1195 (1948); 71, 909 (1949).

3. Anderson, R.C. and Turner, S.E. J. Am. Chem. Soc., 71, 912 (1949).

4. Asmus, E. Z. Anal. Chem., 178, 104 (1960); 183, 321 (1961); 190, 390 (1962).

5. Banerji, S.K. and Dey, A.K. Proc. Symp. Chem. Co-ordination Compounds, Agra, 1959 (2), 198 (1960).

6. Bent, H.E. and French, C.L. J. Am. Chem. Soc., 63, 568 (1941).

7. Betts, R.H. and Michels, R.K. J. Chem. Soc., 5286 (1949).

8. Biedermann, G. and Sillen, L.G. Arkiv. Kemi., 5, 425 (1953).

9. Bjerrum, J. Kgl. danske videns kab, Sals Kab. Mat.-Fys. Medd. 22, 4 (1944).
Chem. Rev., 46, 381 (1950).
'Metal amine formation in aqueous solution', P. Haase, Copenhagen (1941).

10. Bodländer, G. and Storbeck, O. Z. anorg. Chem., 31, 1 (1902).

11. Böttger, W. Z. physik. Chem. Leipzig, 24, 253 (1897).

12. Buděšinský, B. Z. Anal. Chem., 209, 379 (1965).

13. Calvin, M. and Wilson, K.W. J. Am. Chem. Soc., 67, 2003 (1945).

14. Chernyaev, I.I. and Khorunzhenkov, S.I. Bull. Inst. Plat., No.7, 98 (1929).

15. Deford, D.D. and Hume, D.N. J. Am. Chem. Soc., 73, 5321 (1951).

16. Fornaeus, S. 'Thesis Komplex system Hos Kopper' Lund (1948).

17. Frank, H.S. and Oswalt, R.L. J. Am. Chem. Soc., 69, 1321 (1947).

18. Harvey, A.E. and Manning, D.L. J. Am. Chem. Soc., 72, 4488 (1950); 74, 4744 (1952).

19. Irving, H. and Rossotti, H.S. J. Chem. Soc., 3397 (1953); 2904 (1954).

20. Janssen, M.J. Rec. Trav. Chim., 75, 1397 (1956).

21. Job, P. Ann. Chim., 9, 113 (1928).

22. Jones, M.M. J. Am. Chem. Soc., 81, 3188 (1959); 81, 4485 (1959).

23. Jones, M.M. 'Elementary Co-ordination Chemistry', Prentice-Hall Inc. (1964).

24. Jones, M.M. and Innes, K.K. J. physik. Chem., 62, 1005 (1958).

25. Katzin, L.I. and Gebret, E. J. Am. Chem. Soc., 72, 5455 (1950).

26. Kharlamov, I.P. 'Spectrophotometric analysis of alloys', Metallurgia, Moscow, pp. 208 (1968).

27. Kingery, W.D. and Hume, D.N. J. Am. Chem. Soc., 71, 2393 (1949).

28. Koreman, I.M. 'Fotometricheskii, Analiz. Methody opredeleniya Organicheskikh Seedineni', Khimiyia, Moscow, pp. 343 (1970).

29. Kōrtum, G. 'Kolorimetric, photometric und spectrophotometric', Springer Verlag, Berlin (1955).

30. Kraus, K. and Nelson, F. J. Am. Chem. Soc., 72, 3901 (1950).

31. Langmyhr, F.J. and Klausen, K.S. Anal. Chem. Acta, 28, 301 (1963).

32. Leden, I. Z. physik. Chem., A188, 160 (1941).

33. Lewis, J. and Wilkins, R.G. 'Modern Co-ordination Chemistry', Interscience Publishers, Inc., N.Y. (1960).

34. Ley, H. Z. Electrochem., 10, 954 (1904).

35. Ley, H. Ber., 42, 354 (1909).

36. Lingane, J.J. Chem. Rev., 29, 1 (1941).

37. Marczenko, Z. 'Calorimetric determination of elements', WNT, Warsaw, pp. 718 (1968).

38. Martell, A.E. and Calvin, M. 'Chemistry of metal chelate Compounds', Prentice-Hall Inc., Englewood Cliffs, N.J., pp. 175 (1952).

39. Millburn, R.M. and Vosburgh, W.C. J. Am. Chem. Soc., 75, 2449 (1953).

40. Molland, J. J. Am. Chem. Soc., 62, 54 (1940).

41. Morze, H. Z. Phys. Chem., 41, 709 (1902).

42. Murman,R.K. 'Inorganic complex compounds', Reinhold Publishing Corp., Chapman and Hall Ltd., London (1964).

43. Naganen, R. Acta Chem. Scand., 5, 139 (1951).

44. Nasanen, R. Acta Chem. Scand., 3, 179 (1949); 4, 140 (1950); 7, 1261 (1953); 8, 112 (1954).

45. Nernst, W. Z. physik. Chem. Leipzig, 4, 129 (1899).

46. Newman, L. and Hume, D.N. J. Am. Chem. Soc., 79, 4571 (1957).

47. Newton, T.W. and Arcand, G.M. J. Am. Chem. Soc., 75, 2449 (1953).

48. Prideaux, E.B.R. J. Chem. Soc., 99, 1224 (1911).

49. Ringbom, A. and Harju, L. Anal. Chim. Acta, 59, 33 (1972).

50. Rossotti, F.J.C. and Rossotti, H. 'The determination of stability constant', McGraw-Hill, N.Y. (1961).

51. Rossotti, F.J.C. and Rossotti, H. Acta Chem. Scand., 9, 1166 (1955).

52. Schläfer, H.L. 'Komplex bildun in losung', Springer Verlag, Berlin (1961).

53. Schläfer, H.L. and Kling, O. Angew. Chem., 68, 667 (1956).

54. Schubert, J. J. Phys. Colloid Chem., 52, 340 (1948).

55. Schubert, J. and Richter, J.W. J. Phys. Colloid Chem., 52, 350 (1948).

56. Schubert, J. and Richter, J.W. J. Am. Chem. Soc., 70, 4259 (1948).

57. Seth, R.L. and Dey, A.K. J. Inorg. Nucl. Chem., 17, 312 (1961).

58. Sherrill, M.S. Z. physik. Chem. Leipzig, 43, 705 (1903).

59. Skyes, K.W. and Fudge, H.J. J. Chem. Soc., 124 (1952).

60. Sommer, L. and Hniličvkov, M. Bull. Soc. Chim. (France), 36, (1959).

61. Sullivan, J.C. and Hindman, J.C. J. Am. Chem. Soc., 74, 6091 (1952).

62. Taube, H. J. Am. Chem. Soc., 70, 1215 (1948).

63. Vosburgh, W.C. and Cooper, G.R. J. Am. Chem. Soc., 64, 1630 (1942).

64. van Euler, H. Ber., 36, 3400 (1903).

65. Watkins, K.O. and Jones, M.M. J. Inorg. Nucl. Chem., 24, 1235 (1962).

66. Woldbye, F. Acta Chem. Scand., 9, 299 (1955).

67. Yatsmirskii, K.B. Zhur. neorg. Khim., 10, 2306 (1956).

68. Yatsmirskii, K.B. and Vasil'ev, V.P. 'Instability constants of complex compounds', D. Van Nostrand Co., Inc., N.J. (1960).

69. Yoe, J.H. and Jones, A.L. Ind. Eng. Chem., Anal. Ed., 16, 111 (1944).

* * *

CHAPTER III

SPECTROPHOTOMETRIC STUDIES OF METAL CHELATES OF CHROMOTROPE 2R

One of the important aspects of organic complexing agents is their application in colorimetric analysis. The change in colour by the interaction of metal ion with ligand in solution, is the basis of chromogenic reactions, in which measurement of optical density is possible. The use of colour in chemical analysis is as old as the science of chemistry itself. Recently a great impetus to the studies involving absorbance measurements has been offered by the availability of high precision, sensitive and automatic recording spectrophotometers.

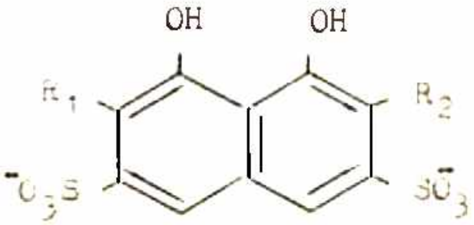
Among the chromogenic reagents, many dyes have offered considerable interest, on account of their tendency of forming metal-dye complexes in solution. In the earlier stages of studies of metal-dye complexes, there was a confusion over the nature of association. Blitz[8] and Weiser[54] expressed doubts about the definite chemical nature of the products formed. They concluded from their studies that the association is purely on account of absorption of metal ion on the dye. Liebermann[24] and Werner[55] considered these as distinct chemical compounds and according to the present ideas, there is a definite bond between the metal and the ligand.

While working with several dyes as a chromogenic reagent for complexation, Green[17], Meyer and Bradshaw[28] and Larson and Hirozawa[23], observed the non-stoichiometric compositions for these complexes, particularly when the solutions of the ligand employed are not too dilute. These deviations were attributed due to the hydrolysis of the metal ion. However, Dey[3] and coworkers concluded from their conductance studies that these ligands behave as colloidal electrolytes. They recommended the use of very dilute solutions of the order of 10^{-4}M, when these ligands behaved as true electrolytes and stoichiometric compositions are observed.

Chromotropic acid is well known as a chromogenic reagent for the determination of several metal ions[3,37,39,47]. In a search for new and potentially useful reagents with better sensitivity and selectivity, many mono-(arylazo) and bis-(arylazo) dyes of chromotropic acid have been synthesised and are in wide use for the determination of numerous[14,26,29,53,56] ions. Recently many reviews have appeared in literature which summarise the co-ordination chemistry and analytical applications of these azo dyes[6,9,12,22,31,40,48]. Barnard and Flaschka[4] have dealt with at considerable length the preparation and analytical applications for the determination of several metal ions individually with various mono-(arylazo) and bis-(arylazo) derivatives of chromotropic acid. High sensitivity, good selectivity and ease of synthesis are some of the factors which are responsible for the widespread use of these chromogenic reagents.

These chromogenic reagents can be divided into the following three groups.

I. 3-arylazo and 3,6-bis (arylazo) derivatives in which the aryl group carries no donor group at the ortho position to the azo link.

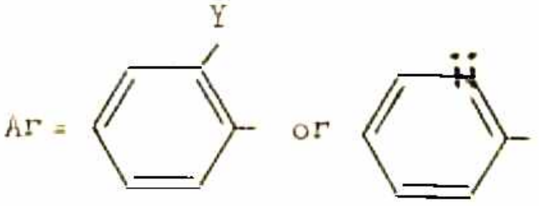


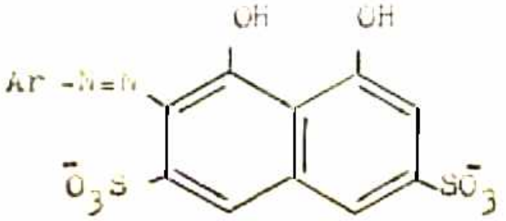
R_1 = Ar-N = N-

R_2 = R_1 or H

Ar = C_6H_5- or $C_{12}H_{11}$ - etc.

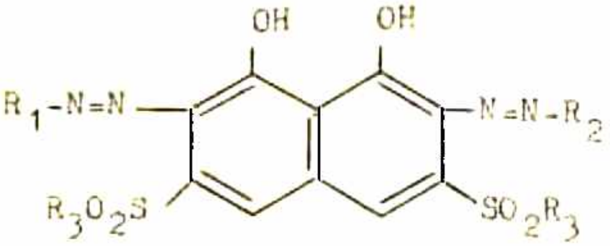
II. 3-arylazo derivatives in which the aryl substituent carries a donor group ortho to the azo group.

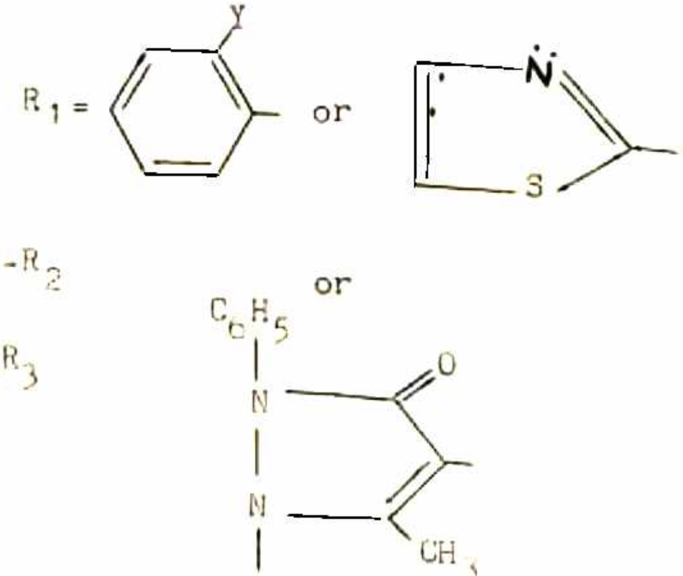




Y = a donor group e.g.
-AsO(OH)$_2$, -PO(OH)$_2$,
-COOH

III. 3,6-bis (arylazo) derivatives in which at least one of the aryl substituent carries a donor group ortho to the azo group.





Y = a donor group e.g. $-OH$, $-SH$, $-COOH$, $-SO(OH)_2$,
$-PO(OH)_2$, $-AsO(OH)_2$, $-B(OH)_2$, $-CH_2N(CH_2COOH)_2$, $-NO_2$ etc.

$R_2 = R_1$ or phenyl, p-substituted phenyl

$R_3 = -OH$, $-NH_2$ or C_6H_5NH-

Among these dyes chromotrope 2R (C.I. 16570, Acid Red 29) i.e. 4,5-dihydroxy-3-phenyl azo-2,7-naphthalene-disulfonic acid, abbreviated as CTR, in this thesis, is the one which has been investigated for the spectrophotometric studies of some metal complexes.

Popa and coworkers have made extensive studies on the metal complexes of chromotrope 2R. In the year 1961 they studied the metal complexes of this reagent with palladium[34] and beryllium[33]. From the results obtained, it has been observed that the method for the determination of palladium is very sensitive, selective and is applicable even in the presence of 650 fold excess of platinum.

Koreman[21] et al. in a search for a reagent for thallium has tried various chromotropic azo dyes. Popa[35] has carried out the spectrophotometric determination of lanthanium at pH 8.0 using borax-boric acid buffer and has given the composition for the metal chelate as 1:1. Prakash and Mushran[36] have made photometric studies of the composition and stability of Iron, Cobalt and Nickel complexes of chromotrope 2R. Shah and Sangal[41] carried out the preliminary investigations on the complexation between azophenyl chromotropic acid and Cu(II), Zn(II), Ga(III), Al(III), Zr(IV), Hf(IV), Fe(III), Co(II), Ni(II), Pd(II), Pr(III), Nd(III), Sm(III), Th(IV) and UO_2(II). Shibata and coworkers[45] have reported the spectrophotometric determinations of Mg(II) in aqueous acetone medium at pH 10.8 and reported a method by which magnesium in traces (0.01 ppm), can be determined with great ease. Moreover, the method is applicable to the direct determination of magnesium in zinc and aluminium alloys.

The metal complexes of rare-earths with chromotrope 2R have been studied by Sangal et al.[11,42,44]. They have made extensive studies on its chelates with Praseodymium, Neodymium, Samarium and Europium and observed that Cu(II), Be(II), Al(III), Ga(III), In(III), Zr(IV), W(VI), Ni(II), Co(II), Pt(IV), La(III), Ce(III), tellurate, citrate, tartrate, oxalate and phthalate interfere in all concentrations in the photometric determination, while Ba(II), Sr(II), Co(II), Br^- and I^- interfere only when present in large amounts. Recently they have reported the composition and stability constants for cerium-chromotrope 2R chelate[43] and worked out suitable conditions for the determination of the metal in micro amounts. Mushran[52] has studied the 1:1 metal to ligand complexes of VO^{+2} with chromotrope 2R, chromotrope 2B and SPANDS at pH 4.4 and have observed the stability constants in the order CTR > SPANDS > CBT and inferred this order as being due to the electrophilic character of the p-substituted group in the ligand molecules.

Apart from the use of chromotrope 2R as a chromogenic reagent for the photometric studies of various metal complexes, it is widely used as a stain[10,27,46] in various biological processes. Betzer[7] has used CTR in fuel cell electrode manufacture for metallic coating. In a recent communication Jain and coworkers[19] have studied the ultrasonic effect on aqueous solution of chromotrope 2R and observed that the decolourisation of aqueous solution of CTR with H_2O_2 on exposure to ultrasonic wave increases with sound intensity and is slower in the presence of nitrogen than in the presence of oxygen. Dioxane, ether, acetone, acrylamine and allylthiourea inhibit decolourisation.

Although some work has been reported on the use of chromotrope 2R as a chromogenic reagent for the photometric determination of various metal ions, but no work has been done on the composition, stability and thermodynamic functions (ΔG, ΔH and ΔS) of the copper, aluminium, gallium, ytterbium, zirconium and hafnium chelates. This, therefore has been undertaken along with the photometric determination, wherever possible. In order to reduce the size of the thesis, the experimental data have been represented graphically.

EXPERIMENTAL

Instruments

All the absorbance measurements have been made on a Perkin-Elmer UV-VIS (model 139) spectrophotometer, using one cm matched quartz cells, equipped with thermoplates to stabilise the temperature. pH measurements have been made on a Beckman (model H2) pH meter using glass-calomel electrode assembly.

Chemicals

Stock solutions of copper sulphate (G.R., E. Merck), ammonium aluminium sulphate (BDH, AnalaR), gallium chloride (E. Merck), ytterbium chloride (K and K Laboratories, Inc., N.Y.), zirconyl chloride (BDH, AnalaR) and hafnyl chloride (A.D. Mackey and Co. Inc., N.Y.) were prepared in carbon dioxide free double distilled water and their metal ion contents determined by usual methods. A 10^{-4}M solution of purified CTR was prepared in double distilled water. Sodium perchlorate (Reidal) solution was used to maintain the constant ionic strength. Solutions of diverse ions were prepared using AnalaR grade salts of the corresponding metal ions.

Preliminary Investigation of the Ligand

Effect of pH on chromotrope 2R solution: In order to study the effect of pH on the reagent, a series of solutions containing the same concentration of the ligand were prepared and their pH was adjusted to different values with AnalaR grade hydrochloric acid and sodium hydroxide. From the observations it can be concluded that between a pH range 2.0-11.5 the reagent has λ_{max} in the range 510-520 nm i.e. the variation of pH in the range described above causes no shift in value of λ_{max}.

Colour formation with inorganic cations

Before going into the detailed study of metal chelates of CTR, it was thought necessary to study the colour formation of reagent with various metal ions. For this a solution of chromotrope 2R was taken in different test tubes and to this were added various metal ion solutions. The colour developed was noted visually and compared against a reagent blank. The results obtained have been summarized in Table 3.1.

RESULTS AND DISCUSSION

Conditions of Study

The solutions of metal as well as the ligand were mixed in certain proportions by diluting with CO_2 free double distilled H_2O. All the studies were carried out at a temperature $25\pm0.1^{\circ}C$. The solutions were kept in a constant temperature precision thermostat (Forma Scientific, model 2095), for half an hour to attain the equilibrium. The pH of the solutions was maintained constant generally by hexamine-perchloric acid buffer, after a preliminary study of the pH effect by using sodium hydroxide and hydrochloric acid had been made. In some cases sodium hydroxide and hydrochloric acid have been used to adjust the pH of the solutions. The conditions of study for all the metals are given in Table 3.2.

Effect of Time and Temperature

It was observed that the formation of these chelates was instantaneous. Moreover, the studies reveal that there was no significant change in the value of absorbance even after twelve hours. The change of temperature has no measurable effect on the absorbance when the ligand was present in a large excess. The order of addition of reagents does not have any appreciable effect on the absorbance of chelates. However, for constant environmental conditions, the metal ions were added to the ligand.

Effect of pH

Solutions containing the same concentration of the reagent and metal ions were prepared at different pH values. The absorbance of these solutions were measured at different wavelengths, after they have attained equilibrium. All the complexes show λ_{max} at 530 nm whilst the ligand shows a λ_{max} at 510 nm against a water blank. Absorbance studies have been made at 580 nm in all cases, where the absorbance due to the ligand itself was found negligible. The pH range in which the chelates are most stable, along with the pH at which the subsequent studies have been undertaken, are recorded in Table 3.2.

Nature of the Complexes Formed

The method of Vosburgh and Cooper has been employed for the determination of the nature of the complexes formed. For this, mixtures containing various proportions of metal and ligand (2:1, 1:0, 1:1, 1:2, 1:3, etc.) have been prepared. The pH of the solutions was adjusted within ±0.1 of required pH, with buffers of the corresponding pH values. The optical density of these solutions was recorded at different wavelengths and from the results it was observed that only one complex is formed under the conditions of study in the systems under investigations. The results have been graphically represented in Plates 1-6 (Fig. A).

Stoichiometry of the Complexes

Three independent methods viz. Job's method of continuous variation, mole ratio method and slope ratio method have been employed to study the empirical formula of the complexes formed, under the experimental conditions.

Job's Method of Continuous Variation

Job's method using equimolecular and nonequimolecular solutions have been used to study the composition of the metal chelates. The metal and the ligand were mixed in fixed proportions (1:9, 1:4, 1:3, 1:2, 1:1.5, 1:1, 1.5:1, 2:1, 3:1, 4:1 and 9:1) so that the total concentration of the metal and the ligand was constant in all the solutions. The total volume was made upto 25 ml and pH adjusted with appropriate buffers. The absorbance was measured for these solutions at wavelengths 570, 580 and 600 nm. However, results obtained only at one wavelength i.e. at 580 nm have been represented graphically in Plates 1-4(Fig. B) and Plates 5,6

(Fig. B and Fig. E). The results reveal that 1:1 (metal:ligand) complexes are formed with copper (II), aluminium (III), ytterbium (III), zirconium (IV) and hafnium (IV), and a 1:2 complex (metal:ligand) has been observed in the case of gallium (III).

Mole Ratio Method

A series of solutions was prepared from the respective metal ion and chromotrope 2R in such a way that the molar ratio of the reagent to the metal varies from 1:0.25 to 1:6.0. The absorbance of these mixtures was measured against water or the reagent as a blank at 570, 580 and 600 nm. Some of the studies performed, have been graphically represented in Plates 1-4 (Fig. C), Plates 5 and 6 (Fig. D).

The results obtained corroborate the composition as obtained by Job's method.

Slope Ratio Method

In this method of Harvey and Manning, the volume of the variable component was varied from 0.0 to 10 ml in the presence of an excess of the concentration of the other component. The ratio of the slopes of the two straight lines obtained by plotting the absorbance against the volume gives the same molar ratio of the metal to ligand as obtained by the other two methods. The results obtained have been graphically represented in Plates 1-4 (Fig. D).

Evaluation of the Stability Constants

The value of log K has been determined by the following three methods described in detail in Chapter II.

(1) Molecular extinction coefficient method.

(2) Mole ratio method.

(3) Dey and coworker's method.

The results obtained have been recorded in Table 3.3, from which it is quite apparent that the value of log K, evaluated from the above methods are in a quite good agreement.

Thermodynamic Functions of the Complexes

The free energy of complex formation (ΔG) is related directly to the stability constant by the expression.

$$\Delta G = -RT \ln K$$

R = universal gas constant

T = temperature in absolute degrees.

For the determination of enthalpy change (ΔH) and entropy change (ΔS), which are accompanied with the complex formation, the value of log K was determined at different temperatures (from 15°-$35^{\circ}C$), at a constant ionic strength 0.1. From the slope of the curves obtained by plotting log K against 1/T, the change in enthalpy has been determined by assuming that the value of ΔH remains constant over the range of temperature studied. The entropy change has, then been determined by using Gibbs. Helmholtz equation

$$\Delta G = \Delta H - T\,\Delta S$$

or $$\Delta S = \Delta H - \Delta G/T$$

The results obtained are given in Tables 3.4-3.7, and represented graphically in Plates 1-4 (Fig. F).

Analytical Applications

Experiments were performed to test the suitability of metal complexes of chromotrope 2R for the photometric determination of metals. Cu(II), Al(III), Yb(III), Zr(IV), Hf(IV) and Ga(III) were investigated for their photometric determination.

Effect of Reagent Concentration

The effect of reagent concentration was observed by varying the concentration of the reagent with respect to the metal ions. It was observed that upto a certain fold molar excess of reagent concentration over that of the metal ion concentration, the value of absorbance increases and then it begins to decrease. The concentration at which the maximum absorbance has been obtained has been kept for the photometric determination of the metal ions. The results reveal that at least ten fold molar excess should be kept in the case of Cu(II), Al(III), Yb(III), Zr(IV) and Hf(IV), whilst a fifty fold molar excess is necessary, for determination of gallium.

Beer's Law and Sensitivity

Calibration curves were prepared for the determination of various metal ions, by varying the concentration of the cations in a large excess of the reagent. The Beer's law is followed upto the portion of the curve upto which the concentration was a linear function of the absorbance. The effective range for the photometric determination was determined with the help of Ringbom plot. The molar absorbtivity or molecular extinction coefficient and sensitivity of the colour reactions, as defined by Sandell , along with the effective range for the photometric determination of various metal ions have been given in Table 3.8.

The Effect of Diverse Ions

The effect of diverse ions was examined in the photometric determination of aluminium, gallium and ytterbium. These metals were selected because of their high molar extinction coefficient. A solution containing a known concentration of metal ion and the dye was taken. The tolerance limit was tentatively taken as the concentration of the foreign ion which affects the absorbance of the metal ligand system by less than ±2%. The results have been tabulated in Tables 3.9-3.11.

Comparison with other Methods

Several sensitive reagents have been used for the determination of aluminium, gallium and ytterbium. The proposed method is simple, rapid and sensitive, but not selective due to large interference by foreign ions. The selectivity can be improved in the determination of these metal ions by suitable masking. Table 3.12 gives a comparative account of the molar absorbtivities of some reagents, which are used for the photometric determination of these metal ions. The results therein reveal that the method using chromotrope 2R as a chelating agent for the photometric determination is comparable in sensitivity with the most of the reagents used for their determination.

÷:÷÷:÷÷

PLATE No. 1

Fig. A. Absorption curves of mixtures of Copper and Chromotrope 2R.

Curve 1. $T_L = 12.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 2. $T_L = 8.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 3. $T_L = 4.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 4. $T_L = 4.0\times10^{-5}M$ $T_M = 0.0\times10^{-5}M$

Fig. B. Job's curves (equimolecular and nonequimolecular solutions) for Cu:CTR chelate.

Curve 1. $T_L = T_M = 4.0\times10^{-4}M$ $\rho = T_L/T_M = 1.0$

Curve 2. $T_L = T_M = 2.0\times10^{-4}M$ $\rho = T_L/T_M = 1.0$

Curve 3. $T_L = 2.0\times10^{-4}M$ $T_L = 4.0\times10^{-4}M$

$\rho = T_L/T_M = 0.5$

Fig. C. Mole ratio curves for Cu-CTR system.

Curve 1. Concentration of constant component (T_L) $= 1.0 \times 10^{-4}M$

Curve 2. Concentration of constant component (T_L) $= 0.6 \times 10^{-4}M$

Fig. D. Slope ratio curves for Cu-CTR system.

Concentration of constant component $= 2.0\times10^{-4}M$

Concentration of variable component $= 4.0\times10^{-5}M - 2.0\times10^{-5}M$

Curve 1 = metal varying

Curve 2 = ligand varying

Fig. E. Beer's law plot for Cu-CTR system.

Fig. F. Plot of log K vs. 1/T.

FIG. A

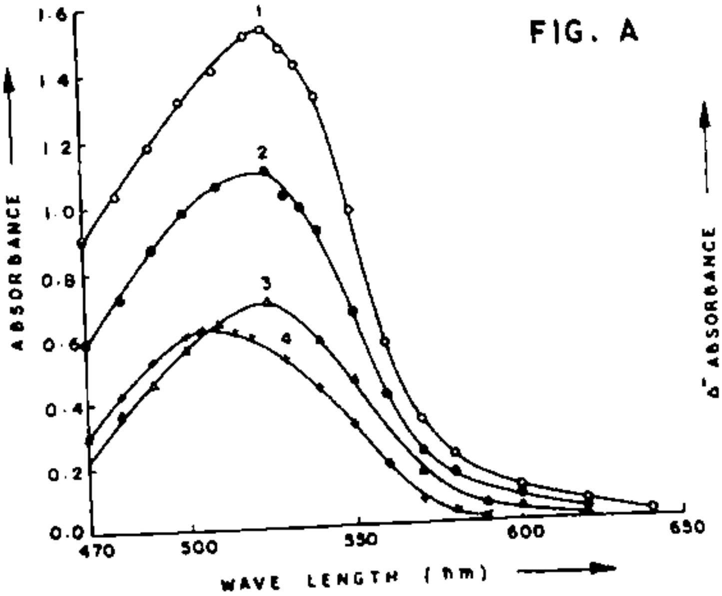


FIG. B

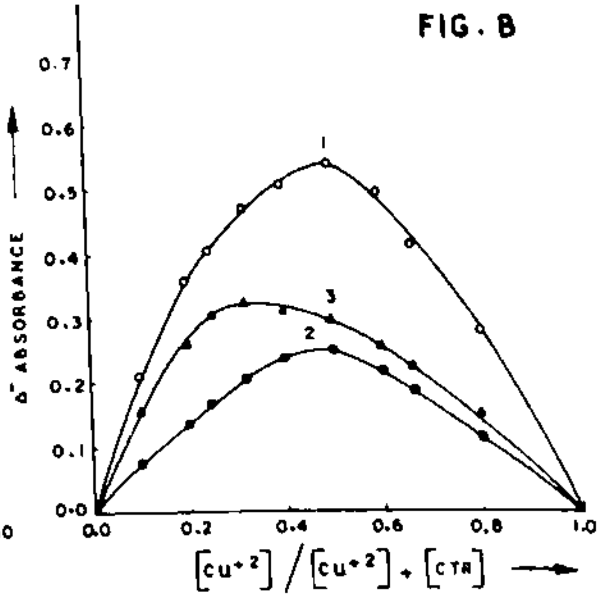


FIG. D

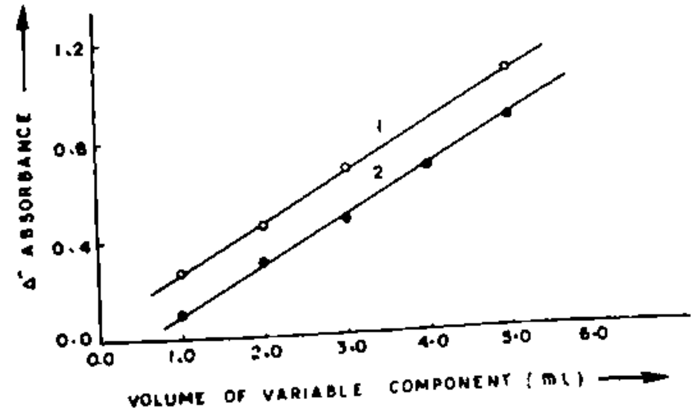


FIG. C

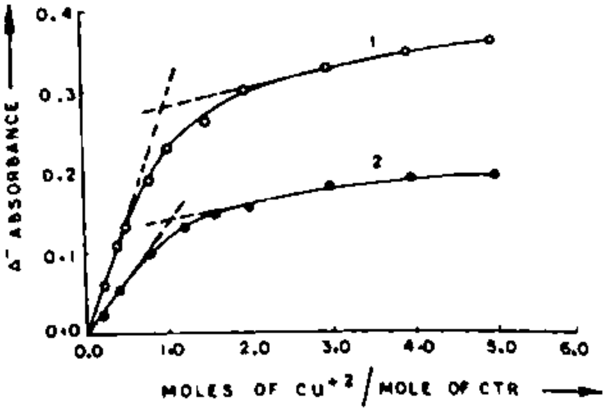


FIG. E

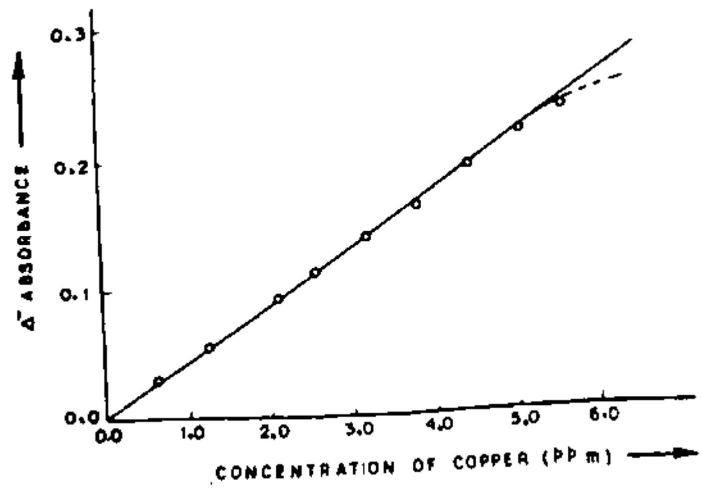


FIG. F

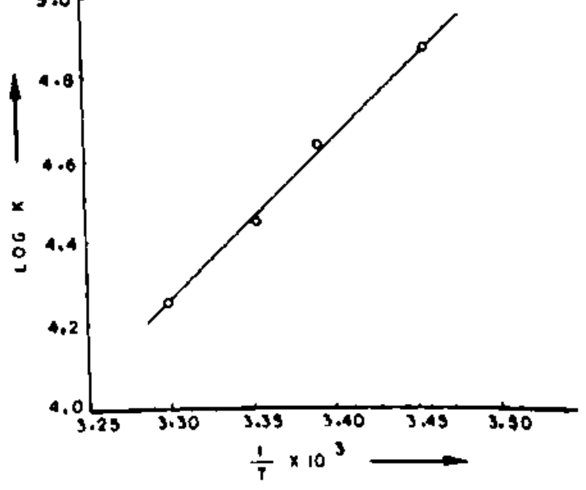


PLATE NO. I

PLATE No. 2

Fig. A. Absorption curves of mixtures of Aluminium and Chromotrope 2R.

Curve 1. $T_L = 12.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 2. $T_L = 8.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 3. $T_L = 4.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 4. $T_L = 4.0\times10^{-5}M$ $T_M = 0.0\times10^{-5}M$

Fig. B. Job's curves (equimolecular and nonequimolecular solutions) for Al-CTR chelate.

Curve 1. $T_L = T_M = 1.25\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 2. $T_L = T_M = 1.00\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 3. $T_L = T_M = 0.833\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 4. $T_L = 1.0\times10^{-4}M$ $T_M = 2.0\times10^{-4}M$

$p = T_L/T_M = 0.5$

Fig. C. Mole ratio curves for Al-CTR chelate.

Concentration of constant component = $8.0\times10^{-5}M$

Curve 1 = at 580 nm

Curve 2 = at 600 nm

Fig. D. Slope ratio curves for Al-CTR chelate

Concentration of constant component = $1.0\times10^{-4}M$

Concentration of variable component = $8.0\times10^{-6}M$ - $4.0\times10^{-5}M$

Curve 1 = metal varying

Curve 2 = ligand varying

Fig. E. Beer's low plot for Al-CTR chelate.

Fig. F. Plot of log K vs. 1/T.

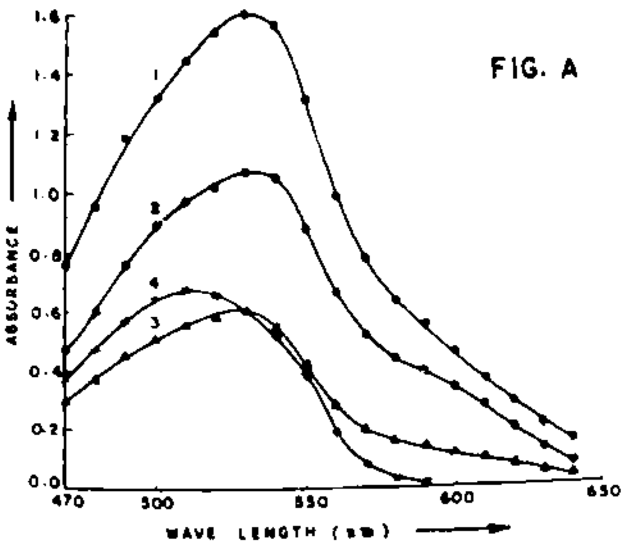


FIG. A

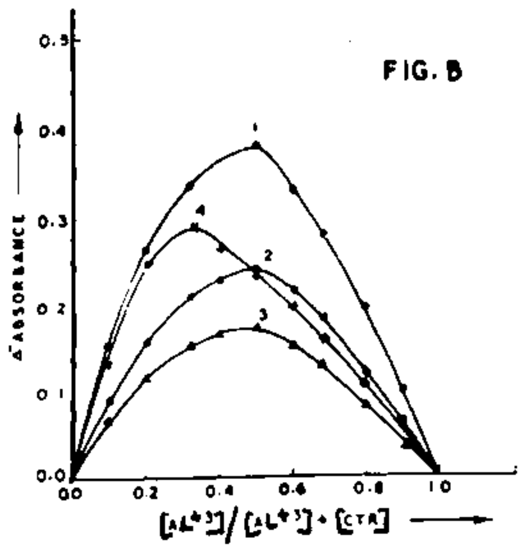


FIG. B

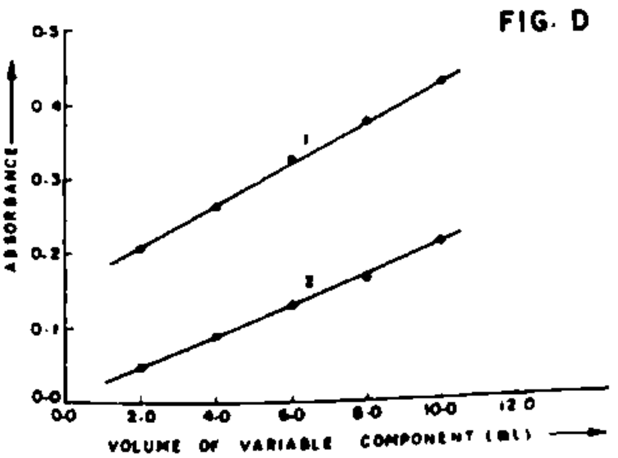


FIG. D

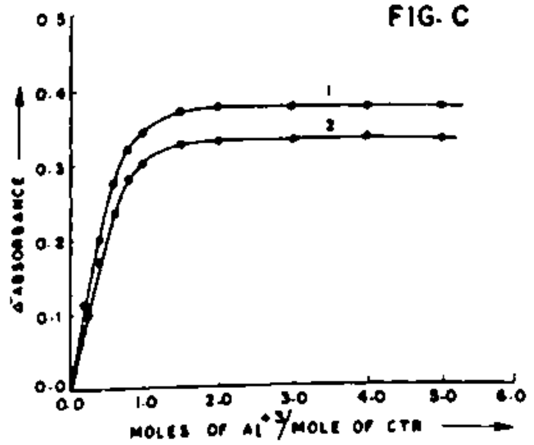


FIG. C

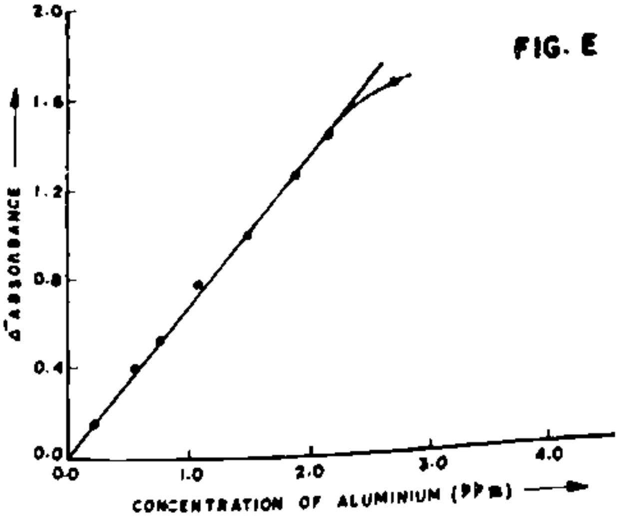


FIG. E

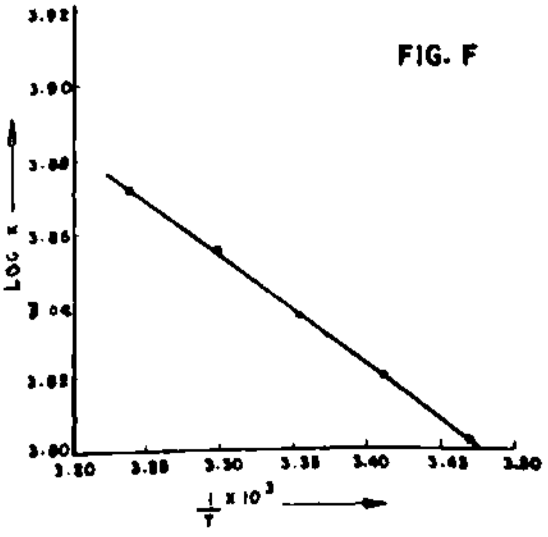


FIG. F

PLATE NO. 2

PLATE No. 3

Fig. A. Absorption curves of mixtures of gallium and chromotrope 2R.

Curve 1. $T_L = 12.0\times10^{-4}M$ $T_M = 4.0\times10^{-4}M$
Curve 2. $T_L = 8.0\times10^{-4}M$ $T_M = 4.0\times10^{-4}M$
Curve 3. $T_L = 4.0\times10^{-4}M$ $T_M = 4.0\times10^{-4}M$
Curve 4. $T_L = 4.0\times10^{-4}M$ $T_M = 0.0\times10^{-4}M$

Fig. B. Job's curves (equimolecular and nonequimolecular solutions) for Ga-CTR chelate.

Curve 1. $T_L = T_M = 2.0\times10^{-4}M$ $p = T_L/T_M = 1.0$
Curve 2. $T_L = T_M = 1.25\times10^{-4}M$ $p = T_L/T_M = 1.0$
Curve 3. $T_L = T_M = 1.00\times10^{-4}M$ $p = T_L/T_M = 1.0$
Curve 4. $T_L = 2.0\times10^{-4}M$ $T_M = 1.0\times10^{-4}M$
$p = T_L/T_M = 2.0$

Fig. C. Mole ratio curves for Ga-CTR chelate.

Curve 1. Concentration of constant component $(T_L) = 8.0\times10^{-5}M$

Curve 2. Concentration of constant component $(T_L) = 6.0\times10^{-5}M$

Fig. D. Slope ratio curves for Ga-CTR system.

Concentration of constant component $= 1.0\times10^{-4}M$
Concentration of variable component $= 8.0\times10^{-4}M - 4.0\times10^{-4}M$

Curve 1 = metal varying
Curve 2 = ligand varying

Fig. E. Ringbom plot for Ga-CTR system

Fig. F. Plot of log K vs. 1/T.

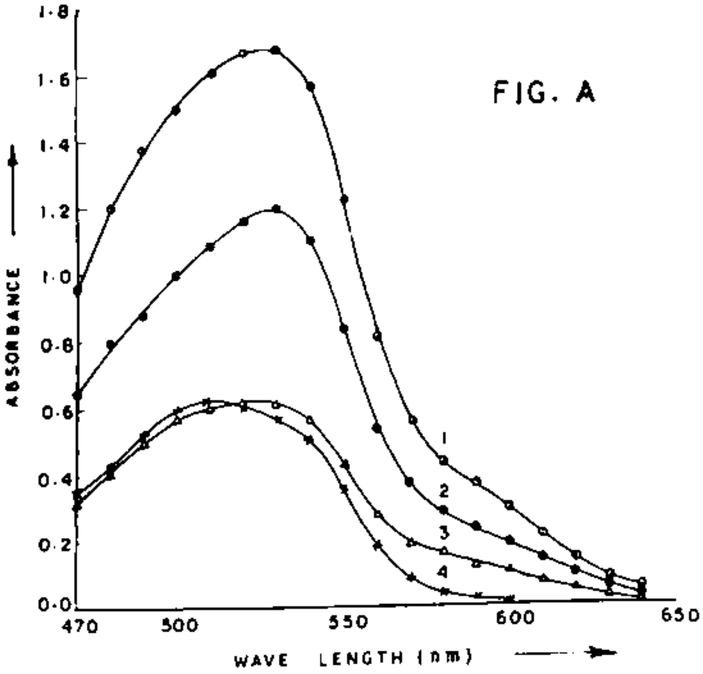


FIG. A

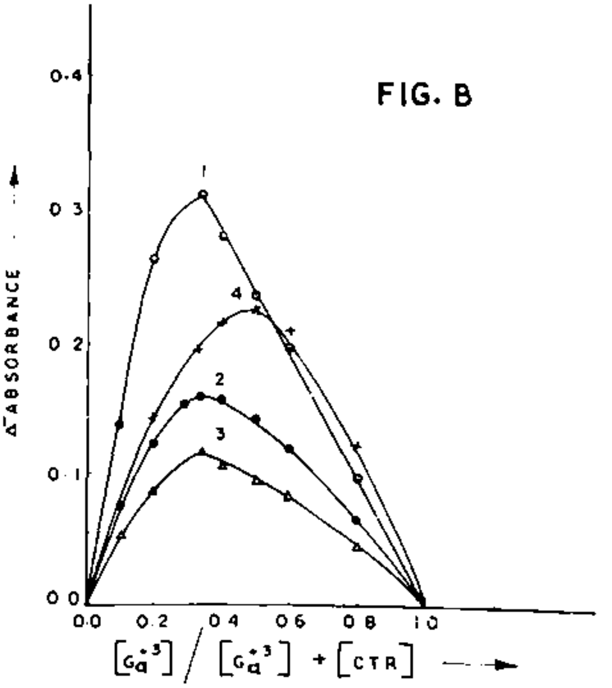


FIG. B

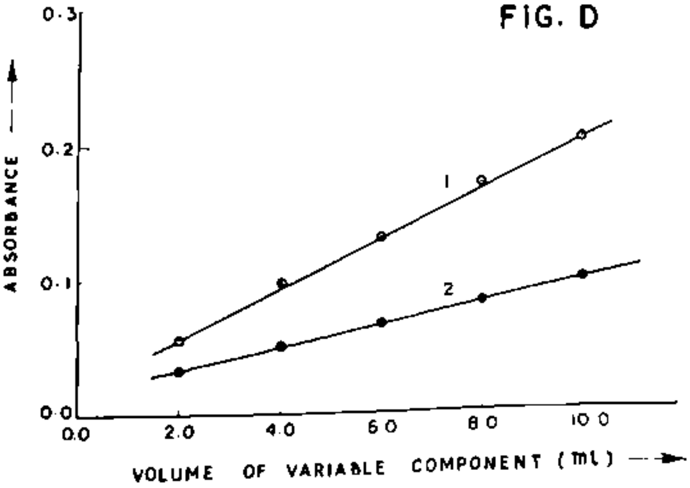


FIG. D

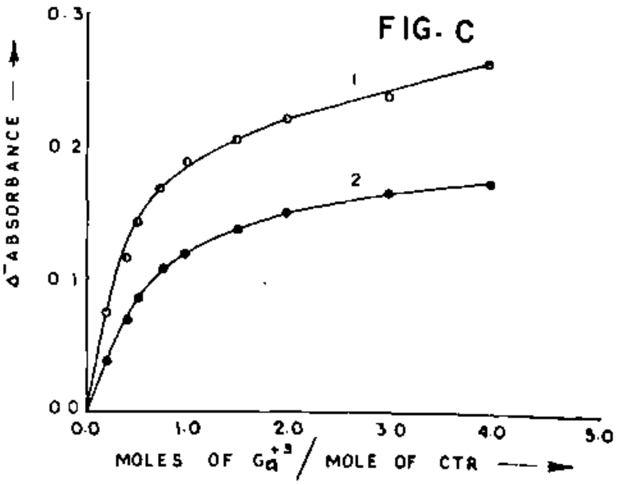


FIG. C

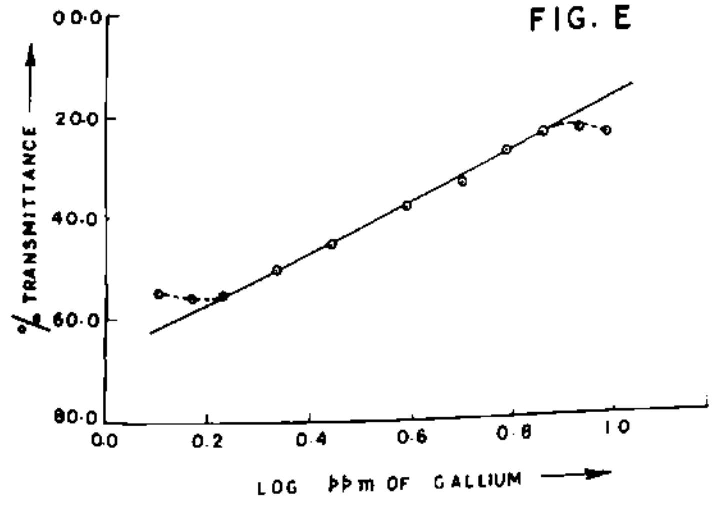


FIG. E

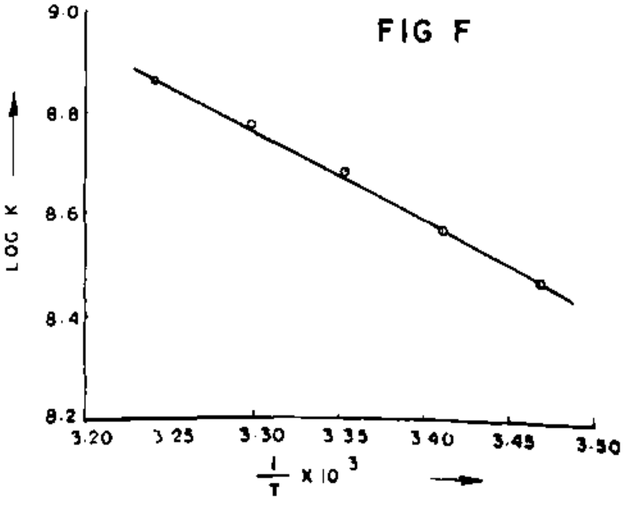


FIG F

PLATE NO. 3

PLATE No. 4

Fig. A. Absorption curves of mixtures of Ytterbium and Chromotrope 2R.

Curve 1. $T_L = 12.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 2. $T_L = 8.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 3. $T_L = 4.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 4. $T_L = 4.0\times10^{-5}M$ $T_M = 0.0\times10^{-5}M$

Fig. B. Job's curves for equimolecular solutions of Yb-CTR chelate.

Curve 1. $T_L = T_M = 2.0\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 2. $T_L = T_M = 1.25\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 3. $T_L = T_M = 1.00\times10^{-4}M$ $p = T_L/T_M = 1.0$

Fig. C. Mole ratio curves for Yb-CTR chelate.

Curve 1. Concentration of constant component $(T_L) = 7.2\times10^{-5}M$

Curve 2. Concentration of comstant component $(T_L) = 4.0\times10^{-5}M$

Fig. D. Slope ratio curves for Yb-CTR chelate

Concentration of constant component $= 2.0\times10^{-4}M$

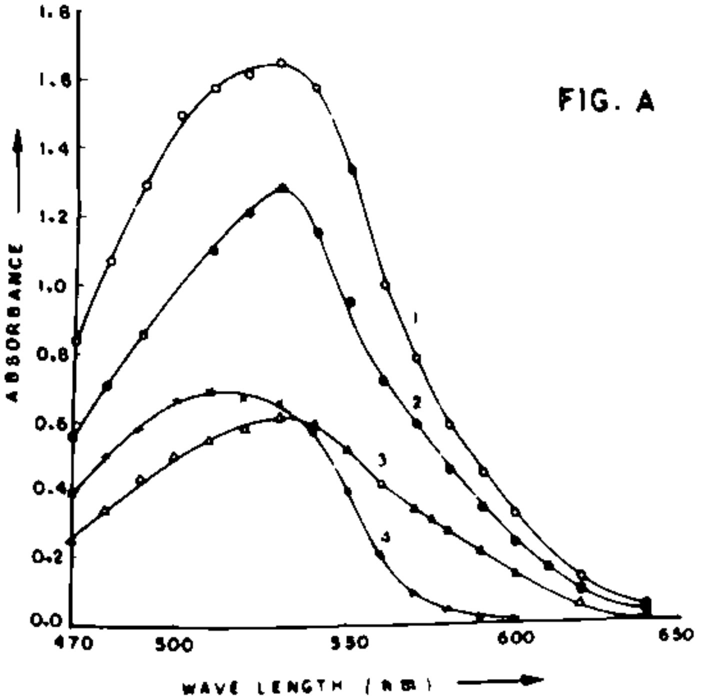
Concentration of variable component $= 4.0\times10^{-5}M - 2.0\times10^{-5}M$

Curve 1 = metal varying

Curve 2 = ligand varying

Fig. E. Beer's law plot for Yb-CTR system.

Fig. F. Plot of log K vs. 1/T.



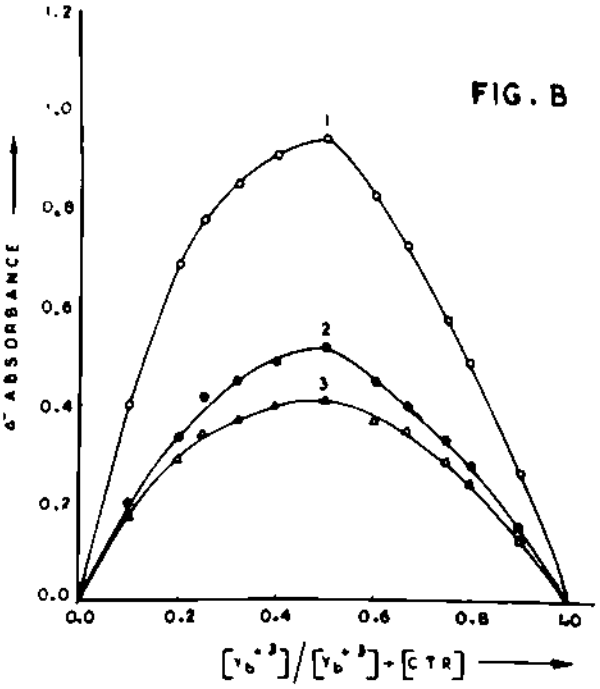


FIG. D

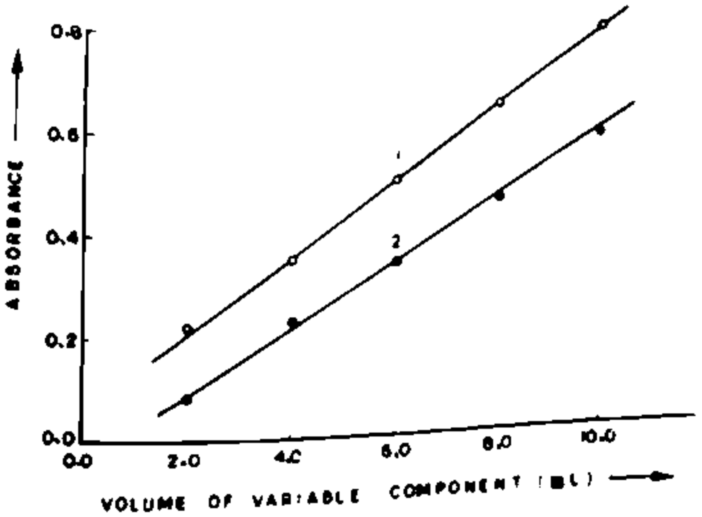


FIG. C

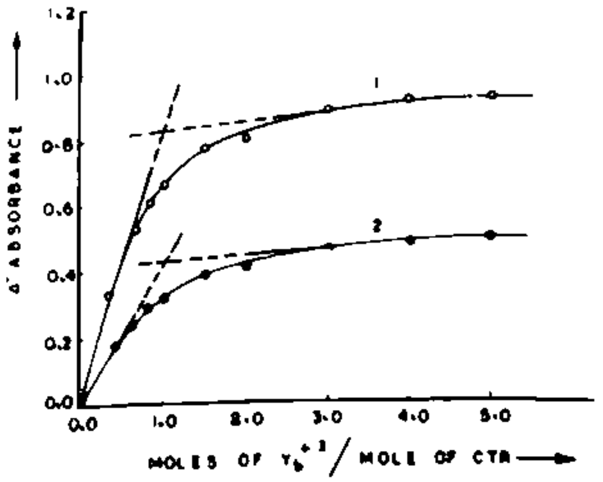


FIG. E

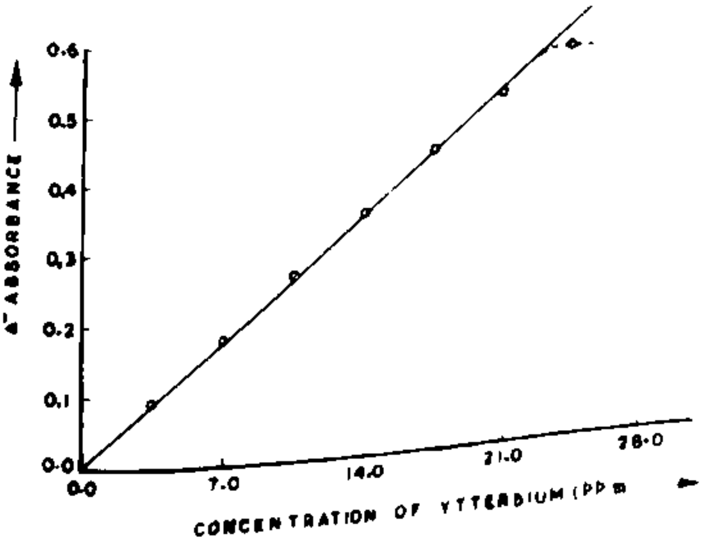


FIG. F

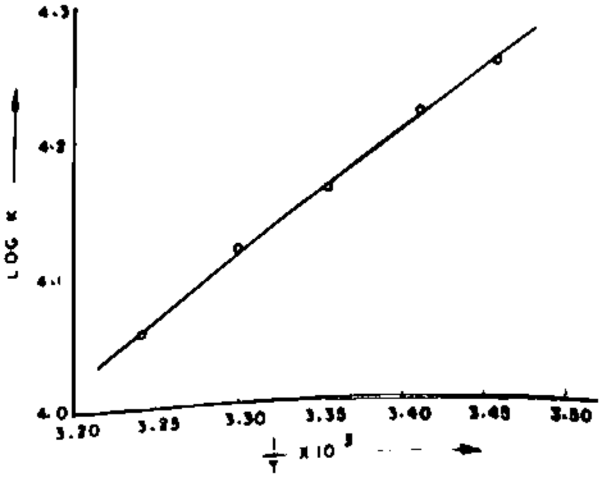


PLATE NO. 4

PLATE No. 5

Fig. A. Absorption curves of mixtures of Zirconium and Chromotrope 2R

Curve 1. $T_L = 8.0\times10^{-4}M$ $T_M = 4.0\times10^{-4}M$

Curve 2. $T_L = 4.0\times10^{-4}M$ $T_M = 4.00\times10^{-4}M$

Curve 3. $T_L = 4.0\times10^{-4}M$ $T_M = 8.00\times10^{-4}M$

Curve 4. $T_L = 4.0\times10^{-4}M$ $T_M = 0.00\times10^{-4}M$

Fig. B. Variation of absorbance with pH for Zr-CTR chelate.

$T_M = 8.0\times10^{-5}M$ $T_L = 8.0\times10^{-5}M$

Fig. C. Job's curves for equimolecular solutions of Zr-CTR chelate.

Curve 1. $T_L = T_M = 5.0\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 2. $T_L = T_M = 2.0\times10^{-4}M$ $p = T_L/T_M = 1.0$

Fig. D. Mole ratio curve for Zr-CTR chelate.

Concentration of constant component $(T_L) = 1.0\times10^{-4}M$

Fig. E. Job's curves for nonequimolecular solution of Zr-CTR chelate.

Curve 1. $T_L = 4.0\times10^{-4}M$ $T_M = 1.0\times10^{-4}M$

$p = T_L/T_M = 4.0$

Curve 2. $T_L = 2.0\times10^{-4}M$ $T_M = 0.5\times10^{-4}M$

$p = T_L/T_M = 4.0$

Fig. F. Ringbom plot for Zr-CTR chelate.

FIG. A

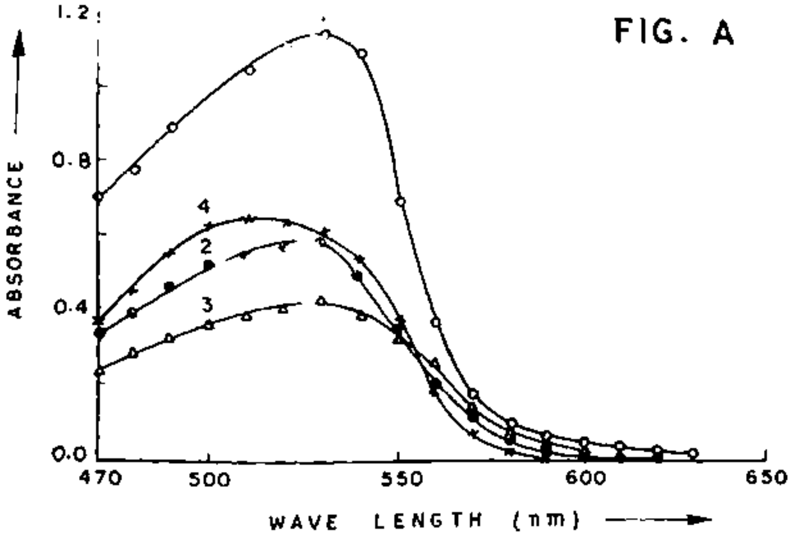


FIG. B

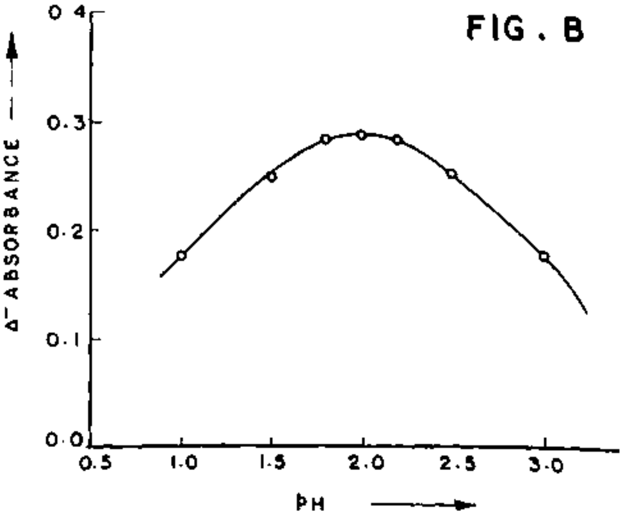


FIG. D

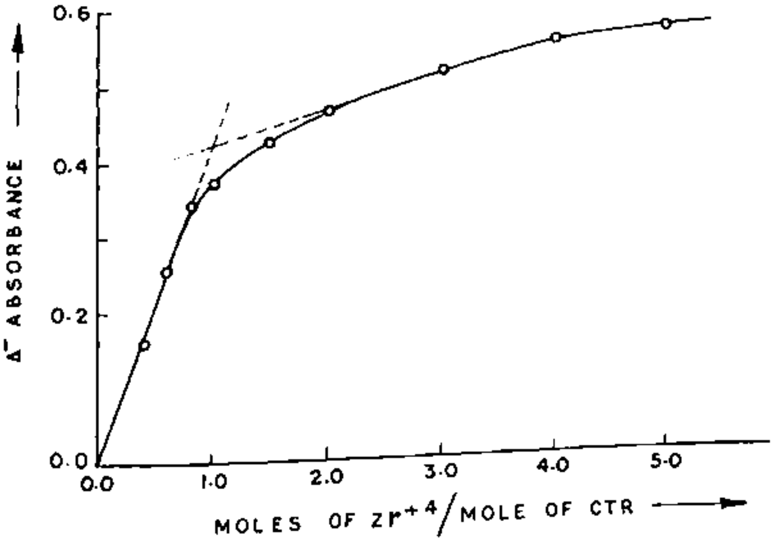


FIG. C

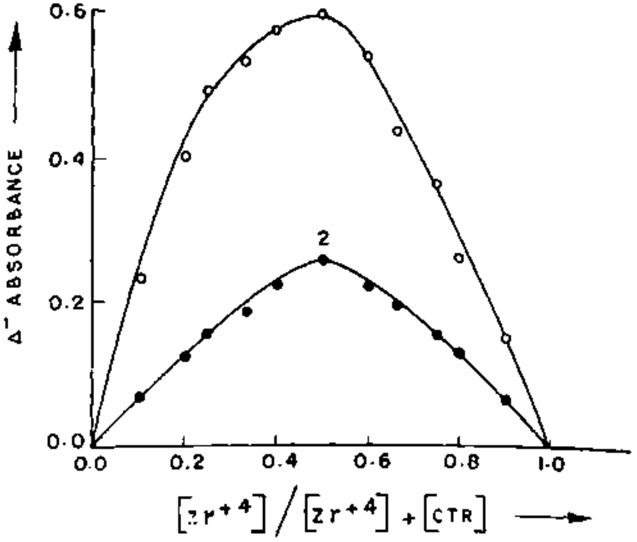


FIG. E

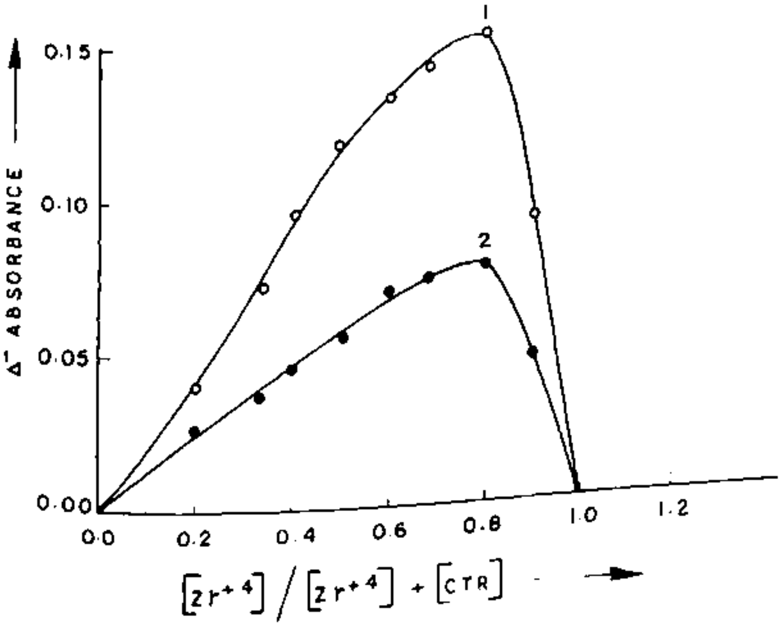


FIG. F

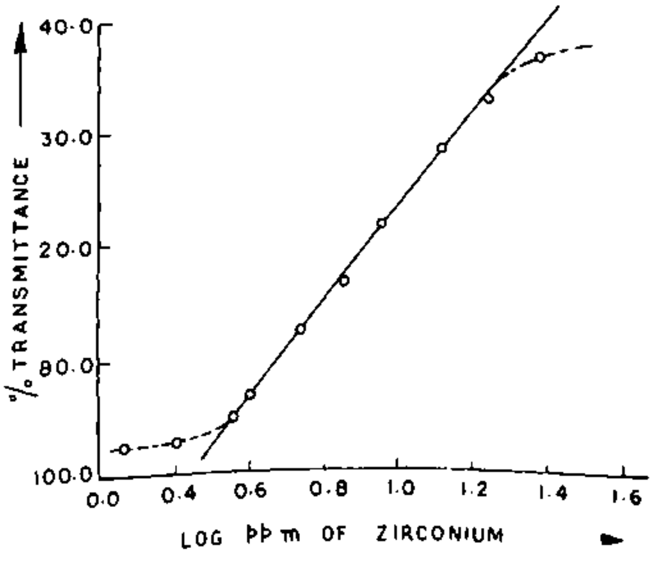


PLATE NO. 5

PLATE No. 6

Fig. A. Absorption curves for mixtures of Hafnium and Chromotrope 2R.

Curve 1. $T_L = 12.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 2. $T_L = 8.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 3. $T_L = 4.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 4. $T_L = 4.0\times10^{-5}M$ $T_M = 0.0\times10^{-5}M$

Fig. B. Variation of absorbance with pH for Hf-CTR chelate.

$T_L = 8.0\times10^{-5}M$ $T_M = 8.0\times10^{-5}M$

Fig. C. Job's curves for equimolecular solution of Hf-CTR chelate.

Curve 1. $T_L = T_M = 2.0\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 2. $T_L = T_M = 1.25\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 3. $T_L = T_M = 1.00\times10^{-4}M$ $p = T_L/T_M = 1.0$

Fig. D. Mole ratio curve for Hf-CTR chelate.

Concentration of constant component $(T_L) = 1.0\times10^{-4}M$

Fig. E. Job's curves for nonequimolecular solutions of Hf:CTR chelate.

Curve 1 = $T_L = 1.25\times10^{-4}M$ $T_M = 2.5\times10^{-4}M$

$p = T_L/T_M = 0.5$

Curve 2 = $T_L = 2.0\times10^{-4}M$ $T_M = 1.0\times10^{-4}M$

$p = T_L/T_M = 2.0$

Fig. F Ringbom plot for Hf-CTR chelate.

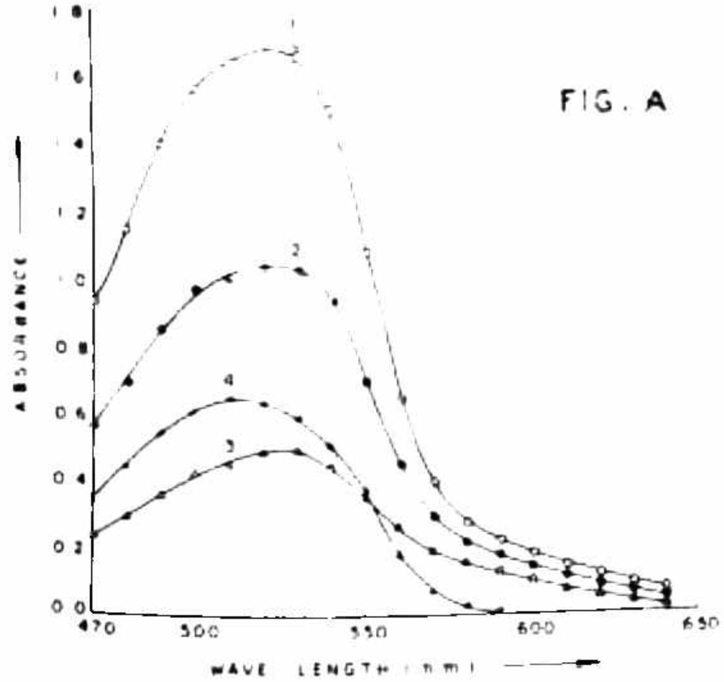


FIG. A

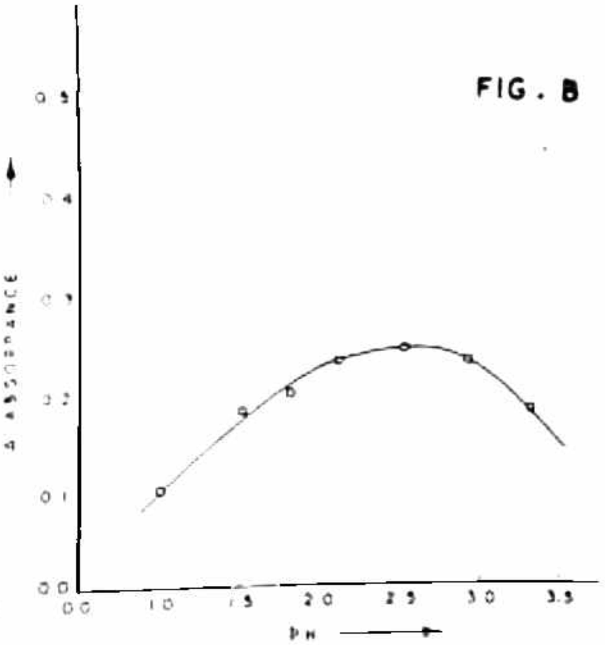


FIG. B

FIG. D

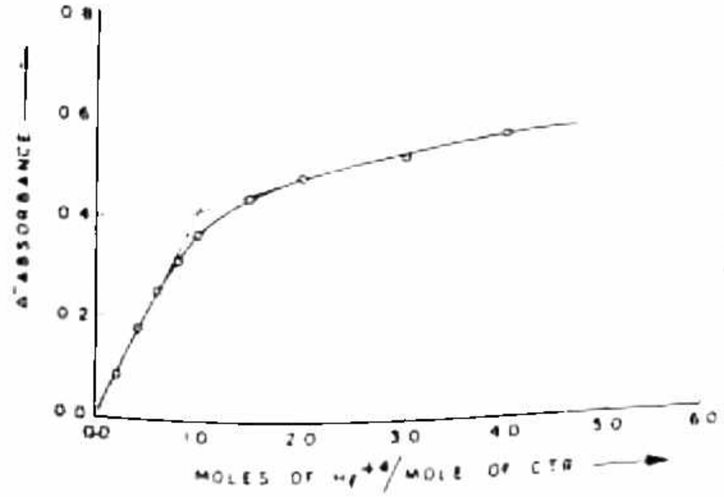


FIG. C

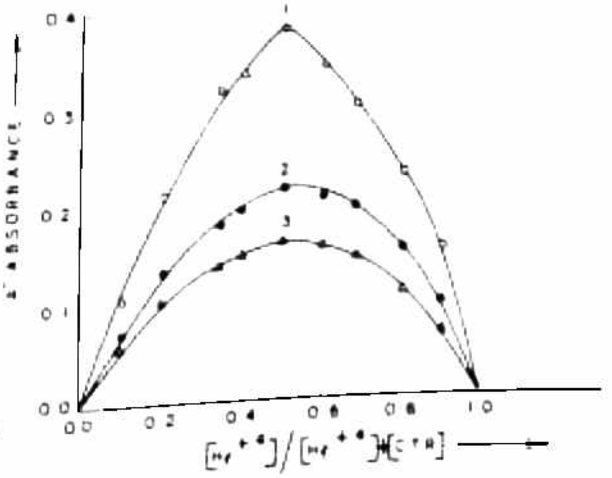


FIG. F

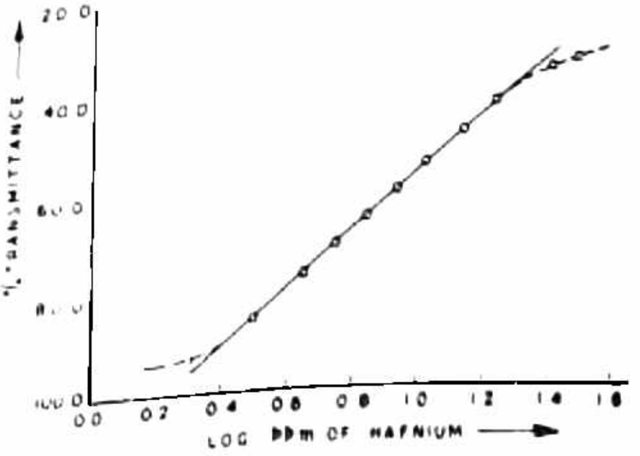


FIG. E

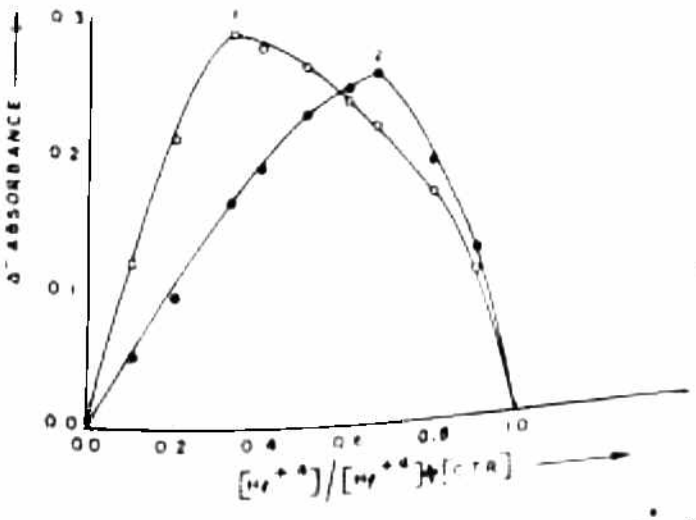


PLATE NO. 6

TABLE 3.1

Colour reactions of Chromotrope 2R with certain metal ions

Colour of the reagent solution - orange red

S.No.	Metal ion	Colour developed	Remark
1.	UO_2(II)	Violet	Sensitive with dilute solutions
2.	Pd(II)	Orange yellow	-
3.	Cu(II)	Pink	-
4.	Mg(II)	Pink	Sensitive with dilute solutions
5.	Co(II)	Orange	-
6.	Ni(II)	Pink	-
7.	Fe(III)	Blackish violet	-
8.	Al(III)	Violet	Sensitive with dilute solutions
9.	Ga(III)	Violet	-
10.	Yb(III)	Violet blue	Sensitive with dilute solutions
11.	Zr(IV)	Violet	Sensitive with dilute solutions
12.	Hf(IV)	Pink violet	Sensitive with dilute solutions

TABLE 3.2

Optimum conditions for the study of metal chelates of Chromotrope 2R

S.No.	Metal chelate	Temperature (^{o}C)	Wavelength at which studies were made (nm)	pH range for the stable existence of chelate	pH(±0.1) at which studies were made	Ionic strength	pH adjusted with
1.	Cu:CTR	25	580	5.0-11.0	6.0	0.1	Hexamine-perchloric acid buffer
2.	Al:CTR	25	580	3.3-7.5	5.0	0.1	Hexamine-perchloric acid buffer
3.	Ga:CTR	25	580	1.0-5.0	3.4	0.1	HCl and NaOH
4.	Yb:CTR	25	580	4.7-8.8	6.9	0.1	Hexamine-perchloric acid buffer
5.	Zr:CTR	25	580	1.0-3.0	2.0	0.1	HCl and NaOH
6.	Hf:CTR	25	580	1.0-3.5	2.0	0.1	HCl and NaOH

TABLE 3.3

Composition and stability of metal chelates of Chromotrope 2R

System	Composition	Molecular extinction method	log K mole ratio method	Dey et al. method	Mean
Cu:CTR	1:1	4.44	4.35	4.29	4.36
Al:CTR	1:1	3.87	4.08	3.93	3.96
Ga:CTR	1:2	8.92	9.00	-	8.96
Yb:CTR	1:1	4.38	4.22	-	4.30
Zr:CTR	1:1	4.41	4.50	4.32	4.41
Hf:CTR	1:1	4.57	4.71	4.60	4.66

✓ Potentiometric results
p.121 indicate 1:2
How this log K is
related to log K_1 and log K_2

p.114 log K^H value

log K_1 - 7.63
log K_2 = 6.64
14.27

TABLE 3.4

Thermodynamic functions of Copper-Chromotrope 2R chelate

pH = 6.0±0.1 μ = 0.1

ΔH = -17.92 kcal/mole

Temperature ^{o}K	log K	ΔG kcal/mole	ΔS e.u./mole
288.15	4.88	-6.44	-39.84
293.15	4.66	-6.25	-39.84
298.15	4.44	-6.05	-39.82
303.15	4.21	-5.84	-39.81

Mean ΔS = -39.83 e.u./mole

TABLE 3.5

Thermodynamic functions of Aluminium-Chromotrope 2R chelate

pH = 5.0±0.1 μ = 0.1

ΔH = +1.42 kcal/mole

Temperature ^{o}K	log K	ΔG kcal/mole	ΔS e.u./mole
288.15	3.80	-5.02	22.31
293.15	3.82	-5.13	22.28
293.15	3.84	-5.24	22.30
298.15	3.86	-5.35	22.31
303.15	3.87	-5.46	22.31

Mean ΔS = 22.30 e.u./mole

TABLE 3.6

Thermodynamic functions of Gallium-Chromotrope 2R chelate

pH = 3.4±0.1 $\mu = 0.1$

$\Delta H = +7.99$ kcal/mole

Temperature °K	log K	ΔG kcal/mole	ΔS e.u./mole
288.15	8.47	-11.18	66.51
293.15	8.57	-11.50	66.48
298.15	8.69	-11.85	66.55
303.15	8.78	-12.17	66.53
308.15	8.86	-12.49	66.46

Mean ΔS = 66.51 e.u./mole

TABLE 3.7

Thermodynamic functions of Ytterbium-Chromotrope 2R chelate

pH = 6.9±0.1 $\mu = 0.1$

$\Delta H = -3.91$ kcal/mole

Temperature °K	log K	ΔG kcal/mole	ΔS e.u./mole
288.15	4.27	-5.63	5.95
293.15	4.23	-5.67	5.98
298.15	4.18	-5.70	6.00
303.15	4.13	-5.73	5.99
308.15	4.08	-5.75	5.96

Mean ΔS = 5.98 e.u./mole

TABLE 3.8

Optimum concentration range for determination, molar absorptivity and sensitivities of metal chelates of Chromotrope 2R

System	Concentration range in which Beer's law is obeyed (ppm)	Optimum concentration range from Ringbom plot (ppm)	Molar absorp-tivity	Sensitivity µg/cm^2
Cu:CTR	0.60- 5.20	1.00- 5.00	7250	0.0080
Al:CTR	0.11- 2.20	0.23- 2.00	19875	0.0014
Ga:CTR	0.70- 7.30	1.60- 7.21	17312	0.0040
Yb:CTR	3.50-21.00	2.90-20.50	25000	0.0068
Zr:CTR	2.50-20.00	3.50-19.05	3875	0.0248
Hf:CTR	2.75-22.23	3.50-21.00	7125	0.0215

TABLE 3.9

Effect of diverse ions on the photometric determination of Aluminium with Chromotrope 2R

Concentration of Aluminium taken = 4.0×10^{-5}M

Diverse ion added (ppm)	Relative % error	Tolerance limit (ppm)
Cu(II) 40	+10.90	7.34
Co(II) 40	-13.04	6.16
Ni(II) 40	- 6.52	12.32
Ba(II) 100	+ 1.30	large excess
Pb(II) 100	- 3.50	large excess
Cd(II) 100	- 4.00	large excess
Sn(II) 40	-67.80	1.19
UO_2(II) 40	+32.69	2.48
Mg(II) 40	-17.39	4.70
Hg(II) 100	+ 2.00	large excess
Pd(II) 40	- 7.10	11.26
Sr(II) 100	+ 4.00	large excess
Ce(III) 40	-42.20	1.89
Tl(III) 100	- 3.50	large excess
La(III) 100	+ 3.10	large excess
W(VI) 40	-78.20	1.02
Mo(VI) 100	-33.30	6.00
NO_3^- 200	+11.40	large excess
Cl^- 200	+ 8.60	large excess
NO_2^- 200	+ 8.60	large excess
ClO_4^- 200	+11.40	large excess
I^- 200	- 7.40	large excess
$C_2O_4^{--}$ 40	-80.70	0.99
$C_4H_4O_6^{--}$ 40	-82.10	0.97
$C_6H_5O_7^{---}$ 40	-87.80	0.91

TABLE 3.10

Effect of diverse ion on the photometric determination of Ytterbium with Chromotrope 2R

Concentration of Ytterbium taken = 4.0 × 10^{-5}M

Diverse ion added (ppm)		Relative % error	Tolerance limit (ppm)
Hg(II)	40	+17.7	4.5
Zn(II)	40	- 4.1	19.5
Cu(II)	20	-53.7	0.8
Cd(II)	40	- 1.5	large excess
Pb(II)	40	+ 6.9	11.6
Co(II)	40	-12.3	6.5
Ni(II)	40	-23.6	1.7
UO_2(II)	40	+ 2.7	29.6
Ba(II)	40	+ 3.5	22.9
Sr(II)	100	+ 1.1	large excess
Be(II)	20	-10.3	3.9
Mg(II)	100	-17.2	11.7
Sn(II)	20	-87.3	0.41
Ce(III)	80	-69.6	0.23
Tl(III)	100	-24.4	8.2
La(III)	100	+26.4	7.6
V(V)	10	-81.6	0.20
Mo(VI)	40	-25.3	3.20
W(VI)	10	-67.1	0.30
Cl^-	40	- 1.9	large excess
Br^-	40	- 1.9	large excess
I^-	100	+ 1.8	large excess
CH_3COO^-	40	-26.0	3.1
SO_3^{--}	100	-17.2	11.7
SO_4^{--}	100	-15.0	13.3
ClO_4^-	40	- 1.3	large excess
NO_3^-	40	- 1.3	large excess
NO_2^-	100	- 2.5	large excess
$C_2O_4^{---}$	20	-70.7	0.51
$C_4H_4O_6^{--}$	20	-86.3	0.46
$C_6H_5O_7^{---}$	10	-81.0	0.25

TABLE 3.11

Effect of diverse ions on the photometric determination of Gallium with Chromotrope 2R

Concentration of Gallium taken = 4.0 × 10^{-5}M

Diverse ion added (ppm)		Relative % error	Tolerance limit (ppm)
Cu(II)	20	- 4.4	9.00
Zn(II)	20	- 9.7	4.10
Sn(II)	20	- 1.0	0.44
Be(II)	100	- 2.0	large excess
Hg(II)	100	+ 5.5	36.40
Co(II)	20	- 3.4	11.80
Ni(II)	20	-18.3	2.20
Ba(II)	100	+ 2.0	large excess
Cd(II)	100	-32.0	6.30
Pb(II)	100	+ 3.0	large excess
Mg(II)	20	-28.2	1.40
Ce(III)	20	-87.6	0.46
Al(III)	5	+66.6	0.15
Tl(III)	40	-13.0	19.10
Th(IV)	5	+92.4	0.11
V(V)	20	-56.5	0.71
Mo(VI)	20	-19.0	2.00
W(VI)	20	-33.1	1.20
Cl^-	100	- 3.2	large excess
Br^-	100	- 0.0	large excess
NO_3^-	100	- 2.1	large excess
SO_4^{--}	100	-45.0	4.40
SO_3^{--}	100	-49.0	4.10
ClO_4^-	100	- 2.1	large excess
CH_3COO^-	20	-41.9	0.96
$C_2O_4^{--}$	20	-36.1	1.10
$C_4H_4O_6^{--}$	20	-66.88	0.60
$C_6H_5O_7^{---}$	20	-61.8	0.65
BO_3^{---}	20	-31.1	1.30

TABLE 3.12

Comparison with other reagents used for spectrophotometric determination of Aluminium, Gallium and Ytterbium

Method	Molar absorptivity	Reference
For Aluminium		
1. Methyl thymol Blue	19,000/590 nm	51
2. 2-(p-sulphophenylazo) 1:8 dihydroxynaphthalene 3:6 disulphonic acid	15,900/570 nm	15
3. Calciochrome	11,500/317 nm	18
4. Anthrazochrome	29,000/590 nm	20
5. 2-Bromo-4,5-dihydroxy -4'-azobenzenesulfonic acid	27,000/455 nm	5
6. Chromotrope 2R	19,875/580 nm	
For Gallium		
1. pyrocatechol violet	11,160/530 nm	1
2. Xylenol orange	16,000/502 nm	32
3. 1-pyrolindine-carbodithioate	2,580	25
4. 6-(2-pyridylazo),3-4 dimethyl phenol	10,000/570 nm	38
5. pyrogallol red	10,000/530 nm	49
6. Chromotrope 2R	17,312/580 nm	

(Contd.)

Table 3.12 (Contd.)

Method	Molar absorp-tivity	Reference
For Ytterbium		
1. Eriochrome Black T	24,000/510 nm	50
2. Diantipyrylazo	23,000/645 nm	10
3. Arsenoazo I	25,000/570 nm	2
4. 4-(2-pyridylazo)-resorcinol	26,000/600 nm	30
5. Pyrocatechol violet	21,000/650 nm	2
6. Methyl thymol blue	21,000/600 nm	2
7. Chromotrope 2R	25,000/570 nm	

REFERENCES

1. Akhmedli, M.K., Bashikirove, E.A., Gluschchenko, E.L. and Zykova, L.I. — Ser. Khim., Nauk., 2, 25 (1965)

2. Akhmedli, M.K. and Granovskaya, P.B. — Azerb. Khim. Zh., 5, 105 (1965)

3. Banerji, S.K. et al. — Nature, 19, 1002 (1963)
Bull. Chem. Soc. Japan, 38(5), 720, (1965)

4. Bernard, A.J. Jr. and Flaschka, H.A. — 'Chelates in analytical chemistry', Marcel Dekker, Inc. New York, Vol. 2, pp. 1 (1969)

5. Basarign, N.N., Akhmedli, M.K. and Kafarova, A.A. — Zh. Anal. Khim., 25, 1497 (1970)

6. Berge, V.H. and Rohde, K.H. — Z. Chem., 9(5), 178 (1969)

7. Betzer, M., Heath, C.E. Jr. and Tramy, B. — Esso Research Engineering Co., U.S. 3, 234, 0-50 (Cl. 136-86), Feb. 8, 1966, App. June 1, 1961.

8. Biltz, W. — Ber., 38, 4143 (1965).

9. Buděšinsky, B. — Chelates Anal. Chem., 2, 1 (1969), Collect. Czech. Chem. Commun., 29(11), 2758 (1964).

10. Buděšinsky, B. and Vrzalova, D. — Anal. Chim. Acta, 36(2), 246 (1966)

11. Dabhade, S.B. and Sangal, S.P. — Microchem. J., 14(2), 190 (1969)

12. Datta, S.K. — Z. Anal. Chem., 167, 105 (1959); 168, 347 (1959); 173, 369 (1960)

13. Dey, A.K. — J.Calloid Science, 3, 473 (1948)

14. Dey, A.K. et al. — Microchem. J. 9(3), 282 (1965).
J. Indian Chem. Soc., 40, 275 (1963); 45(11), 777 (1964).
J. Inorg. Nucl. Chem. 26(9), 1803 (1964).

15. Garg, V.C., Shrivastava, S.C. and Dey, A.K. Proc. Acad. Sci., 37, 203 (1966)

16. Grey, P., Bereczky, E., Master, M.D. and Nevsimel, C. Stain Technol., 33, 215 (1958)

17. Green, D.E. Analyt. Chem., 20, 370 (1948)

18. Ishii, H. and Einage, H. Bull. Chem. Soc., Japan, 39(8), 1721 (1966).

19. Jain, S.K., Prakash, O. and Prakash, S. Bull. Soc. Chim. (France), 1, 91 (1972)

20. Kafarova, A.A., Akhmedli, M.K., and Basargin, N.N. Veh. Zap. Azerb. Inst. Ser. Khim., Nauk. 1, 23 (1959).

21. Koreman, I.M., Potemkina, V.G. and Fedrova, L.S. Zhur. Anal. Chim., 11, 307 (1956)

22. Kuznetsov, V.I. and Nemodruk, A.A. Zh. Obshch. Khim., 35(5), 879 (1965); J. Gen. Chem. (USSR), 26, 3657 (1956)

23. Larson, E.M. and Hirozawa, S.T. J. Inorg. Nucl. Chem., 3, 198 (1956).

24. Liebermann, F. Ber., 26, 1574 (1898).

25. Likussar, W., Sagan, C. and Boltz, D.F. Mikrochim. Acta, 4, 683 (1970)

26. Mazumdar, A.K. et al. Z. Anal. Chem., 174, 197 (1960); 176, 170 (1960); Talanta, 18, 968 (1970)

27. Menzier, D.W. Stain Technol., 37, 45 (1962)

28. Meyer, A. and Bradshaw Analyst, 77, 476 (1952)

29. Miyata, H. et al. Bull. Chem. Soc., Japan, 33, 95 (1960); 36(8), 885 (1963); 40, 141 (1967); 40, 2085 (1967).

30. Munshi, K.N. and Dey, A.K. — Anal. Chem., 36(10), 2003 (1964)

31. Negoiu, D., Isvoranu, C., Kriza, A. and Negoiu, M. — Analet. Univ. Bucuresti, Ser. Stiint. Nat., 13(2), 89 (1964)

32. Ottomo, M. — Bull. Chem. Soc., Japan, 38(2), 624 (1965)

33. Popa, Gr., Negoiu, D. and Vasilescu, C. — Acad. Rep. Populare, Romine, Studii Cercetari Chim., 9, 629 (1961).

34. Popa, Gr., Paralescu, I. and Baiulescu, Gh. — Acad. Rep. Populare Romine, Studii, Cercetari Chim., 9, 85 (1961).

35. Popa, Gr., Paralescu, I. and Balanel, E. — Ser. Stiint. Nat., 10, 203 (1961)

36. Prakash, O. and Mushran, S.P. — Chim. Anal. (Paris), 49(9), 473, (1967).

37. Rehman, S.M.F. and Malik, A. — J. Inorg. Nucl. Chem., 26(2), 385 (1964); J. Prakt. Chem., 21(1-2), 109 (1963); Indian J. Chem., 1(10), 424 (1963).

38. Rakhamatulloeva, K.Z., Rakhamatullaeva, M.A., and Shoeizov, N. — Uzb. Khim. Zh., 14, 25 (1970)

39. Sangal, S.P. — J. Prakt. Chem., 26(3-4), 137 (1964); Bull. Chem. Soc. Japan, 36(16), 1349 (1963).

40. Savvin, S.B. — Talanta, 15(7), 601 (1968); 15(12), 1494 (1968); 16(3), 423 (1969). Tr. Kom. Anal. Akad., Nauk. (SSSR), 17, 163 (1969); 17, 1753 (1969).

41. Shah, V.L. and Sangal, S.P. — Chim. Anal. (Paris), 50(11), 582 (1968).

42. Shah, V.L. and Sangal, S.P. — Microchem. J., 14(2), 261 (1969)

43. Shah, V.L. and Sangal, S.P. Microchem. J., 15(4), 548 (1970)

44. Shah, V.L. and Sangal, S.P. Chim. Anal. (Paris), 53(1), 47 (1971).

45. Shibata, S., Uchimi, A., Sasaki, S. and Goto, K. Anal. Chim. Acta, 44(2), 345 (1969)

46. Singh, C. Stain Technol., 38, 103 (1963)

47. Sommer, L. and Coworkers Chem. Listy, 52, 1485 (1958).
Z. Anal. Chem., 104, 299 (1958).
Bull. Soc. Chim. (France), 862 (1959).

48. Sommer, L. et al. Chem. Listy, 50, 1580 (1956).
Chemist Analyst. 56(12), 9 (1967)

49. Srivastava, K.C. Chim. Anal. (Paris), 53, 525 (1971)

50. Takano, T. Bunseki Kagaku, 16(1), 27 (1967)

51. Tikhonov, I.N. Zh. Anal. Khim. 213(3), 275 (1966)

52. Verma, J.R. and Mushran, S.P. Rev. Chim. Miner. 8(2), 339 (1971)

53. Virgil, A. and Dragusin, I. Rev. Roum. Chim., 14(11), 1367 (1969); 14(12), 1511 (1969).

54. Weiser, H.B. and Porter, E.E. J. Phys. Chem., 31, 1824 (1927).

55. Werner, A. Ber., 41, 1062 (1908).

56. Zollinger, Hch. Helv. Chim. Acta, 34, 600 (1951).

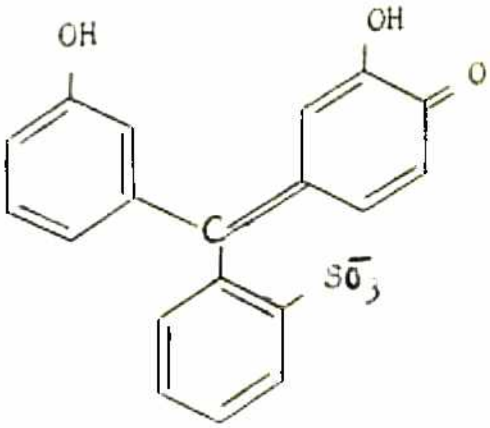
* * *

CHAPTER IV

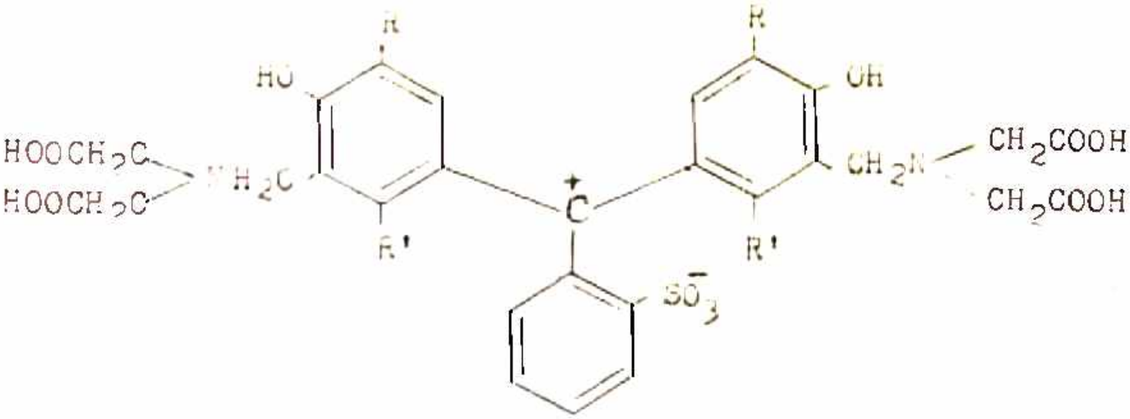
SPECTROPHOTOMETRIC STUDIES OF METAL CHELATES OF BROMOPYROGALLOL RED

One of the important classes of dyes which stand out prominently for their varied applications, is the sulphonephthalein group of dyes. Besides their use in dyeing, printing, chrome-mordanting, their other applications are manifold. A number of them possess the interesting property of forming coloured products with metal ions, which forms the basis for the estimation of these metal ions. The coloured metal chelates may be soluble or insoluble depending on the concentrations, as well as the nature of the metal ion. The colour formation reaction is specific or selective in many cases, due to which these dyes have found use as metallochromic indicators, spot reagents and colorimetric reagents for the determination of microamounts of metal ions.

The chief among the sulphonephthlein dyes are pyrocatechol violet, xylenol orange, methyl-thymol blue, aluminon, pyrogallol red and bromopyrogallol red, the structures of which may be represented as

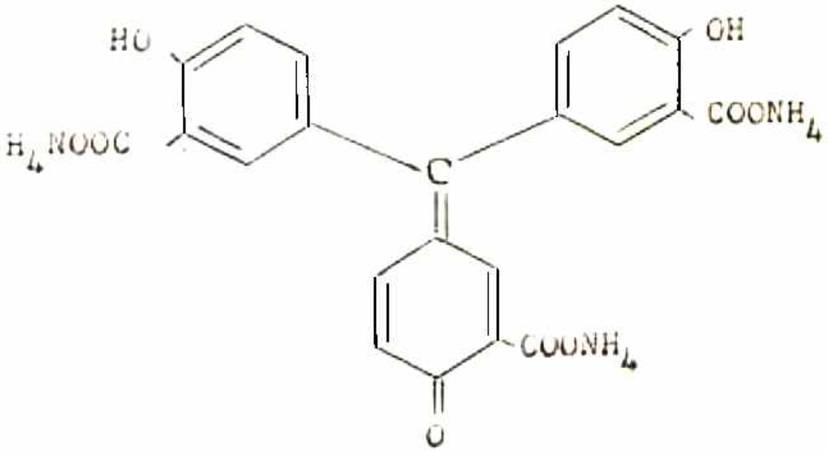


Pyrocatechol violet

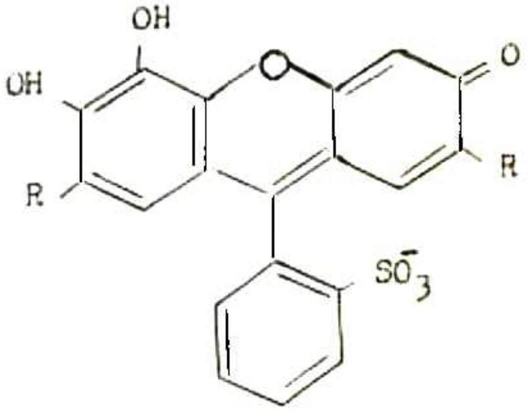


Xylenol Orange : R = $-CH_3$, R' = $-H$

Methyl Thymol Blue : R = $-CH(CH_3)_2$, R' = $-CH_3$



Aluminon



Pyrogallol Red : R = $-H$

Bromopyrogallol Red : R = $-Br$

The preparation of pyrogallol red was first reported in 1898 by Sohon[49], who obtained it by condensation of p-sulphobenzoic anhydride with pyrogallol. Leminger[32] has discussed the preparation and properties of many sulphothelein indicators such as phenol red, tetrachlorophenol sulphonephthalein bromophenol purple, o-cresol red, thymol blue, bromothymol blue, pyrocatechol violet, pyrogallol red and bromopyrogallol red. Suk[52] has concluded from the photometric studies that bromopyrogallol red exhibits acid-base properties in analogy with other sulphonephthalein compounds. Akhmedli et al.[3] have obtained the dissociation constants of bromopyrogallol red by isobestic point method.

Suk, Malát and Jeničkova[53] have used it as a complexometric indicator for the ethylenediamine tetraacetate titration of several metal ions including Bi(III), Ni(II), Co(II), Po(II), Mg(II), Mn(II), Ce(III) and the rare earths under a variety of pH conditions. Vodák and Leminger[66] have advocated this reagent as a spot test reagent for the detection of silver ion, but the test is subject to interference from practically all cations except those of the alkali metals.

West and coworkers[14,67] have undertaken the colour systems formed with silver ion with eighteen metallochromic reagents including Solochrome Black T, o-Cresolphthalein Complexan, PAN, PAR, Catechol Violet, Glycine Thymal blue, Pyrogallol red and Bromopyrogallol red and have found that Bromopyrogallol red gives a specific colour with silver ion.

EDTA eliminates the interference due to some ions which lower the sensitivity. This method is also used for determining silver[15] in trace amounts and is more reproducible than the earlier methods using dithiozone and p-dimethylaminobenzenalrhodanine. Lisitsyna[31] and coworkers have described a sensitive and selective spectrophotometric method, which is based on the formation of a coloured ion association of Ag-phenanthroline complex with BPR anion. This method is applicable for the determination of silver in its ores.

Lukyanov[32] has given a method for the photometric determination of uranium after separating the interfering ions with 1-nitroso-2-naphthol in the presence of complexone III or by chromatography. Bashirov[6] has studied the blue violet complex of copper with bromopyrogallol red. Photometric determination of cadmium with 1-10 phenanthroline and bromopyrogallol red has been made by Deguchi[18].

Pandey and Sangal[38] have carried out the studies on its chelate with aluminium, gallium and indium and have made suggestions for the structures of the chelates formed. Talipan et al.[56] have found a technique for the photometric determination of indium and have inferred that alkaline earth metals, BO_3^{--}, SO_4^{--}, Cl^-, NO_3^-, acetate and citrate do not interfere. Photometric determinations of titanium and lanthanum have been made by Suk et al.[51,54] A highly sensitive spectrophotometric method for the determination of trace amounts of scandium in silicate rocks has been described by Shimizu[48]. Christopher and West[10] have proposed a simple and rapid method for the estimation of antimony by using this reagent, which compares well with most sensitive of the techniques used at present for the determination of antimony. Thierig and Umland[60] have suggested a method for the quantitative estimation of tin in trace amount, which is independent of the oxidation state of tin. Bromopyrogallol reacts with niobium[7] at pH 5.8 in a tartarate medium containing EDTA and CN^- as masking agent and forms 1:2 and 1:3 (Nb:BPR) complexes in the presence and absence of EDTA respectively. The authors inferred that the colour system is stable and reproducible, and the proposed method seems to be the most sensitive among a large number of visible-range spectrophotometric methods proposed so far for niobium(V).

Pandeyand Sangal[37] have done the preliminary studies on the Cu(II), Sc(III), Y(III), Al(III), Ga(III), In(III), Pr(III), Nd(III), Sm(III), Th(IV), Zr(IV), Hf(IV) and Mo(VI) chelates of bromopyrogallol red and pyrogallol red. Vasilenko and coworkers[64] have found that the interaction between thorium and bromopyrogall red proceed with the formation of 1:4 and 1:2 complexes, the formation of which depends on the pH of the medium. Popa[41] has presented a method for the determination of germanium in cupriferrous ore with bromopyrogallol red as described by Nazarenko and Ravitzhaya[34]. The photometric determination of Zr(IV) has been carried out in detail by Takayoshi[55]. Honsa and Suk[25] have used bromopyrogall red as a colorimetric reagent for the photometric determination of molybdenum.

Harrington and Steed[24] have estimated ytterium and cerium with this chromogenic reagent after precipitating these ions as fluoride and then separating the pure solution on an ion exchange column. Poluektov et al.[39] have determined neodymium in a mixture containing ytterium in the presence of nitrilotriacetic acid. Sandu and coworkers[40] have determined lanthanum and cerium in salts of ytterium subgroup rare earth elements, photometrically by masking the reaction with nitrilotriacetic acid. Recently Akhmedli[1] has developed a new extraction-photometric method for determining rare earth elements of ytterium subgroup which is applicable even in the presence of 35 fold thorium, 250 fold titanium, 58 fold calcium, 508 fold barium, 360 fold fluoride and 600 fold phosphate excesses.

Bromopyrogallol red is also used for the estimation of anions. West and Dangell[13] have estimated macro and micro amounts of cynide ion by using 1,10 phenanthroline and bromopyrogallol indicator system. The method is based on the fact that cynide ions prevent the formation of strongly absorbing ternary complex between Ag(I) and 1,10 phenanthroline, and bromopyrogallol in nearly neutral solution. Similarly various workers[10,17] have tried the indirect photometric determination of trace amounts of sulphide, cynide and iodine ions.

Costache and Popa[11,12] have calculated the activation energies, pre-exponential factor and the true rate constant for the cobalt catalysed reaction between H_2O_2 and bromopyrogallol red. Moreover they have estimated traces of cobalt with this reagent kinetically, which is based on the oxidation of bromopyrogallol red by H_2O_2 catalysed by cobalt, leading to a colourless product. Barbig[4] and coworkers have carried out the thin layer chromatographic study of plasma bromosulphonephthalein metabolites in normal subjects. Bromopyrogallol red can be used in the amperometric titration of uranium[61] in a solution of tri-n-octylaminebenzene ethanol using dropping mercury electrode at -0.98V.

The work presented here reports the chelates of Lead (II), Nickel (II), Cobalt (II), Ytterbium (III), Praseodymium (III) and Tungsten (VI) with bromopyrogallol red i.e. 5,5' dibromopyrogallol sulphonephthalein which is abbreviated as BPR throughout this work. As no significant work is reported in literature, a systematic work regarding the composition, stability and thermodynamic functions of these metals was undertaken. In order to reduce the bulk of the thesis, the results obtained have been represented graphically or presented in tables.

EXPERIMENTAL

Instruments

The details of instruments used for the absorbance and pH measurements is same as that described in Chapter III.

Reagents

Stock solutions of lead acetate, nickel sulphate, cobalt sulphate (all BDH, AnalaR), ytterbium chloride, Praseodymium chloride (K and K Laboratories, Inc., N.Y.) and sodium tungstate (BDH AnalaR) were prepared by dissolving them in carbon dioxide free double distilled water and their metal content was estimated by the usual manner. A 10^{-4}M solution of purified sample of bromopyrogallol red (G.R., E. Merck) was prepared in double distilled ethyl alcohol. To maintain the desired ionic strength sodium perchlorate (Reidel) solution of known concentration was employed. Solutions of various diverse ions were prepared from the AnalaR grade salts of the corresponding metal ions.

Preliminary investigations of the reagent

Effect of pH on Bromopyrogallol Red:

Bromopyrogallol red behaves as an acid-base indicator and changes colour with the variation of hydrogen ion concentration of the solution, which is responsible for the shift in λ_{max}, when the pH of the solution is varied. A number of solutions were prepared containing 6.0×10^{-5}M BPR in 50% ethanol and their pH was adjusted to different values by AnalaR grade sodium hydroxide and hydrochloric acid. The absorbance spectra of the solutions was plotted, and the results obtained have been summarised in Table 4.1.

Colour formation with inorganic ions:

For studying the colorimetric reactions of BPR with metallic ions, 2 ml of bromopyrogall red solution was taken in different test tubes and to this was added different metal ions. The colour change developed was noted visually and compared with an equal amount of reagent diluted with water to the same extent. The colour reactions of the cations tested have been recorded in Table 4.2.

RESULTS AND DISCUSSION

Conditions of study

Appropriate dilutions of the stock solutions were made by adding double distilled water, keeping the final solution 50% ethanolic in every mixture. All the studies were undertaken at 30±0.1°C. The individual solutions and mixtures were kept in a precision thermostat (Forma Scientific Model 2095) maintained at 30±0.1°C, for half an hour to attain the equilibrium. The pH of the solutions was adjusted mostly with hexamine-perchloric acid buffer. The conditions of study for all the metal complexes have been summarised in Table 4.3.

Effect of time and temperature

The chelate formation was observed to be instantaneous in all the cases. In almost every case, except cobalt, there was no significant variation in the values of absorbance even after six or eight hours. In the case of cobalt it was observed that the colour of the solutions fades away as the time lapses. To stabilise the colour formation 1 c.c. of 3% gelatin solution was added in every solution. After the addition of gelatin, the colouration was stable at least for six to eight hours. Changes in temperature were found to have no measurable effect on absorbance, when the ligand was in excess. The order of addition of reagents had no effect on absorbance of the chelates. However, in the present studies, the ligand solution was taken first, to ensure the uniformity.

Effect of pH on the complexes

With a view to study the effect of pH on the absorbance of the chelate, a series of solutions containing a fixed amount of metal ion and BPR were prepared and their pH adjusted to different values with AnalaR grade sodium hydroxide and hydrochloric acid. The absorbance spectra was recorded for each metal chelate. The pH range in which the chelates were most stable, the pH at which the subsequent studies were undertaken and buffers used to adjust the final pH values, have been recorded in Table 4.3.

Nature of the complexes formed

To investigate the nature of complexes formed, the method of Vosburgh and Cooper[65] was employed, in a way, similar to that as described in Chapter III. The absorbances of various mixtures were measured at various wavelength and the spectra recorded. The results have been graphically represented in Plates 7-11 and 13 (Fig. A). The results reveal that only one complex is formed under the conditions of study, in all the systems except in the case of praseodimium where two complexes are formed under different values of pH and wavelength.

Stoichiometry of the chelate

The empirical formula of the various complexes have been established by the three independent methods.

(i) Continuous variation method

Job's method of continuous variation using equimolecular as well as nonequimolecular solutions was adopted to study the molar compositions of the coloured complexes formed under the conditions of study. The experimental details of the method are same as described in Chapter III. The results obtained have been graphically represented in Plates 7-11 and 13 (Fig. B), and Plate 12 (Fig. A). The results reveal that a 1:1 (metal:ligand) complex is formed with Lead, Nickel, Ytterbium and Tungsten, whilst Cobalt forms a 1:2 (Co:BPR) complex. Praseodymium forms both 1:1 and 1:2 (metal:ligand) complexes under different sets of pH and wavelength.

(ii) Mole ratio method

For the determination of composition of the metal complexes, mole ratio method of Yoe and Jones was employed. A series of solutions was prepared from the respective metal ion and BPR in such a way that the molar ratio of the metal to the ligand varied from 1:0.25 to 1:5.0. The absorbances of these solutions were measured at the λ_{max} of the chelate against a reagent blank. The results obtained have been embodied in the graphs in Plates 7-11 and 13 (Fig. C) and Plate 12 (Fig. B). The results obtained by this method corroborate the same compositions as revealed by the previous method.

(iii) Slope ratio method

In this method, the volume of the variable component was varied from 1 to 5 ml, in the presence of an excess concentration of the other component. The ratio of the slopes of the two straight lines shows the same composition as by the other two methods. The results obtained are represented graphically in Plates 7-11 and 13 (Fig. D) and Plate 12 (Fig. C).

Evaluation of stability constants

The stability constants of these chelates have been determined by the following two different methods.

(i) Molecular extinction coefficient method.
(ii) By using data from mole ratio curves.

The results obtained have been recorded in Table 4.4 from which it is quite evident that the values of log K by the two different methods are in a good agreement.

Thermodynamic functions of the complexes

The free energy of chelate formation has been calculated by using the equation

$$\Delta G = - RT \ln K$$

To calculate the values of enthalpy and entropy changes during the chelate formation, the stability constants were calculated at different temperatures. From the slope of the curve obtained by plotting log K against 1/T (Plates 7-10 (Fig. F) and Plates 11,12 (Fig. E)), the value of enthalpy (ΔH) has been determined by assuming that its value remains constant in the range of temperature under investigation. Knowing the values of free energy of formation (ΔG) and enthalpy change (ΔH), the value of entropy change (ΔS), has been determined by Gibbs- Helmholtz equation described earlier.

The results obtained have been summarised in Tables 4.5-4.11.

Analytical applications

To test the analytical potentialities of the various metal chelates of bromopyrogallol red the following experiments were performed:

Effect of reagent concentration

The effect of increase in concentration of the ligand over that of the metal ion, on the absorbance of the various complexes formed at λ_{max} (against a reagent blank) was observed. It was seen that the absorbance value increases as the concentration of the BPR is increased and becomes maximal at a certain molar excess of BPR concentration over that of the metal ion. It was found that at least three fold molar excess of BPR is essential for the photometric determination of Lead (II), Nickel (II), Ytterbium (III) and Tungsten (VI) whilst a 5 to 6 fold molar excess of BPR is required to be maintained for the spectrophotometric determination of cobalt (II) and praseodymium (III).

Beer's law and sensitivity

Calibration curves for the determination of Pb(II), Ni(II), Co(II), Yb(III), Pr(III) and W(VI) with bromopyrogallol red were prepared using standard procedures (Plates 7-10, Fig. E and Plate 12, Fig. D). The range over which the Beer's law was obeyed has also been studied. The optimum concentration range for the photometric determination was obtained by the Ringbom method[42]. Molar absorptivity, and sensitivity as defined by Sandell's notation[45] at λ_{max} (against a reagent blank), for $I_o/I = 0.001$, were also calculated for each system. The results have been summarized in Table 4.12.

Standard procedure for determination

Transfer an aliquot amount of the metal ion (upto which Beer's law is obeyed) to a 25 ml flask and add at least three fold concentration of BPR in the photometric determination of Pb(II), Ni(II), Yb(III), W(VI), whilst a 5 to 6 fold molar excess of the reagent as added in the case of Co(II) and Pr(III). The solution may then be made upto the mark after adjusting the pH to the required value such that the final solution is 50% ethanolic. Add 1 ml of 3% gelatin in the case of Co(II) so as to stabilise the colour formation. After allowing the mixtures to stand for a sufficient time to attain equilibrium, their absorbance values were noted. The concentration of the metal ion was then estimated from the calibration curve corresponding to the value of absorbance.

The effect of diverse ions

The effect of diverse ions was examined with a known concentration of metal ion and the dye, in the presence of various foreign ions. The tolerance limit was tentatively assumed to be the concentration of the diverse ion which affects the absorbance of the complex by less than ±2.0%. The effect of various foreign ions on the photometric determination of various metals under investigation, have been summarized in Tables 4.13-4.18.

Comparison with other methods

Although various organic reagents have been used for the determination of different metal ions under investigations, the method for the spectrophotometric determination of metal ions using Bromopyrogallol Red as a chromogenic agent is simple, rapid and sensitive. However, to determine these metal ions in alloys or rocks, the interfering ions must be masked with the usual masking agents or by column chromatography using various resins. Tables 4.19-4.21 present a comparative account of some of the reagents used for the photometric determination of Nickel, Cobalt, Ytterbium, Praseodymium, Lead and Tungsten. The results indicate that this method, for the determination of these metal ions is not less good as the other methods available at present.

PLATE No. 7

Fig. A. Absorption curves for mixtures of Lead and Bromopyrogallol Red.

Curve 1. $T_L = 6.0\times10^{-5}M$ $T_M = 2.0\times10^{-5}M$

Curve 2. $T_L = 4.0\times10^{-5}M$ $T_M = 2.0\times10^{-5}M$

Curve 3. $T_L = 2.0\times10^{-5}M$ $T_M = 2.0\times10^{-5}M$

Curve 4. $T_L = 2.0\times10^{-5}M$ $T_M = 0.0\times10^{-5}M$

Fig. B. Job's curves (equimolecular and nonequimolecular solutions) for Pb:BPR chelate.

Curve 1. $T_L = T_M = 1.25\times10^{-4}M$ $p = \frac{T_L}{T_M} = 1.0$

Curve 2. $T_L = T_M = 1.00\times10^{-4}M$ $p = \frac{T_L}{T_M} = 1.0$

Curve 3. $T_L = 1.25\times10^{-4}M$ $T_M = 2.50\times10^{-4}M$

$p = T_L/T_M = 0.5$

Fig. C. Mole ratio curves for Pb:BPR chelate.

Curve 1. Concentration of Lead $(T_M) = 4.0\times10^{-5}M$

Curve 2. Concentration of Lead $(T_M) = 2.0\times10^{-5}M$

Fig. D. Slope ratio curves for Pb:BPR chelate

Concentration of the constant component = $1.0\times10^{-4}M$

Concentration of the variable component = $4.0\times10^{-6}M$ - $2.0\times10^{-5}M$

Curve 1.= metal varying

Curve 2 = ligand varying

Fig. E. Ringbom plot for Pb:BPR chelate

Fig. F. Plot of log K vs. 1/T

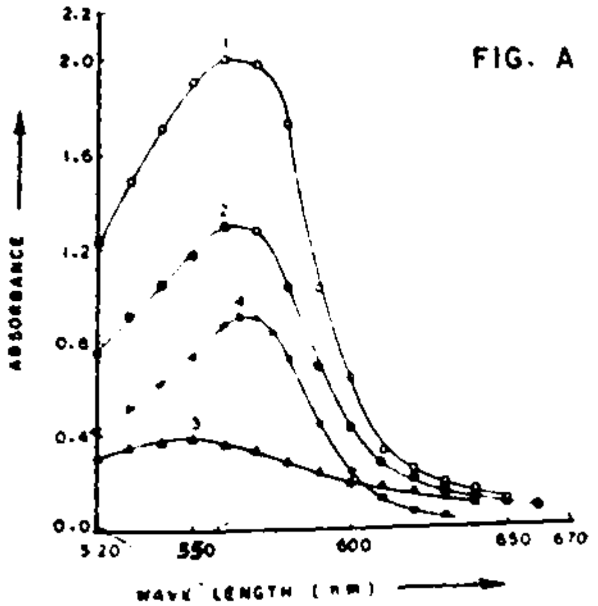


FIG. A

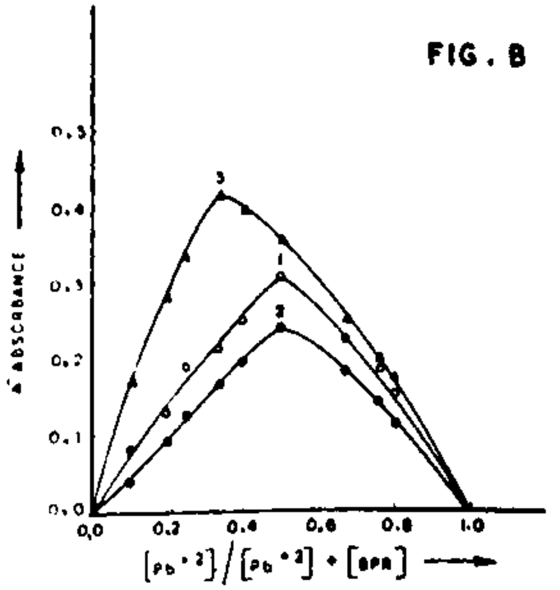


FIG. B

FIG. D

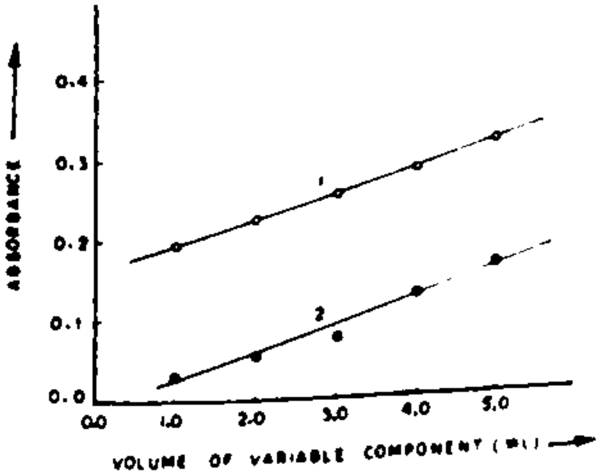


FIG. C

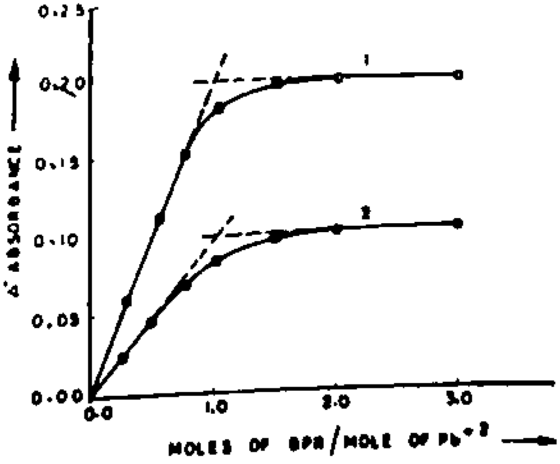


FIG. E

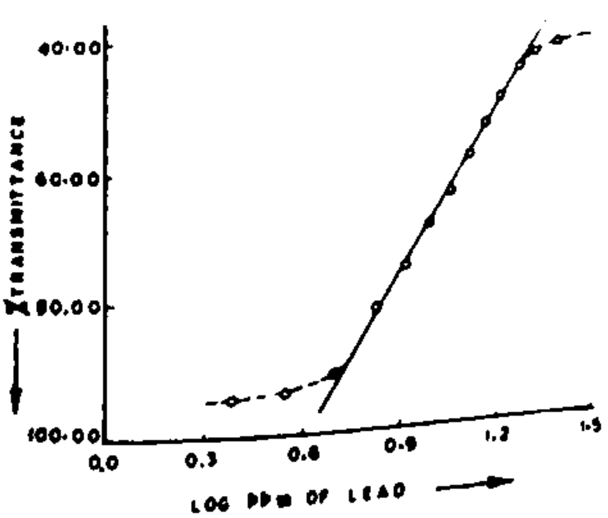


FIG. F

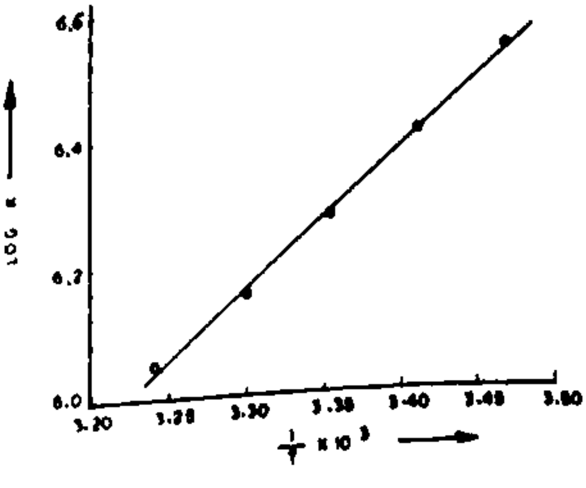


PLATE NO 7

PLATE No. 8

Fig. A. Absorption curves for mixtures of Nickel and Bromopyrogallol Red.

Curve 1. $T_L = 8.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 2. $T_L = 4.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 3. $T_L = 4.0\times10^{-5}M$ $T_M = 8.0\times10^{-5}M$

Curve 4. $T_L = 8.0\times10^{-5}M$ $T_M = 0.0\times10^{-5}M$

Fig. B. Job's curves (equimolecular and nonequimolecular solutions) for Ni:BPR chelate.

Curve 1. $T_L = T_M = 1.0\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 2. $T_L = T_M = 0.00\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 3. $T_L = 1.0\times10^{-4}M$ $T_M = 2.0\times10^{-4}M$ $p = T_L/T_M = 0.5$

Fig. C. Mole ratio curves for Ni:BPR chelate.

Curve 1. Concentration of Nickel (T_M) = $4.0\times10^{-5}M$

Curve 2. Concentration of Nickel (T_M) = $2.0\times10^{-5}M$

Fig. D. Slope ratio curves for Ni:BPR chelate.

Concentration of the constant component = $6.0\times10^{-5}M$

Concentration of the variable component = $4.0\times10^{-6}M$ - $2.0\times10^{-5}M$

Curve 1 = metal varying

Curve 2 = ligand varying

Fig. E. Beer's law plot for Ni:BPR chelate.

Fig. F. Plot of log K vs 1/T.

FIG. A

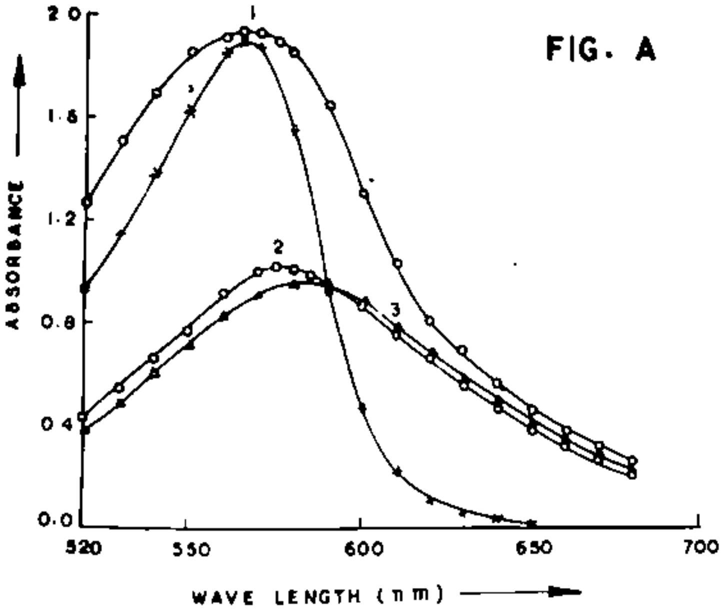


FIG. B

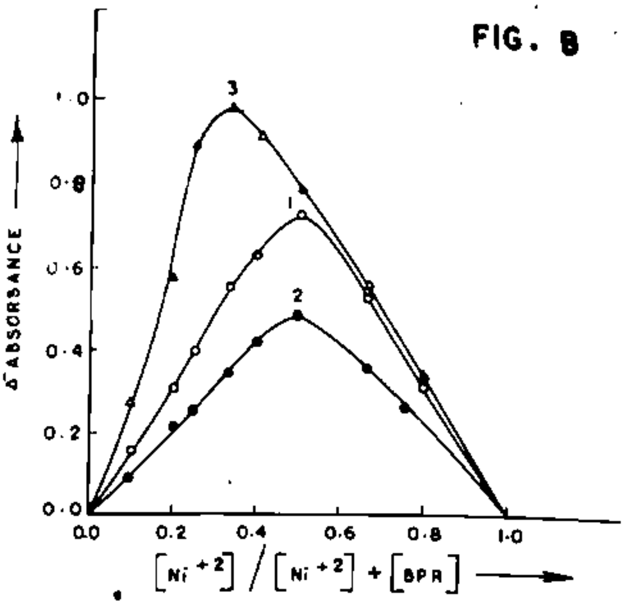


FIG. D

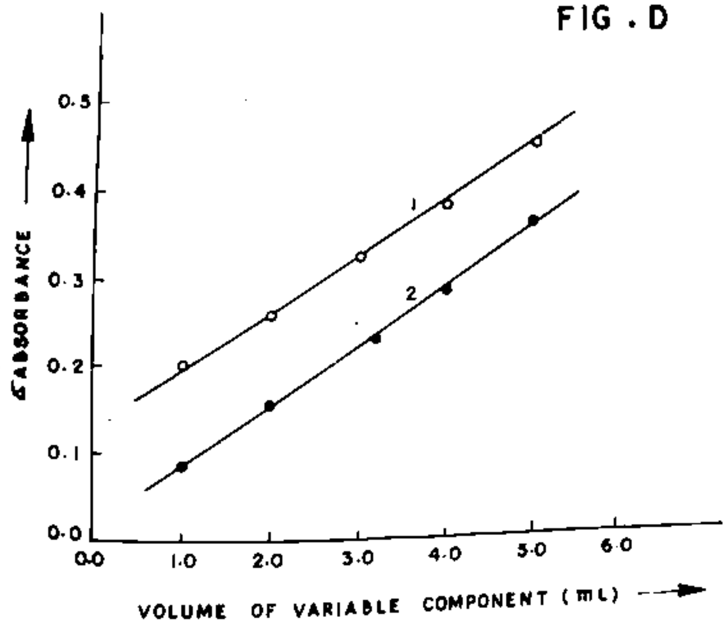


FIG. C

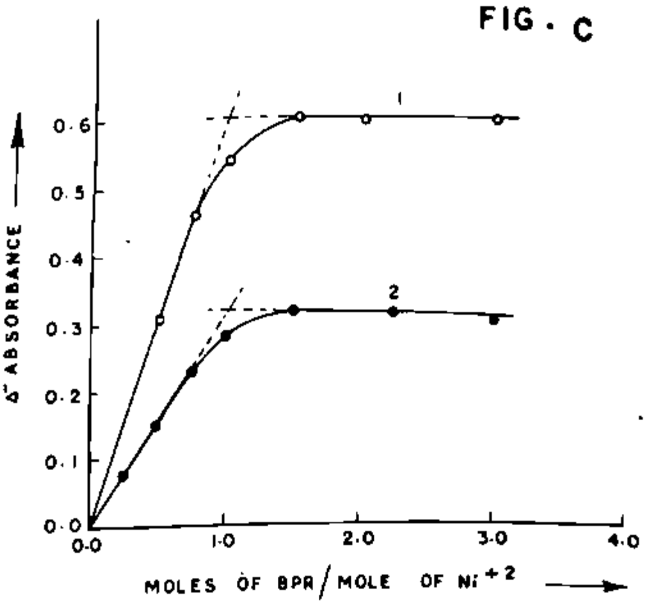


FIG. E

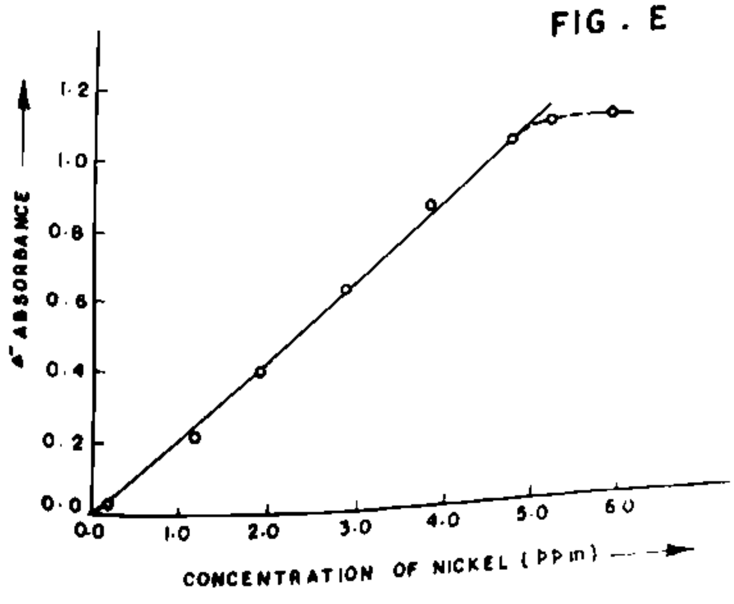


FIG. F

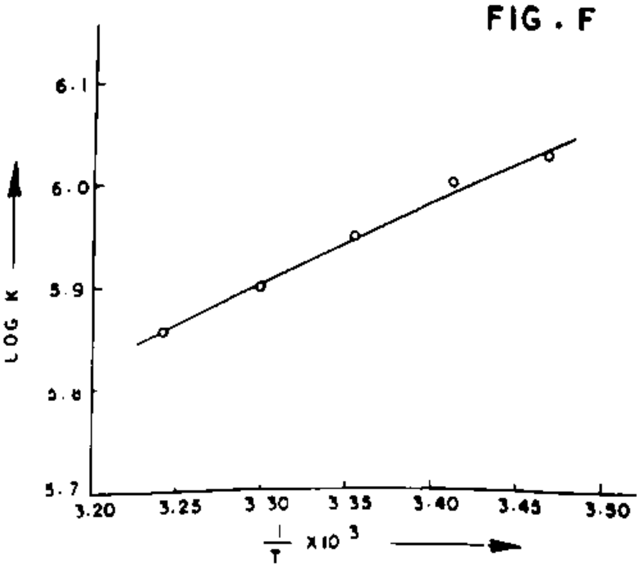


PLATE NO. 8

PLATE No. 9

Fig. A. Absorption curves for mixtures of Cobalt and Bromopyrogallol Red.

Curve 1. $T_L = 6.0\times10^{-5}M$ $T_M = 2.0\times10^{-5}M$

Curve 2. $T_L = 4.0\times10^{-5}M$ $T_M = 2.0\times10^{-5}M$

Curve 3. $T_L = 2.0\times10^{-5}M$ $T_M = 2.0\times10^{-5}M$

Curve 4. $T_L = 2.0\times10^{-5}M$ $T_M = 0.0\times10^{-5}M$

Fig. B. Job's curves (equimolecular and nonequimolecular solutions) for Co:BPR chelate.

Curve 1. $T_L = T_M = 2.0\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 2. $T_L = T_M = 1.0\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 3. $T_L = 2.0 \times 10^{-4}M$ $T_M = 1.0\times10^{-4}M$

$p = T_L/T_M = 2.0$

Fig. C. Mole ratio curves for Co:BPR chelate

Curve 1. Concentration of cobalt (T_M) $= 4.0\times10^{-5}M$

Curve 2. Concentration of cobalt (T_M) $= 2.0\times10^{-5}M$

Fig. D. Slope ratio curves for Co:BPR chelate

Concentration of the constant component $= 1.2\times10^{-4}M$

Concentration of the variable component $= 4.0\times10^{-6}M$ - $2.0\times10^{-5}M$

Curve 1 = metal varying

Curve 2 = ligand varying

Fig. E. Ringbom plot for Co:BPR chelate

Fig. F. Plot of log K vs. 1/T

FIG. A

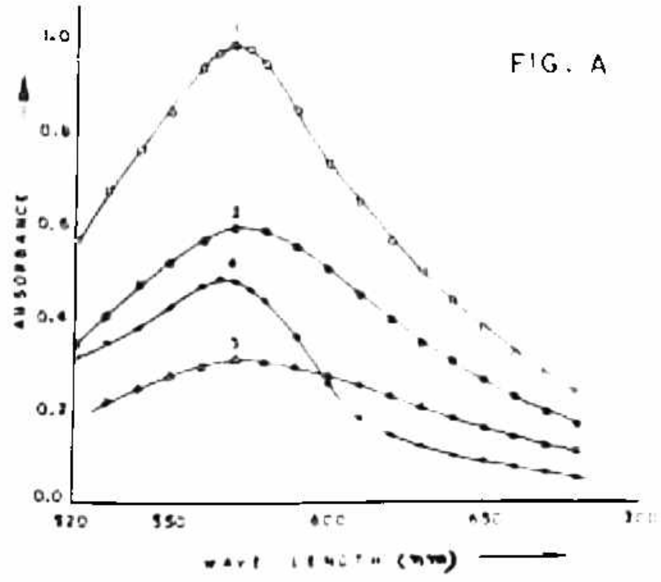


FIG. B

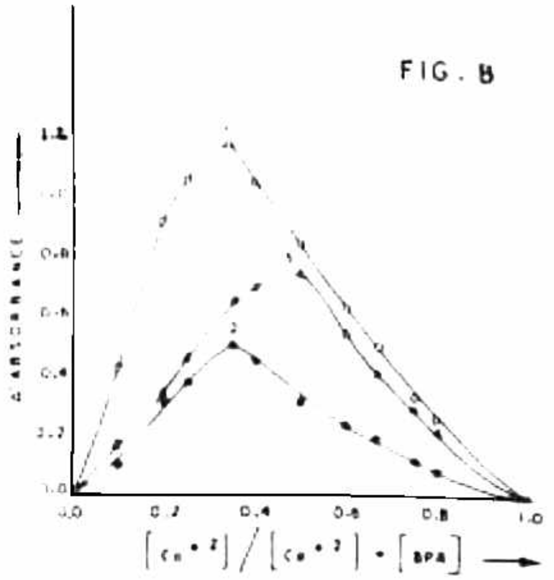


FIG. D

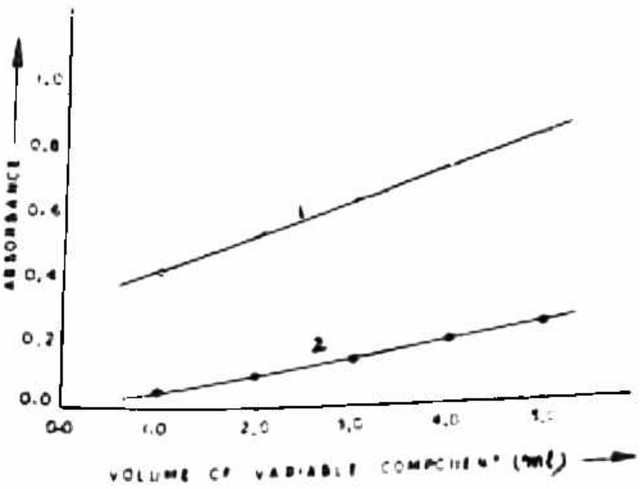


FIG. C

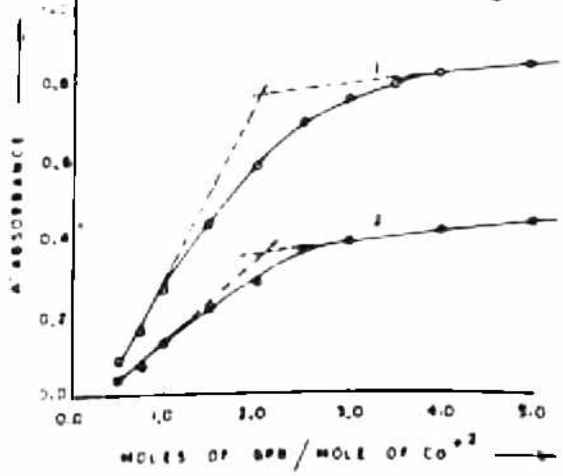


FIG. E

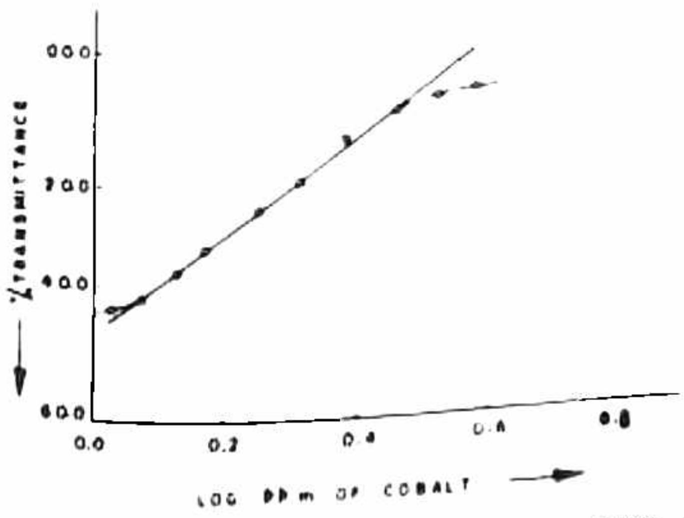


FIG. F

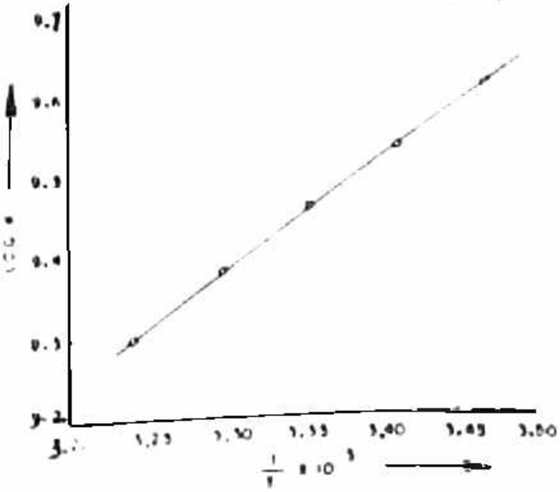


PLATE NO. 9

PLATE No. 10

Fig. A. Absorption curves for mixtures of Ytterbium and Bromopyrogallol Red.

Curve 1. $T_L = 4.8 \times 10^{-5}M$ $T_M = 1.6 \times 10^{-5}M$

Curve 2. $T_L = 3.2 \times 10^{-5}M$ $T_M = 1.6 \times 10^{-5}M$

Curve 3. $T_L = 1.6 \times 10^{-5}M$ $T_M = 1.6 \times 10^{-5}M$

Curve 4. $T_L = 1.6 \times 10^{-5}M$ $T_M = 0.0 \times 10^{-5}M$

Fig. B. Job's curves (equimolecular and nonequimolecular solutions) for Yb:BPR chelate.

Curve 1. $T_L = T_M = 6.66 \times 10^{-5}M$ $p = T_L/T_M = 1.0$

Curve 2. $T_L = T_M = 5.00 \times 10^{-5}M$ $p = T_L/T_M = 1.0$

Curve 3. $T_L = 5.00 \times 10^{-5}M$ $T_M = 1.00 \times 10^{-4}M$

$p = T_L/T_M = 0.5$

Fig. C. Mole ratio curves for Yb:BPR chelate.

Curve 1. Concentration of Ytterbium (T_M) = $4.0 \times 10^{-5}M$

Curve 2. Concentration of Ytterbium (T_M) = $2.0 \times 10^{-5}M$

Fig. D. Slope ratio curves for Yb:BPR chelate.

Concentration of the constant component = $8.0 \times 10^{-5}M$

Concentration of the variable component = $2.0 \times 10^{-6}M$ - $1.0 \times 10^{-5}M$

Curve 1 = metal varying

curve 2 = ligand varying

Fig. E. Ringbom plot for Yb:BPR chelate.

Fig. F. Plot of log K vs. 1/T.

FIG. A

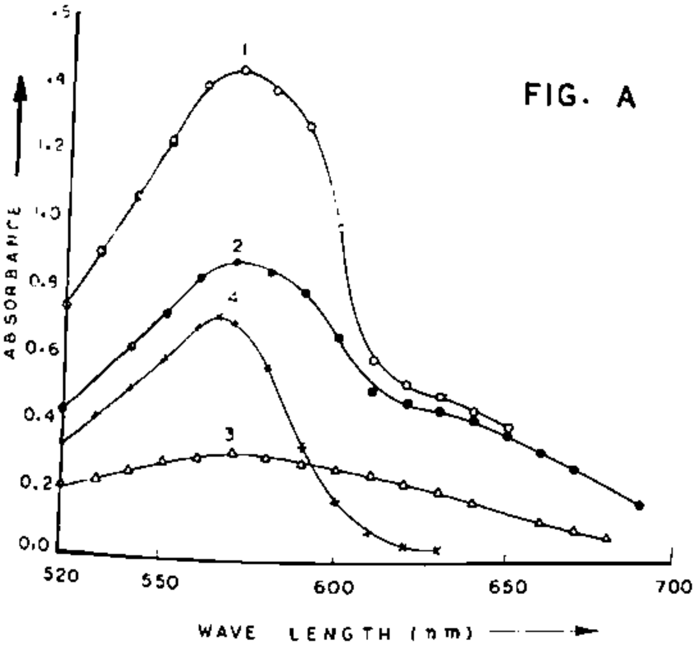


FIG. B

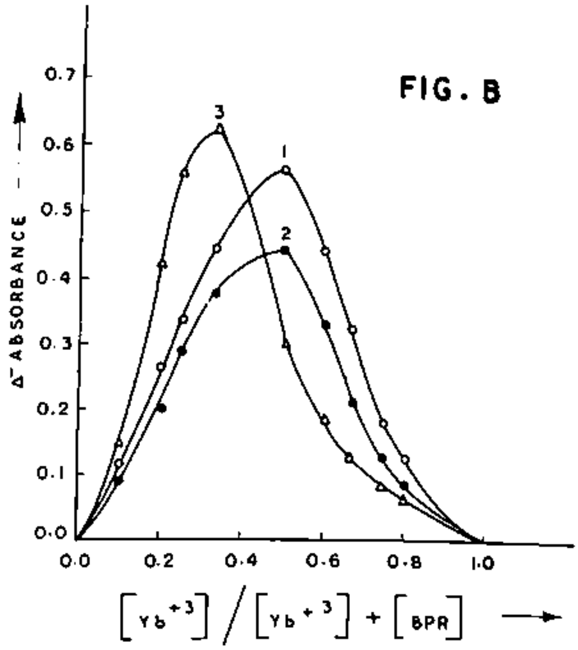


FIG. D

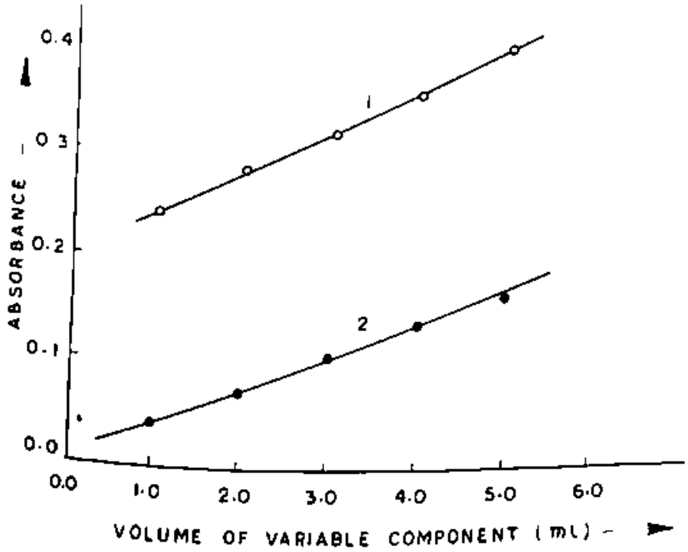


FIG. C

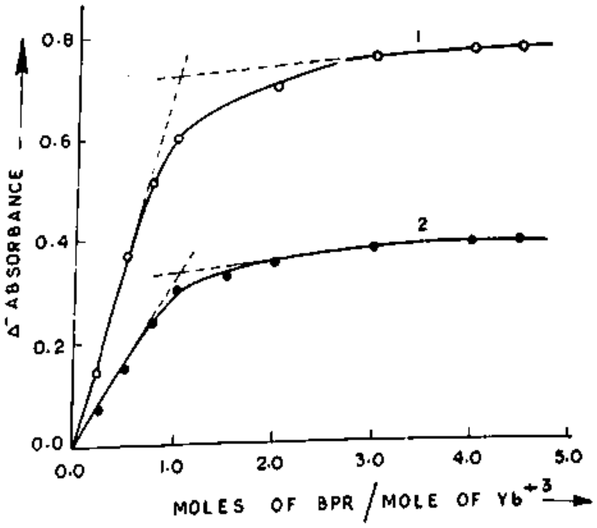


FIG. E

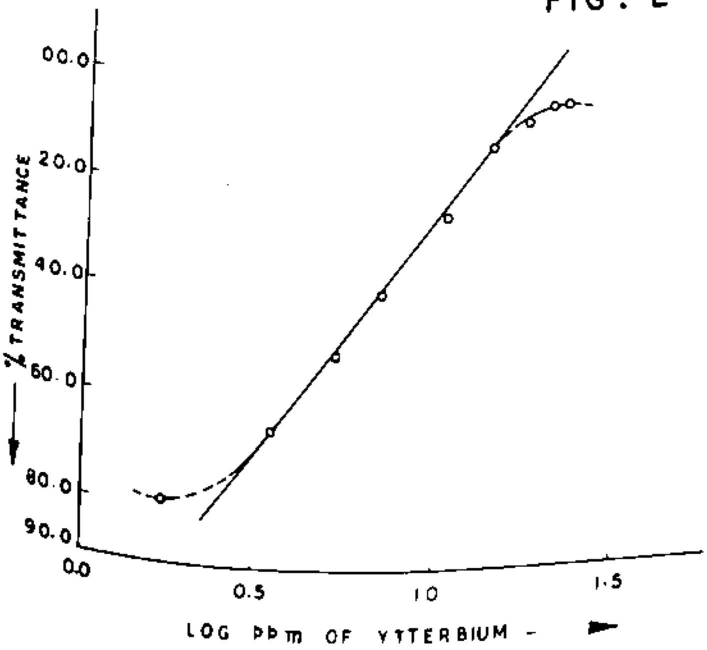


FIG. F

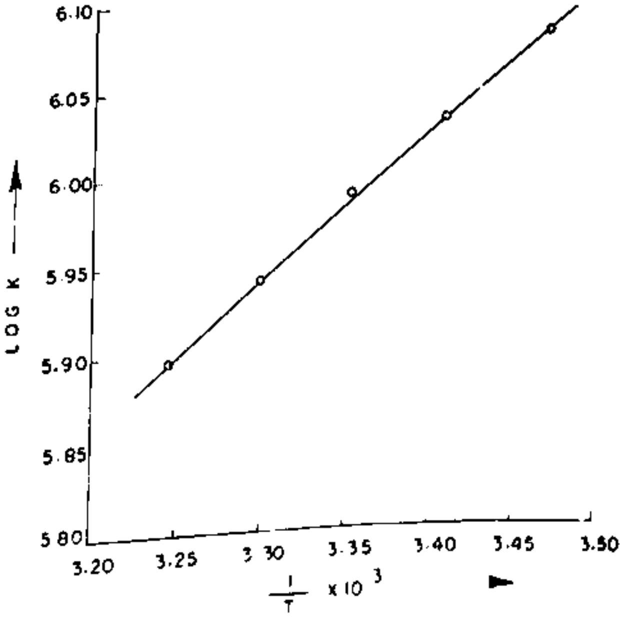


PLATE NO. 10

PLATE No. 11

Fig. A. Absorption curves for mixtures of Praseodymium and Bromopyrogallol Red.

Curve 1. $T_L = 6.0\times10^{-5}M$ $T_M = 2.0\times10^{-5}M$

Curve 2. $T_L = 4.0\times10^{-5}M$ $T_M = 2.0\times10^{-5}M$

Curve 3. $T_L = 2.0\times10^{-5}M$ $T_M = 0.0\times10^{-5}M$

Fig. B. Job's curves (equimolecular and nonequimolecular solutions) for Pr:BPR chelate at 620 nm.

Curve 1. $T_L = T_M = 1.0\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 2. $T_L = T_M = 0.66\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 3. $T_L = 0.66\times10^{-4}M$ $T_M = 1.32\times10^{-4}M$

$T_L/T_M = 0.5$

Fig. C. Mole ratio curves for Pr:BPR chelate.

Curve 1. Concentration of Praseodymium $(T_M)=4.0\times10^{-5}M$

Curve 2. Concentration of Praseodymium $(T_M)=2.0\times10^{-5}M$

Fig. D. Slope ratio curves for Pr:BPR chelate.

Concentration of the constant component = $1.0\times10^{-4}M$

Concentration of the variable component = $4.0\times10^{-6}M$ - $2.0\times10^{-5}M$

Curve 1 = metal varying

Curve 2 = ligand varying

Fig. E. Plot of log K vs. 1/T.

FIG. A

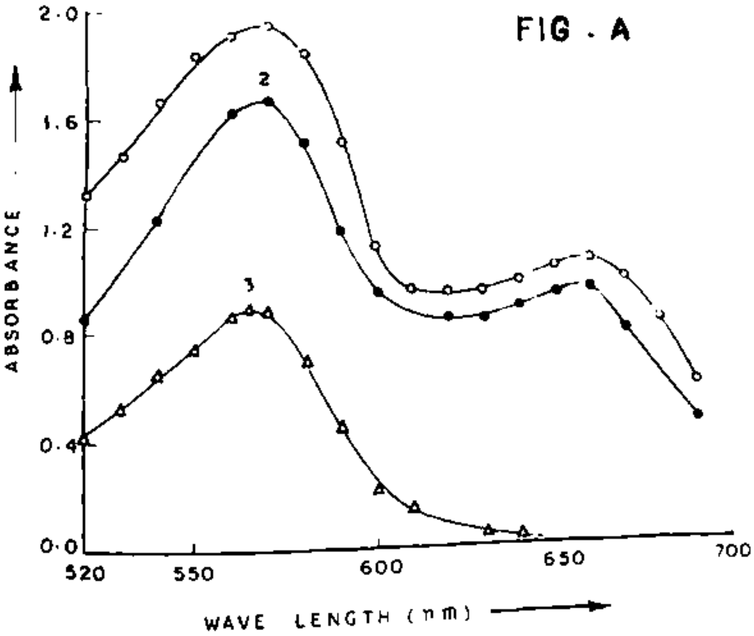


FIG. B

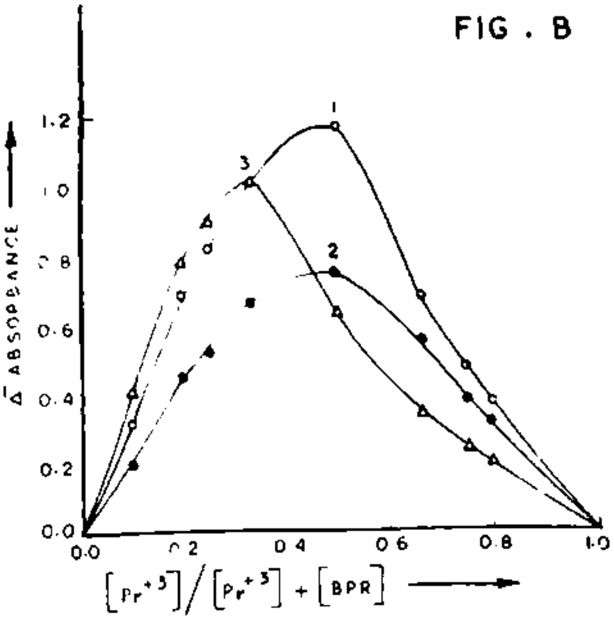


FIG. D

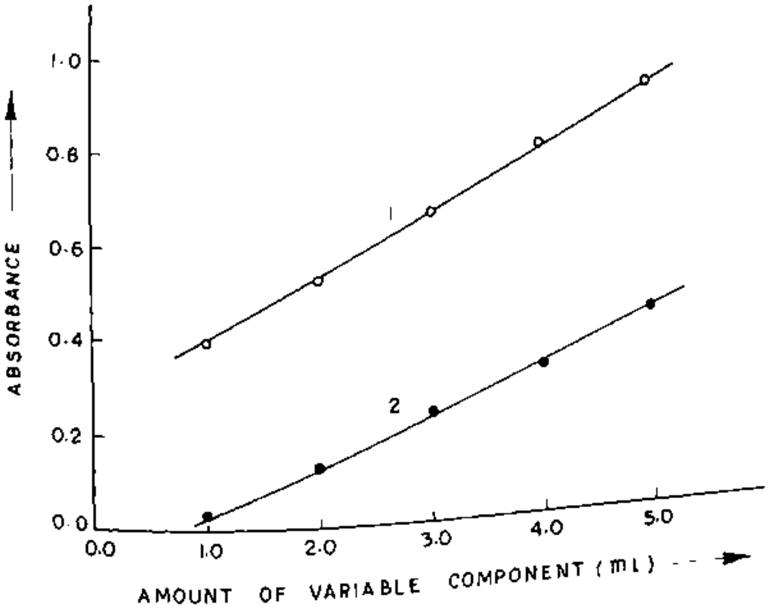


FIG. C

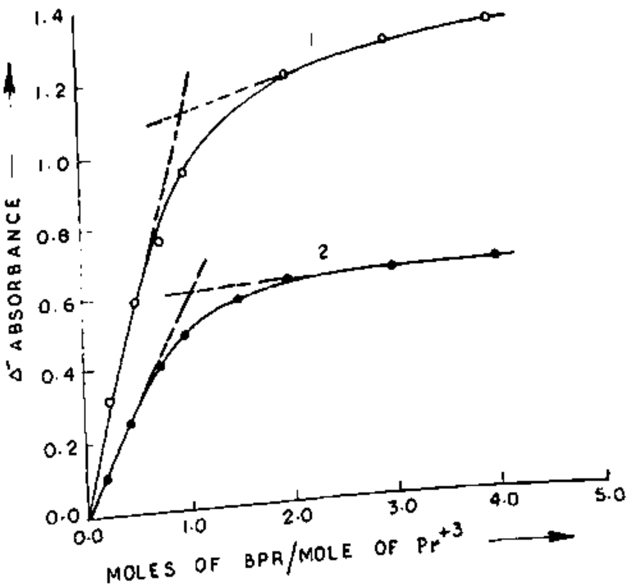


FIG. E

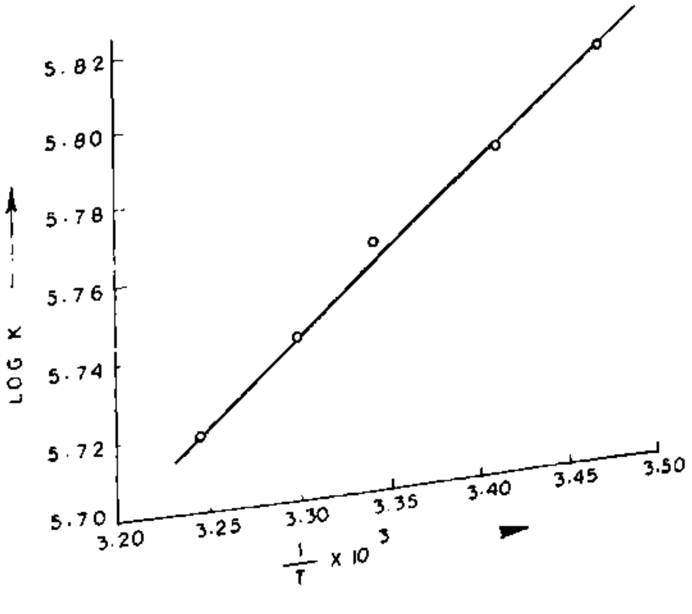


PLATE NO. II

PLATE No. 12

Fig. A. Job's curves (equimolecular and nonequimolecular solutions) for Pr:BPR chelate at 650 nm.

Curve 1. $T_L = T_M = 1.0\times10^{-4}$M $\quad p = T_L/T_M = 1.0$

Curve 2. $T_L = T_M = 0.5\times10^{-4}$M $\quad p = T_L/T_M = 1.0$

Curve 3. $T_L = 0.5\times10^{-4}$M $\quad T_M = 0.25\times10^{-4}$M

$p = T_L/T_M = 2.0$

Fig. B. Mole ratio curve for Pr:BPR chelate.

Concentration of Praseodymium (T_M) = 2.0×10^{-5}M

Fig. C. Slope ratio curves for Pr:BPR chelate.

Concentration of the constant component = 1.0×10^{-4}M

Concentration of the variable component = 2.0×10^{6}M - 1.0×10^{-5}M

Curve 1 = metal varying

Curve 2 = ligand varying

Fig. D. Beer's law plot for Pr:BPR chelate

Fig. E. Plot of log K vs. 1/T

FIG. A

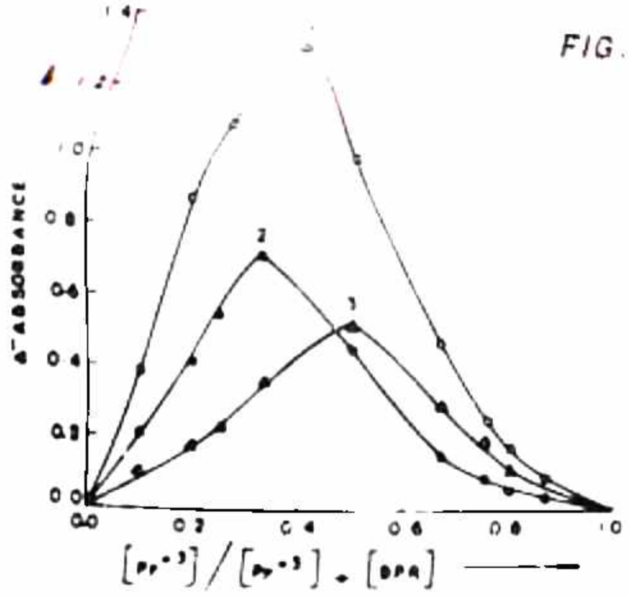


FIG. B

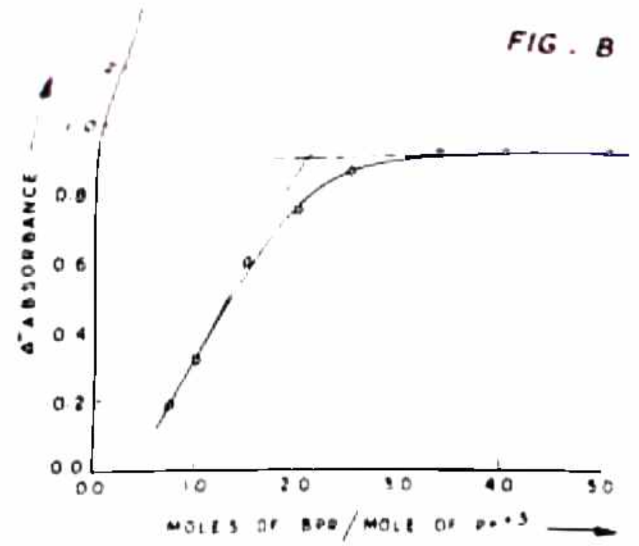


FIG. D

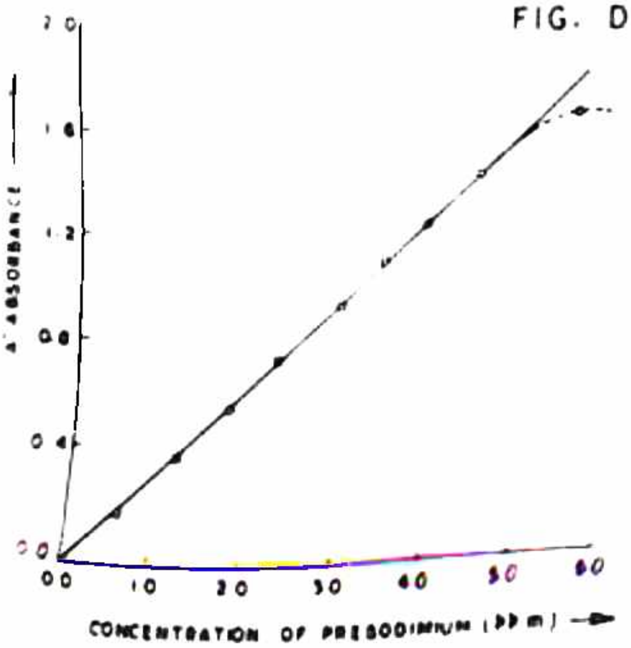


FIG. C

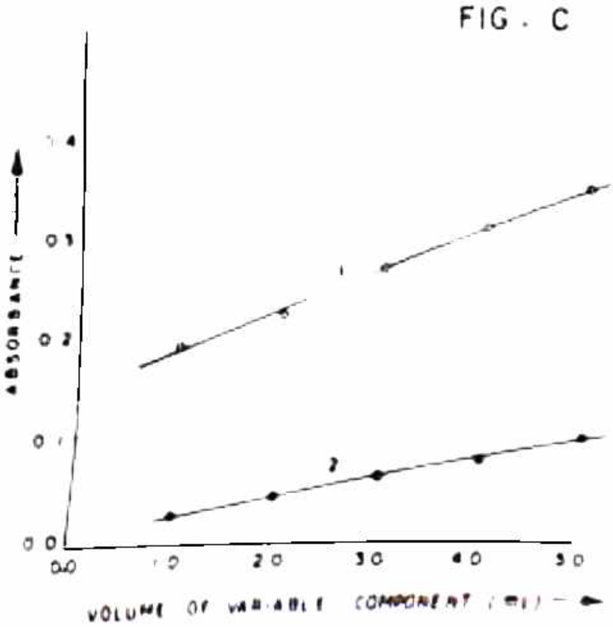


FIG E

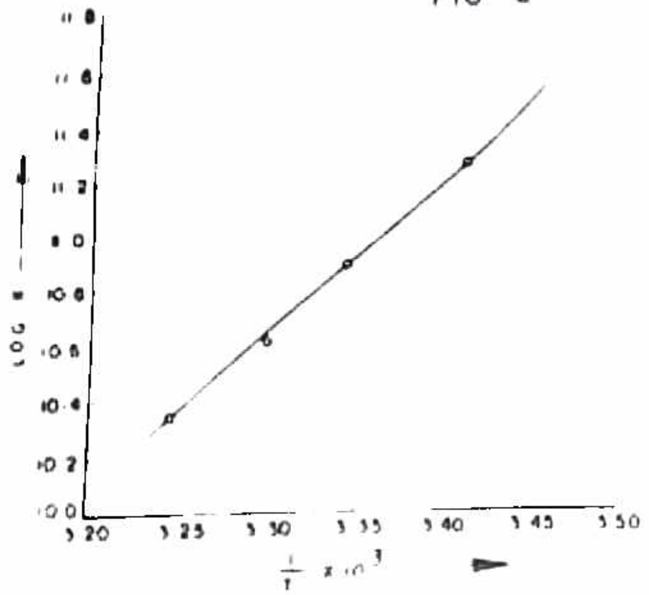


PLATE NO. 12

PLATE No. 13

Fig. A. Absorption curves for mixtures of Tungsten and Bromopyrogallol Red.

Curve 1. $T_L = 8.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 2. $T_L = 4.0\times10^{-5}M$ $T_M = 8.0\times10^{-5}M$

Curve 3. $T_L = 4.0\times10^{-5}M$ $T_M = 4.0\times10^{-5}M$

Curve 4 $T_L = 4.0\times10^{-5}M$ $T_M = 0.0\times10^{-5}M$

Fig. B. Job's curves (equimolecular and nonequimolecular solutions) for W:BPR chelate.

Curve 1. $T_L = T_M = 2.00\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 2. $T_L = T_M = 1.25\times10^{-4}M$ $p = T_L/T_M = 1.0$

Curve 3. $T_L = 2.00\times10^{-4}M$ $T_M = 4.0\times10^{-4}M$

$p = T_L/T_M = 0.5$

Fig. C. Mole ratio for W:BPR chelate.

Curve 1. Concentration of tungsten (T_M) = $8.0\times10^{-5}M$

Curve 2. Concentration of tungsten (T_M) = $4.0\times10^{-5}M$

Fig. D. Slope ratio curves for W:BPR chelate.

Concentration of the constant component = $8.0\times10^{-5}M$

Concentration of the variable component = $4.0\times10^{-6}M$ - $2.0\times10^{-5}M$

Curve 1 = metal varying

Curve 2 = ligand varying

Fig. E. Beer's law plot for W:BPR chelate.

Fig. F. Plot of log K vs. 1/T.

FIG. A

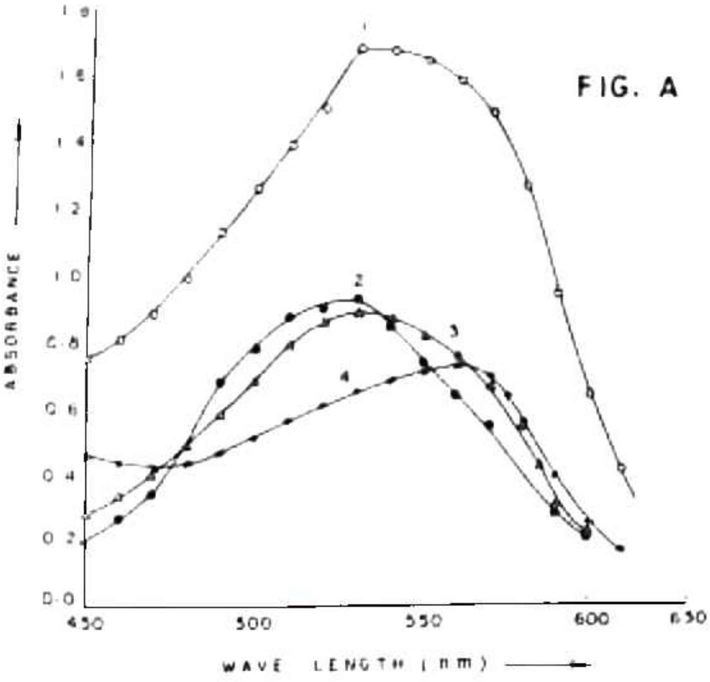


FIG. B

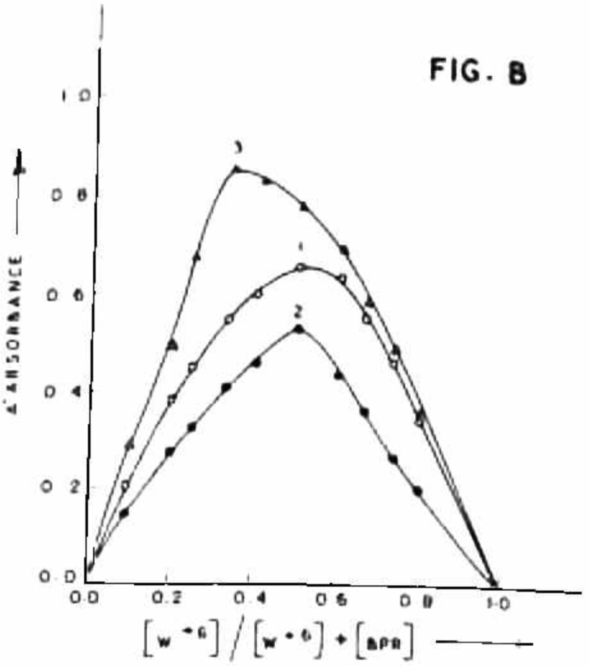


FIG. D

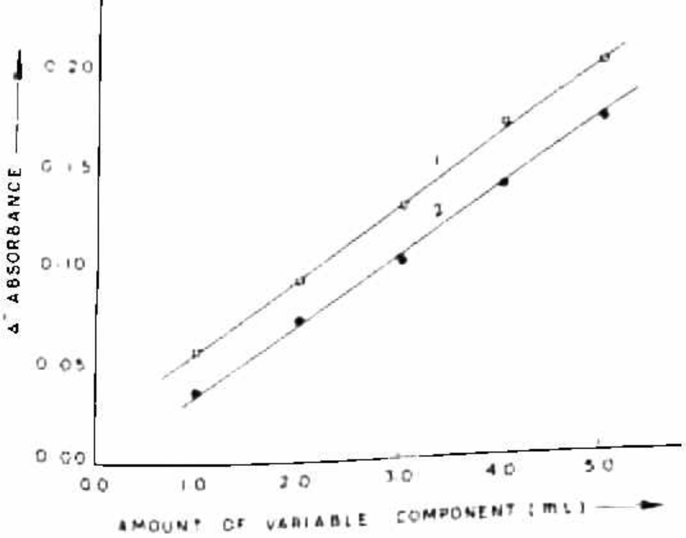


FIG. C

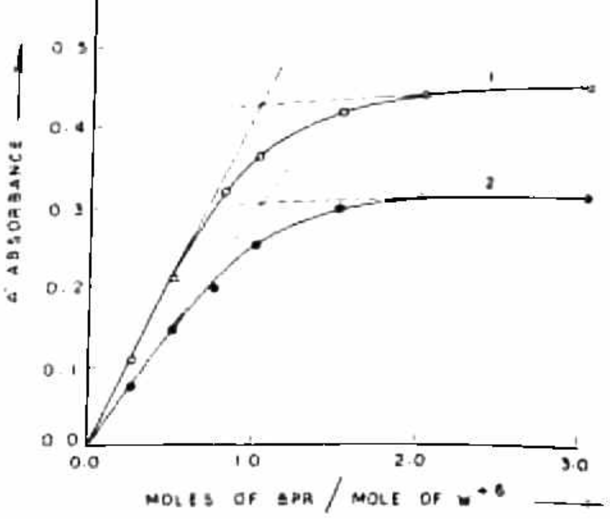


FIG. E

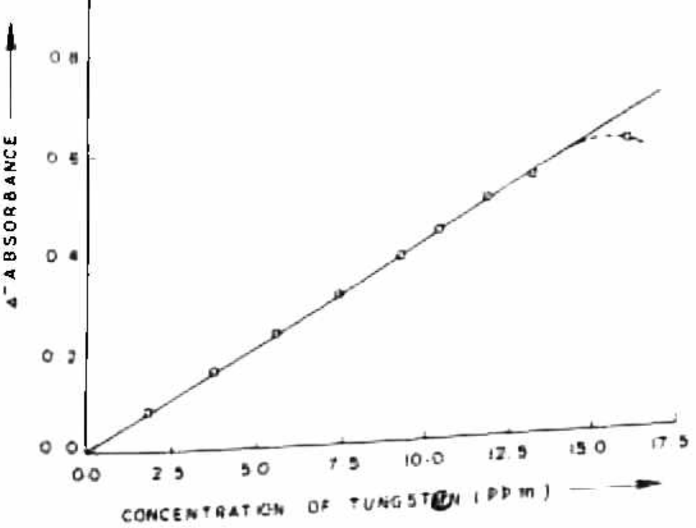


FIG. F

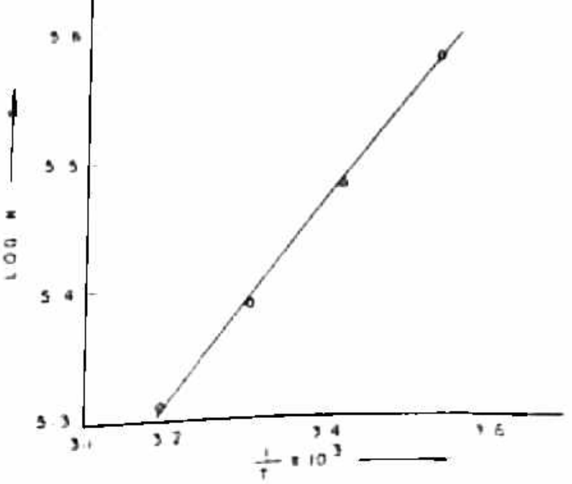


PLATE NO. 13

TABLE 4.1

Shift in λ_{max} with change in pH of BPR solutions

pH	Colour	λ_{max} (nm)
1.0-2.8	orange yellow	440
3.0-5.8	light raspbery	440,565
6.5-9.7	violet	565
> 10	blue	600

TABLE 4.2

Colour reaction of metal ions with Bromopyrogallol Red

Colour of the reagent solution = orange red

S.No.	Metal ion	Colour observed	Remarks
1.	Ag(I)	Yellow	Sensitive with dilute solution
2.	Cu(II)	Blue violet	-
3.	UO_2(II)	Blue violet	Sensitive
4.	La(III)	Blue	Very sensitive
5.	Pb(II)	Blue	Most sensitive with dilute solution
6.	Co(II)	Purple	"
7.	Ni(II)	Purple	"
8.	Yb(III)	Violet	Most sensitive
9.	Pr(III)	Violet	Most sensitive
10.	Mg(II)	Pinkish tinge	-
11.	Zn(II)	Pinkish tinge	-
12.	Be(II)	Violet	Sensitive with dilute solution
13.	Cr(III)	Violet black	-
14.	Fe(III)	Black	-
15.	V(V)	Light yellow	-
16.	W(VI)	Violet	Most sensitive even in dilute solution

TABLE 4.3

Optimum conditions for the study of metal chelates of Bromopyrogallol Red

S.No.	Metal chelate	Temperature °C	Wavelength at which studies were made (nm)	Ionic strength	pH range for the stable existence of the chelate	pH (±0.1) at which the studies were made	pH adjusted with
1.	Pb:BPR	20	630	0.1	3.7-8.6	5.5	HMT*-$HClO_4$
2.	Ni:BPR	30	620	0.1	5.2-9.0	6.8	HMT-$HClO_4$
3.	Co:BPR	30	620	0.1	5.6-9.7	6.5	HMT-$HClO_4$
4.	Yb:BPR	30	620	0.1	4.8-9.3	6.3	HMT-$HClO_4$
5.	Pr:BPR	30	620 and 650	0.1	1.6-9.5	7.2 and 4.0	HMT-$HClO_4$ and $KHC_8H_4O_4$-Hcl
6.	W:BPR	20	510	0.1	2.3-6.0	4.7	$KHC_8H_4O_4$-NaOH

HMT* = Hexamine or Hexamethylene tetramine

TABLE 4.4

Composition and stability of the metal chelates of Bromopyrogallol Red

System	Composition M:L	log K		
		Molecular extinction coefficient method	Mole ratio method	Mean
Pb:BPR	1:1	6.39	6.57	6.48
Ni:BPR	1:1	5.89	5.68	5.79
Co:BPR	1:2	9.40	9.38	9.39
Yb:BPR	1:1	5.94	6.23	6.09
Pr:BPR	1:1	5.75	5.53	5.64
	1:2	10.59	10.74	10.66
W:BPR	1:1	5.56	5.64	5.60

TABLE 4.5

Thermodynamic functions of the Lead-Bromopyrogallol Red complex

pH = 5.5±0.1 μ = 0.1

ΔH = -10.46 kcal/mole

Temperature °K	log K	$-\Delta G$ kcal/mole	$-\Delta S$ e.u./mole
288.15	6.56	8.65	6.26
293.15	6.41	8.60	6.33
298.15	6.28	8.56	6.36
303.15	6.16	8.54	6.33
308.15	6.05	8.52	6.26
		Mean ΔS =	-6.31 e.u./mole

TABLE 4.6

Thermodynamic functions of the Nickel-Bromopyrogallol Red complex

pH = 6.8±0.1 μ = 0.1

ΔH = -3.86 kcal/mole

Temperature °K	log K	$-\Delta G$ kcal/mole	ΔS e.u./mole
288.15	6.03	7.97	14.24
293.15	6.00	8.05	14.28
298.15	5.95	8.11	14.25
303.15	5.89	8.17	14.32
308.15	5.85	8.26	14.26
		Mean ΔS =	14.27 e.u./mole

TABLE 4.7

Thermodynamic functions of Cobalt-Bromopyrogallol Red complex

pH = 6.5±0.1 μ = 0.1

ΔH = -6.35 kcal/mole

Temperature °K	log K	$-\Delta G$ kcal/mole	ΔS e.u./mole
288.15	9.61	12.68	21.97
293.15	9.53	12.78	21.95
298.15	9.46	12.90	21.96
303.15	9.38	13.01	21.99
308.15	9.30	13.11	21.92
		Mean ΔS =	21.96 e.u./mole

TABLE 4.8

Thermodynamic functions of Ytterbium-Bromopyrogallol Red complex

pH = 6.3±0.1 μ = 0.1

ΔH = -3.54 kcal/mole

Temperature °K	log K	$-\Delta G$ kcal/mole	ΔS e.u./mole
288.15	6.07	8.01	15.51
293.15	6.03	8.09	15.52
298.15	5.99	8.17	15.57
303.15	5.94	8.25	15.53
308.15	5.90	8.31	15.53
		Mean ΔS =	15.53 e.u./mole

TABLE 4.9

Thermodynamic functions of Praseodymium-Bromopyrogallol Red complex

pH = 7.2±0.1 μ = 0.1

ΔH = -1.84 kcal/mole

Temperature °K	log K	-ΔG kcal/mole	ΔS e.u./mole
288.15	5.81	7.66	20.20
293.15	5.79	7.76	20.19
298.15	5.76	7.89	20.23
303.15	5.74	7.97	20.21
308.15	5.72	8.06	20.18

Mean ΔS = 20.20 e.u./mole

TABLE 4.10

Thermodynamic functions of Praseodymium-Bromopyrogallol Red complex

pH = 4.0±0.1 μ = 0.1

ΔH = -28.55 kcal/mole

Temperature °K	log K	-ΔG kcal/mole	-ΔS e.u./mole
288.15	11.75	15.49	45.30
293.15	11.25	15.10	45.86
298.15	10.88	14.85	45.80
303.15	10.59	14.69	45.73
308.15	10.34	14.58	45.33

Mean ΔS = 45.60 e.u./mole

TABLE 4.11

Thermodynamic functions of Tungsten-Bromopyrogallol Red complex

pH = 4.7±0.1 μ = 0.1

ΔH = -3.83 kcal/mole

Temperature °K	log K	$-\Delta G$ kcal/mole	ΔS e.u./mole
283.15	5.89	7.25	12.07
288.15	5.48	7.36	12.01
303.15	5.39	7.47	12.00
313.15	5.30	7.60	12.02

Mean ΔS = 12.02 e.u./mole

TABLE 4.12

Optimum concentration range for determination, molar absorptivity and sensitivities of metal chelates of Bromopyrogallol Red

System	Concentration range in which Beer's law is obeyed (ppm)	Optimum concentration range from Ringbom plot (ppm)	Molar absorptivity	Sensitivity $\mu g/cm^2$
Pb:BPR	0.8-14.6	3.0-13.5	5000	0.0140
Ni:BPR	0.25-4.75	0.3-4.3	16000	0.0037
Co:BPR	0.2-3.0	0.3-2.9	29000	0.0022
Yb:BPR	1·0- 14·0	2.9-13.0	19850	0.0087
Pr:BPR	0.5-5.16	0.8-4.9	46500	0.0031
W:BPR	0.8-14.5	2.0-13.6	8000	0.0023

TABLE 4.13

Effect of diverse ions on the photometric determination of Lead with Bromopyrogallol Red

Concentration of Lead taken = 4.0×10^{-5}M

Diverse ion added (ppm)		Relative % error	Tolerance limit (ppm)
Ag(I)	100	+1.6	large excess
UO_2(II)	20	+73.0	0.55
Sn(II)	10	+ 4.0	5.0
Cu(II)	10	+81.0	0.24
Cd(II)	200	-19.7	20.3
Hg(II)	200	+ 6.9	large excess
Be(II)	200	+ 9.6	41.6
Mg(II)	200	- 2.6	large excess
Zn(II)	24	+20.3	2.4
Ba(II)	200	+20.3	19.6
Sr(II)	200	+12.3	32.4
Tl(III)	200	+ 4.2	large excess
La(III)	8	+64.7	0.26
Al(III)	20	+18.2	2.2
Ce(III)	2	+73.6	0.05
Th(IV)	10	+34.1	0.59
W(VI)	80	-41.1	3.9
Mo(VI)	100	+ 8.8	22.7
CH_3COO^-	200	+ 4.43	large excess
Cl^-	200	+ 1.3	large excess
I^-	200	- 1.8	large excess
NO_3^-	200	- 1.9	large excess
$C_2O_4^{--}$	200	+15.2	26.3
SO_4^{--}	200	+ 1.3	large excess
$C_4H_4O_6^{--}$	200	- 1.9	large excess
$C_6H_5O_7^{---}$	100	-17.7	11.6
BO_3^{---}	200	+ 8.0	50.0

TABLE 4.14

Effect of diverse ions on the photometric determination of Nickel with Bromopyrogallol Red

Concentration of Nickel taken = 4.0 × 10^{-5}M

Diverse ion added (ppm)		Relative % error	Tolerance limit (ppm)
UO_2(II)	120	+29.9	8.3
Cd(II)	40	-44.5	1.89
Pb(II)	40	-63.1	1.27
Cu(II)	40	-12.4	6.47
Ba(II)	200	-52.2	7.7
Be(II)	40	-45.3	1.8
Zn(II)	40	-23.7	3.3
Mg(II)	200	+ 3.1	large excess
Sr(II)	200	-48.49	8.2
Sn(II)	20	-74.25	0.5
La(III)	200	+ 9.6	41.7
Tl(III)	100	-34.4	5.9
Ce(III)	40	+20.6	0.4
Th(IV)	200	- 6.1	large excess
W(VI)	100	-19.6	10.3
Mo(VI)	200	- 4.1	large excess
CH_3COO^-	200	+ 7.5	51.9
Cl^-	200	+ 8.6	49.0
Br^-	200	+ 3.1	large excess
ClO_4^-	200	0.0	large excess
NO_3^-	200	+ 1.1	large excess
SO_4^{--}	200	+ 3.1	large excess
$C_2O_4^{--}$	200	-10.8	37.2
$C_4H_4O_6^{--}$	200	- 3.1	large excess
$C_6H_5O_7^{---}$	40	-50.0	1.6
BO_3^{---}	200	+ 3.1	large excess

TABLE 4.15

Effect of diverse ions on the photometric determination of Cobalt with Bromopyrogallol Red

Concentration of Cobalt taken = 4.0 × 10^{-5}M

Diverse ion added (ppm)		Relative % error	Tolerance limit (ppm)
Cd(II)	10	-73.6	0.3
Pb(II)	20	-18.0	2.2
Cu(II)	40	0.0	40.0
Ba(II)	200	+41.0	9.8
Be(II)	20	-47.0	0.8
Zn(II)	100	-17.0	11.8
Sr(II)	200	+45.0	9.1
Sn(II)	200		0.0
Ni(II)	200	-32.0	12.5
La(III)	200	+85.0	4.7
Tl(III)	200	-26.0	15.4
Ce(III)	100	-17.0	11.8
Th(IV)	200	+45.0	9.1
W(VI)	120	-68.6	3.5
Mo(VI)	80	-53.6	3.0
CH_3COO^-	200	+ 9.0	44.4
Cl^-	200	- 6.0	large excess
I^-	200	- 2.0	large excess
NO_3^-	200	- 6.0	large excess
ClO_4^-	200	- 6.0	large excess
SO_4^{--}	200	-30.0	13.3
$C_2O_4^{--}$	200	+ 8.4	47.9
$C_4H_4O_6^{--}$	200	-28.4	14.1
$C_6H_5O_7^{---}$	80	-71.0	2.2
BO_3^{---}	200	- 8.0	50.0

TABLE 4.16

Effect of diverse ions on the photometric determination of Ytterbium with Bromopyrogallol Red

Concentration of Ytterbium taken = 4.0×10^{-5}M

Diverse ion added (ppm)		Relative % error	Tolerance limit (ppm)
Ba(II)	200	- 7.3	large excess
Cu(II)	200	-30.6	13.1
Pb(II)	40	-75.8	1.1
Sn(II)	20	-65.7	0.6
Zn(II)	200	-46.7	8.6
Ni(II)	40	-38.9	2.1
Cd(II)	60	-61.3	2.0
Tl(III)	200	-21.9	18.3
Ce(III)	40	-21.9	3.8
La(III)	40	- 4.9	16.3
Th(IV)	200	-21.1	19.0
W(VI)	200	-28.4	14.1
Mo(VI)	240	+20.8	23.1
CH_3COO^-	200	+ 6.5	large excess
Cl^-	200	+ 5.1	large excess
ClO_4^-	200	- 5.7	large excess
I^-	200	- 0.5	large excess
NO_3^-	200	- 3.4	large excess
SO_4^{--}	200	+ 2.8	large excess
$C_2O_4^{--}$	200	+ 6.8	large excess
$C_4H_4O_6^{--}$	200	-15.0	26.8
$C_6H_5O_7^{---}$	200	-87.6	4.5
BO_3^{---}	200	-10.9	36.7

TABLE 4.17

Effect of diverse ions on the photometric determination of Praseodymium with Bromopyrogallol Red

Concentration of Praseodymium taken = 4.0×10^{-5}M

Diverse ion added (ppm)		Relative % error	Tolerance limit (ppm)
Ni(II)	20	+ 5.8	6.9
Mg(II)	200	- 3.5	large excess
Cd(II)	24	-57.7	0.8
Cu(II)	20	-60.4	0.7
Pb(II)	20	-77.9	0.5
Zn(II)	20	-73.0	0.6
Ce(III)	12	-69.3	0.3
Tl(III)	200	+ 2.3	large excess
La(III)	20	-15.1	2.7
Th(IV)	20	- 6.9	5.8
Mo(VI)	80	-32.5	4.9
CH_3COO^-	200	+22.6	17.7
NO_2^-	200	+12.8	31.3
Br^-	200	- 3.5	large excess
I^-	200	- 4.6	large excess
ClO_4^-	200	+ 1.1	large excess
SO_3^{--}	200	+10.5	38.1
$C_2O_4^{--}$	200	+25.6	15.6
$C_4H_4O_6^{--}$	160	-18.6	17.2
$C_6H_5O_7^{---}$	200	-80.0	4.7
BO_3^{---}	200	-57.7	6.9

TABLE 4.18

Effect of diverse ions on the photometric determination of Tungsten with Bromopyrogallol Red

Concentration of Tungsten taken = 4.0×10^{-5}M

Diverse ion added (ppm)		Relative % error	Tolerance limit (ppm)
UO_2(II)	20	+48.0	0.83
Cd(II)	100	+22.9	8.5
Ba(II)	200	-12.5	31.2
Be(II)	100	-33.3	6.0
Zn(II)	100	-54.5	3.4
Mg(II)	200	-16.6	24.0
Sr(II)	100	-36.7	5.4
Sn(II)	200	+50.0	8.0
Tl(III)	100	-45.0	4.5
Ce(III)	40	-34.6	2.3
Al(III)	100	-22.1	9.1
CH_3COO^-	200	+8.33	46.9
Cl^-	200	- 6.6	large excess
ClO_4^-	200	+ 2.1	large excess
NO_3^-	200	- 8.6	46.5
SO_4^{--}	200	- 8.6	46.5
$C_2O_4^{--}$	200	- 2.1	large excess
$C_4H_4O_6^{--}$	200	-35.4	11.3
$C_6H_5O_7^{---}$	80	-42.0	3.9
BO_3^{---}	200	+13.3	30.1

TABLE 4.19

Comparison with other reagents used for the spectrophotometric determination of Nickel and Cobalt

Method	Molar absorptivity	Reference
For Nickel		
1) N-methylanabasine-α'-azo-hydroxyquinoline	1.29×10^4/500 nm	57
2) 8-hydroxy-5 quinoline-sulphonic acid	1.30×10^4/400 nm	28
3) Mercaptothioazolyl-azo-naphthol	1.50×10^4/638 nm	20
4) p-dihydroxydithiobenzoic acid	1.50×10^4/530 nm	44
5) 2,3-bis (salicylideneamino-benzofuran)	1.22×10^4/535 nm	26
6) Bromopyrogallol Red	1.60×10^4/620 nm	
For Cobalt		
1) 1-(2-pyridylazo)-2-naphthol	2.5×10^4/640 nm	23
2) 7-nitroso-8-hydroxyquinoline)-5-sulphonic acid	1.1×10^4/528 nm	21
3) Furildioxime	1.84×10^3/350 nm	27
4) Mercaptothioazolyl-azo-naphthol	1.18×10^4/680 nm	20
5) 4-(2-thiazolylazo) resorcinol	2.5×10^4/570 nm	22
6) Bromopyrogallol Red	2.9×10^4/620 nm	

TABLE 4.20

Comparison with other reagents used for the spectrophotometric determination of Ytterbium and Praseodymium

Method	Molar absorptivity	Reference
For Praseodymium		
1) Diantipylylazo	2.30×10^4/645 nm	8
2) Arsenoazo (I)	1.67×10^4/584 nm	
3) Chromotrope 2R	3.00×10^3/590 nm	47
4) Xylenol orange	1.70×10^4/570 nm	5
5) Stilbazo (I)	1.27×10^4/536 nm	59
6) 1-methyl-6'-(4-hydroxy-3-totylazo) anabasine	3.30×10^4	29
7) Bromopyrogallol Red	4.65×10^4/650 nm	
For Ytterbium		
1) Xylenol orange	2.10×10^4/570 nm	5
2) Chromotrope 2R	2.50×10^4/570 nm	9
3) Diantipyrylazo	2.30×10^4/645 nm	8
4) Pyrocatechol violet	2.10×10^4/650 nm	2
5) Methyl thymol blue	2.10×10^4/600 nm	2
6) Bromopyrogallol Red	1.985×10^4/620 nm	

TABLE 4.21

Comparison with other reagents used for the spectrophotometric determination of Tungsten and Lead

Method	Molar absorptivity	Reference
For Tungsten		
1) Phenylfluorone	$8.50\times10^3/453$ nm	9
2) Quinalizarin	7875/530 nm	50
3) 8-Mercaptoquinoline	$3.67\times10^3/412$ nm	33
4) Tiron	$7.60\times10^3/313$ nm	62
5) Benzohydroxyamic acid	$6.50\times10^3/290$ nm	40
6) Bromopyrogallol Red	$8.00\times10^3/510$ nm	
For Lead		
1) 1-(2-pyridylazo)2-naphthol	5.30×10^3	35
2) Quinalizarin	$5.00\times10^3/655$ nm	36
3) 7- α-(o-Methoxy-carbonylaniline)-8-quinolinol	$4.50\times10^3/410$ nm	65
4) 2-carboxy-2'-methoxy-5'-sulpho-formazylbenzene	$1.00\times10^4/590$ nm	63
5) Bromopyrogallol Red	$5.00\times10^3/630$ nm	

REFERENCES

1. Akhmedli, M.K., Ayubova, A.M. and Imamverdieva, F.B. — Azerb. Khim. Zh., 2, 138 (1971)

2. Akhmedli, M.K. and Granovskaya, P.B. — Azerb. Khim. Zh., 5, 105 (1965)

3. Akhmedli, M.K. and Imamverdieva, F.B. — Azerb. Khim. Zh., 3, 122 (1966)

4. Barbig, L., Sardini, D., Maggi, C.A. and Sanna, G.P. — Biol. Lat. 21(3), 389 (1970)

5. Barnard, A.J. Jr. and Flashka, H.A. — 'Chelates in analytical chemistry' Mescell Dekker, Inc., New York, Vol. 1, p. 20 (1967)

6. Bashirov, E.A., Akhmedli, M.K. and Abdullavoa, T.E. — Azerb. Khim. Zh., 1, 114 (1967)

7. Belcher, R., Ramakrishna, T.V. and West, T.S. — Talanta, 12(7), 681 (1965)

8. Buděšinský, B. and Vrzalova, D. — Anal. Chim. Acta, 36(2), 246 (1966)

9. Buganov, Kh.G., Bagdasarov, K.N. and Tateav, O.A. — Sb. Statei Moldykh. Uch. Dagest Fil. Akad. Nauk., SSSR, 198 (1968)

10. Christopher, D.H. and West, T.S. — Talanta, 13(3), 507 (1966)

11. Costache, D. — Stud. Univ. Babes- Balyai, Ser. Chem., 16(2), 130 (1971).

12. Costache, D. and Popa, Gr. — Rev. Roum. Chim., 15(9), 1349 (1970)

13. Dagnall, R.M., ElGhomry, M.T. and West, T.S. — Talanta, 15(1), 107 (1968).

14. Dagnall, R.M. and West, T.S. — Talanta, 8, 711 (1961).

15. Dagnall, R.M. and West, T.S. — Talanta, 11(11), 1533 (1964).

16. Deguchi, M., Abe, R. and Okumura, I. — Bunseki Kagaku, 18(10), 1248 (1969)

17. Deguchi, M. and Sakai, K. — Kagaku Keisatsu Kenkyushu Hokoku, 22(3), 164 (1969); 22(3), 168 (1969).

18. Deguchi, M., Tanno, K. and Sakai, K. — Bunseki Kagaku, 19(9), 1291 (1970)

19. Dhupar, S.C., Srivastava, K.C. and Banerji, S.K. — J. Ind. Chem. Soc., 49(4), 425 (1972).

20. Domaglina, E. and Zoreba, S. — Chem. Anal. (Warsaw), 15, 1227 (1970)

21. Dong, H.L. — Daehan Hwakak Howejee, 9(2), 101 (1965).

22. Frei, R.W. and Navretil, O. — Anal. Chim. Acta, 52, 221 (1970)

23. Goldstein, G., Manning, D.L. and Menis, O. — Anal. Chem., 31, 192 (1959)

24. Herrington, J. and Steed, K.C. — Anal. Chim. Acta, 22, 180 (1960)

25. Honsa, I. and Suk, V. — Collect. Czech. Chem. Commun., 35(4), 1283 (1970)

26. Ishii, H. and Einaga, H. — Bunseki Kagaku, 19, 1351 (1970)

27. Jones, J.L. and Gastfeild, J. — Anal. Chim. Acta, 51, 130 (1970)

28. Kambara, T., Matsumae, S. and Hasebe, K. — Bunseki Kagaku, 19, 1239 (1970)

29. Krukovskaya, E.L., Talipov, Sh.T. and Lenchenko, T.A. — Izv. Akad. Nauk. Kaz. SSR, Ser. Khim., 19(3), 6 (1969)

30. Leminger, O. — Chem. Prümyst, 5(30), 7 (1955)

31. Lisitsyna, D.N. and Shcherbov, D.P. — Zh. Metal, 1971 Abstr. No. 3K7

32. Luk'yanov, V.F. and Duderova, E.P. — Zhur. Anal. Khim., 16, 60 (1961)

33. Nazarenko, V.A. and Poluektova, E.N. — Zh. Anal. Khim., 26, 1331 (1971)

34. Nazarenko, V.A. and Ravitzkaya, R.V. — Zavod. Lab., 24, 9 (1958)

35. Negoiu, D., Kriza, A. and Baloiu, L. — Analete Univ. Bueuresti, Ser. Stiint. Nat., 13(1), 165 (1964)

36. Nemirovskaya, A.F. — Tr. Novocherk Politekhn. Inst., 143, 45 (1963).

37. Pandey, S.C. and Sangal, S.P. — J. Prakt. Chem., 311(2), 328 (1959)

38. Pandey, S.C. and Sangal, S.P. — Chim. Anal. (Paris), 15(11), 555 (1969).

39. Polektov, N.S., Ovahar, L.A., Ornichenko, S.F. and Lauer, R.S. — Zavod. Lab., 37(8), 895 (1971).

40. Poluektova, E.N. and Nazarenko, V.A. — Zh. Anal. Khim., 22(5), 746 (1967).

41. Popa, Gr. and Paralescu, I. — Talanta, 15, 272 (1968)

42. Ringbom, A.A. — Z. Anal. Chem., 115, 332 (1939)

43. Roeibish, G. — Anal. Chim. Acta, 47, 539 (1969)

44. Rudzitis, G., Postare, S. and Jansons, E. — Zh. Anal. Khim., 25, 2407 (1970)

45. Sandell, S.B. — 'Colorimetric determination of traces of metals', Inc. New York (1959)

46. Sandu, M.A., Poluektov, N.S. and Lauer, R.S. — Ukr. Khim. Z., 37(8), 820 (1971).

47. Shah, V.L. and Sangal, S.P. — Chim. Anal. (Paris), 53(1), 47 (1971)

48. Shimizu, T. — Talanta, 14(4), 473 (1967)

49. Sohon, M.D. — Amer. Chem. J., 20, 257 (1898)

50. Srivastava, K.C. — Unpublished work.

51. Suk, V. — Collect. Czech. Chem. Commun., 31(1), 367 (1966)

52. Suk, V. — Collect. Czech. Chem. Commun., 31(8), 3127 (1966)

53. Suk, V., Malát, M. and Jeničkova, A. — Chem. Listy, 49, 1798 (1955)

54. Suk, V., Nemcova, I. and Malát, M. — Collect. Czech. Chem. Commun., 30(8), 2538 (1965)

55. Takayoshi, S. and Yuko, F. — Bull. Chem. Soc. Japan, 42(8), 2272 (1969)

56. Talipan, Sh.T., Abdullaeva, Kh.S. and Gor'kovaya, G.P. — Uzbeksh. Khim. Zh., 6(5), 16 (1962)

57. Talipov, Sh.T., Dzhiyanhaeva, R.Kh. and Andrushko, G.S. — Nauchn. Tr. Tashkentsk. Gos. Univ., 264, 106 (1964)

58. Tataeev, O.A. — Materialy 4-oi(Chetvertoei) Nauchn. Konf. Aspirantov Sb. 133 (1962)

59. Tataev, O.A. and Bagdasarov, K.N. — Peredovye Methody Khim. Technol. i. Kontrolya Proizv., 249 (1964)

60. Thierig, D. and Umland, F. — Fresenus' Z. Anal. Chem., 221, 229 (1966)

61. Tserkovnitskaya, I.A. and Bykhovtseva, T.T. — Zh. Anal. Khim., 19(5), 574 (1964)

62. Tsuneo, S. Kimiko, K., Sakuko, O. and Kyoich, H. — Bunseki Kagaku, 15(2), 120 (1966)

63. Uchimi, A. and Iida, H. — Nippon Kagaku Zasshi, 89(8), 776 (1968)

64. Vasilenko, V.D., Shanya, M.V. and Bolbas, V.I. — Z. Anal. Khim., 22(12), 1818 (1967)

65. Vosburgh, W.C. and Cooper, G.R. — J. Am. Chem. Soc., 72, 5455 (1950)

66. Vodák, Z. and Leminger, O. — Chem. Listy, 50, 2028 (1956)

67. West, T.S. — Analyst., 87, 630 (1962)

* * *

CHAPTER V

POTENTIOMETRIC STUDIES OF SOME BIVALENT METAL CHELATES OF CHROMOTROPE 2R

Most complexing agents in general, and chelating agents in particular, exhibit acid-base properties, and the complexation of a metal ion is accompanied by either a release or a consumption of hydrogen ion. Consequently, the complexation reactions can be followed via pH measurements, which can be performed most readily with a glass electrode. This convenient approach was demonstrated quite early by Bjerrum[6] and Schwarzenbach[34]. Commonly, an aqueous medium is employed, but for water insoluble compounds other media can be used, for example dioxane-water mixtures[10]. From the potentiometric titration curves for the ligands it is possible to evaluate the number of protons that are neutralized and to calculate the respective acid dissociation constants.

When a chelating agent is neutralised in the presence of a metal ion that is capable of being complexed, the form of the titration curve will change in a characteristic manner. The stability constant of the chelates formed may then be determined from the nature of the curve. The analysis of the titration curve also enables the determination of the stability of any protonated chelates formed. Typical examples of this technique can be found in the work of Schwarzenbach and coworkers[35] and in a recent paper of Schacher[32]. Application of the potentiometric method to the analysis of more complicated systems where polynuclear chelates are formed have been reported by Grimes and coworkers[19], Bohigian and Martell[7,8] and

Schrøder[33].

As discussed earlier in Chapter III, chromotropic acid has been used for the photometric determination of various metal ions. However, some workers have also reported potentiometric studies on the metal chelates of chromotropic acid with a view to determine the stepwise stability constants.

Zollinger[37] determined the dissociation constants of 1st and 2nd OH groups of many dihydroxynaphthalene sulphonic acids potentiometrically. He concluded from these studies that there exists strong hydrogen bonding between OH groups in the 1,8 positions, very weak hydrogen bonding between OH groups in the 2,3 positions and no hydrogen bonding between OH groups in the 2,8 positions. Buděšinský[9] has reported the acidity of several chromotropic acid derivatives by potentiometric and spectrophotometric methods.

The course of reaction between chromotropic acid and titanium was followed potentiometrically by Sommer[29]. Athavale and coworkers[1,2] have studied the stepwise formation of metal chelates of some bivalent and trivalent metal ions. Bartusek[4,5] made potentiometric investigations of Beryllium and Uranium chelates of chromotropic acid. The potentiometric titration of ligand solution with Mn(III)[25] showed a 1:1 molar ratio for the complex. Jöntti[21] concluded from his studies on metal chelates of chromotropic acid the order of stabilities as $Al^{+++} < Cu^{++} < Cr^{+++} < UO_2^{++}$.

Less stable compounds were formed with Co^{+2}, Ni^{+2} and Mn^{+2}, while no chelation was noted with Ca^{+2}, Sr^{+2} and Ba^{+2}. Mehrotra and Dubey[16,17] have reported the potentiometric titration of beryllium and aluminium. Dey[3] used Irving and Rossotti titration technique, to determine the stepwise protonation constants of chromotropic acid and stepwise formation constant of chelates with uranium and thorium. Recently Gonia and coworkers[18] have determined the thermodynamic functions related to aluminium and chromotropic acid chelate. Many workers[11,12,14,20,24,31] have used chromotropic acid as secondary reagent for the study of mixed ligand chelates using this technique. Martell and coworkers[13,15,26] have investigated the hydrolytic tendencies of metal chelate compounds potentiometrically.

However, no work appears in literature on the potentiometric studies of derivatives of chromotropic acid. Miyata and coworkers[22,23,27,28] have made detailed studies on the chelate formation of o-substituted phenylazo chromotropic acids with alkaline earth metals i.e. with calcium, barium, strontium and magnesium. Recently Petrova and coworkers[30] have made a comparative study potentiometrically of colour reactions of bisazo-substituted chromotropic acids.

While working on chromotrope 2R chelates spectrophotometrically, certain amount of interest was induced to study the stepwise stability constants of some bivalent metals potentiometrically, at different ionic strengths as no work is reported in literature except on some alkaline earths (Mg, Ca, Ba and Sr) very recently by Miyata[28].

The method followed is essentially the Bjerrum-Calvin titration technique as modified by Irving and Rossotti which is described at length in Chapter II. A suitable program was formed for the IBM 1130 computer to calculate the various values of $\bar{n}_A$, $\bar{n}$ and pL, the knowledge of which is essential for calculating the stepwise proton ligand stability constants and the stepwise metal-ligand stability constants.

EXPERIMENTAL

Apparatus

A Beckman pH meter (model H_2) with glass-calomel electrode assembly was used for pH measurements. Standard Beckman buffer supplied with the instrument, was used to check the value of pH at regular intervals of time, to ensure the accuracy of the results.

Reagents

A purified sample of chromotrope 2R (E. Merck) was used to prepare a M/100 solution in carbon dioxide free double distilled water. Uranyl nitrate, copper sulphate, beryllium sulphate, lead nitrate, mercuric chloride, cadmium sulphate, nickel sulphate, cobalt sulphate and zinc sulphate (all BDH, AnalaR) were dissolved in appropriate amount of double distilled water and their content estimated by usual methods[36]. Sodium perchlorate (Reidel) solution was used to maintain the required ionic strength, as per-chlorate ion, of all the anions, has the least complexation tendency towards metal ions. Sodium hydroxide (E. Merck) solution was prepared and kept over lime overnight and then standardised against oxalic acid. The strength of analytical grade perchloric acid (J.T. Baker Chemical Co., Phillipsburg, N.J.) solution was determined by titrating against standard sodium hydroxide potentiometrically. All the studies were performed at room temperature (15±1.0°C).

Calvin-Bjerrum pH titration technique

The following mixtures were titrated against 1.0N sodium hydroxide pH-metrically in aqueous medium using a microburrete. The mixtures were stirred magnetically, and the pH noted after each addition.

(A) 5 ml of N/5 perchloric acid + x ml of 2.5M sodium perchlorate

(B) Mixture A + 75 ml of M/100 chromotrope 2R

(C) Mixture B + 15 ml of M/100 metal ion solution

The value for x was 1 ml, 2 ml, 3 ml and 5 ml for maintaining the overall ionic strength 0.025, 0.050, 0.075 and 0.125 respectively. Carbon dioxide free double distilled water was added in the first two mixtures to make the total volume 100 ml. A molar ratio of 1:5 of metal to ligand was maintained to fulfil the maximum co-ordination number of the metal.

The volume of alkali used in each mixture was plotted against the pH of the corresponding solution and the formation curves so obtained are represented in plates 14-17 (Fig. A, Fig. C and Fig. D). Curves 1 and 2 in Fig. A represent the titration curves for perchloric acid + sodium perchlorate and perchloric acid + ligand + sodium perchlorate respectively. Curves 1 to 9 in Fig. C and Fig. D are the titration curves in the presence of Nickel, Cobalt, Berylium, Cadmium, Uranyl ion, Lead, Zinc, Mercury and Copper respectively.

The additional amount of sodium hydroxide needed to reach the same pH values in the presence of metal ions is clearly due to the liberation of hydrogen ion on account of complex formation between the ligand and the metal ions. It is seen that the titration curves almost concide at higher pH values at which the reagent is completely ionised. This shows that metal complexes are hydrolysed to a very small extent at high pH values.

<u>Proton-ligand stability constants</u>

For the calculation of metal ligand stability constant, a prior determination of proton-ligand stability is necessary. The observations made during the titration of mixtures A and B containing perchloric acid and perchloric acid + chromotrope 2R respectively, were used to calculate the formation constants of the proton ligand system. Chromotrope 2R (4,5 dihydroxy-3(-phenylazo) 2:7 naphthalene disulphonic acid) possesses two ionisable hydrogen atoms in the two -OH groups present in ortho position to each other. However, the titration curve 2 in Fig. A of plates 14-17 shows only one inflection, indicating the dissociation of one of the hydrogen atom in the range of pH in which titrations were carried out.

Calculation of $\bar{n}_A$

The value of y in the expression given below which was used to calculate $\bar{n}_A$ (the average number of protons dissociated during the course of titration) was taken as unity as only one proton gets dissociated.

$$\bar{n}_A = y + \frac{(v' - v'')\ (N^o + E^o)}{(V^o + v')\ T_L} \qquad (5.1)$$

where T_L = total concentration of chromotrope 2R = 7.5×10^{-4}M

E^o = initial concentration of perchloric acid = 0.01M

V^o = total initial volume of mixtures = 100 ml

N^o = normality of sodium hydroxide = 1.0M

v' and v'' = volumes of sodium hydroxide added in the absence and in the presence of chromotrope 2R to reach the same value of pH

T_L, E^o, N^o and V^o being known, the value of $\bar{n}_A$ can be ascertained by reading the values of v' and v'' at various pH values from the curves 1 and 2 in graphs represented in Fig. A (plates 14-17). The values of $\bar{n}_A$ at various pH values have been calculated using a suitable program on IBM 1130 computer. The results obtained at various ionic strengths are embodied in Fig. B (plates 14-17). However, the representative results at one ionic strength only, are presented in Table 5.1.

The proton ligand formation curves were obtained by plotting the graphs between $\bar{n}_A$ and pH. Various computational methods viz. interpolation at half $\bar{n}_A$ values (H) and interpolation at various $\bar{n}_A$ values (V) have been applied to determine the proton-ligand stability constant at different ionic strengths. The thermodynamic stability constant was obtained by extraploting these values to zero ionic strength. The values of the proton-ligand stability constants so obtained are enlisted in Table 5.2.

Metal-ligand stability constants

The formation of metal complexes in solution has been found to take place in a stepwise manner. The value of stepwise formation constant is obtained by applying various computational methods by plotting $\bar{n}$ against pL. The value of $\bar{n}$ i.e. the average number of ligand molecules attached, per metal ion, is given by

$$\bar{n} = \frac{(v''' - v'')\left[N^o + E^o + T_L\ (y - \bar{n}_A)\right]}{(V^o + v'')\ \bar{n}_A . T_M} \qquad (5.2)$$

where

T_M = total concentration of metal present in solution

= 0.0025M

v''' = the volume of sodium hydroxide used in mixture C to reach the same pH as in the case of mixtures A and B.

The other terms in the expression 5.2 have their usual meaning.

The free ligand exponent, pL has been evaluated from the expression.

$$pL = \log_{10}\left[\frac{(\beta_1^H[H] + \beta_2^H[H]^2 + \ldots)}{(T_L - \bar{n}\,T_M)} \cdot \frac{V^o + v'''}{V^o}\right] \qquad (5.3)$$

β_1^H and β_2^H are the reciprocal acid dissociation constants of the ligand. The results obtained are presented in Tables 5.3-5.6 only at one ionic strength for the metals under investigation.

The metal-ligand formation curves are obtained by plotting $\bar{n}$ against pL (Plates 14-17, Fig. E and Fig. F) for all the nine metals. The value of $\bar{n}$ varies between 0.0-2.0 in the case of UO_2(II), Cu(II), Be(II), Zn(II), and Hg(II), while for Co(II), Ni(II), Pb(II) and Cd(II) between 0.0-1.0 indicating that two complexes are formed in the former and only one metal chelate is formed in the latter case. The stepwise stability constants of the metal-chromotrope 2R chelates are then evaluated by applying the various computational methods viz. (i) interpolation at half $\bar{n}$ values (H), (ii) interpolation at various $\bar{n}$ values (V), and (iii) mid point slope method. The results obtained are fitted in Tables 5.7-5.12.

Thermodynamic stability constants

The thermodynamic stability constants were obtained by extrapolation of the stability constants obtained at various ionic strengths to zero ionic strength. The stepwise stability constants were extrapolated to zero ionic strength to give thermodynamic stability constants $\log K_1^{\mu=0}$ and $\log K_2^{\mu=0}$. Their sum has been represented as calculated $\log \beta_2^{\mu=0}$ (cal.). The values of overall stability constants $\log \beta_2$ were similarly extrapolated to give experimental $\log \beta_2^{\mu=0}$ (exp.). These are embodied in Table 5.13.

PLATE No. 14

Temperature = $15 \pm 1.0^{\circ}$ Ionic strength = 0.025

Fig. A. Titration curves for proton-CTR system

Curve 1 = $HClO_4$ Curve 2 = $HClO_4$+CTR

Fig. B. Formation curve for proton-CTR system

Fig. C. Titration curves for CTR metal chelates

Curve 1 = Ni-CTR Curve 2 = Co-CTR

Curve 3 = Be-CTR Curve 4 = Cd-CTR

Curve 5 = UO_2-CTR

Fig. D. Titration curves for CTR metal chelates

Curve 6 = Pb-CTR Curve 7 = Zn-CTR

Curve 8 = Hg-CTR Curve 9 = Cu-CTR

Fig. E. Formation curves for CTR metal chelates

Curve 1 = Ni-CTR Curve 2 = Co-CTR

Curve 3 = Be-CTR Curve 4 = Cd-CTR

Curve 5 = UO_2-CTR

Fig. F. Formation curves for CTR metal chelates

Curve 6 = Pb-CTR Curve 7 = Zn-CTR

Curve 8 = Hg-CTR Curve 9 = Cu-CTR

FIG. A

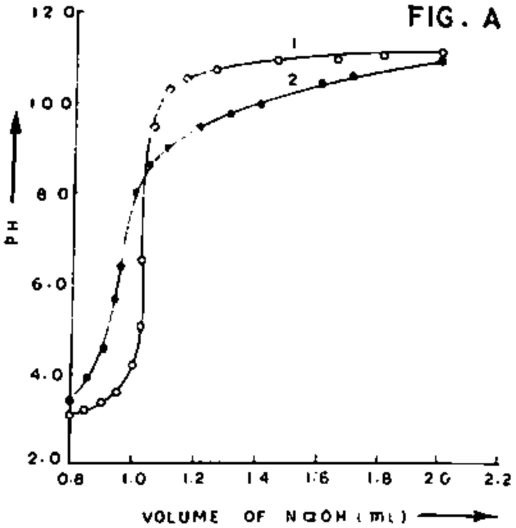


FIG. B

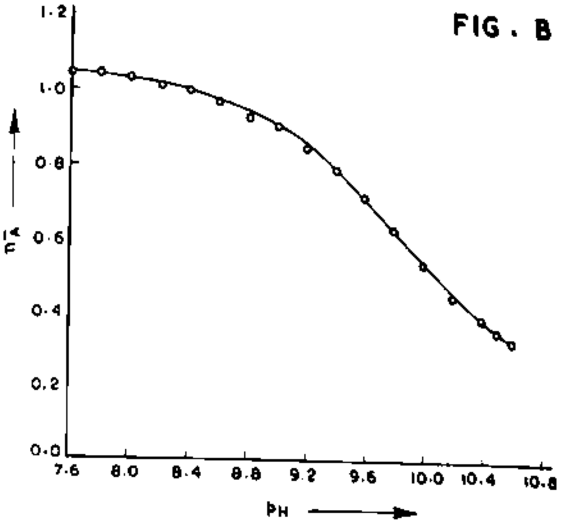


FIG. C

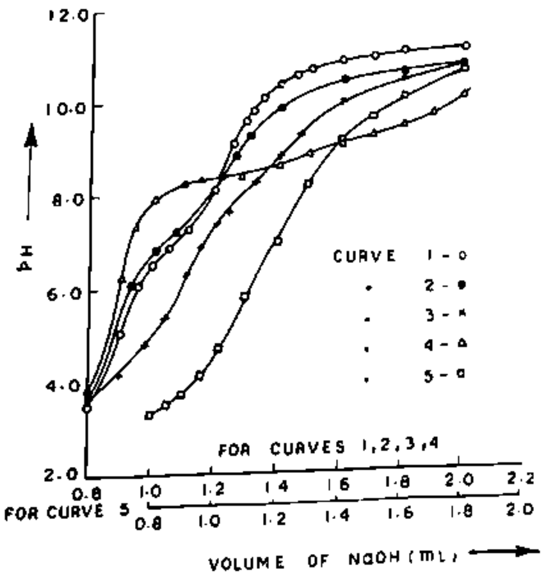


FIG. D

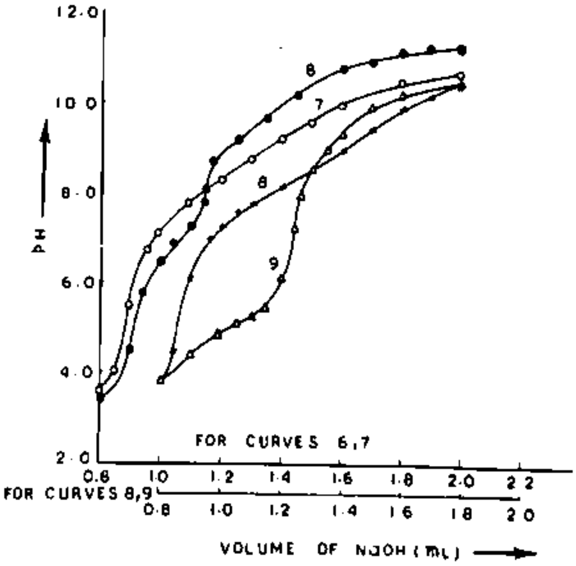


FIG. E

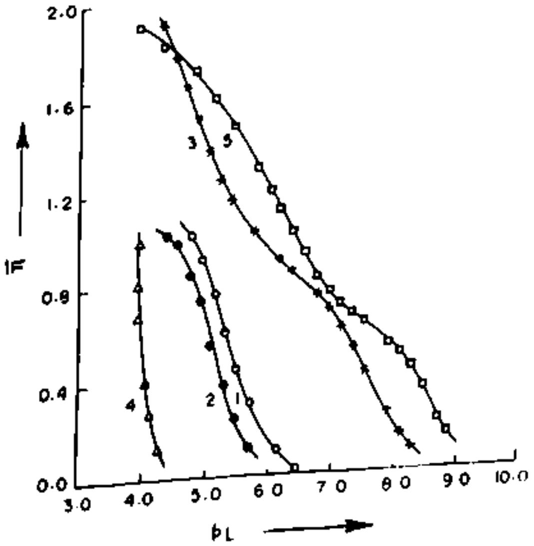


FIG. F

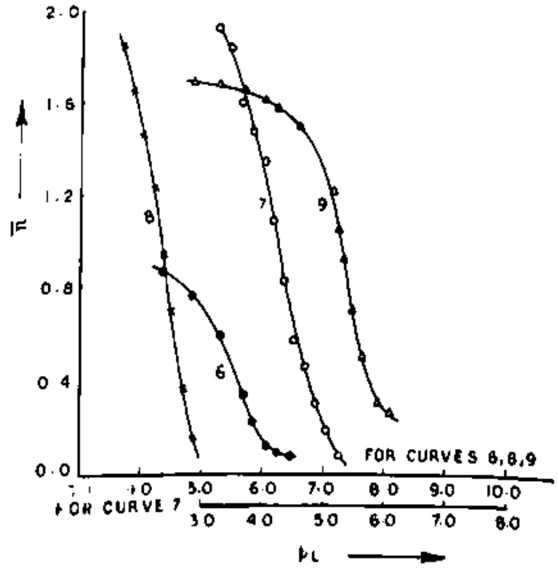


PLATE NO 14

PLATE No. 15

Temperature = 15±1.0°C   Ionic strength = 0.050

Fig. A. Titration curves for proton-CTR system

Curve 1 = $HClO_4$ Curve 2 = $HClO_4$+CTR

Fig. B. Formation curve for proton-CTR system

Fig. C. Titration for CTR metal chelates

Curve 1 = Ni-CTR   Curve 2 = Co-CTR

Curve 3 = Be-CTR   Curve 4 = Cd-CTR

Curve 5 = UO_2-CTR

Fig. D. Titration curves for CTR metal chelates

Curve 6 = Pb-CTR   Curve 7 = Zn-CTR

Curve 8 = Hg-CTR   Curve 9 = Cu-CTR

Fig. E. Formation curves for CTR metal chelates

Curve 1 = Ni-CTR   Curve 2 = Co-CTR

Curve 3 = Be-CTR   Curve 4 = Cd-CTR

Curve 5 = UO_2-CTR

Fig. F. Formation curves for CTR metal chelates

Curve 6 = Pb-CTR   Curve 7 = Zn-CTR

Curve 8 = Hg-CTR   Curve 9 = Cu-CTR

FIG . A

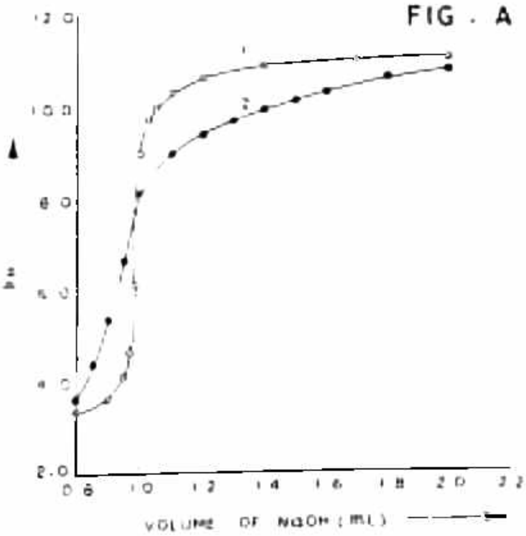


FIG . B

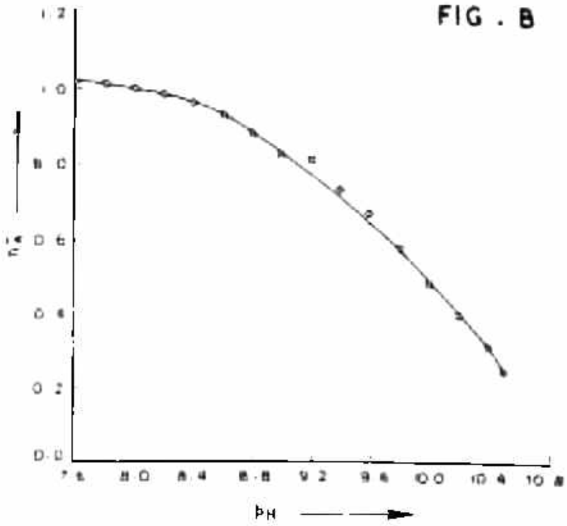


FIG . C

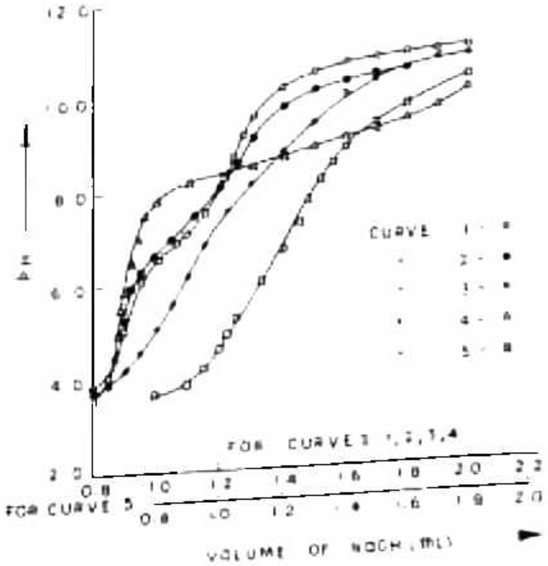


FIG . D

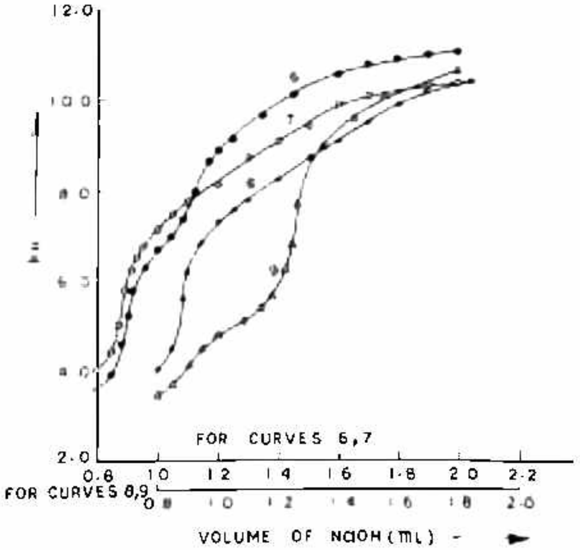


FIG . E

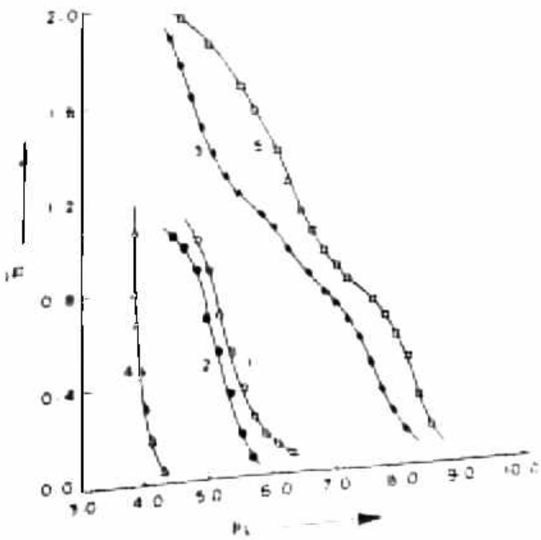


FIG . F

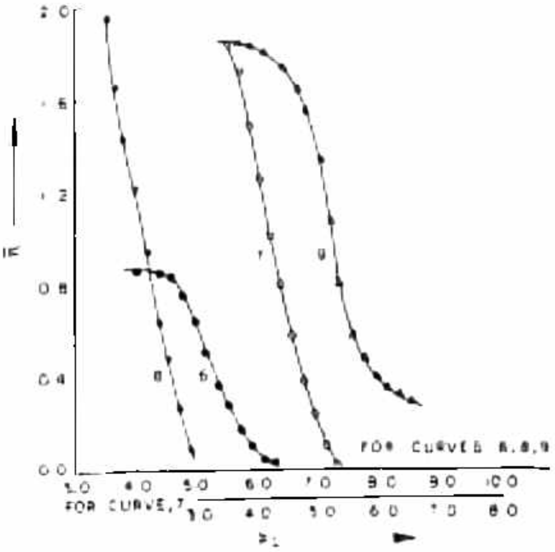


PLATE NO . 15

PLATE No. 16

Temperature = 15±1.0°C Ionic strength = 0.075

Fig. A. Titration curves for proton-CTR system

Curve 1 = $HClO_4$ Curve 2 = $HClO_4$+CTR

Fig. B. Formation curve for proton-CTR system

Fig. C. Titration curves for CTR metal chelates

Curve 1 = Ni-CTR Curve 2 = Co-CTR

Curve 3 = Be-CTR Curve 4 = Cd-CTR

Curve 5 = UO_2-CTR

Fig. D. Titration curves for CTR metal chelates

Curve 6 = Pb-CTR Curve 7 = Zn-CTR

Curve 8 = Hg-CTR Curve 9 = Cu-CTR

Fig. E. Formation curves for CTR metal chelates

Curve 1 = Ni-CTR Curve 2 = Co-CTR

Curve 3 = Be-CTR Curve 4 = Cd-CTR

Curve 5 = UO_2-CTR

Fig. F. Formation curves for CTR metal chelates

Curve 6 = Pb-CTR Curve 7 = Zn-CTR

Curve 8 = Hg-CTR Curve 9 = Cu-CTR

FIG. A

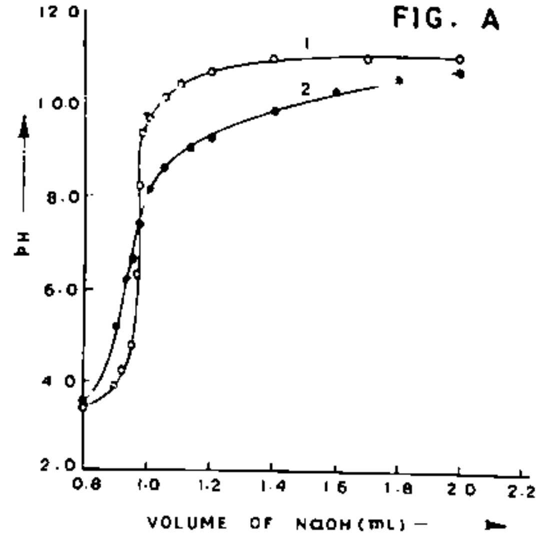


FIG. B

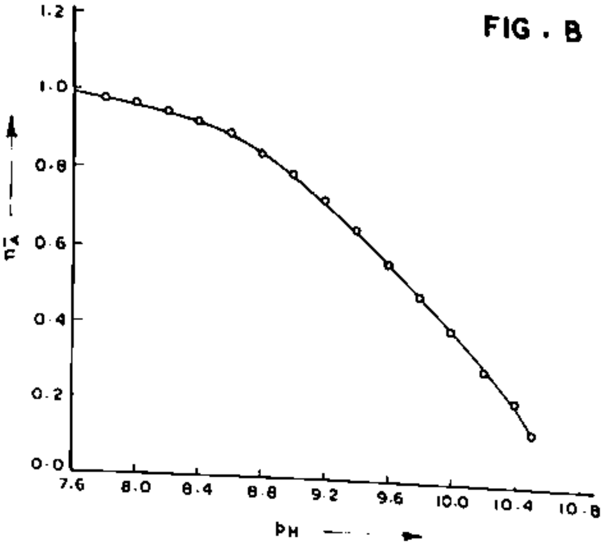


FIG. C

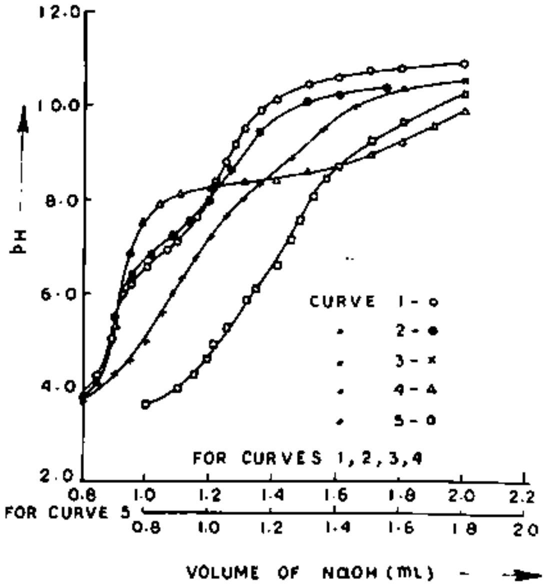


FIG. D

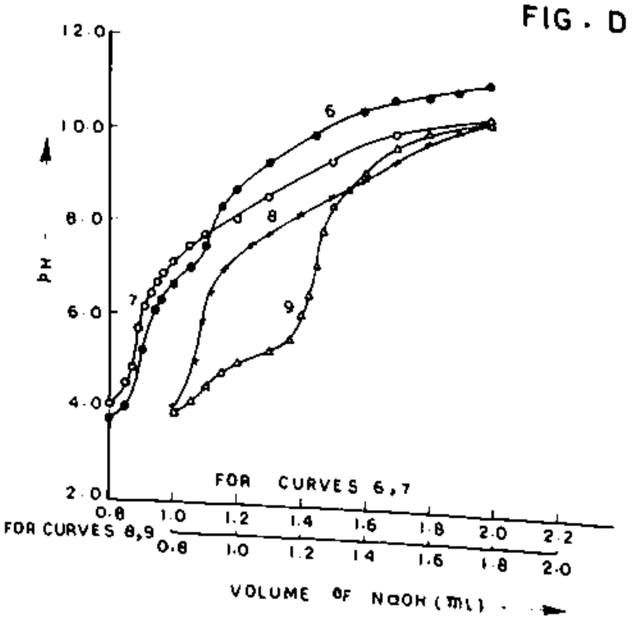


FIG. E

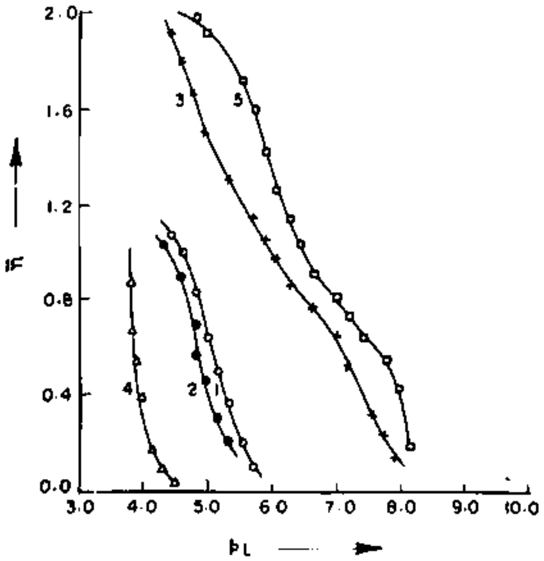


FIG. F

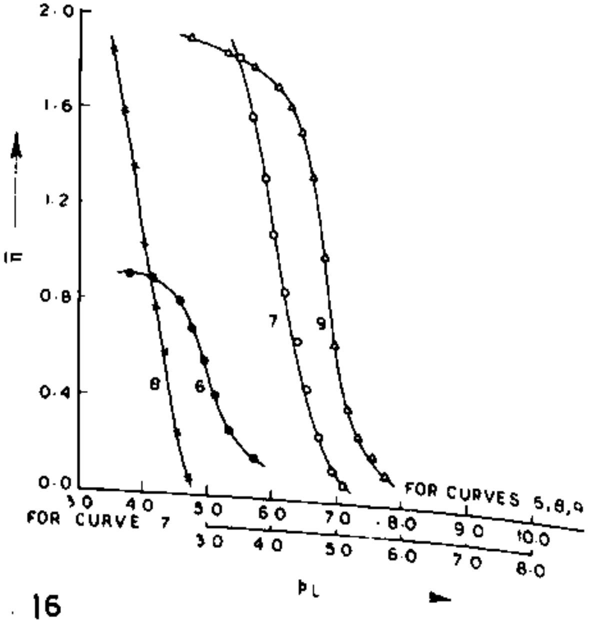


PLATE NO. 16

PLATE No. 17

Temperature = 15±1.0°C   Ionic strength = 0.125

Fig. A. Titration curves for proton-CTR system

Curve 1 = $HClO_4$ Curve 2 = $HClO_4$+CTR

Fig. B. Formation curve for proton-CTR system

Fig. C. Titration curves for CTR metal chelates

Curve 1 = Ni-CTR   Curve 2 = Co-CTR

Curve 3 = Be-CTR   Curve 4 = Cd-CTR

Curve 5 = UO_2-CTR

Fig. D. Titration curves for CTR metal chelates

Curve 6 = Pb-CTR   Curve 7 = Zn-CTR

Curve 8 = Hg-CTR   Curve 9 = Cu-CTR

Fig. E. Formation curves for CTR metal chelates

Curve 1 = Ni-CTR   Curve 2 = Co-CTR

Curve 3 = Be-CTR   Curve 4 = Cd-CTR

Curve 5 = UO_2-CTR

Fig. F. Formation curves for CTR metal chelates

Curve 6 = Pb-CTR   Curve 7 = Zn-CTR

Curve 8 = Hg-CTR   Curve 9 = Cu-CTR

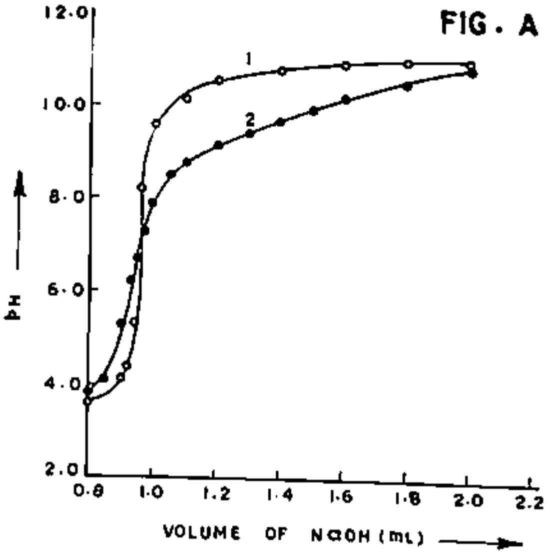


FIG. A

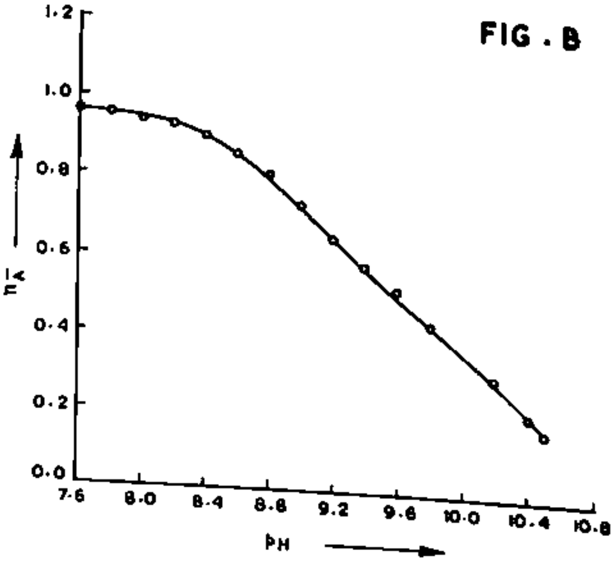


FIG. B

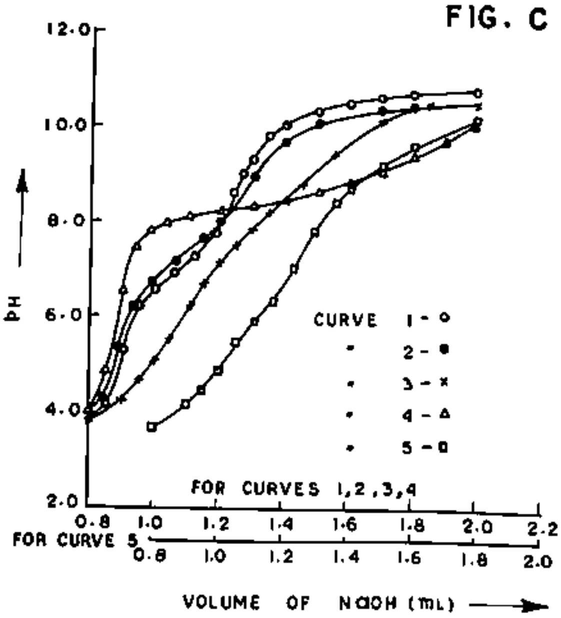


FIG. C

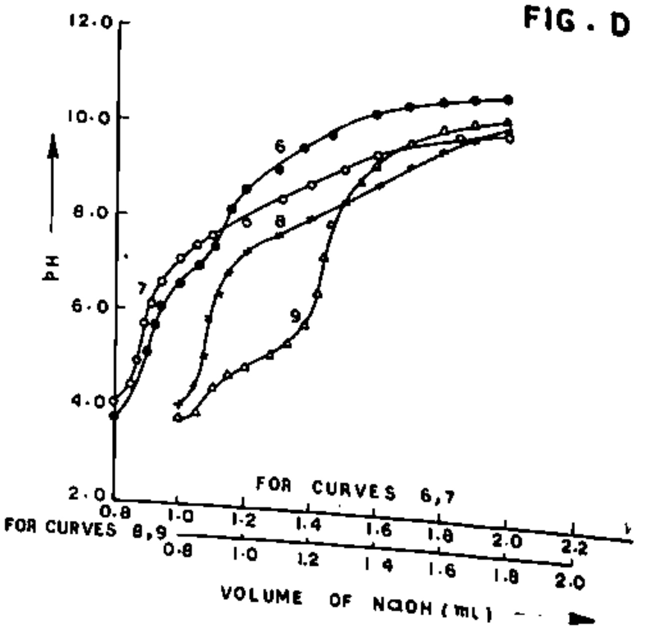
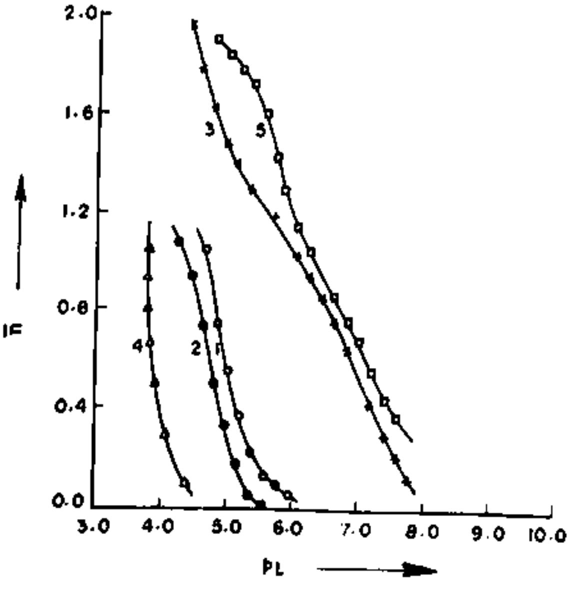


FIG. D

FIG. E



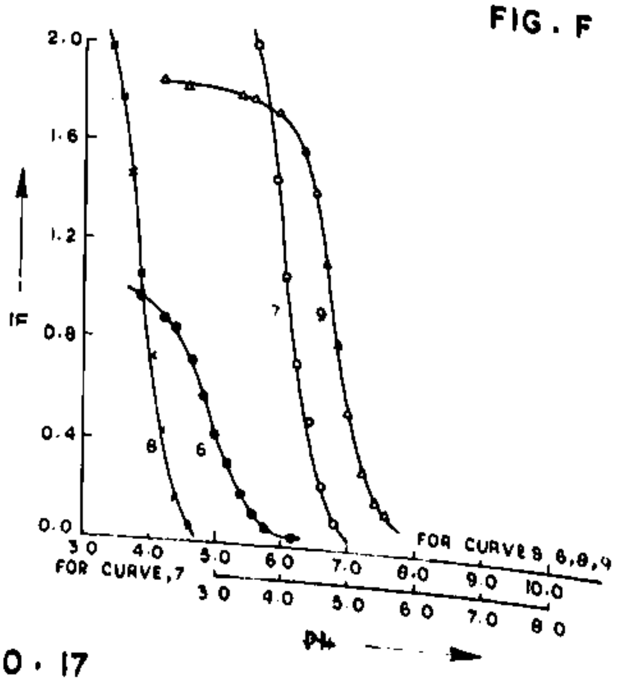


FIG. F

PLATE NO. 17

TABLE 5.1

T_L = 0.0075M
V^o = 100.0 ml
μ = 0.125

N^o = 1.0N
χ = 1.0
Plate 17 (Fig. B)

S.No.	pH	v'	v"	$\bar{n}_A$
1.	3.6	0.800	-	-
2.	3.8	0.865	0.800	1.0867
3.	4.0	0.895	0.837	1.0774
4.	4.2	0.910	0.857	1.0707
5.	4.4	0.923	0.870	-
6.	4.6	0.927	0.880	1.0627
7.	4.8	0.931	0.887	1.0587
8.	5.0	0.935	0.894	1.0547
9.	5.2	0.938	0.899	1.0520
10.	5.4	0.943	0.904	-
11.	5.6	0.944	0.910	1.0453
12.	5.8	0.945	0.916	1.0386
13.	6.0	0.949	0.925	1.0320
14.	6.2	0.950	0.930	1.0266
15.	6.4	0.950	0.940	1.0133
16.	6.6	0.952	0.947	1.0066
17.	6.8	0.952	0.955	0.9959
18.	7.0	0.953	0.963	0.9866
19.	7.2	0.954	0.968	0.9799

(Contd.)

Table 5.1 (Contd.)

S.No.	pH	v'	v"	$\bar{n}_A$
20.	7.4	0.954	0.975	0.9719
21.	7.6	0.955	0.983	0.9613
22.	7.8	0.956	0.990	0.9533
23.	8.0	0.958	0.999	0.9426
24.	8.2	0.960	1.010	0.9306
25.	8.4	0.963	1.030	0.9066
26.	8.6	0.966	1.070	0.8572
27.	8.8	0.970	1.110	0.8079
28.	9.0	0.970	1.167	0.7372
29.	9.2	0.978	1.240	0.6505
30.	9.4	0.987	1.300	0.5825
31.	9.6	1.000	1.360	0.5199
32.	9.8	1.025	1.445	0.4400
33.	10.0	1.057	1.540	0.3496
34.	10.2	1.105	1.625	0.3073
35.	10.4	1.195	1.745	0.2144
36.	10.5	1.235	1.820	0.1681

TABLE 5.2

Proton-ligand stability constants of Chromotrope 2R at various ionic strengths

Ionic strength	log K^H		Mean log K^H
	H	V	
0.025	10.08	10.04	10.06
0.050	9.96	9.92	9.94
0.075	9.77	9.71	9.74
0.125	9.65	9.59	9.62
0.000	By usual extrapolation method		10.22

TABLE 5.3

T_L = 0.0075M
N^o = 1.0N
u = 0.125

T_M = 0.0025M
V^o = 100 ml
Plate 17 (Fig. E)

S.No.	UO_2(II)		Be(II)		Cd(II)	
	$\bar{n}$	pL	$\bar{n}$	pL	$\bar{n}$	pL
1.	0.235	7.774	0.112	7.763	0.103	4.375
2.	0.380	7.588	0.206	7.572	0.291	4.052
3.	0.449	7.394	0.312	7.381	0.375	3.907
4.	0.565	7.205	0.421	7.192	0.660	3.837
5.	0.681	7.017	0.523	7.002	0.802	3.751
6.	0.765	6.826	0.639	6.813	0.937	3.746
7.	0.862	6.636	0.761	6.626	1.078	3.760
8.	0.958	6.446	0.862	6.436	-	-
9.	1.053	6.257	0.957	6.246	-	-
10.	1.150	6.068	1.034	6.055	-	-
11.	1.293	5.884	1.092	5.861	-	-
12.	1.429	5.701	1.189	5.672	-	-
13.	1.600	5.522	1.251	5.478	-	-
14.	1.723	5.338	1.312	5.287	-	-
15.	1.775	5.145	1.400	5.097	-	-
16.	1.839	4.954	1.487	4.908	-	-
17.	1.899	4.762	1.627	4.726	-	-
18.	1.990	4.575	1.777	4.546	-	-
19.	-	-	1.922	4.366	-	-

TABLE 5.4

T_L = 0.0075M

N^o = 1.0N

μ = 0.125

T_M = 0.0025M

V^o = 100 ml

Plate 17, Fig. E

S.No.	Ni(II)		Co(II)	
	$\bar{n}$	pL	$\bar{n}$	pL
1.	0.013	6.155	0.013	5.555
2.	0.058	5.959	0.046	5.358
3.	0.097	5.762	0.172	5.169
4.	0.130	5.565	0.335	4.984
5.	0.230	5.374	0.521	4.802
6.	0.384	5.189	0.728	4.622
7.	0.556	5.005	0.940	4.445
8.	0.757	4.825	1.089	4.261
9.	1.062	4.658	-	-

TABLE 5.5

T_L = 0.0075M

T_M = 0.0025M

N^o = 1.0N

V^o = 100 ml

μ = 0.125

Plate 17, Fig. F

S.No.	Cu(II)		Pb(II)	
	$\bar{n}$	pL	$\bar{n}$	pL
1.	0.162	7.568	0.025	6.356
2.	0.199	7.371	0.045	6.157
3.	0.314	7.182	0.058	5.959
4.	0.555	7.005	0.065	5.759
5.	0.829	6.833	0.130	5.565
6.	1.148	6.607	0.197	5.371
7.	1.433	6.501	0.318	5.182
8.	1.595	6.321	0.435	4.993
9.	1.696	6.135	0.588	4.808
10.	1.739	5.940	0.728	4.622
11.	1.787	5.747	0.858	4.436
12.	1.797	5.548	0.881	4.238
13.	1.808	5.150	0.945	4.045
14.	1.819	4.951	0.977	3.849
15.	1.832	4.553	1.003	3.652
16.	1.839	4.354	1.030	3.455
17.	1.854	4.156	-	-

TABLE 5.6

T_L = 0.0075M

T_M = 0.0025M

N^o = 1.0M

V^o = 100.0 ml

μ = 0.125

Plate 17, Fig. F.

S. No.	Hg(II)		Zn(II)	
	$\bar{n}$	pL	$\bar{n}$	pL
1.	0.061	4.559	-	-
2.	0.172	4.369	0.115	4.764
3.	0.440	4.194	0.265	4.578
4.	0.735	4.023	0.515	4.401
5.	1.068	3.859	0.742	4.224
6.	1.470	3.706	1.085	4.061
7.	1.766	3.544	1.472	3.906
8.	1.984	3.375	1.777	3.746
9.	2.188	3.205	2.023	3.580

TABLE 5.7

Values of stability constants for UO_2-CTR chelate at different ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.025	log K_1	8.02	8.08	7.74	
	log K_2	5.45	5.54	5.62	
	log K_c	13.45	13.62	13.36	13.48
0.050	log K_1	8.05	7.67	7.64	
	log K_2	5.75	5.68	5.77	
	log K_c	13.80	13.35	13.41	13.52
0.075	log K_1	7.81	7.64	7.63	
	log K_2	5.70	5.69	5.67	
	log K_c	13.51	13.33	13.30	13.38
0.125	log K_1	7.34	7.35	7.53	
	log K_2	5.66	5.56	5.57	
	log K_c	13.00	12.91	13.10	13.00

TABLE 5.8

Values of stability constants for Be-CTR chelate at different ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.025	log K_1	7.50	7.40	7.35	
	log K_2	4.80	4.84	4.93	
	log K_c	12.30	12.24	12.28	12.27
0.050	log K_1	7.41	7.37	7.27	
	log K_2	4.85	4.91	4.93	
	log K_c	12.26	12.28	12.20	12.25
0.075	log K_1	7.25	7.21	7.25	
	log K_2	4.86	4.93	4.90	
	log K_c	12.11	12.14	12.15	12.14
0.125	log K_1	7.05	7.09	7.20	
	log K_2	4.93	5.02	4.84	
	log K_c	11.98	12.11	12.14	12.04

TABLE 5.9

Values of stability constants for Cu-CTR chelate at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.025	log K_1	7.63	7.64	7.78	
	log K_2	6.64	6.60	6.57	
	log K_c	14.27	14.24	14.35	14.29
0.050	log K_1	7.65	7.80	7.70	
	log K_2	6.58	6.56	6.50	
	log K_c	14.23	14.36	14.20	14.27
0.075	log K_1	7.15	7.19	7.49	
	log K_2	6.49	6.24	6.16	
	log K_c	13.64	13.43	13.65	13.57
0.125	log K_1	6.95	7.05	7.29	
	log K_2	6.45	6.27	6.13	
	log K_c	13.40	13.32	13.42	13.38

TABLE 5.10

Values of stability constants for Zn-CTR chelate at different ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.025	log K_1	4.60	4.65	4.71	
	log K_2	3.90	3.85	3.80	
	log K_c	8.50	8.50	8.51	8.50
0.050	log K_1	4.60	4.64	4.73	
	log K_2	3.83	3.74	3.67	
	log K_c	8.43	8.38	8.40	8.41
0.075	log K_1	4.50	4.53	4.61	
	log K_2	3.76	3.82	3.71	
	log K_c	8.26	8.35	8.32	8.31
0.125	log K_1	4.36	4.41	4.54	
	log K_2	3.89	3.87	3.66	
	log K_c	8.25	8.28	8.20	8.25

TABLE 5.11

Values of stability constants for Hg-CTR chelate at different ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.025	log K_1	4.58	4.64	4.73	
	log K_2	3.82	3.89	3.97	
	log K_c	8.40	8.53	8.70	8.54
0.050	log K_1	4.48	4.50	4.55	
	log K_2	3.78	3.78	3.75	
	log K_c	8.26	8.28	8.30	8.28
0.075	log K_1	4.34	4.36	4.43	
	log K_2	3.73	3.64	3.69	
	log K_c	8.07	8.00	8.12	8.06
0.125	log K_1	4.11	4.15	4.25	
	log K_2	3.70	3.68	3.52	
	log K_c	7.81	7.83	7.77	7.80

TABLE 5.12

Values of stability constants for Co-CTR, Ni-CTR, Pb-CTR and Cd-CTR chelates at various ionic strengths

Metal ion	Ionic strength	log K		
		H	V	Mean
Co^{+2}	0.025	5.20	5.24	5.22
	0.050	5.16	5.15	5.16
	0.075	4.93	4.97	4.95
	0.125	4.83	4.81	4.82
Ni^{+2}	0.025	5.40	5.44	5.42
	0.050	5.35	5.39	5.37
	0.075	5.13	5.16	5.14
	0.125	5.05	5.12	5.08
Pb^{+2}	0.025	5.37	5.39	5.38
	0.050	5.14	5.16	5.15
	0.075	5.05	5.03	5.04
	0.125	4.90	4.92	4.91
Cd^{+2}	0.025	4.04	4.08	4.06
	0.050	3.93	3.96	3.95
	0.075	3.90	3.97	3.93
	0.125	3.90	3.91	3.91

TABLE 5.13

Values of thermodynamic stability of Chromotrope 2R chelates at 15°±1.0°C

$\log K_n$	UO_2(II)	Be(II)	Cu(II)	Zn(II)	Hg(II)	Co(II)	Ni(II)	Pb(II)	Cd(II)
$\log K_1^{\mu=o}$	8.20	7.60	8.20	4.72	3.94	5.25	5.45	5.65	4.14
$\log K_2^{\mu=o}$	5.02	4.90	7.00	4.00	4.80	-	-	-	-
$\log \beta_2^{\mu=o}$ (calc.)	13.22	12.56	15.20	8.72	8.74	-	-	-	-
$\log \beta_2^{\mu=o}$ (exp.)	13.31	12.50	15.15	8.66	8.70	5.25	5.45	5.65	4.14

REFERENCES

1. Athavale, V.T. Mathur, P.K. and Sathe, R.M. J. Inorg. Nucl. Chem., 29, 1947 (1967)

2. Athavale, V.T., Sathe, R.M. and Mahadevan, N. J. Inorg. Nucl. Chem., 30(11), 3107 (1968)

3. Banerjee, A. and Dey, A.K. J. Inorg. Nucl. Chem., 30(4), 995 (1968)

4. Bartusek, M. and Ruzickova, J. Collect Czech. Chem. Commun., 31(1), 207 (1966)

5. Bartusek, M. and Zelimka, J. Collect. Czech. Chem. Commun., 32(3), 992 (1967)

6. Bjerrum, J. 'Metal amine formation in aqueous solutions,' P. Haase, Copenhagen (1941)

7. Bohigian, T.A. and Martell, A.E. Inorg. Chem., 4, 1264 (1965)

8. Bohigian, T.A. and Martell, A.E. J. Am. Chem. Soc., 89, 832 (1967)

9. Buděšinský, B. Talanta, 16(9), 1277 (1969)

10. Calvin, M. and Wilson, J. J. Am. Chem. Soc., 67, 2003 (1945)

11. Carey, G.H., Bogucki, R.F. and Martell, A.E. Inorg. Chem., 3(9), 1288 (1964)

12. Carey, G.H. and Martell, A.E. J. Am. Chem. Soc., 89(12), 2859 (1967)

13. Chaberek, S. Jr., Glustafson, R.L., Courtney, R.C. and Martell, A.E. J. Am. Chem. Soc., 81, 515 (1959)

14. Condike, G.F. and Martell, A.E.	J. Inorg. Nucl. Chem., 31(8), 2455 (1969)
15. Courtney, R.C., Glustafson, R.L., Chaberek, S. Jr. and Martell, A.E.	J. Am. Chem. Soc., 80, 2121 (1958), 81, 519 (1959)
16. Dubey, S.N. and Mehrotra, R.C.	J. Less Common metals, 9(2), 123 (1965)
17. Dubey, S.N. and Mehrotra, R.C.	J. Indian Chem. Soc., 42(10), 685 (1965)
18. Gonia, T., Bocaniciu, L. and Olariu, M.	Rev. Roum. Chim., 16(12), 1849 (1971)
19. Grimes, J.H. Huggard, A.J. and Wilford, S.F.	J. Inorg. Nucl. Chem., 25, 1225 (1963)
20. Intorre, B.J. and Martell, A.E.	J. Am. Chem. Soc., 83, 3618 (1961)
21. Jöntti, O.	Souman Kemistilethi, 30B, 136 (1957)
22. Katayama, T. Miyata, H. and Toêi, K.	Bull. Chem. Soc., Japan, 44, 2712 (1971), 44, 3040 (1971)
23. Kina, K., Miyata, H. and Toêi, K.	Bull. Chem. Soc., Japan, 44, 1855 (1971)
24. Lal, K. and Aggarwal, R.P.	J. Less Common Metals, 12(4), 269 (1967)
25. Malik, A. and Rehman, S.M.F.	J. Inorg. Nucl. Chem., 25(9), 1193 (1963)
26. Martell, A.E., Chaberek, S. Jr., Westerback, S. and Hyytiainen, H.	J. Am. Chem. Soc., 79, 3036 (1957)
27. Nagamori, S. and Miyata, H.	Bull. Chem. Soc., Japan, 44, 3476 (1971)

28. Nakashima, S., Miyata, H. and Tôei, K. — Bull. Chem. Soc., Japan, <u>41</u>, 2632 (1968)

29. Oka'c, A. and Sommer, L. — Chem. Listy, <u>47</u>, 659 (1953)

30. Petrova, T.V., Savvin, S.B. and Dzherayan, T.G. — Zh. Anal. Khim., <u>27(1)</u>, 10 (1972).

31. Sathe, R.M., Mahadevan, N. and Shetty, S.Y. — Indian J. Chem., <u>6(12)</u>, 755 (1968)

32. Shacher, G. — J. Inorg. Nucl. Chem., <u>28</u>, 845 (1966).

33. Schrøder, K.H. — Acta. Chem. Scand., <u>19</u>, 1797 (1965), <u>20</u>, 8811 (1966)

34. Schwarzenbech, G. — Helv. Chim. Acta, <u>28</u>, 218 (1945)

35. Schwarzenbech, G. and Coworkers — Helv. Chim. Acta, <u>28</u>, 828 (1945), <u>30</u>, 1303 (1947), <u>32</u>, 1543 (1949), <u>34</u>, 1503 (1951)

36. Vogel, A.I. — 'Textbook of quantitative inorganic analysis', 3rd Edn., Longmans, London (1961)

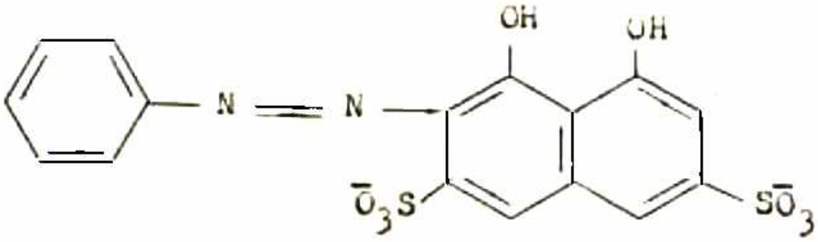
37. Zollinger, Hch. and Bücher, W. — Helv. Chim. Acta, <u>34</u>, 591 (1951)

CHAPTER VI

DISCUSSION

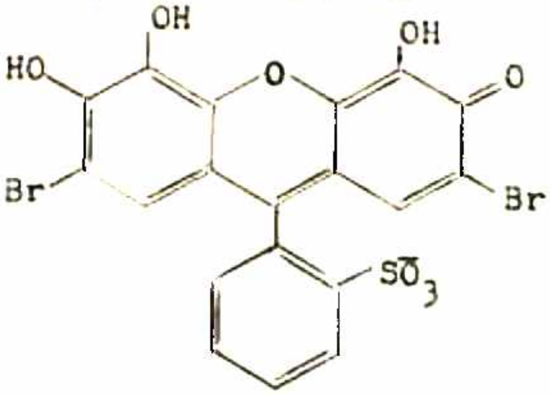
In course of these investigations, detailed studies have been carried out on some metal complexes of Chromotrope 2R and Bromopyrogallol Red, which have the following structures.

I.



(Chromotrope 2R)

II.

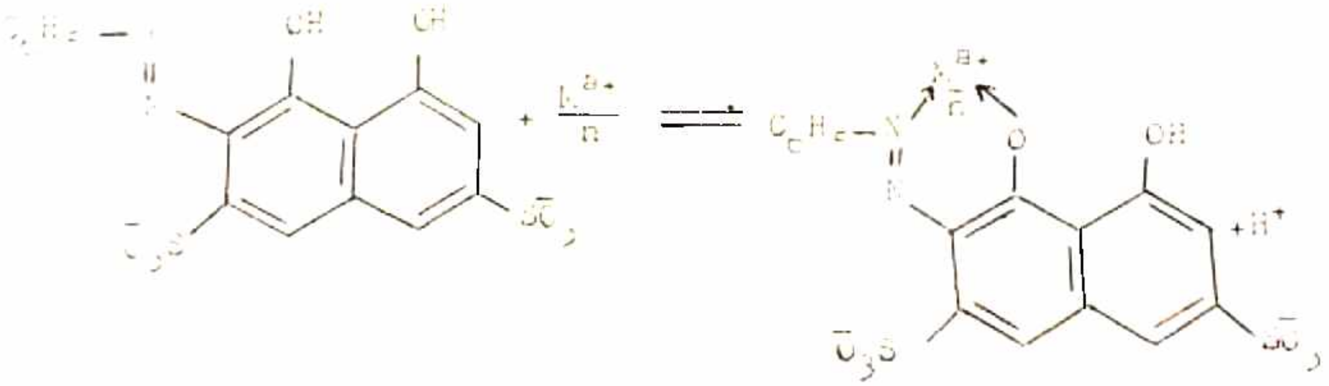


(Bromopyrogallol Red)

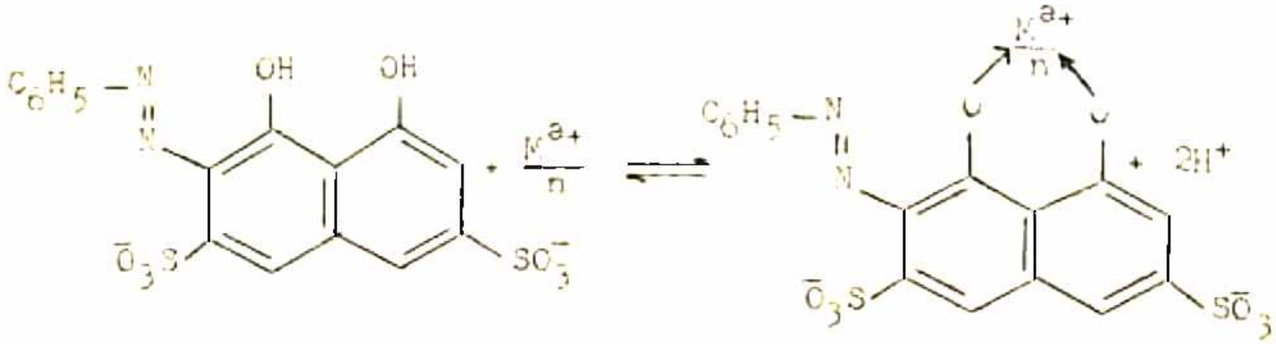
Metal Chelates of Chromotrope 2R

Chromotrope 2R behaves as a bidentate ligand and as such there are two alternative positions where the chelation ring can be formed:

I. between the hydroxyl group in the 4-position of chromotropic acid entity and the remote nitrogen in the azo group.



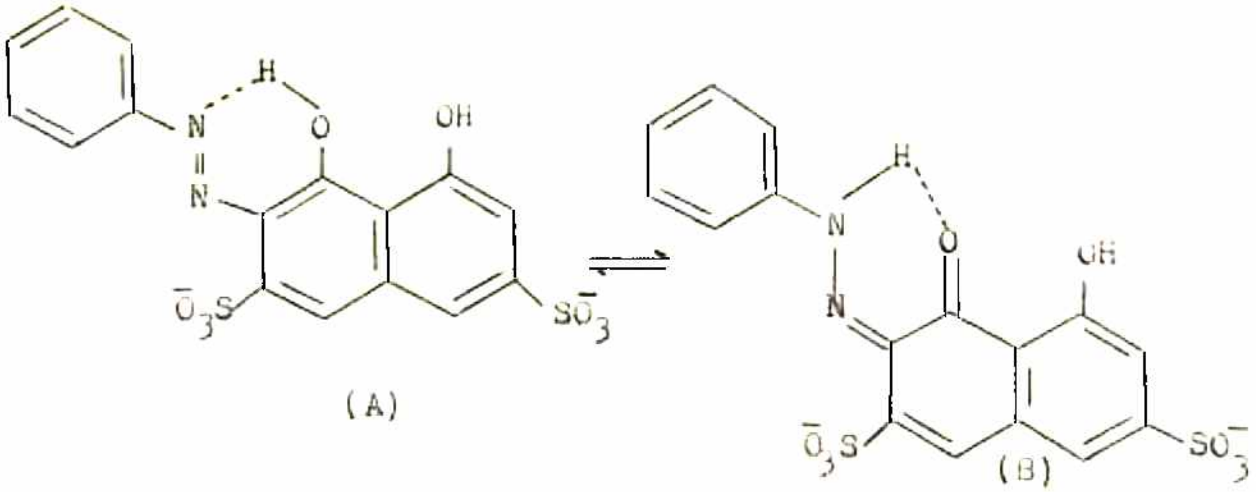
II. between the peri-hydroxyl groups of the chromotropic acid component.



Sommer[23] has predicted both the possibilities for chelation and is of the view that the mode adopted depends on the bonding properties of the metal ions. Buděšinský[2] and Dey[10] have reported the structures of metal chelates of this dye, which involve in them the two hydroxyl groups at peri-position to one another. Buděšinský from further studies has concluded that the chelation by (I) proceeds, when the aryl substituent carries a donor group ortho to the azo group. However, Miyata and coworkers[15] have made suggestions that the chelation takes place between one of the naphthoic hydroxyl group (at 4 position) and nitrogen of the azo group.

The λ_{max} of the ligand, which may be attributed to the π-π^* transition of the conjugated π-electron system, and the λ_{max} of the complex (against water) are almost the same. This suggests that the π system is not involved in chelation, thus lending support to the assumption that the two peri-hydroxyls are used in complex formation. However, this suggestion for possible structures is tentative, as this does not form a part of these studies. To establish the structures of the metal chelates of CTR fully, further investigations are necessary.

The absorption maxima of the dye solution, which lies in the range 510-520 nm, does not change significantly over the pH range 2.0-11.5. This factor offers an analytical advantage for this dye, since reagent blank will show a little, if any, pH dependence[24]. CTR shows the well known tautomeric equilibrium[26] as expressed by



Structure 'A' is acidic and occurs predominantly in alkaline medium whilst structure 'B' is basic and predominates in acidic media.

Part A: Spectrophotometric Studies

The stabilities of the metal complexes depend on a number of factors which are a function of the nature of the metal ion and the ligand itself. It is a well known observation that the stability of the metal complexes, is a linear function of the ionisation potential of the metal ions. Moreover, electronegativity, which indicates the relative attraction for electron pairs, also determines the stability. Two elements of very different electronegativities are expected to form ionic bonds, whilst two elements having lesser difference in electronegativity, have greater tendency to form covalent bond, which contributes to the greater stability of the complex compounds. Table 6.1 records the first and second ionisation potentials together with the Pauling's electronegativity of the metals under investigation.

The order of stability of metal complexes of CTR does not lead to any quantitative correlation as the metal ions studied are of different oxidation states. However, an attempt is made to compare the stabilities of the complexes of these metal ions, whose oxidation states are same. Thus, for metal complexes of trivalent ions i.e. Al(III), Ga(III) and Yb(III), the order observed is:

Ga(III) > Yb(III) > Al(III)

The reason for the greater stability of Ga(III) complex seems to be because of number of ligands attached per metal ion, is twice the number of ligands attached in the case of aluminium and ytterbium. This may also be attributed to the high value of ionisation potential (I_3) for gallium ion. Moreover, the closer proximity of its electronegativity value to that of aluminium is also responsible for its high stability. The sequence of stability Yb(III) > Al(III) may be attributed to greater ionisation potential ($I_1 = 6.2$) of Yb(III) than that of aluminium ($I_1 = 5.984$). The formation of 1:2 complex between Ga(III) and CTR, as opposed to 1:1 complexes with other metal ions, could be connected with energetics of the chelation reaction.

Chelates of Zr(IV) and Hf(IV) have been studied at pH 2.0. The atomic sizes of these metals permit the formation of complexes, with co-ordination number upto 8. Hydrolysis does occur and it is very doubtful, if M^{4+} aquo ions exist even in strong acidic solutions. The order of stability observed is:

Hf(IV) > Zr(IV)

which can be due to the higher second ionisation potential of Hf(IV) than that of Zr(IV). Moreover, Hf(IV) has a smaller ionic radius than Zr(IV), which might partially explain the slightly higher stability of Hf:CTR complex.

The greater stability of Cu(II) complex can be ascribed to its being weakly basic in nature, as a result of which, this aquires a greater stability resulting in the formation of a very stable complex. Apart from this, Cu(II) has higher ionisation potential ($I_1 = 7.633$) as compared to other metals. Further Pauling's electronegativity value (1.9) is in close proximity to that of nitrogen and oxygen. This renders it to be more capable of covalent bond formation, which leads to its greater stability.

Thermodynamic functions of metal complexes of CTR

From an examination of the thermodynamic functions of the metal complexes of CTR, it is clear that all the complexation reactions under investigations are spontaneous, as is evident from the negative value of free energy of formation (ΔG).

The change in heat content (ΔH) is dependent on the difference of bond energies of the reactants and the product and also the solvation of all the species (ions or molecules) involved in complexation reaction. This can provide valuable information regarding the nature of the metal-ligand bonding as well as the sterochemistry of the complexes. For essentially electrostatic interactions, endothermic changes are observed, since the electrostatic forces will vary with temperature in the same way as the macroscopic dielectric constant of water. The larger exothermic heat changes are observed in the case of covalent bond formation.

During investigations it was observed, that while Cu(II) and Yb(III) complexes are formed exothermically, Al(III) and Ga(III) complexes are formed endothermically.

The positive ΔH in the latter two cases is indicative of the fact that energy is required for the replacement of ligated solvent molecules by CTR. As Al(III) and Ga(III) belong to the same group of periodic table, we can expect them to behave similarly in most chemical reactions. This is borne out by the endothermic character of these reactions with CTR.

Calvin and Bailer[5] showed that heat and entropy effects contribute equally to the free energy of the formation or indirectly to the stability of the metal complexes. According to Latimar et al.[16] entropy changes are mainly due to two factors.

(1) Change in entropy due to the replacement of water molecules bound to the metal ion by the ligand molecule.

(2) Charge effect.

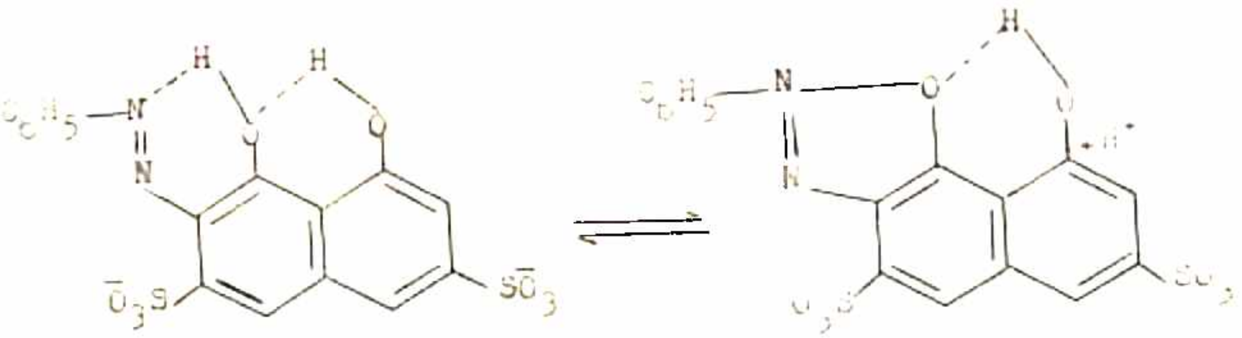
Entropies of the reactions when there is a reduction in the total number of ions, are generally positive, while entropies of the reactions between cations and neutral molecules, with no net reduction of charge are negative and do not favour complexation. It was observed during these investigations that except for the Cu(II)-CTR system, all other complexation reactions have a positive value for ΔS. The negative value of ΔS in the former case may be due to the strong complex-solvent interaction.

In the spectrophotometric method for the estimation of various ions, the results obtained reveal that the method using CTR as a chromogenic reagent compares well with the other methods used at present for the photometric determination of aluminium, gallium and ytterbium. A comparison of these as a function of molecular extinction coefficient is represented in Table 3.12. In spite of various advantages such as sensitivity, speed and water solubility, the method suffers from interference of a number of cations. However, the interference due to anions is comparatively lesser.

Part B: Potentiometric Studies of Metal Complexes of CTR

In course of these studies, proton-ligand stability constant and stepwise stability constants of some bivalent metal complexes of chromotrope 2R have been determined potentiometrically using Bjerrum-Calvin pH titration technique as described by Irving and Rossotti.

As is evident from the structure of CTR, the reagent possesses two hydroxyl groups at peri-position to one another. As such the reagent should give two inflexions in the formation curve, but as one inflexion is observed, only one proton is dissociated under the conditions of studies. The extremely high value of second dissociation constant is possibly due to the formation of a strong hydrogen bridge after the first step of dissociation.



This phenomenon has been observed by a number of workers[12,19,27] while making studies on chromotropic acid and its various derivatives. The value of pK_1 determined for CTR agrees well with the values obtained earlier by various workers[9,20]. The order of stability constant of bivalent metal complexes of CTR, taking into consideration only log K_1 values is:

$$UO_2(II) > Cu(II) > Be(II) > Ni(II) > Pb(II) > Co(II) > Zn(II) \sim Hg(II) > Cd(II)$$

The order observed is similar to that observed by Maley and Mellor[18] and Irving and Williams[14], except for a few irregularities. The higher value of $UO_2(II)$ than Cu(II) complex can be justified on the basis that it has been generally observed that with **-O-O-** donors, $UO_2(II)$ forms stronger complexes than Cu(II) and this order is reversed in ligands with -O-N- donors[25]. According to Maley and Mellor, order for zinc, cadmium and mercury complexes should be Zn > Cd > Hg. But in the case of CTR complexes operative in the first step of complexation of Cu(II)-CTR complex, but it is not sufficient to stabilise the complex to an extent greater than the stability of UO_2 (1:1) complex.

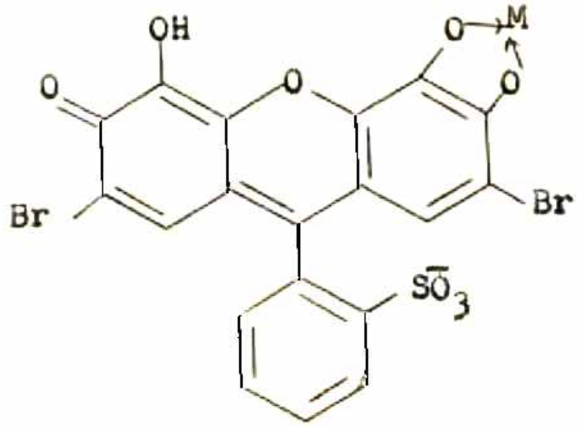
In all the cases it is observed that $\log K_1 > \log K_2$. This is so, on account of statistical reasons as the presence of a co-ordinating ligand causes repulsion for an incoming ligand of a similar type.

All the complexes except the 1:2 complexes of Be(II) and UO_2(II), show a decrease in stabilities with an increase in ionic strength. This decrease may be attributed due to the formation of a dense ionic atmosphere around the metal ions and the screening effect which reduce the rate of recombination of the metal ion with the ligand molecule. In the case of Be(II) and UO_2(II), where the stability increases with increasing ionic strength may be due to the lowering of the activity coefficient of the ionic species.

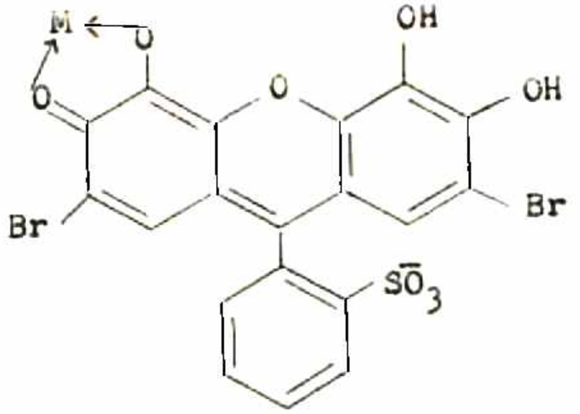
Metal Complexes of Bromopyrogallol Red (BPR)

In case of BPR, the chelation can take place in three possible ways described below:

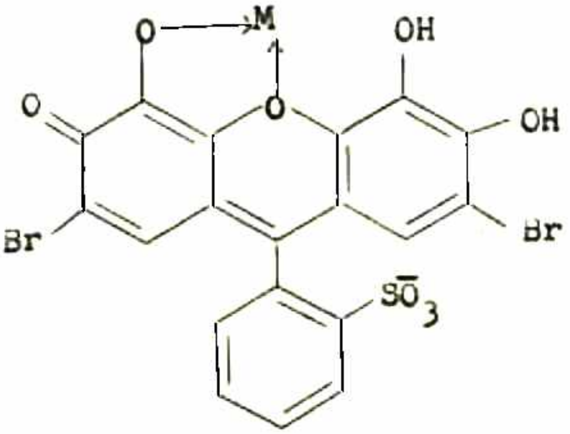
I. between the phenolic -OH groups which are in peri-position to one another.



II. between the -OH group and the ketonic - O group of the same ring.



III. between the -OH group and the -O- group in the adjacent ring.

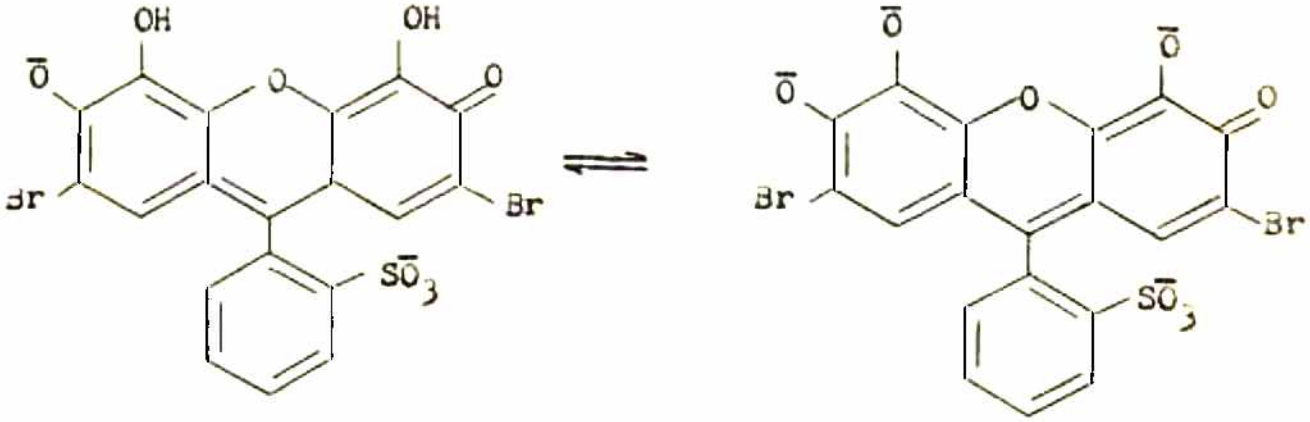


The absorption spectra of BPR and its metal chelates are similar. This suggests that the π energy levels of BPR and the complexes are of similar energy. It would therefore be reasonable to assume that the chelation occurs through the two vicinal hydroxyl groups in which case the conjugated π system is more or less uneffected. This conclusion, as may be seen, is further supported by the oxidation studies of West et al.[8] A complete picture of the structure can only be obtained by further studies, which do not form the aim of the present work.

BPR behaves as an acid-base indicator like other sulphonephthalein dyes, and changes colour with the variation of pH. The equilibrium may be repsented as

$$\begin{array}{ccccccccc} H_4BPR & \rightleftharpoons & H_3BPR^- & \rightleftharpoons & H_2BPR^{-2} & \rightleftharpoons & HBPR^{-3} & \rightleftharpoons & BPR^{-4} \\ \text{orange red} & & \text{red} & & \text{light raspoery} & & \text{violet} & & \text{blue} \end{array}$$

The red form predominates in the acid medium while violet form predominates in the alkaline media.



Red form in acidic medium

Violet or alkaline form

Preliminary absorption spectra was plotted for the reagent and mixtures of the reagent and metal ion. The reagent shows maximum absorbance at 565 nm. The effect of the metal ion is to cause a decrease in the absorbance at 565 nm, accompanied by an absorbance increase for the complex which exhibit maximal value at about 620 nm, in the case of lead, nickel, cobalt, ytterbium and proseodymium, whilst in the case of tungsten the maxima is at 510 nm.

An examination of the stability constant data of BPR complexes reveals the order

Co(II) > Pb(II) > Yb(III) > Ni(II) > Pr(III) > W(VI)

Cobalt and praseodymium are different in so far as both form 1:2 complexes. Praseodymium also forms an identifiable 1:1 complex. This order of stability cannot be fruitfully correlated because the metal ions studied belong to different groups. It may be noted that the fact that Co(II) and Pr(III) form 1:2 complexes may be connected with the energy considerations of the chelation reaction.

However, some conclusions may be drawn, about the order of stability of metal complexes of BPR which belong to same group of the periodic table. For metals of bivalent ions the order observed is

Co(II) > Pb(II) > Ni(II)

The stability of cobalt complex is greatest, because Co(II) forms 1:2 complex, whilst Pb(II) and Ni(II) form 1:1 complex. Moreover, the ionisation potential of Co(II) is higher than that of Ni(II) and Pb(II), which also contributes towards its greater stability. The order Pb > Ni has also been observed by a number of workers[21,22].

For the 1:1 metal complexes of BPR with trivalent metal ions the trend of stability is:

Yb(III) > Pr(III)

Yb(III), having a greater ionization potential than that of Pr(III), would be expected to form more stable complexes, which is borne out by the experimental results.

The thermodynamics of these systems show that all metals react spontaneously with BPR, as is evident by the negative value of free energy of formation. Except in the case of Pb(II), the values of entropy change (ΔS), for other complexation reactions are positive, showing a greater amount of disorder in the product than in the reactants. The Pb(II)-BPR system has a negative ΔS value, which shows that the product is more ordered than the reactants. This may also be due to the formation of highly symmetrical species or due to very strong complex-solvent interactions. All the reactions are exothermic, as is evidenced by the negative heat of formation (ΔH). A point of interest is the low value of heat of formation of 1:1 Pr(III)-BPR chelate (-1.84 kcal/mole) as compared to the 1:2 complex (-28.55 kcal/mole). This suggests that in the first step of complexation reaction i.e. the replacement of the co-ordinated solvent molecules by the ligand molecules, a large amount of energy is consumed which is just compensated by the bond energy released due to the complex species formed. In the subsequent step, however, the replacement of solvent molecules by the ligand is not such an energy consuming process.

At present a large number of organic reagents are in use, for the photometric determination of Pb(II), Co(II), Ni(II), Yb(III), Pr(III) and W(VI). The proposed method using BPR as a chromogenic reagent is simple, rapid and sensitive, but selective only to a limited extent. Tables 4.19-4.21 give a comparative account of the molar absorptivities of some reagents used for these metals, which clearly indicates that BPR is comparable in sensitivity with the other reagents used at present.

While investigating the BPR complex with Co(II), it was observed that the optical density of the system decreases with the time. This may be accounted for the possible air oxidation of cobalt, from the divalent to the trivalent state. This phenomenon has also been observed by a large number of workers[1,4,7,17] while studying complexes of this metal. The metal is probably bound to BPR in a square planer configuration like Co(II)-phthalocyanine[8] and Co(II)-dimethylglyoxime[9]. This is speculative, however, because it is known that the d^7 configuration of the metal ion can assume either square planer (dsp^2) or tetrahedral (sp^3) symmetry depending on the environment. The suggestion of an equilibrium mixtures may be plausible in some cases. A distorted octahedral configuration has also been suggested as possibility[6]. Such a structure will require promotion of a 'd' electron to an outer '5s' or '4d' orbital. Two solvent molecules then conceivably occupy two elongated, weakly bonding sites of the metal. Magnetic moments measurements would possibly aid in the elucidation of the structure. The stabilisation of the colour system by the addition of gelatin is the phenomenon related to 'gelatin sensitisation' effect noted by Feigal[11] in connection with hydrophobic solutions.

These studies clearly reveal the stoichiometry of the coloured bodies, but do not present any evidence of its physical nature. The only pertinent evidence available from the studies is that the complexes precipitate out from solutions and are easily coagulated at the interface on standing. This happens despite the presence of sulphonic acid groups in the periphery positions of the organic reagent, remote from the chelating center of the molecule, is indicative of the colloidal nature and suggests that an absorption system i.e. lake formation may be involved in the complex formation.

TABLE 6.1

Metal ion	Ionisation potential (e.v.)		Pauling's electro-negativity
	I_1	I_2	
Cu(II)	7.724	20.090	1.90
Pb(II)	7.415	14.970	1.80
Ni(II)	7.630	18.150	1.80
Co(II)	7.860	17.050	1.80
Ga(III)	6.000	20.430	1.80
Al(III)	5.984	18.740	1.50
Yb(III)	6.200	-	-
Pr(III)	5.760	-	-
Zr(IV)	6.950	13.970	1.40
Hf(IV)	5.500	14.900	1.30
W(VI)	7.980	14.000	1.70
N	14.540	29.605	3.04
O	13.614	35.146	3.44

REFERENCES

1. Bailer, J.C. Jr. and Callis, C.F. J. Am. Chem. Soc., 74, 6018 (1952).

2. Barnard, A.J. Jr. and Flashka, H.A. 'Chelates in analytical Chemistry', Marcel Dekker, Inc., N.Y., p. 9 (1969)

3. Bjerrum, J. 'Stability constant - Part I Organic ligands,' The Chemical Society, London, p. 95 (1957)

4. Callis, C.F., Neilson, N.C. and Bailer, R.H. J. Am. Chem. Soc., 74, 3461 (1952)

5. Calvin, H. and Bailer, R.H. J. Am. Chem. Soc., 68, 949 (1946)

6. Cartell, E. and Fowles, G.W.A. 'Valency and molecular structure', Butterworths, London (1956)

7. Cheng, K.L. and Bray, R. Anal. Chem., 27, 1827 (1955)

8. Christopher, D.H. and West, T.S. Talanta, 13, 507 (1966)

9. Cotton, F.A. and Wilkinson, G. 'Advanced inorganic chemistry', Ind. Edn., Interscience (1966)

10. Dey, A.K. Proceedings - Fifty-seventh Science Congress, Kharagpur, p. 21 (1970)

11. Feigal, F. 'Specific, selective and sensitive reactions', p. 465 (1949)

12. Hellor, J. and Schwarzenbach, G. Helv. Chim. Acta, 34, 1876 (1951)

13. Irving, H. and Rossotti, H.S. J. Chem. Soc., 2904 (1954)

14. Irving, H. and Williams, R.J.P. J. Chem. Soc., 3192 (1953)

15. Katayama, T., Miyata, H. and Tôei, K. Bull. Chem. Soc., Japan, 44, 3040 (1971)

16. Latimar, W.M. and Jolley, W.L. J. Am. Chem. Soc., 75, 548 (1953)

17. Liu, J. CH.I. Thesis, University of Illinois (1951)

18. Maley, L.E. and Mellor, D.P. Nature, 159, 370 (1947); 161, 436 (1948)

19. Miyata, H. Z. Anal. Chem., 245, 322 (1959)

20. Miyata, H. Bull. Chem. Soc., Japan, 36(4), 362 (1963)

21. Monk, C.B. Trans. Faraday Society, 47, 297 (1951)

22. Pederson, K.J. Atta Chem. Scand., 3, 670 (1949)

23. Sommer, L. and Cenek, M. Chemist Analyst, 56, 9 (1967)

24. Sommer, L. and Hnilčková, M. Collect Czech. Chem. Commun., 22, 209 (1957)

25. Vartak, D.G. and Menon, K.R. J. Inorg. Nucl. Chem., 31, 3141 (1969)

26. Zollinger, H. 'Chemie der azofarbstaffe', Biskhouses, Basel and Stuttgart (1958)

27. Zollinger, H. and Büchler, W. Helv. Chim. Acta, 34, 391 (1951)

* * *

SUMMARY

The work described in this thesis concerns with a detailed study of metal complexes of chromotrope 2R and bromopyrogallol red, the former being an azo dye while the latter belongs to the sulphonphthalein group of dyes. In course of these studies, metal chelates of chromotrope 2R and bromopyrogallol have been investigated spectrophotometrically whereas potentiometric studies have been carried out on some bivalent metal ions complexes of chromotrope 2R.

Part A: Spectrophotometric Investigations

The principal aim of the spectrophotometric studies has been to investigate the optimum conditions for complex formation, the composition, stability and thermodynamic functions such as free energy of formation (ΔG), enthalpy change (ΔH) and entropy change (ΔS), which are associated with the formation of metal complexes in solution. The dyes selected for the present studies are chromotrope 2R and bromopyrogallol Red. The application of these chromogenic reagents for the micro determination of certain metal ions and the effect of foreign ions on the photometric determination of metal ions have also been attempted, and the results obtained have been reported at length in course of this presentation.

Part B: Potentiometric Studies

This part of the thesis deals with the study of metal chelates of chromotrope 2R with some bivalent metal ions. Stepwise stability constants of the metal complexes and the reagent itself have been obtained at various ionic strengths, and the thermodynamic stability constants have been obtained by the method of extrapolation to zero ionic strength.

The work has been presented in six chapters. The first chapter describes in brief the introduction of co-ordination chemistry with special reference to the theories of co-ordination and the analytical importance of metal complexes in various fields of science.

Chapter II deals with the methods used for discerning the composition and the stability of the metal chelates, both by spectrophotometric as well as by potentiometric methods. For the stoichiometry of metal to ligand in various metal complexes, in solution, the following methods have been used in this work, which are based on absorbance measurements.

(1) Job's method of continuous variation using equimolecular and nonequimolecular solution.

(2) Mole ratio method of Yoe amd Jones.

(3) Slope ratio method of Harvey and Manning.

The results obtained by these methods indicate the same stoichiometry.

The apparent or conditional stability of the metal complexes have been determined using the following three methods:

(1) Method of Banerji and Dey,

(2) Mole ratio method,

and (3) Molecular extinction coefficient method.

For the determination of thermodynamic functions, which are associated with the complex formation, in solution, the value of stability constants have been obtained by the molecular extinction coefficient method at different temperatures in the range 15°C-35°C. The value of free energy of formation was obtained directly by using van't Hoff isotherm. Assuming that the enthalpy remains constant over the range of temperature under investigations, the value of ΔH was obtained by plotting a graph between log K vs 1/T, the slope of which is equal to $-\frac{\Delta H}{4.57}$, or by using van't Hoff isochore. The entropy change (ΔS) was then obtained by Gibbs Helmholtz equation.

The stepwise protonation constant of chromotrope 2R and the stepwise metal-ligand stability constants have been determined using Bjerrum-Calvin pH titration technique as described by Irving and Rossotti. All the values of $\bar{n}_A$, $\bar{n}$ and pL which are used to determine the stability constants, were calculated by programming in the IBM 1130 computer and results checked by manual calculations. The computational methods employed for the analysis of the formation curves, to determine the protonation constant of the ligand and the stepwise metal-ligand stability constants are listed below.

(i) Interpolation at half $\bar{n}$ values (H).

(ii) Interpolation at various $\bar{n}$ values (V).

(iii) Mid point slope method (M).

A detailed investigation of metal complexes of Copper (II), Aluminium (III), Gallium (III), Ytterbium (III), Zirconium (IV) and Hafnium (IV) with chromotrope 2R has been described in Chapter III, by spectrophotometric method. The results obtained have been recorded in Table I.

Chapter IV describes the spectrophotometric studies of metal complexes of bromopyrogallol red with Lead (II), Nickel (II), Cobalt (II), Ytterbium (III), Praseodymium (III) and Tungsten (VI). Some of the representative results have been recorded in Table II.

The potentiometric studies on the metal complexes of chromotrope 2R with some bivalent metal ions i.e. Uranyl ion (II), Copper (II), Beryllium (II), Mercury (II), Zinc (II), Nickel (II), Cobalt (II), Cadmium (II) and Lead (II) have been embodied in Chapter V. The results obtained have been recorded in Tables III and IV.

The last chapter describes the discussion of the results obtained.

The present work has thrown considerable light on the composition, stability and thermodynamic functions of metal complexes of Chromotrope 2R and Bromopyrogallol Red, which have not been investigated earlier. The stability constants of the metal complexes of CTR with some bivalent metal ions have also been determined at various ionic strengths i.e. 0.025, 0.050, 0.075, and 0.125, and by the extrapolation of log K to zero ionic strength, the thermodynamic stability constants ($\log K_1^{\mu=0}$, $\log K_2^{\mu=0}$ and $\log \beta_2^{\mu=0}$) have been obtained.

:::::::::::::

TABLE I

Characteristics of Metal Complexes of Chromotrope 2R

Temperature = 25°C Ionic strength = 0.1

System	pH	λ_{max} (nm)	Compo-sition M:L	Molar absorp-tivity	Sensitivity	log K	-ΔG kcal/mole	ΔH kcal/mole	ΔS e.u./mole
Cu:CTR	6.0±0.1	580	1:1	7250	0.0080	4.44	6.05	-17.92	-39.82
Al:CTR	5.0±0.1	580	1:1	19875	0.0014	3.84	5.24	+ 1.42	+22.30
Ga:CTR	3.4±0.1	580	1:2	17312	0.0040	8.69	11.85	+ 7.99	+66.55
Yb:CTR	6.9±0.1	580	1.1	25000	0.0068	4.16	5.70	- 3.91	+ 6.00
Zr:CTR	2.0±0:1	580	1:1	3875	0.0248	4.41	6.02	-	-
Hf:CTR	2.0±0.1	580	1:1	7125	0.0215	4.57	6.23	-	-

TABLE II

Characteristics of metal complexes of Bromopyrogallol Red

Temperature = 30°C Ionic strength = 0.1

System	pH	λ_{max} (nm)	Composition M:L	Molar absorptivity	Sensitivity $\mu g/cm^2$	log K	$-\Delta G$ kcal/mole	$-\Delta H$ kcal/mole	ΔS e.u./mole
Pb:BPR	5.5±0.1	630	1:1	5,000	0.0140	6.16	8.54	10.46	- 6.33
Ni:BPR	6.8±0.1	620	1:1	16,000	0.0037	5.89	8.17	3.86	+ 14.32
Co:BPR	6.5±0.1	620	1:2	29,000	0.0022	9.38	13.01	6.35	+ 21.99
Yb:BPR	6.3±0.1	620	1:1	19,850	0.0087	5.94	8.25	3.54	+ 15.53
Pr:BPR	7.2±0.1	620	1:1	35,500	0.0042	5.74	7.97	1.84	+ 20.21
	4.0±0.1	650	1:2	40,500	0.0031	10.59	14.09	28.55	+45.73
W:BPR	4.7±0.1	510	1:1	8,000	0.0023	5.39	7.47	3.83	+12.00

TABLE III

Values of stability constants of CTR metal chelates

Metal	Ionic strength	log K_1		Average	log $K_1^{\mu=0}$
		(H)	(V)		
H^+	0.025	10.08	10.04	10.06	10.22
	0.050	9.96	9.92	9.94	
	0.075	9.77	9.71	9.74	
	0.125	9.65	9.59	9.62	
Pb^{+2}	0.025	5.37	5.39	5.38	5.65
	0.050	5.14	5.16	5.15	
	0.075	5.05	5.03	5.04	
	0.125	4.90	4.92	4.91	
Ni^{+2}	0.025	5.40	5.44	5.42	5.45
	0.050	5.35	5.39	5.37	
	0.075	5.13	5.16	5.14	
	0.125	5.05	5.12	5.08	
Co^{+2}	0.025	5.20	5.24	5.22	5.25
	0.050	5.16	5.15	5.16	
	0.075	4.93	4.97	4.95	
	0.125	4.81	4.82	4.82	
Cd^{+2}	0.025	4.04	4.08	4.06	4.14
	0.050	3.93	3.96	3.95	
	0.075	3.90	3.97	3.93	
	0.125	3.90	3.91	3.91	

TABLE IV

Values of stability constants of CTR metal chelates

Metal	Ionic strength	log K_1			log K_2			Average log β_2	log $K_1^{\mu=0}$	log $K_2^{\mu=0}$	log $\beta_2^{\mu=0}$ cal.	log $\beta_2^{\mu=0}$ exp.
		(H)	(V)	(M)	(H)	(V)	(M)					
Cu^{+2}	0.025	7.63	7.64	7.78	6.64	6.60	6.57	14.29	8.20	7.00	15.20	15.15
	0.050	7.65	7.80	7.70	6.58	6.56	6.50	14.27				
	0.075	7.15	7.19	7.49	6.49	6.24	6.16	13.57				
	0.125	6.95	7.05	7.29	6.45	6.27	6.13	13.38				
UO_2^{+2}	0.025	8.02	8.08	7.74	5.43	5.54	5.62	13.48	8.20	5.00	13.20	13.32
	0.050	8.05	7.67	7.64	5.75	5.68	5.77	13.52				
	0.075	7.81	7.64	7.63	5.70	5.69	5.67	13.40				
	0.125	7.34	7.35	7.53	5.60	5.56	5.57	13.00				
Be^{+2}	0.025	7.50	7.40	7.35	4.80	4.84	4.93	12.27	7.60	4.90	12.50	12.40
	0.050	7.41	7.37	7.27	4.85	4.91	4.93	12.25				
	0.075	7.25	7.21	7.25	4.86	4.93	4.90	12.14				
	0.125	7.05	7.09	7.20	4.93	5.02	4.84	12.04				
Zn^{+2}	0.025	4.60	4.65	4.71	3.90	3.78	3.69	8.44	4.75	4.00	8.7	8.68
	0.050	4.60	4.64	4.65	3.83	3.74	3.75	8.40				
	0.075	4.50	4.53	4.55	3.76	3.82	3.76	8.32				
	0.125	4.36	4.41	4.34	3.89	3.89	3.60	8.24				
Hg^{+2}	0.025	4.58	4.64	4.73	3.82	3.89	3.97	8.54	4.81	3.94	8.75	8.70
	0.050	4.48	4.50	4.55	3.78	3.78	3.75	8.28				
	0.075	4.34	4.36	4.43	3.73	3.64	3.69	8.06				
	0.125	4.11	4.15	4.25	3.70	3.68	3.52	7.80				

APPENDIX I

COMPUTER PROGRAM FOR THE CALCULATION OF $\bar{n}_A$ AND $\bar{n}$

```
PAGE   1    3241CC05

// JCB T                                                  3241CC05

LCG CRIVE   CART SPEC   CART AVAIL   PHY DRIVE
  CCCC        CCCA        CCCA         CCCO

V2 MC8   ACTLAL 16K  CCNFIG 16K

// FCR
*ICCS(25C1 READER,14C3 PRINTEP)
*CNE WCRC INTEGERS
*LIST SCURCE PRCGRAM
      REAL NC, NBARA(5C), NBAR(50)
      CIMENSICN C(5C),C1(5C)
      CIMENSICN V1(5C), V2(5C), V3(50)
    1 REAC(8,3)NSET
      IF (NSET)2,46,2
    2 REAC (8,4C)Y,NC,EC,VC,TL,TM
      REAC(8,3)N
    3 FCRMAT(I2)
      REAC(8,1C)(V1(I),I=1,N),(V2(I),I=1,N)
      KCUNT=1
   4C FCRMAT(8F1C.6)
   15 REAC (8,1C) (V3(I),I=1,N)
   1C FCRMAT(8F1C.3)
      CCNS2=(NC+EC)
      CCNS1=CCNS2/TL
      CC 2C I=1,N
      C(I)=V2(I)-V1(I)
      C1(I)=V3(I)-V2(I)
      NBARA(I)=Y+CCNS1*(V1(I)-V2(I))/(V0+V1(I))
   20 NBAR(I)=(V3(I)-V2(I))*(CCNS2+(Y-NBARA(I))
     +*TL)/((VC+V2(I))*NBARA(I)*TM)
      NCNT=1
      JI=N
      JJ=1
      IF(N-25)29,29,28
   28 NCNT=2
      JI=25
   29 IPAGE=0
      CC 34 I3=1,NCNT
      IPAGE=IPAGE+1
      WRITE(5,30)KCUNT,IPAGE
   30 FCRMAT(1H1,//,15X,'SET NC',I3,30X,'PAGE',I2,/)
      WRITE(5,31)
   31 FCRMAT(15X,65('-'))
      WRITE(5,32)
   32 FCRMAT(61X,'--',14X,'-',/,16X,'S NO',10X,'V2-V1',10X,'V3-V2',11X,'NA',14X,
     +'NA',14X,'N',/)
      WRITE(5,31)
      WRITE(5,33)(I,C(I),C1(I),NBARA(I),NBAR(I),I=JJ,JI)
   33 FCRMAT(15X,I5,4F15.4,/)
      JJ=26
      JI=N
   34 WRITE(5,31)
      KCUNT=KCUNT+1
      IF(KCUNT-NSET) 15,15,45
   45 GC TC 1
   46 CALL EXIT
      END

FEATURES SUPPCRTED
 CNE WCRC INTEGERS
 ICCS

CCRE REQUIREMENTS FCR
 CCMMCN       0  VARIABLES      730   PRCGRAM     416

ENC CF CCMPILATICN

// XEQ
```

APPENDIX II

COMPUTER PROGRAM FOR THE CALCULATION OF FREE LIGAND EXPONENT, pL

```
PAGE   1    2241CCC5

// JCB T                                                     2241CC05

LCG CRIVE    CART SPEC    CART AVAIL   PHY CRIVE
  CCCC         CCCA         CCCA         CCCC

V2 MC8    ACTUAL 16K  CCNFIG 16K

// FCR
*ICCS(25C1READER,14C3PRINTER)
*CNE WCRC INTEGERS
*LIST SCURCE PRCGRAM
      REAL NBAR(5C)
      CIMENSICN PH(5C),V111(5C),VC3(5C),PL(5C)
    2 FCRMAT (I2,2E12.4,3F1C.5)
    5 READ (8,2) N,B1,B2,TL,TM,VC
      IF (N) 2C,2C,25
   25 WRITE(5,9)
    9 [illegible],'PH',13X,'VO+V3',14X,'NBAR',14X,'PL',/,6
     1[illegible],'-----',14X,'-----',14X,'--',//)
      [illegible] (V111(I),I=1,N),(NBAR(I),I=1,N)
    1 [illegible]
      CC 1C I=1,N
      [illegible]
      VC3(I)=VC+V111(I)
      PLCG=(B1*H+B2*H*H)*VC3(I)/((TL-TM*NBAR(I))*VO)
   1C PL(I)=ALCG(PLCG)*.4343
      CC 12 I=1,N
   12 WRITE (5,15)  I,PH(I),VC3(I),NBAR(I),PL(I)
   15 FCRMAT (//,8X,I3,4(1CX,F1C.3))
      GC TC 5
   2C CALL EXIT
      END

FEATURES SUPPCRTEC
 CNE WCRC INTEGERS
 ICCS

CCRE REQUIREMENTS FCR
 CCMMCN      C  VARIABLES     522   PRCGRAM     288

END CF CCMPILATICN

// XEQ
```