SURFACTANT IMPROVED SPECTROPHOTOMETRY DETERMINATION OF SOME METALS

by

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A thesis submitted to the Postgraduate School, Ahmadu Bello University, in partial fulfilment of the requirements for the degree of:
MASTER OF SCIENCE in ANALYTICAL CHEMISTRY.

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FEBRUARY, 1983.

DECLARATION

I hereby declare that this thesis has been written by me and that it is a record of my own research work. It has not been presented in any previous application for a higher degree. All quotations are indicated and the sources of information are specifically acknowledged by means of references.

S U P E R V I S O R	C A N D I D A T E
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THESIS RECOMMENDATION

We hereby recommend that the thesis prepared by Mr. O. Durotimi entitled, "Surfactant improved spectrophotometric determination of some metals" be accepted in partial fulfilment of the requirements for the degree of M.Sc. Analytical Chemistry.

Internal Examiner	External Examiner
DATE	DATE

DEDICATION

This thesis is fondly
dedicated to my daughter
Ibukun Bolanle Durotimi.

ACKNOWLEDGEMENTS

I have received much good counsel from my supervisor, Dr. J.Y. Olayemi who has been incessant in his help. I have constantly drawn on his expert knowledge, untiring encouragement and impartial supervision. I am sincerely most grateful.

My sincere thanks go to Dr. H.T. Bozimo, the Head of the Department of Chemistry for making available to me the facilities necessary for this project.

I thank the Council of the Kwara State College of Education, Ilorin for making it possible for me to undertake this course.

My special thanks are due to my wife, Oluremi and daughter, Ibukun whose patience constantly spurred me to work hard and especially for letting me spend these months which I would have normally spent with them.

Much thanks to my friends and colleagues, Abayomi, Idowu, Tola and Kunle for it was both a pleasure and stimulus to work with them.

Finally, I would like to take this opportunity to express my thanks to my long time friend Zacchaeus Ibiyemi and his wife for their various contributions to the success of this work.

OLATUNDE DUROTIMI.

ABSTRACT

The procedure for producing a calibration curve for the determination of aluminium, conper, zinc and chromium in trace amounts is described. It involves the use of a sensitive spectrophotometric method based on the formation of intensely coloured micellar improved ternary systems. The systems studied are: Zn - PGR, Cr - PGR as well as Al - CV and Cu - CV.

On investigating the interaction between (PGR) and zinc or chromium, the wavelength of maximum absorption of 520nm was recorded for the PGR - Zn system and 414nm for the Cr - PGR system with corresponding extinction coefficient values of 13,66 x 10^3 $l.mole^{-1}$ cm^{-1} and 18.94 $l.mole^{-1}$ cm^{-1} . From the results, the stoichiometry of the Zn - PGR complex was either $Zn(PGR)_5$ or Zn_2PGR but it was impossible to deduce that of the Cr - PGR complex.

The binary systems were sensitized by the addition of cetyltrimethylammonium bromide (CTAB). The wavelength of maximum absorption for the ternary systems are 600nrn for Zn - PGR - CTAB and 572nm for Cr-PGR-CTAB with corresponding extinction coefficient values of 15.40 x 10^3 $l.mole\text{-}^{1}.cm\text{-}^{1}$ 15.53 $l.mole^{-1}$. cm^{-1}. The composition of the ternary complex was deduced using the mole ratio method. A formula of $Zn[PGR)_4(CTAB)_{10}]$ or $Zn_4((PGR)_2(CTAB)_5\}$ is proposed for the zinc complex.

Similarly, the interaction between (CV) and aluminium or copper was investigated. The wavelength of maximum absorption of 578nm was recorded for the Al-CV system and 610nm for the Cu-CV system with corresponding extinction coefficients of 2.C5 x 10^3 $l.mole^{-1}$ cm^{-1} and 2.69 x 10^4 l.mole-^{1} cm-^{1}.

The stiochiometry of the Cu - CV complex was $Cu(CV)_2$ while that of Al - CV was A1CV. On the addition of (CTAB) to these binary systems, the composition of the corresponding ternary system was deduced using the mole ratio method. For the Cu-CV - CTAB complex, a formula of $Cu[CV_2(CTAB)_6)$ or Cu(CV - $(CTAB)_3J_2$ was proposed while $A1CV(CTAB)_2$ was proposed for the Al-CV-CTAB system. The wavelength of maximum absorbance for Cu-CV-CTAB is 698nm and 696nm for the Al-CV-CTAB with an extinction coefficient of 3.10 x 10^4 $l.mole^{-1}.cm^{-1}$ and 35.97 x 10^3 $l.mole^{-1}$ cm^{-1} respectively.

Even though no attempts were made to mask interfering ions, the selectivity of the method was studied by investigating the interference of some cations and anions on each of the systems. The interference effects were recorded in percentage form.

TABLE OF CONTENTS

		Page
Title		i
Declaration		ii
Thesis recommendation		iii
Dedication		iv
Acknowledgement		v
Abstract		vi
List of tables		x
List of figures		xiii
Chapter		
1.	Introduction	1
	Surface active agents or Surfactants	1
	Analysis of metallic elements	8
	Surfactants in trace metal analysis	15
2.	Study of pyrogallol red	20
	Interaction between pyrogallol red and zinc or chromium(III) ions	30
	Determination of the optimum conditions for pyrogallol red (PGR) and cetyl trimethylammonium bromide (CTAB) interactions	35
	Study of the M^{n+} - PGR - CTAB system	41
	Interference study	51
3.	Study of catechol violet	56
	Interaction of catechol violet with metal ions	65
	Determination and maximising the conditions for catechol violet (CV) and cetyltrimethyl ammonium bromide (CTAB) interactions	72

Chapter		Page
	Study of the ternary system of M^{n+} - CV - CTAB	75
	Interference study	85
4.	Summary and conclusions	90
	Recommendations	94
	Suggestions for further Investigation ..	97
References		99

LIST OF TABLES

Page

Table 2.1: Variation of pH and absorbance of aqueous (PGR) solution with increase in buffer concentration .. 27

2.2a: Extinction coefficient of Zn^{2+} in PGR - Zn^{2+} at different (PGR) concentrations 31

2.2b: Extinction coefficient of Cr^{3+} in PGR - Cr^{3+} at different (PGR) concentrations 35

2.3: Mole ratio of [CTAB]/[PGR] for specific interaction at different (PGR) concentrations 38

2.4: Extinction coefficient of Zn^{2+} in Zn - PGR - CTAB for different (PGR) concentrations 44

2.5 Extinction coefficient of Cr^{3+} for different (PGR) concentrations in the presence of (CTAB) 51

2.6 Interference (%) of some ions in the determination of zinc using (PGR) and (CTAB) as reagents 52

Page

Table 2.7: Extinction coefficient and λ_{max} of the chloride compared with the nitrate salts of zinc 53

2.8: Interference (%) of some ions in the determination of chromium using (PGR) and (CTAB) as reagents 54

2.9: Extinction coefficient and λ_{max} of the chloride compared with the nitrate salts of chromium 55

3.1: Dependence of pH and absorbance of (CV) on concentration of $NaHCO_3$/NaOH .. 64

3.2: Variation of extinction coefficient of Cu^{2+} in Cu-CV system with (CV) concentration 69

3.3 Variation of extinction coefficient of Al^{3+} in Al-CV system with (CV) concentration 72

3.4 Mole ratio of [CTAB]/[CV] at different (CV) concentrations in the CV-CTAB system 75

3.5: Variation of the extinction coefficient of Cu^{2+} in Cu-CV-CTAB with (CV) concentration 80

Page

Table 3.6 Molar ratio of $[CV]/[Cu^{2+}]$ in the ternary system of Cu-CV-CTAB .. 81

3.7 Extinction coefficients for Al^{3+} in the ternary system of Al-CV-CTAB .. 83

3.8: Mole ratio of $[CV]/[Al^{3+}]$ in the ternary Al-CV-CTAB 85

3.9 Interference (%) of some ions in the determination of copper using (CV) and (CTAB) as reagents 86

3.10: Extinction coefficient and λ_{max} of the chloride compared with the nitrate salts of copper 87

3.11: Interference (%) of some ions in the determination of aluminium using (CV) and (CTAB) as reagents 88

3.12 Extinction coefficient and λ_{max} of the chloride compared with the nitrate salts of aluminium 89

LIST OF FIGURES

Page

Figure 2.1: Potentiometric titration of pyrogallol red with both sodium hydroxide and hydrochloric acid 22

2.2 Spectrophotometric titration of pyrogallol red solution with both sodium hydroxide and hydrochloric acid 24

2.3 Variation of λ_{max} of aqueous solution of 1.6×10^{-5}M pyrogallol red with pH 25

2.4 Beer-Lambert's law calibration curve for pyrogallol red solution 29

2.5a Beer-Lambert's law calibration curve for PGR-Zn^{2+} complex 32

2.5b Beer-Lambert's law calibration curve for PGR-Cr^{3+} complex 34

2.6a Variation of change of {PGR} at 550nm with {CTAB} 37

2.6b Variation of {PGR} with {CTAB} at constant absorbance 39

2.7 Effect of {CTAB}/{PGR} on absorbance 40

Page

Figure 2.8 Variation of absorbance of CTAB/PGR system with $\{Zn^{2+}\}$ for different [PGR] and constant {CTAB}/[PGR] of 2.6 43

2.9a Variation of change of [PGR] with λ_{max} 45

2.9b Variation of extinction coefficient with change in [PGR] 46

2.10 Calibration curve for Cr^{3+} at 572nm using different [PGR] but keeping {CTAB}/[PGR] at 2.6. 50

3.1 Potentiometric titration of catechol violet solution with both sodium hydroxide and hydrochloric acid .. 58

3.2 Spectrophotometric titration of catechol violet solution with both sodium hydroxide and hydrocholoric acid 61

3.3 Variation of λ_{max} of aqueous catechol violet with pH. 62

3.4 Beer-Lambert law calibration curve for catechol violet solution 66

Page

Figure 3.5: Beer-Lambert law calibration curve for CV - Cu^{2+} complex 68

3.6: Beer-Lambert law calibration curve for CV-Al^{3+} complex 71

3.7 Absorption spectra of CTAB/CV complex at 600nm 74

3.8 Variation of (CTAB) concentration with {CV} 76

3.9 Absorption spectra of CV-Cu^{2+} system and Cu-CV-CTAB system 78

3.10 Absorption spectra of Cu-CV-CTAB complex 79

3.11 Absorption spectra of Al-CV-CTAB complex 84

CHAPTER ONE

1. INTRODUCTION.

1.1 SURFACE ACTIVE AGENTS OR SURFACTANTS

Surfactants are substances that alter the conditions prevailing at interfaces e.g. cleansing materials - soaps, greases, glues and gums. They have found wide use in almost all branches of the chemical industry most especially in detergency, textile industry and biological research. Each surfactant molecule or monomer has two distinct regions in its chemical nature. One is a hydrocarbon chain, the hydrophobic region and the other is the ionized group or the water soluble group, the hydrophilic region. An example of a surfactant is cetyltrimethylammonium bromide (CTAB) with a chemical formula, $C_{16}H_{33}N^{+}(CH_3)_3Br^{-}$. As a class, these substances which include soaps, detergents are called, "surface active agents, association colloids or colloidal surfactants" (1)

Hartley (2), described the existence in one compound of two moities as amphipathy. This dual nature of surface active agents is responsible for their surface activity, micellization and solubilization. It is the presence of the hydrophilic group that renders each of the substances soluble in water at an appropriate temperature.

1.1.1 Types of Surfactants.

The usual classification of non-ionic, anionic cationic or switterionic surfactants depend upon the nature of the head groups. The hydrophobic part can be of different length. It can contain unsaturated portions, aromatic groups, can be branched or can be partly or completely halogenated. The principal types and their characteristics are:

(i) Cationic surfactants: These ionize in solution with the head group carrying a positive charge e.g. cetyltrimethylammonium bromide (CTAB), $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$ and cetylpyridinium chloride (CPC) $C_5H_5N^+C_{12}H_{25}Cl^-$.

(ii) Anionic surfactants: These ionize with the head group carrying a negative charge e.g. potassium laurate, $CH_3(CH_2)_{10}COO^-K^+$.

(iii) Non-ionic surfactants: These do not ionize in solution. They only behave like organic molecules.

(iv) Ampholytic surfactants: These can behave as either anionic, cationic or non-ionic, depending on the pH of the solution.

(v) Zwitterionic surfactants: These ionize to carry equal number of positive and negative charges, simultaneously and are thereby neutral.

Most of the surface active agents are synthetic but a few are naturally occurring e.g. lecithin.

1.1.2 The micellization.

At very low concentrations, those surface active agents which carry ionized groups behave like ordinary strong electrolytes and are completely dissociated. As the concentration of the surface active agents in solution is increased sufficiently, formation of small aggregates of colloidal size is observed. Those aggregates of colloidal dimension are called micelles. It is interesting to note that in the early stages, the concept of micelles met with some resistance, before acceptance as can be realized from the following quotation from Mcbain (3).

> so novel was this finding that when in 1925 some of the evidence for it was presented to the Colloid Committee for the advancement of Science in London, it was dismissed by the chairman, a leading international authority with the words, Nonsense McBain.

The word micelle is used in a variety of ways. According to the Webster Dictionary (4) for example, a micelle is a unit of structure built up from polymeric molecules or ions as:

a) an ordered region in a natural or synthetic fibre (as of cellulose, silk or rayon).

b) a highly associated particle of colloidal solution (colloidal micelles of soaps and detergents).

c) an organic colloidal particle ranging in size from one micron to one millimicron and found in coal and some shales.

In this work, definition (b) from Webster for micelle is the only one relevant. It refers to aggregates of amphiphilic electrolytes in aqueous solution.

Numerous investigators have shown that micelle formation begins or becomes appreciable over a narrow range of concentration of the surfactant in solution. The International Union of Pure and Applied Chemist (IUPAC) Manual of Symbols and terminology Appendix II, Part I (5) states that:

> surfactants in solution are often associated colloids, that is they tend to form micelles, meaning aggregates of colloidal dimensions existing in equilibrium with the molecule or ions from which they are formed.

There is a relatively small range of concentration separating the limit below which virtually no micelles

are detected and the limit above which virtually all additional surfactants form micelles. This range is known as the critical micelle concentration (usually abbreviated as c.m.c.) The relatively small range of concentration mentioned above is narrow enough, however to allow the critical micelle concentration values to be determined quite precisely in many cases. One of the most practical uses of the (c.m.c) is in the calculation of the monomeric and micellar concentrations. However since micelles are not generally strongly surface active, the practical significance of the (c.m.c) is that, it is the equilibrium concentration where surface chemistry ends and colloid chemistry begins according to Hinze (6).

1.1.3 Size, shape and structure of micelles.

Though there is a general agreement on the presence of micelles in strong solutions of surface active agents, there is a disagreement as to their shapes, kinds and mechanism of formation (1,7). Both McBain (3) and Hartley (2) suggest different types of micellar structure. McBain assummed two types of micelles. One is a spherical, fully ionized micelle of not more than ten like ions, existing only in dilute solutions of the surfactants. The other is a micelle with little or no ionic charge, called lamellar micelle composed of alternate layers of water and double amphipathic molecules and formed

above the (c.m.c). Hartley(2), however proposed yet an undoubtedly simpler model, in which he believed that the micelles are liquid and essentially spherical, and that their interior approximates the random distribution of liquid paraffin, but with the hydrophylic end of the chain constrained to remain at the surface of the micelle. Debye and Anacker,(8) suggested that neither a spherical nor a disc - shaped micelle is formed, but rather a rod like micelle having the general shape of a stack of coins is what obtains.

The size, shape and charge of micelles have been studied mostly by light scattering and diffusion techniques. It is believed that the micelle is a compact roughly spherical body with a liquid like hydrocarbon core. These hydrocarbon chains are inside, remote from the solvent and the polar head groups are usually at the surface (or outside) of the spherical particle which is rough.

Generally the shape and size of micelles depend on the concentration, temperature and the molecular structure of the respective surface active agent.

1.1.4 Solubilization.

Solubilization as defined by McBain and Hutchinson (7) is a particular mode of bringing into solution substances that are otherwise insoluble in a given medium,

involving the previous presence of a colloidal solution whose particles take up and incorporate within or upon themselves the otherwise insoluble material. However this definition does not take cognizance of what happens in the colloidal structure when a third component is incorporated. The modern usage of the word solubilization has given it a more general meaning, i.e. the preparation of a thermodynamically stable isotropic solution of a substance normally insoluble or very slightly soluble in a given solvent by the introduction of an additional amphiphilic component or components. Such a definition encompasses dilute and concentrated solutions. While Hartley (9) pointed out that solubilization occurred only above the (c.m.c), Elworthy, et al, (10) suggested that the increased solubility of a solubilizate in a surfactant solution was due to some form of attachment of the solubilizate to the exterior of the micelle or solution in it. Shinoda, (11) showed that the addition of solubilizates tend to lower the critical micelle concentration. Shinoda added that some of the factors that can affect the amount of a given substance which can be solubilized include, polarity, polarizability, chain length, chain branching, molecular size and shape etc. Klevens (12) pointed out that in most cases, increasing the length of the alkyl chain in a straight chain compound or substituents on a benzene ring decreases the solubility

in a surfactant solution and that unsaturated compounds are more soluble than their saturated counterparts, while cyclization results in enhanced solubility. In most cases, however solubilization increases with temperature.

Surfactants are used as solubilizing agents primarily because they form ternary complexes with metal ions and chelometric dyestuffs, which are sensitive in spectrophotometric analysis. Surfactants can solubilize a number of solutes which are otherwise insoluble or sparingly soluble in the bulk solvent. As a result of this, surfactants used in micellar system possess a unique feature and property that should be amenable to analytical system and hence are very useful in helping to overcome many of the potential analytical problems e.g. solubility problems of required analytical reagents, slowness of analytical reactions, problems due to undesirable side attractions and lack of sensitivity or selectivity of spectral methods. And since only very small amounts of surfactants are used, there will be essentially no loss in sensitivity due to dilution.

1.2 ANALYSIS OF METALLIC ELEMENTS.

A large number of reagents and methods are known for the determination of nickel, copper(II), aluminium and chromium. Some of the methods and reagents are

common to the four ions (13-16). The determination of nickel in steel is generally based on its separation as the dimethylglyoximate and the subsequent determination by direct weighing or volumetric or photometric methods. Similarly copper can be determined gravimetrically as Copper(II) thiocyanate after reduction to Copper(I) by hydrogen sulphide. Since the classification of analytical methods is based on the final measurement step in the procedure, some of the standard methods that have been used in the determination of metallic elements include: gravimetric, volumetric and physicochemical methods. Incidentally, since some of these methods are mostly used for bulk determinations, they cannot be used satisfactorily to estimate trace or minute quantities of metal ions. The methods that are reliable in the determination of trace amounts of metals are therefore discussed in details below.

1.2.1 Colorimetric methods.

This is a branch of quantitative analysis in which the quantity of a coloured constituent is determined by measuring the amount of light passing through the solution of the constituent. A colorimeter is often used. In this method, the substance to be determined is converted to some compound which imparts to its solution a distinct colour, the intensity of

which varies in proportion to the amount of the compound in solution. Two types of constituents are encountered.

(a) The constituent itself may be coloured and can thus be determined directly e.g. the determination of permanganate ion.

(b) The constituent may be caused to react with a substance to form a coloured compound e.g. the determination of copper(II), after its reaction with ammonia to form a deep blue complex ion.

Colorimetirc methods are in general restricted to the determination of very small quantities of metals. The following terms are in common use in colorimetric measurements.

$$T = \frac{I}{I_o} \qquad .....(1 - 1)$$

$$A = \log \frac{I_o}{I} \qquad .....(1 - 2)$$

where, T is transmittance of solution, I is intensity of light transmitted, I_o is intensity of incident light and A is absorbance.

1.2.2 Spectrophotometric methods.

These measure the amount of nearly monochromatic light transmitted by an absorbing medium. Desired range of wavelengths is often used e.g. the ultraviolet

and visible regions. A spectrophotometer is often used. From a quantitative view point, spectrophotometric methods have certain advantages over colorimetric methods.

(a) They permit easy selection of optimum wavelengths for comparison and it is possible to determine more than one component in a single compound.

(b) They are more sensitive and permit the determination of microgram quantities in many cases.

Usually in spectrophotometric methods, a curve is plotted to show the relations between the wavelength and absorbance or between concentration and absorbance. Spectrophotometric methods are remarkable for their versatility, sensitivity and precision. A very extensive range of concentration of absorbing species may be covered usually from macroquantities to traces.

1.2.3 Sensitivity of spectrophotometric methods.

Strictly speaking, sensitivity refers to the slope of a calibration curve. The acceptable numerical expression of the sensitivity of spectrophotometric methods is the extinction coefficient or molar absorptivity (ε) at the wavelength of maximum absorbance (λ_{max}). Usually (ε) is represented by the equation,

$$(\varepsilon) = \frac{A}{c.l} \qquad \ldots(1 - 3)$$

where A is absorbance, c is concentration (mole/l), l is path length (cm). and (ε) is expressed in $l.mole^{-1}\ cm^{-1}$.

For very sensitive spectrophotometric method (ε) is usually very large and sometimes greater than 1×10^4 $l.mole^{-1}\ cm^{-1}$. The sensitivity of spectrophotometric methods is sometimes discussed in literature in terms of the smallest concentration of the absorbing substance that can be reliably determined i.e. the lower limit of determination. In such cases, additional information should be given e.g. the solution volume, path length of cuvette, type of instrument etc.

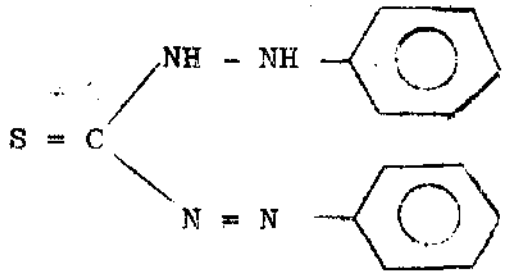
1.2.4 Selectivity of spectrophotometric methods.

According to the definition recommended by the Analytical Division of IUPAC, a reagent which reacts with a limited number of elements is considered to be selective. A reagent may be called specific if it gives a reaction with only one element in certain circumstances. Accordingly one may speak of selective and specific spectrophotometric methods. The selectivity of colour reactions and the corresponding spectrophotometric methods depend on; the nature of the reagent used, the oxidation state of the element, the pH of the medium as well as the nature of the complexing agent used to mask interfering ions.

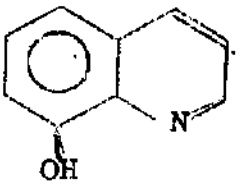
Since there exists rather few specific reagents and reactions, the selectivity of most methods is improved by choosing a suitable pH for the reaction medium. With some spectrophotometric methods the most suitable pH range is rather narrow owing to the nature of the colour reaction and or the effect of other ions. Increased selectivity of spectrophotometric methods is obtained mainly by masking the interfering ions. The measurement of the absorbances of two coloured complexes at different wavelengths lead to enhanced selectivity.

1.2.5 Colour systems used in spectrophotometry.

Almost all the colour systems used in spectrophotometric methods involve complex formation of some kind (17). The largest group makes use of the bifunctional organic reagents to form chelate complexes with metal ions, e.g.

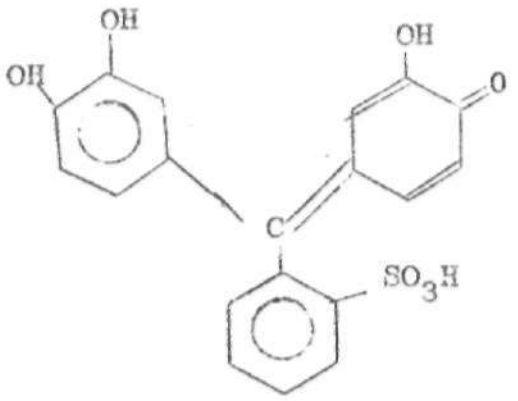


dithizone

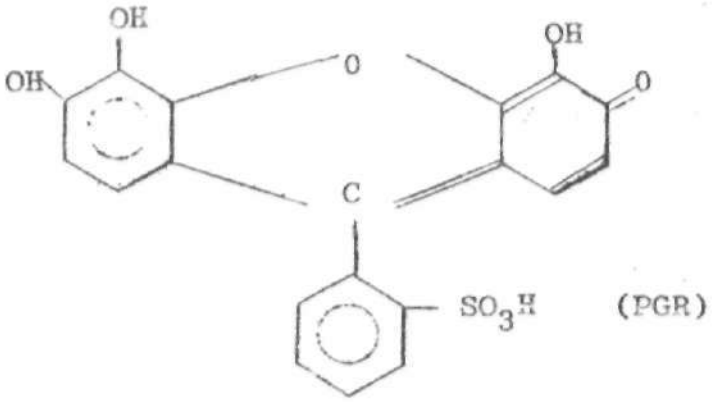


oxine

Another group uses organic reagents to form water soluble anionic or cationic chelate complexes with metal ions. These reagents have hydrophilic groups in their structure, usually the sulphonic acid groups. These include the triphenyl methane reagents e.g. pyrocatechol violet.



It forms intensely coloured complexes and provides the basis of sensitive spectrophotometric determinations of a number of metals. The xanthene reagents also belong to this group e.g. bromopyrogallol red(BPGR) or pyrogallol red (PGR).



(PGR)

These reagents undergo stepwise dissociation and change their colours according to the pH of the medium. They react with many metals to form chelate complexes. The metal-indicator complexes are usually one to one, but occasionally one to two (18) complexes may be obtained.

1.3 SURFACTANTS IN TRACE METAL ANALYSIS

Most of the analytical work done using surfactants and micellar systems concern their application to UV-Visible absorption spectral methods, particularly those involving metal ion determination. Though fairly new, the use of micellar systems in atomic absorption spectroscopy (AAS), fluorescence, analytical phosphorimetry and electroanalytical techniques e.g. polarography have been recognized and amply documented according to Hinze (6). For quite some times it has been known that acid base indicators have altered their colours in the presence of micelle forming detergents. Studying the effect of anionic, cationic and non-ionic detergents on a large number of dyes, Hartley (19) found that the greatest colour change occurs when the charge on the detergent micelles is opposite to that of the indicator ion. Typical among the already reported studies of binary complexes of metal chelometric indicators are the reactions involving the triphenyl methanes e.g. catechol violet (CV) and Xylenol orange (20) for the

determination of chromium. Other azo dyes have been suggested for the determination of zinc e.g. xylenol orange (21) and methylthymol blue (22). Similarly, the metal-chelometric indicator reaction between Bi(III) and (XO) (23) had been investigated by spectrophotometry. A characteristic of this binary complex is that it absorbs strongly in the visible region (550 ± 60nm). Of course in the determination of aluminium, methods using (XO), methylthymol blue as well as the structurally related (PGR) have become popular though their sensitivity is rather low. A considerable enhancement of sensitivity is obtained when the ternary complex of aluminium with (XO) and (CTAB) is formed (24). Though the method of the determination of metal ions involving their complexation with chelometric indicators have become popular, the beneficial effects produced by the addition of surfactants have been found to be very significant. Over the last three decades there have been a large number of reports of such surfactant and micellar improved UV absorption methods for the determination of metal ions. The absorbance of the ternary complex is often directly proportional to the metal ion concentration over a measurable concentration range. The addition of surfactants has a dramatic effect upon these methods and systems especially:

(i) it results in many cases to marked colour changes.

(ii) the addition of metal ions lead to the formation of intensely coloured complexes over a wide pH range.

(iii) bathochromic shift is observed for the ternary complex, which helps to lesson spectra overlap problems.

Consequently the micellar improved methods are better than the ordinary methods notably since they show greater sensitivity, better selectivity, improved precision and reproducibility as well as an extension of pH range, where complexes can be formed.
Even though Svoboda and Chromy (25) have described the use of xylenol orange (XO) in conjuction with long chain surface active agents as a general colour reaction for many metal ions, quite recently, the binary metal ion complexes of organic dyestuff e.g. xylenol orange (XO) have been sensitized by the addition of long chain cationic surfactants e.g. (CTAB) (26). This mode of reaction is considered to be generally applicable and one of the most sensitive methods available for spectrophotometric determination of many metal ions. Dagnal, et al (27) reported that the use of ternary complexes as indicators in visual titration should prove very useful and give a more distinct end point, because of the relatively large shift in the wavelength of maximum absorption. By means of photometric titration and method of continous variation, Bailey, et al (28)

showed that the Sn(IV)-CV-CTAB complex has a stoichiometry of 1 to 2 to 4. Aston et al (29) investigated the ternary system of Sn-CV-CTAB and Sn-CV-brilliant green ($C_{27}H_{34}N_2O_4S$) and reported that (CTAB) serves as a counter cation as well as a dispersant. A sensitive spectrophotometric method has been developed for the microdetermination of Uranium(VI). This is based on the formation of a blue ternary complex with (PGR) and cetylpyridinium chloride. Kumar, et al (30) on investigating this ternary system reported a complex of composition UO_2^{2+} + $(PGR)_2(CPC)_4$. Quite recently, Abii (31) developed a very sensitive spectrophotometric method for the determination of nickel. She reported presence of binary complexes of XO-CTAB at pH 10.5 with the mole ratios of 1:2 and 1:6 respectively. In the presence of nickel possibility of formation of ternary complexes of $Ni\{XO(CTAB)_2\}_4$ and $Ni\{XO(CTAB)_6\}_4$ respectively has been reported.

The use of cationic surfactants to obtain better conditions in molecular absorption spectrophotometry based on the formation of ternary complexes with cations and organic dyes has therefore been a useful innovation in Analytical Chemistry.

Consequently the present studies were undertaken in order to explore the analytical importance of such colour reactions, especially the attendant bathochromic

shift, the increase in sensitivity, selectivity and extinction coefficient. Attempts were made to optimize the reactions, i.e. determine the time for stable colour formation, the wavelength of maximum absorption, the stoichiometry of binary and ternary complexes and the optimum range of concentration of the absorbing species over which Beer Lambert law is obeyed.

Some preliminary studies were undertaken to find out which of the three chelometric indicators namely, pyrogallol red (PGR), catechol violet (CV) and gallein ($C_{20}H_{12}O_7$) had any specific interaction with any of a variety of metal ions e.g. Co^{2+}, Ni^{2+}, Al^{3+} Zn^{2+}, Cd^{2+}, Fe^{2+}, Cr^{3+}, Ba^{2+}, Mg^{2+}, Sr^{2+} and Cu^{2+}. It was observed from this auxiliary studies that there was a specific interaction between Zn-PGR, Cr-PGR as well as Al-CV and Cu-CV. By specific interaction it is meant that there was a wavelength of maximum absorption (λ_{max}), increase in absorption with increase in metal concentration etc. Since (CTAB) had been successfully used with (XO) in this laboratory. It was decided to investigate its effect on these binary complexes.

CHAPTER 2

2.1 STUDY OF PYROGALLOL RED.

2.1.1 Preparation of solutions:

(i) Pyrogallol red (PGR) ($C_{19}H_{12}O_8S$), (4×10^{-4}M)

0.01602g of pyrogallol red was dissolved in distilled deionized water and made up to $100cm^3$ in a standard volumetric flask.

(ii) Sodium hydroxide (10^{-2}M)

10g of sodium hydroxide was dissolved in distilled deionized water and made up to $500cm^3$ in a standard volumetric flask. $2cm^3$ of this solution was measured with a pipette and made up to $100cm^3$ in a standard flask to obtain the required 10^{-2}M solution.

(iii) Hydrochloric acid (10^{-2}M)

Standard HCl solution in ampoule was appropriately diluted with distilled deionized water in a standard flask to obtain a 10^{-2}M solution.

2.1.2 Potentiometric titration of aqueous solution of pyrogallol red with sodium hydroxide and hydrochloric acid.

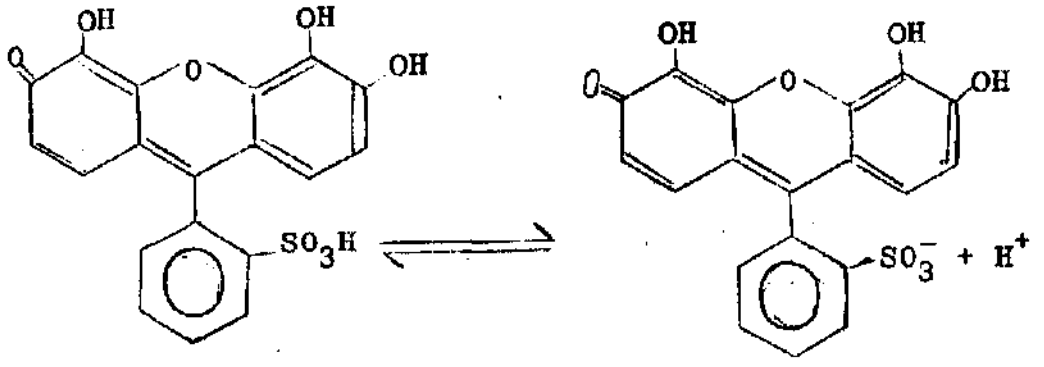
2.1.2.1 Method:

$2cm^3$ of the stock solution of pyrogallol red (4×10^{-4}M) was accurately measured into a $50cm^3$ standard volumetric flask and made up to the $50cm^3$ mark with distilled deionized water. The solution was poured into a $100cm^3$ beaker and

titrated potentiometrically with NaOH or HCl using a PW 9418 Philips PYE Unican pH meter. A plot of pH against the equivalents of sodium hydroxide or hydrochloric acid was made in fig. 2.1.

2.1.2.2 Results and Discussion:

From the pH of 4.40 obtained, it is evident that aqueous untreated pyrogallol red solution is essentially acidic. The ionization steps during interaction with a base in an aqueous medium is as shown below.



Since it readily releases a proton to a strong base the titration curve shows an initial steep rise in pH, on the addition of 10^{-2}M NaOH. The potentiometric titration curve indicates that the aqueous (PGR) solution was not maximally buffered until around the pH of 10.0. Similarly in the acid range, buffer effect was not noticed until at pH of about 2.2.

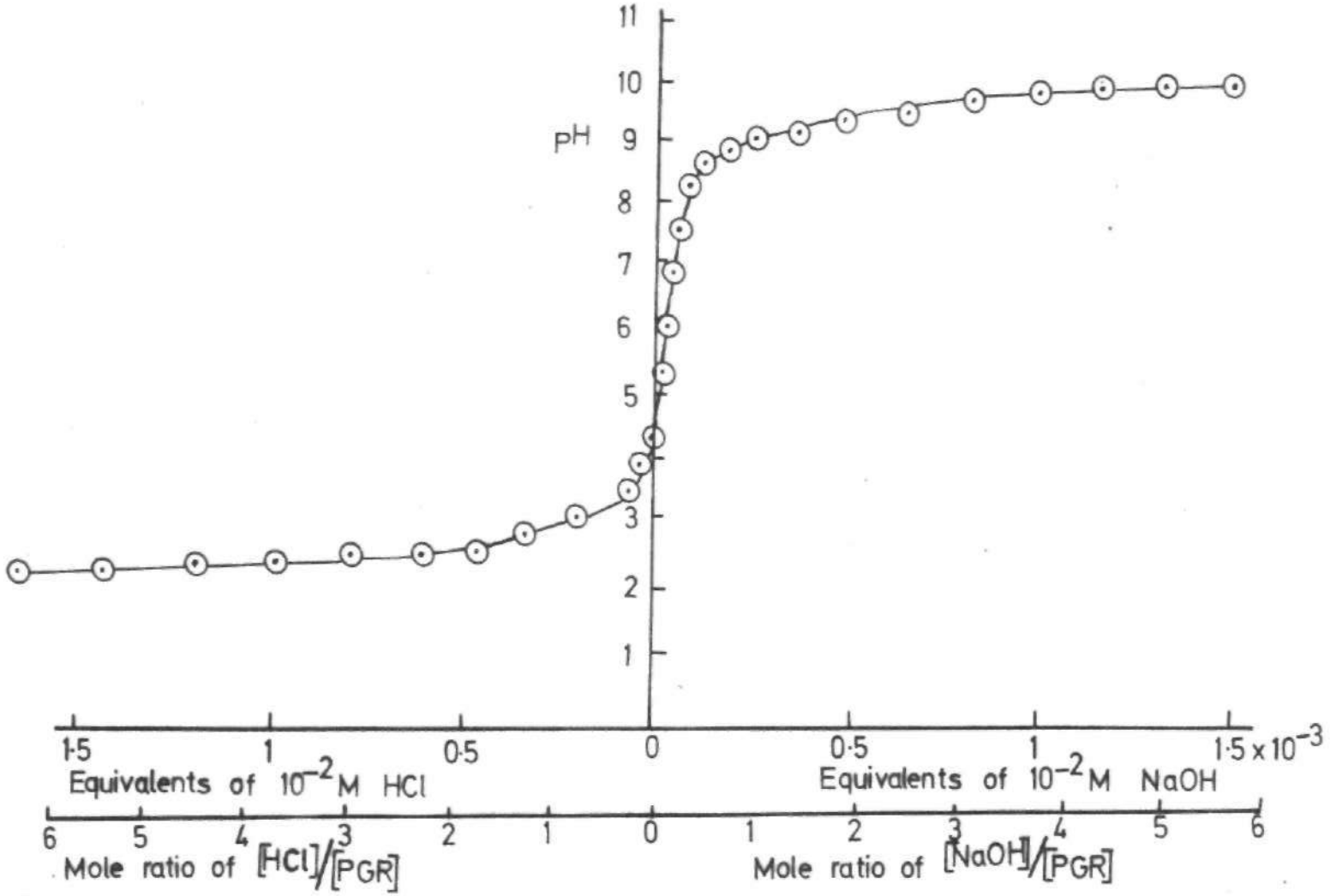


Fig 2·1 Potentiometric titration of pyrogallol red with both sodium hydroxide and hydrochloric acid $[PGR] = 1{\cdot}6 \times 10^{-5}$ M.

2.1.3 Spectrophotometric study of aqueous solution of pyrogallol red at different pH.

2.1.3.1 Method:

$2cm^3$ of the stock (PGR) solution ($4 \times 10^{-4}M$) and $30cm^3$ of $10^{-2}M$ NaOH were mixed in a standard $50cm^3$ volumetric flask and made to the mark with distilled deionized water. The absorption spectrum of the solution was determined using a Unicam SP 1750 UV spectrophotometer. The pH of the solution was also taken after 30 minutes of preparation. This study was repeated with the same concentration of (PGR) but,

(i) different volumes of the $10^{-2}M$ NaOH solution

or

(ii) different volumes of $10^{-2}M$ HCl solution.

2.1.3.2 Results and Discussion.

A plot of the different absorbances against corresponding pH values is shown in fig 2.2. Also a plot of the λ_{max} of the absorbance of the solutions against pH is shown in fig. 2.3. The absorbance is quite high at pH 10.5 and tends to increase at higher pH values. On fig. 2.3, in the alkaline region and above pH 10.0, the λ_{max} is fairly constant. The solution was also resistant to pH changes as seen on fig. 2.1. However in the acid region, the λ_{max} decreased gradually as the solution became more acidic.

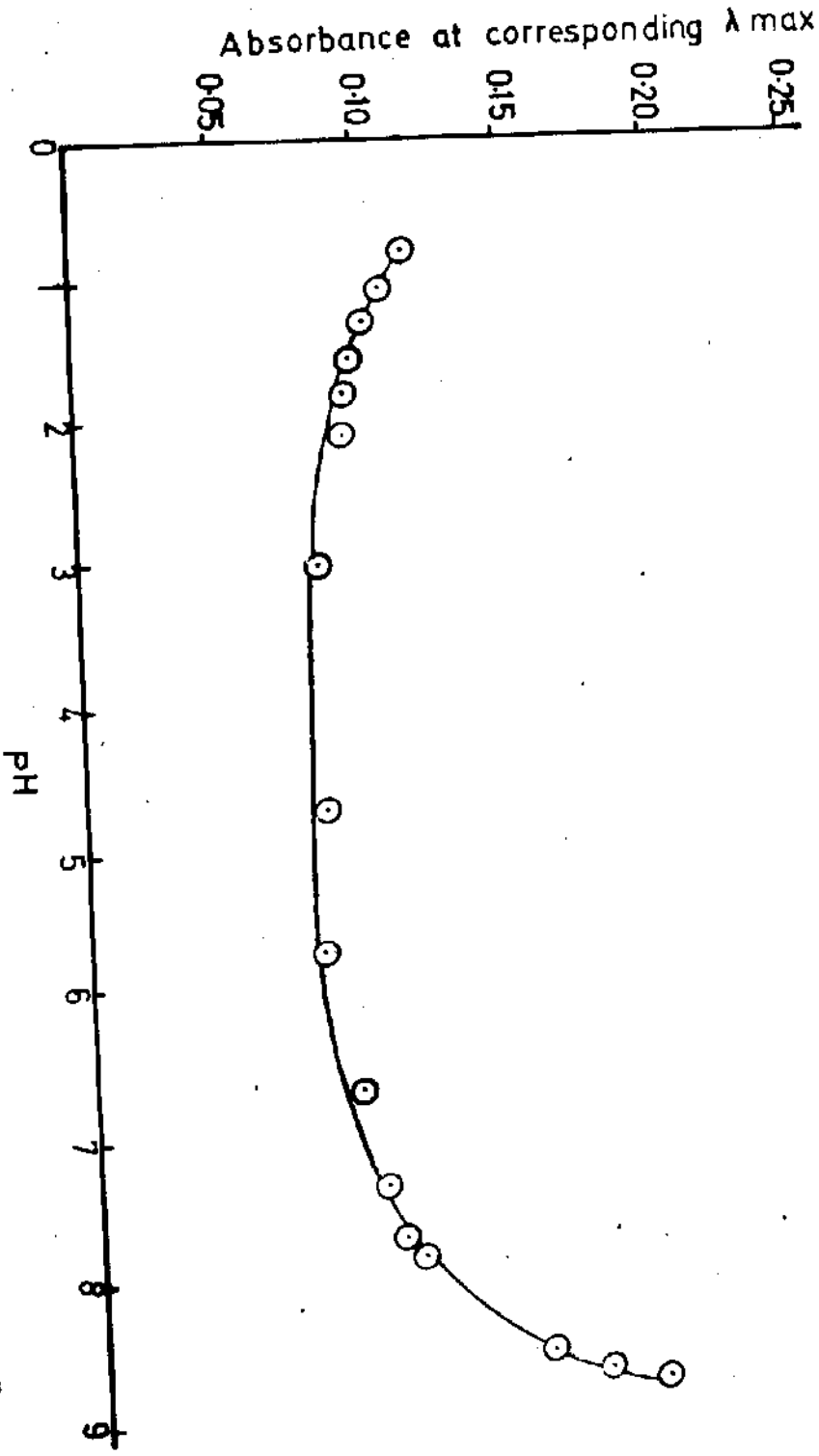


Fig 2.2 Spectrophotometric titration of pyrogallol red solution with both sodium hydroxide and hydrochloric acid $[PGR] = 1.6 \times 10^{-5}$ M.

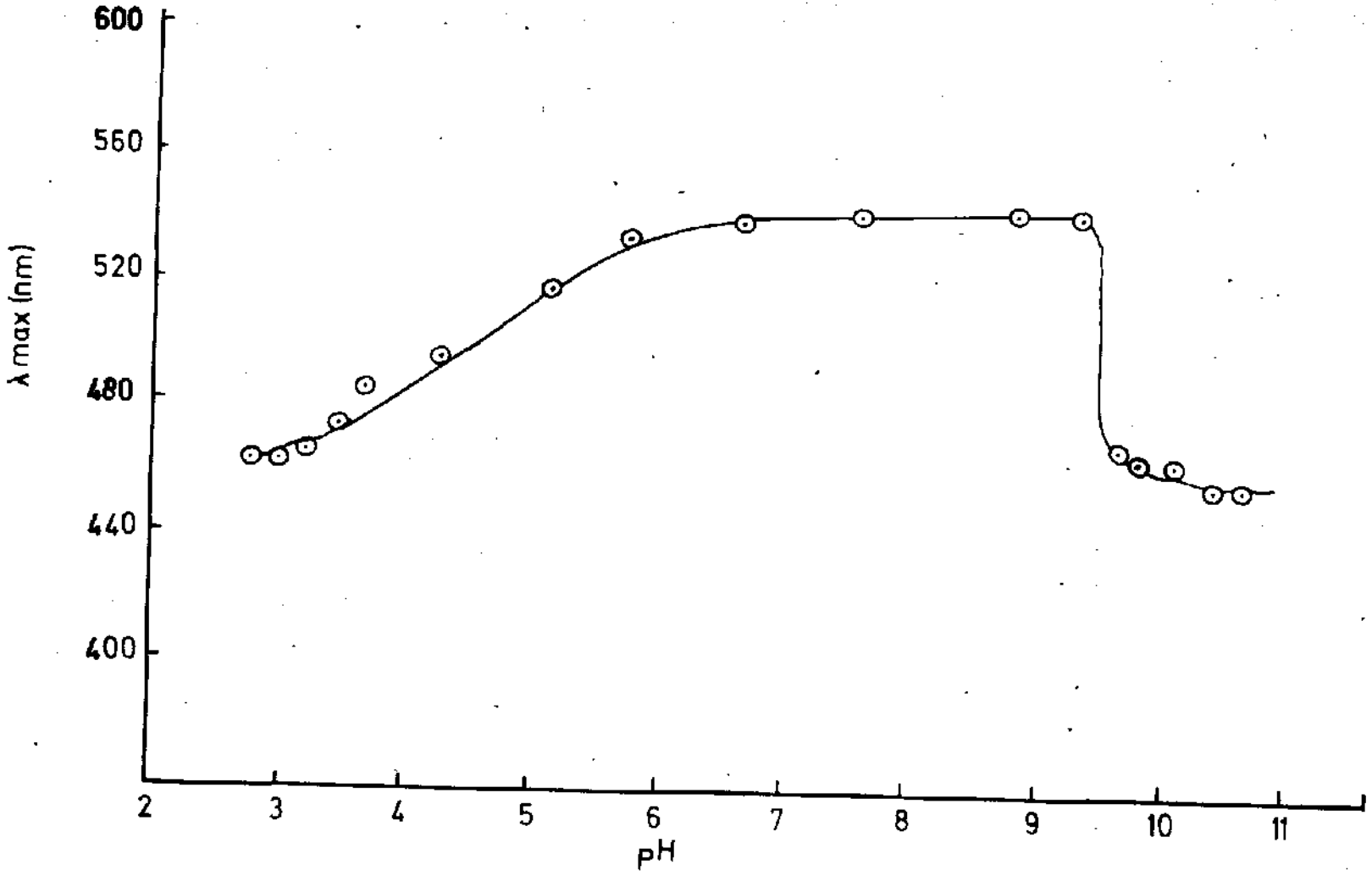


Fig 2-3 Variation of λmax of aqueous solution of $1{\cdot}6\times10^{-6}$M pyrogallol red with pH.

For the purpose of the studies reported therefore, the alkaline range pH 10.5 was chosen because,

(i) the absorbance is reasonably high,

(ii) the solution is highly buffered against pH changes, and

(iii) the λ_{max} remains reasonably constant.

2.1.4 Effect of concentration of $NaHCO_3$/NaOH buffer (pH 10.5) on the absorbance of pyrogallol red.

2.1.4.1 Reagents.

$NaHCO_3$/NaOH buffer (32) at pH 10.5. (2.5×10^{-2}M)

$500cm^3$ of 5×10^{-2}M $NaHCO_3$ [4.2g/l] and $178cm^3$ of 0.1M NaOH [4g/l] were mixed together and diluted with distilled deionized water to $1000cm^3$ in a standard volumetric flask.

2.1.4.2 Method.

Investigation of the wavelength of maximum absorbance of pyrogallol red and the determination of the amount of buffer required for maximum buffer action were carried out. In this, $2cm^3$ of 4×10^{-4}M pyrogallol red was accurately measured into a $50cm^3$ standard flask. $2cm^3$ of buffer pH 10.5 was added and the mixture was made up to $50cm^3$ with distilled deionized water in a standard flask. Other similar solutions were prepared using the same volume ($2cm^3$) of 4×10^{-4}M pyrogallol red, but different volumes of the stock 2.5×10^{-5}M buffer solution.

The UV absorbance of each solution was taken at the wavelength of maximum absorbance for each solution using 10mm quartz cells, and distilled deionized water as reference The pH of each solution was also determined.

2.1.4.3 Result and Discussion.

The table below shows the pH, the wavelength of maximum absorption and the absorbance for the solution prepared.

Volume of (2.5×10^{-2}M) Carbonate buffer (cm^3)	pH	λmax (nm)	Absorption at λmax
2	9.85	458	0.255
4	10.05	456	0.230
6	10.15	456	0.233
10	10.30	456	0.231
15	10.40	456	0.220
20	10.40	456	0.247
25	10.50	456	0.256
30	10.50	456	0.246
35	10.50	456	0.224

Table 2.1: Variation of pH and absorbance of aqueous (PGR) solution with increase in buffer concentration.

Aqueous alkaline pyrogallol red (pH 10.5) has a wavelength of maximum absorption of 456nm. Also from table 2.1, about $25cm^3$ of the stock $NaHCO_3/NaOH$ buffer ($2.5 \times 10^{-2}M$) was required to effectively buffer the reaction medium against pH changes. $25cm^3$ of stock $NaHCO_3/NaOH$ buffer was therefore used in subsequent studies.

2.1.5 Investigation of Beer-Lambert law for aqueous pyrogallol red solution.

2.1.5.1 Method.

$0.50cm^3$ of pyrogallol red ($4 \times 10^{-4}M$) solution was accurately measured into a $50cm^3$ standard flask. $25cm^3$ of buffer pH 10.5 was added and the mixture made up to $50cm^3$ with distilled deionized water. Other solution mixtures were prepared with different volumes of (PGR) and $25cm^3$ of the buffer. The UV absorbance of each solution at 456nm was recorded after five minutes of mixing when the absorbance characteristics were steady.

2.1.5.2 Results and Discussion.

A plot of absorbance against concentration is shown in fig. 2.4. The absorption of the aqueous (PGR) solution at pH 10.5 obeyed Beer-Lambert's law at very low concentrations i.e. below about $2.4 \times 10^{-5}M$ of the indicator. As a result of this $2.5cm^3$ of the $4 \times 10^{-4}M$ stock, ($2 \times 10^{-5}M$) of (PGR) i.e. $2 \times 10^{-5}M$ experimental concentration was used for subsequent studies.

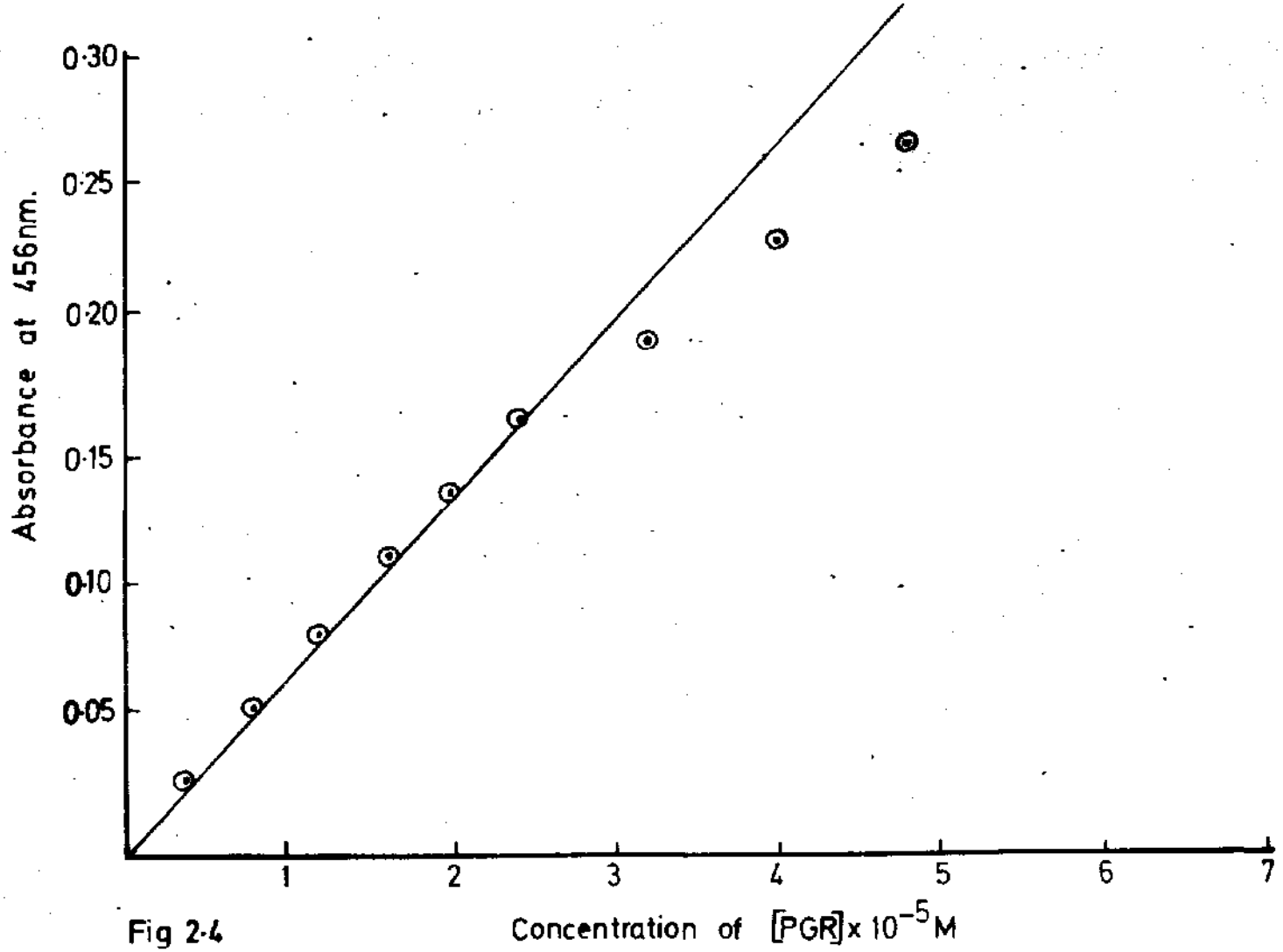


Fig 2·4 Beer-Lambert's law calibration curve for pyrogallol red solution.

2.2 INTERACTION BETWEEN PYROGALLOL RED AND ZINC OR CHROMIUM (III) IONS.

2.2.1 Reagents.

Appropriate quantities of the analytical grade of the metallic salts $Zn(NO_3)_2.6H_2O$ or $CrCl_3.6H_2O$ were dissolved in distilled deionized water in a $500cm^3$ standard flask and made to the mark, and kept as primary stock. $1cm^3$ of the above stock solution (10^4ppm) was accurately measured into a $100cm^3$ standard flask and made to the mark with distilled deionized water to obtain a solution of 100ppm of M^{n+}, referred to as a secondary stock solution for the experiments that follow.

2.2.2 Interaction of (PGR) with Zn^{2+}.

2.2.2.1 Method.

$2.5cm^3$ aliquots of 4×10^{-4}M aqueous (PGR) solution were accurately measured into different $50cm^3$ standard flasks. $25cm^3$ of the stock bicarbonate buffer pH 10.5 was added to each flask followed by different volumes of the 100ppm Zn^{2+} solution. Each solution was made up to the mark with distilled deionized water. The wavelength of maximum absorbance and the corresponding absorbance value for each solution were determined using the UV spectrophotometer. The reference was the buffered indicator solution of the same strength as the experimental solution but without the zinc ions. One hour of waiting was allowed for each solution before

spectra reading were taken, based on the results of an auxiliary kinetic experiment showing constant absorbance characteristics after about one hour of mixing the reagents. The experiment was repeated using $1.5cm^3$, $4cm^3$ and $5cm^3$ of (PGR) solution.

2.2.2.2 Results and Discussion.

The aqueous PGR-Zn^{2+} system of pH 10.5 has its wavelength of maximum absorption at 520nm. A plot of the absorbance against concentration for the system at this λ_{max} is shown in fig. 2.5a. Beer-Lambert law is obeyed below about 9.2×10^{-6}M zinc when 2×10^{-5}M (PGR) is used and below about 1.2×10^{-5}M zinc when 3.2×10^{-5}M (PGR) is used. The extinction coefficient of the system increased with increase in (PGR) concentration as shown below. This suggests that the system tends to be more sensitive for the determination of zinc at higher concentrations of (PGR). However the concentration of (PGR) required for optimum sensitivity appeared not much higher than 4.0×10^{-5}M.

Concentration of (PGR) used x 10^5M	Extinction coefficient (l. $mole^{-1}$ cm^{-1}) x 10^{-3}
1.2	7.62
2.0	10.78
3.4	13.06
4.0	13.66

Table 2.2a Extinction coefficient of Zn^{2+} at different (PGR) concentrations.

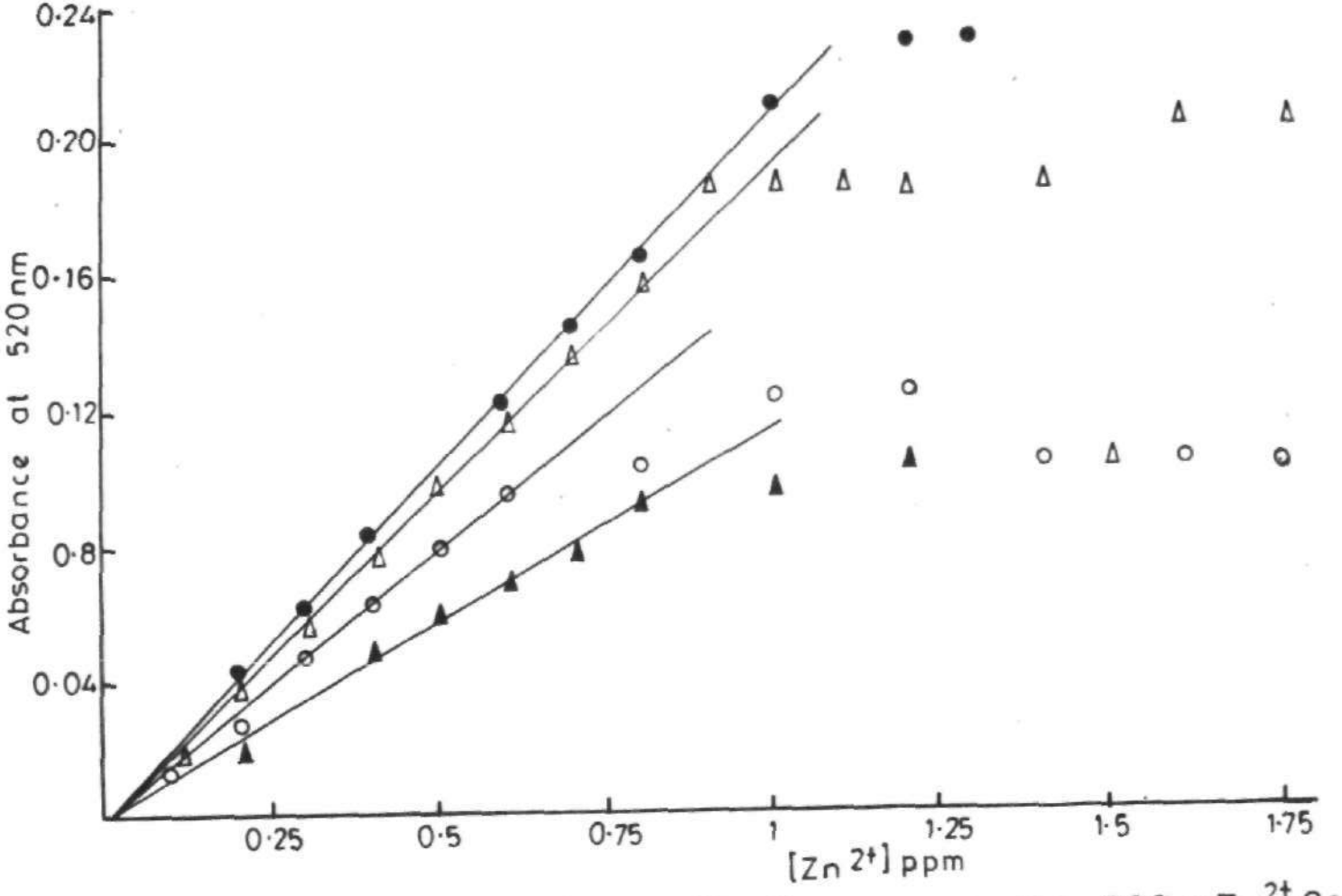


Fig. 2·5a Beer–Lambert's law calibration curves for PGR $-Zn^{2+}$ Complex
(○) [PGR]= 2×10^{-5}M (△) [PGR] = $3{\cdot}2 \times 10^{-5}$ M
(●) [PGR]= $4{\cdot}0 \times 10^{-5}$ M (▲) [PGR] = $1{\cdot}2 \times 10^{-5}$ M

2.2.3 Interaction of PGR with Cr^{3+}

2.2.3.1 Method.

$2.5cm^3$ aliquots of 4×10^{-4}M aqueous (PGR) solution were accurately measured into different $50cm^3$ standard flasks. $25cm^3$ of the stock bicarbonate buffer pH 10.5, was added to each flask followed by different volumes of the 10^4ppm Cr^{3+} solution greater than $2.5cm^3$. Each solution was made up to the mark with distilled deionized water. The wavelength of maximum absorbance and the corresponding absorbance value for each solution were determined using the UV spectrophotometer. The reference was the buffered indicator solution of the same strength as the experimental solution without chromium ions. The spectra reading were taken after 15 minutes of mixing the reagents when the absorbance characteristics were constant. This time of waiting prior to absorbance measurement was established in an auxiliary kinetic experiment. The experiment described was repeated using $1.5cm^3$, $4cm^3$ and $5cm^3$ of (PGR).

2.2.3.2 Results and Discussion.

The aqueous PGR - Cr^{3+} system at pH 10.5 has its wavelength of maximum absorption at 414nm. A plot of the absorbance against concentration for the system at this λ_{max} is shown in fig. 2.5b. Below 500ppm, the solutions did not show any λ_{max}, hence the absorbances were not recorded. However, there is a linear relationship

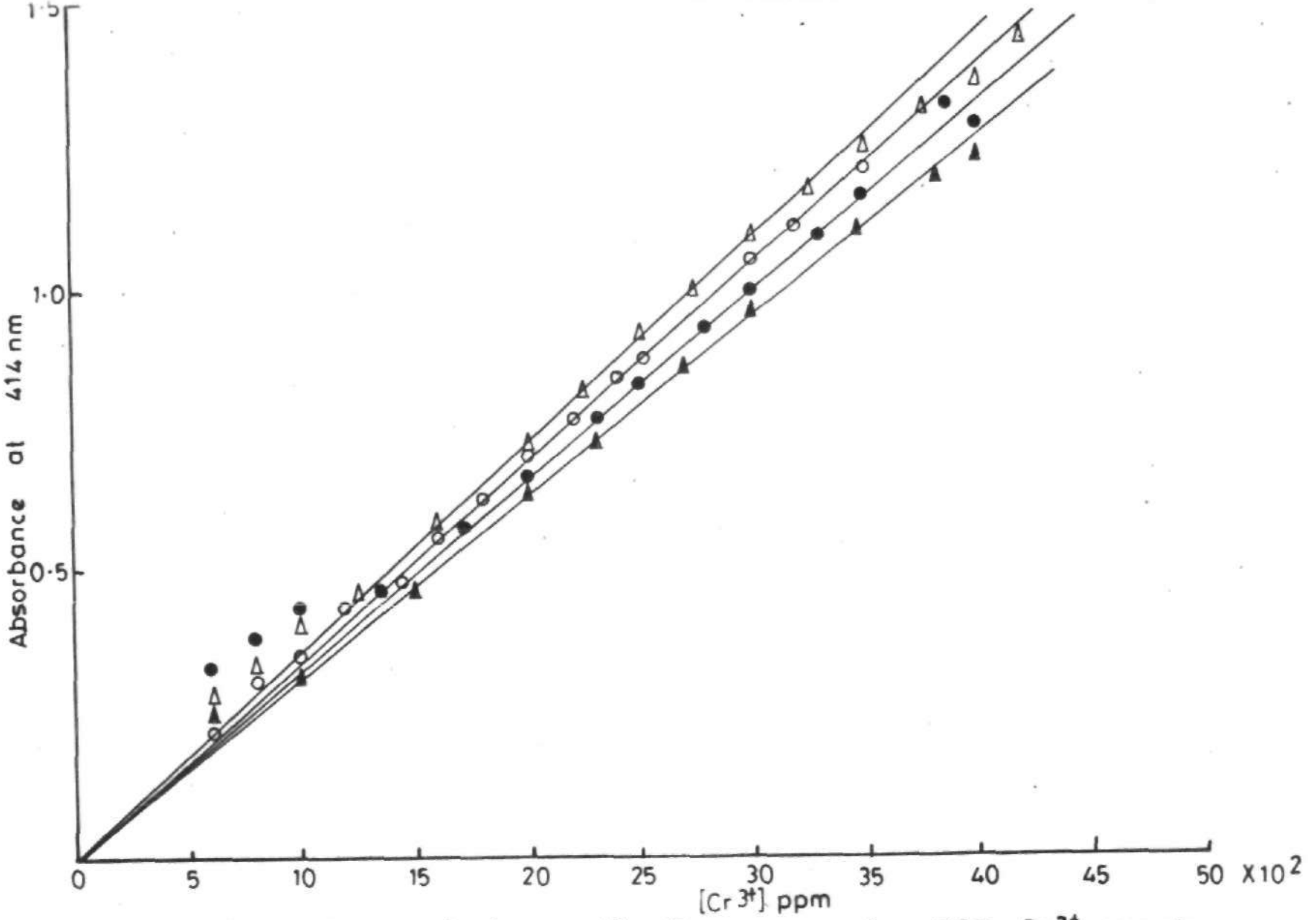


Fig. 2·5b Beer–Lambert's law calibration curve for PGR–Cr^{3+} complex

(o) [PGR] = $2{\cdot}0 \times 10^{-5}$ M
(Δ) [PGR] = $3{\cdot}2 \times 10^{-5}$ M
(●) [PU] = $4{\cdot}0 \times 10^{-5}$ M
(▲) [PGR] = $1{\cdot}2 \times 10^{-5}$ M

between 600ppm and very high concentrations up to about 3500ppm investigated.

The extinction coefficient for the system was calculated and shown below. The extinction coefficient increases with increase in [PGR] until a maximum was reached when 3.2×10^{-5}M (PGR) was used.

Concentration of (PGR) used x 10^{5}M	Extinction coefficient $l.mole^{-1}\ cm^{-1}$
1.2	16.64
2.0	18.23
3.2	18.94
4.0	17.53

Table 2.2b Extinction coefficient of Cr^{3+} in PGR - Cr^{3+} at different (PGR) concentrations.

2.3 DETERMINATION OF THE OPTIMUM CONDITIONS FOR PYROGALLOL RED (PGR) AND CETYLTRIMETHYLAMMONIUM BROMIDE (CTAB) INTERACTION.

2.3.1 Reagents.

Cetyltrimethylammonium bromide $\{CH_3(CH_2)_{15}\}(CH_3)_3NBr$ (CTAB), (4×10^{-4}M)

0.14578g of (CTAB) was accurately weighed and dissolved with distilled deionized water and made to the mark in a $1000cm^3$ standard flask.

2.3.2 Method.

3.5cm^3 of 4 x 10^{-4}M aqueous (PGR) solution was accurately measured into a 50cm^3 standard flask. 25cm^3 of the stock bicarbonate buffer at pH 10.5 was added followed by 1cm^3 of 4 x 10^{-4}M (CTAB). The mixture of solutions was made to the mark with distilled deionized water. The wavelength of maximum absorption and the absorbance were determined using the UV spectrophotometer, and buffered indicator solution of the same strength without (CTAB) as reference. The experiment was carried out using different but increasing volumes of 4 x 10^{-4}M (CTAB), and various volumes of stock (PGR) solution between 0.5 and 4.0cm^3. All the UV absorption measurements were made 10 minutes after mixing the reagents when the absorbance values remained constant.

2.3.3 Results and Discussion.

The aqueous CTAB - PGR system at pH 10,5 had its wavelength of maximum absorption at 550nm. A plot of the absorbance against concentration of (CTAB) in the solution at λ_{max} is shown in fig. 2.6a. Each of the curves has two segments. The composition of CTAB - PGR at the point of intersection was calculated in each case by the mole ratio methods.

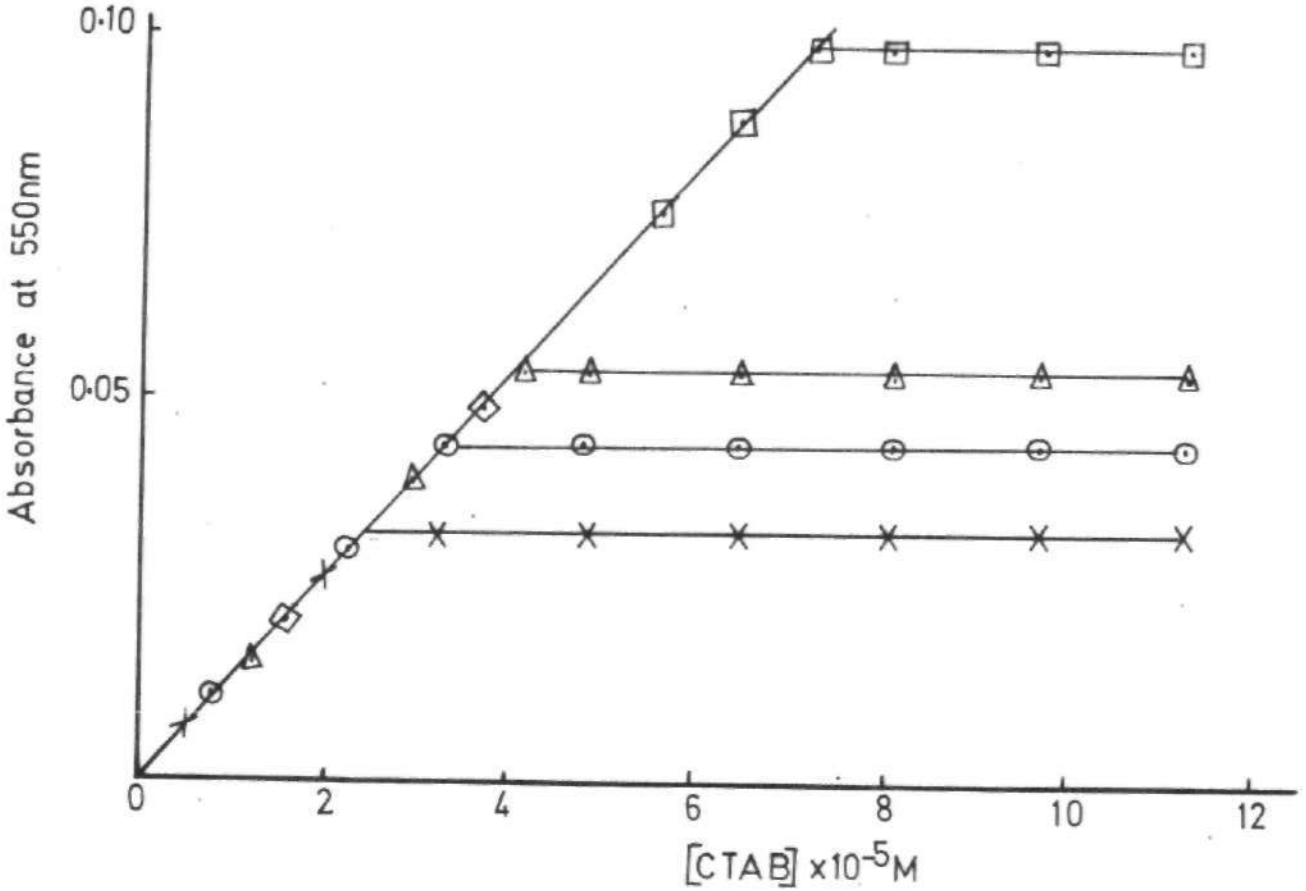


Fig 2·6a Variation of change of [PGR] at 550nm with [CTAB]

(X) [PGR] = 6×10^{-6}M (△) [PGR] = 2×10^{-5}M

(⊙) [PGR] = $1{\cdot}2 \times 10^{-5}$M (⊡) [PGR] = $2{\cdot}8 \times 10^{-5}$M

Concentration of (PGR) used x 10^5	Concentration of (CTAB) at intercept x 10^5	Mole ratio of [CTAB]/[PGR]
2.8	7.2	2.57
2.0	4.8	2.40
1.2	3.2	2.67
0.6	2.4	4.00

Table 2.3 Mole ratio of [CTAB]/[PGR] for specific interaction at different [PGR] concentrations.

From table 2.3, the last value of mole ratio is clearly much higher than the rest. The average of the remaining three values was found to be 2.55. Also the gradient of the straight line plot in fig. 2.6b of the concentration of(CTAB) at the point of maximum absorbance against concentration of (PGR) used for the first three points is 2.56.

The effect of the concentration of CTAB) and (PGR) on the absorbance of PGR - CTAB system was further investigated keeping the mole ratio of [CTAB]/[PGR] at 2.6. The results are presented in fig. 2.7. From the slope of this graph, the extinction coefficient of the CTAB - PGR system was calculated to be 9.38 x 10^3 l. $mole^{-1}$ cm^{-1} at λ_{max} of 550nm. The extinction coefficient for aqueous alkaline (PGR) pH 10.5 was determined to be

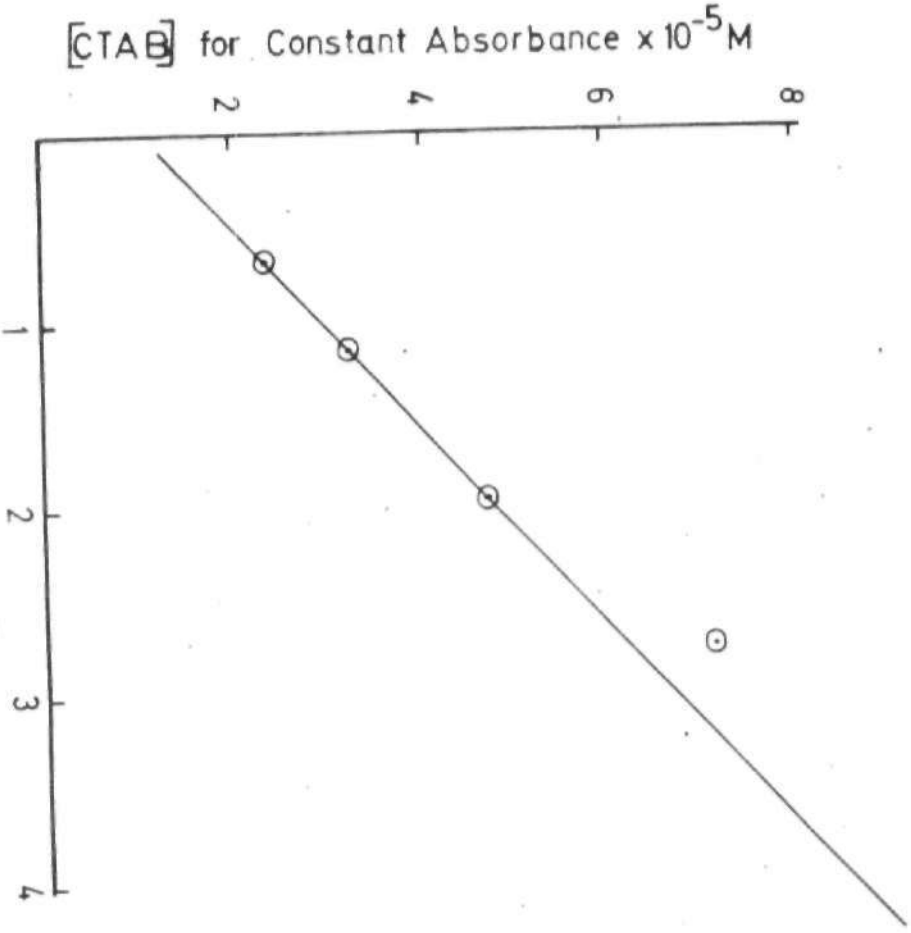


Fig 2.6b Variation of [PGR] with [CTAB] at constant absorbance

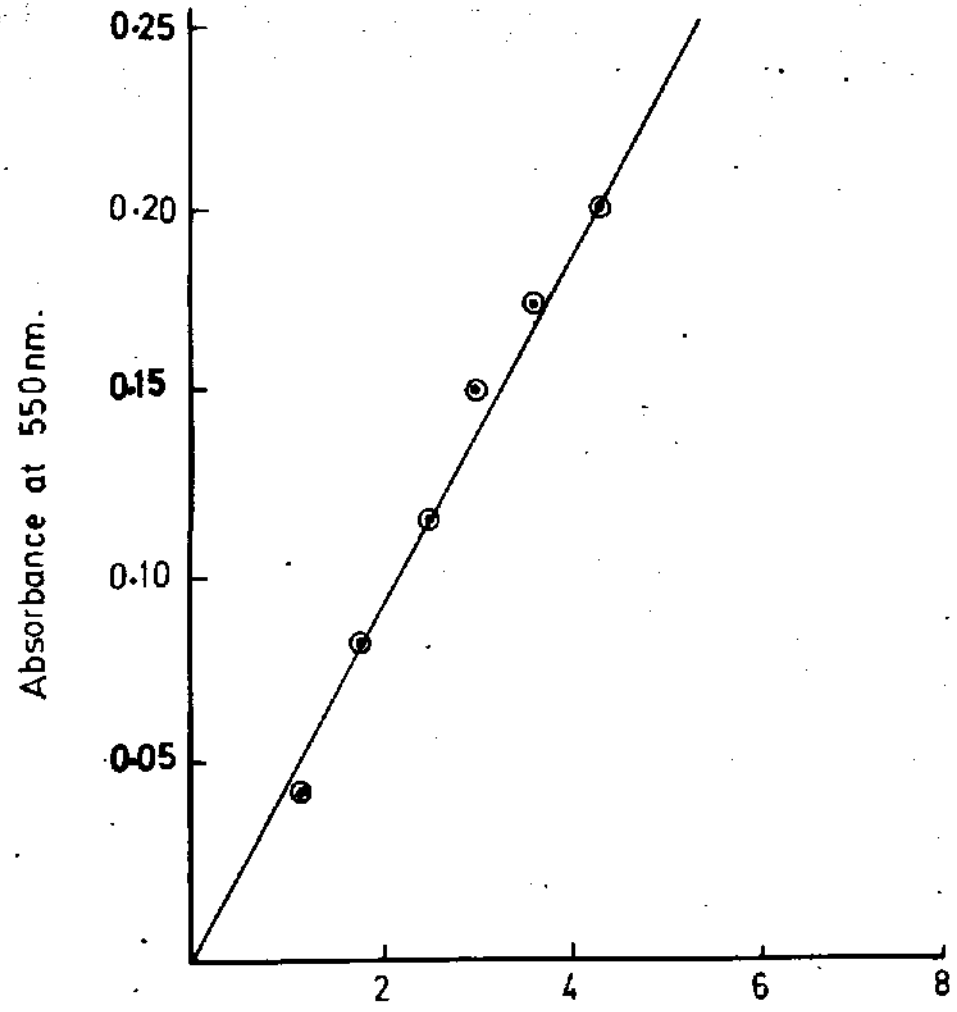


Fig 2·7

Effect of [CTAB]/[PGR] on Absorbance

[CTAB]/[PGR] = 2·6

7.14×10^3 l.mole^{-1}. cm^{-1} from fig. 2.4 at λ_{max} of 456nm. Hence the addition of (CTAB) to aqueous alkaline (PGR) produced a bathochromic shift of about 94nm from 456nm to 550nm. The mole ratio of [CTAB]/[PGR] to produce this bathochromic shift is 2.6 with a molar concentration of (PGR) above 1×10^{-5}M. There is a marked increase in the extinction coefficient of aqueous alkaline (PGR) solution at pH 10.5 when (CTAB) is added. This increase in extinction coefficient indicates an appreciable increase in the sensitivity of the method in determining the concentration of (PGR) in the solution.

2.4 STUDY OF THE M^{n+}-PGR-CTAB SYSTEM.

2.4.1 The Zn-PGR-CTAB system.

2.4.1.1 Method.

$2cm^3$ aliquots of aqueous (PGR), (4×10^{-4}M) solution were accurately measured into different $50cm^3$ standard flasks. $25cm^3$ of the stock bicarbonate buffer solution pH 10.5 was added to each flask followed by $5.2cm^3$ of 4×10^{-4}M (CTAB) solution and different volumes of the 100 ppm Zn^{2+} solution. The solution mixture in the flasks were made up to the $50cm^3$ mark with distilled deionized water. The UV spectrum of the bluish-violet solution was taken at the wavelength of maximum absorption using a reagent blank as reference containing the same concentration of both (PGR), (CTAB) and buffer as in the experimental solution. The UV spectrum of each

solution was taken as soon as mixing was completed.

The molar concentration of (CTAB) was varied but keeping the [CTAB]/[PGR] at 2.6.

2.4.12 Results and Discussion

The plot of the absorbance against the concentration of zinc in the Zn - PGR - CTAB system is shown in fig. 2.8.

It was found that the wavelength of maximum absorbance increased with increase in the molar concentration of (CTAB). It is interesting to note that from the shape of the graphs, that there are two distinct sets of lines, an upper set and a lower set which probably indicates the formation of two types of complexes.

For the lower set, the detection limit of Zn^{2+} was between 7.65×10^{-6}M and 1.6×10^{-5}M whereas for the upper set, much lower concentrations, below 6.1×10^{-6}M could be detected. Furthermore at higher (PGR) concentration (upper set) there is a marked increase in absorbance. This would lead to a much higher sensitivity in the detection of very low zinc concentrations. With the lower set there is a remarkable decrease in the absorbance which suggests that it might be used for determining higher concentrations of zinc and over a wider range of zinc concentrations than could be carried out with the upper set.

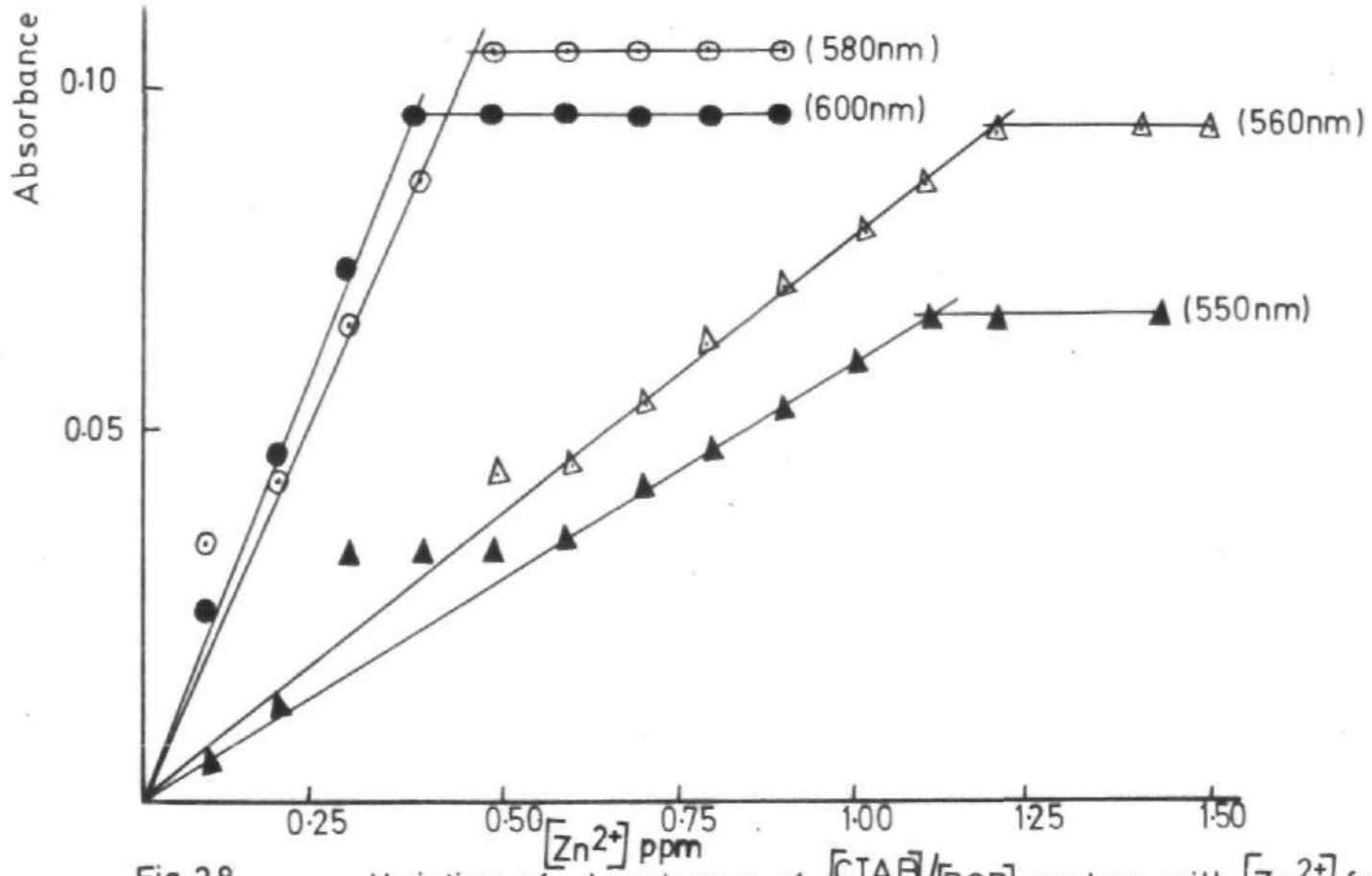


Fig 2·8 Variation of absorbance of [CTAB]/[PGR] system with $[Zn^{2+}]$ for different [PGR] and constant [CTAB]/[PGR] of 2·6

(▲) [PGR] = 8×10^{-6} M (⊙) [PGR] = $2{\cdot}4 \times 10^{-5}$ M

(△) [PGR] = $1{\cdot}6 \times 10^{-5}$ M (●) [PGR] = $3{\cdot}2 \times 10^{-5}$ M

Fig. 2.9a shows a linear increase of wavelength of maximum absorbance of Zn - PGR - CTAB complex with molar concentration of (PGR) using a blank of 2.6 mole ratio of (CTAB)/(PGR). From the slope of the lines in fig. 2.8, the extinction coefficient of the respective Zn-PGR-CTAB complexes were calculated and are shown in table 2.4.

Concentration of (PGR) x 10^{5}M	Extinction coefficient ($l.mole^{-1}$ cm^{-1}) x 10^{-3}
0.8	4.00
1.6	4.90
2.4	14.40
3.2	15.40

Table 2.4. Extinction coefficient of Zn^{2+} in Zn - PGR - CTAB for the different (PGR) concentrations.

From the plot of extinction coefficient against the concentration of (PGR) used in fig. 2.9b, the molar composition of the Zn - PGR - CTAB complex was calculated as follows:

The point of deflection of the upper set of lines in fig. 2.8 corresponds to 0.45ppm of Zn^{2+}. This is equal to 6.88 x 10^{-6}M of zinc. This corresponds to 3.2 x 10^{-5}M of (PGR) as seen in fig. 2.9b, at the point of maximum and constant value of the extinction coefficient.

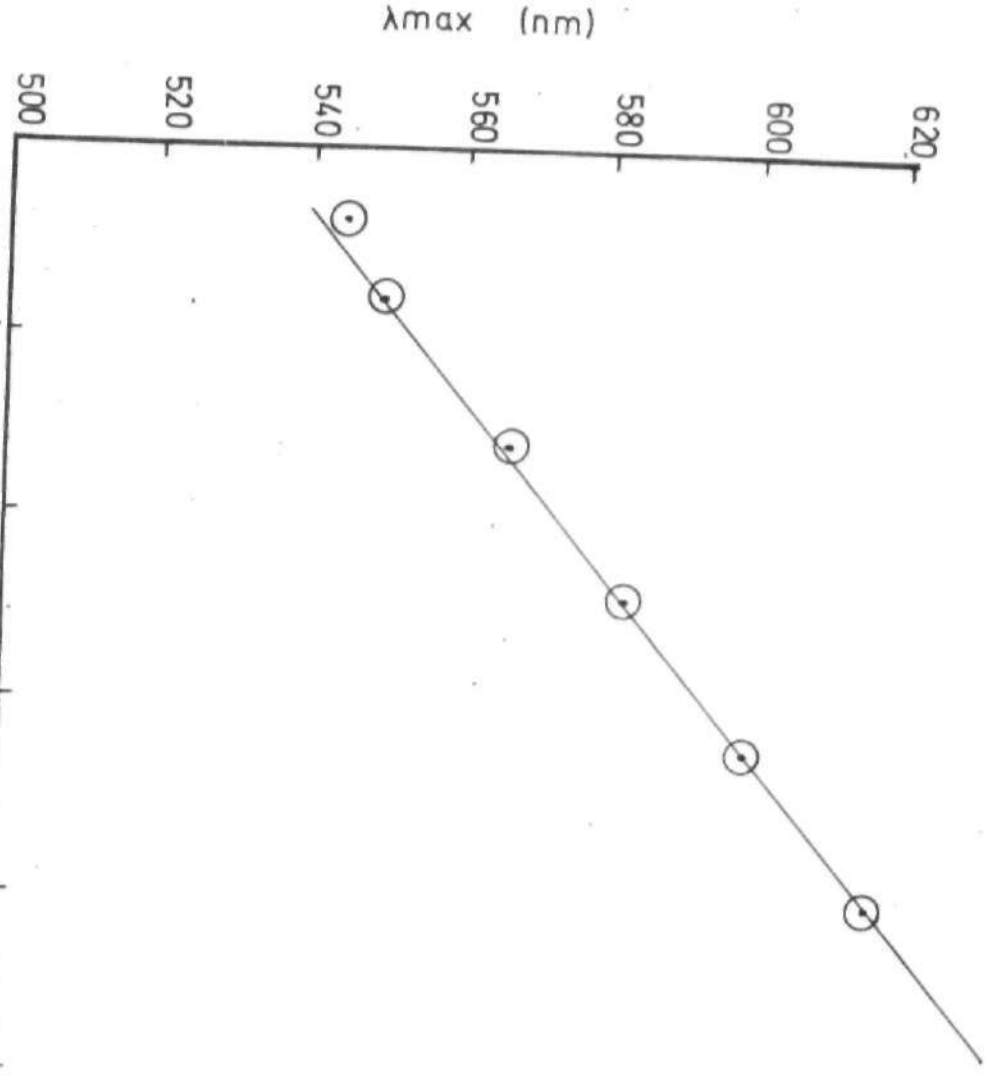


Fig 2·9a Variation of change of [PGR] with λmax.

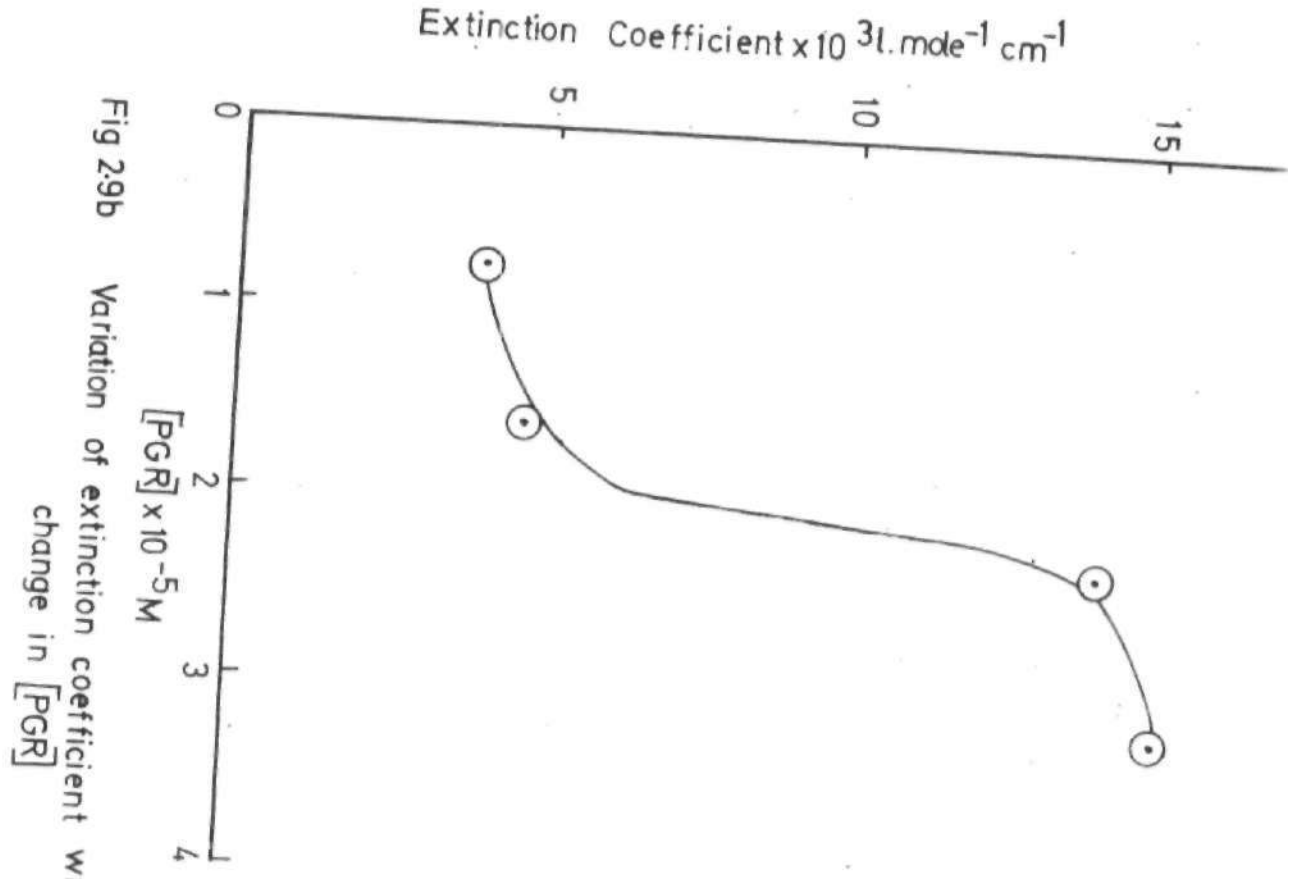


Fig 2.9b Variation of extinction coefficient with change in [PGR]

Therefore $\frac{[PGR]}{[Zn^{2+}]} = \frac{3.20 \times 10^{-5}M}{6.88 \times 10^{-6}M}$

$= 4.65$

Thus the molar ratio of $[PGR]/[Zn^{2+}]$ is 5, giving a formular, $Zn(PGR)_5$ or its multiple.

Similarly, at the point where the extinction coefficient is smallest and constant,

$$\frac{[PGR]}{[Zn^{2+}]} = \frac{8.00 \times 10^{-6}}{1.68 \times 10^{-5}}$$

$$= 0.50$$

The formular for this complex is Zn_2PGR. Considering the specific $[CTAB]/[PGR]$ ratio of 2.6, the stoichiometry of the Zn - PGR - CTAB complex at the highest extinction coefficient is calculated as $Zn\ (PGR)_4(CTAB)_{10}$, while for the lowest value of extinction coefficient it is $Zn_4(PGR)_2(CTAB)_5$.

The use of (CTAB) in the determination of Zn^{2+} in the presence of (PGR) causes a bathochromic shift of at least 10nm where extinction coefficient is smallest, and a value of at least 50nm with the highest value of extinction coefficient. Apart from an increase in the absorbance values, which depicts an increased sensitivity of the method, there is also an enhanced extinction coefficient when (CTAB) is added, because in the absence

of (CTAB), the extinction coefficient was 12.74 x 10^3l. $mole^{-1}$ cm^{-1}, while it was 15.40 x 10^3l. $mole^{-1}$ cm^{-1} when (CTAB) was added when 3.2 x 10^{-5}M (PGR) was used. The results also suggest a possibility of two types of complexes existing, possibly at different concentrations of (PGR).

2.4.2 The Cr - PGR - CTAB system.

2.4.2.1 Method.

$4cm^3$ aliquots of aqueous (PGR), (4 x 10^{-4}M) solution were accurately measured into different $50cm^3$ standard flasks. $25cm^3$ of the stock bicarbonate buffer solution, pH 10.5 was added to each flask, followed by $10.4cm^3$ of 4 x 10^{-4}M (CTAB) solution and different volumes of the 10^4ppm Cr^{3+} stock solution. The solution mixture in the flasks was made up to the $50cm^3$ mark with distilled deionized water. The UV spectrum of the deep green solution was taken at the wavelength of maximum absorption using a reagent blank as reference containing the same concentration of both (PGR), (CTAB) and buffer as in the experimental solution. The spectra readings were taken after 15 minutes of mixing the reagents when the absorbance characteristics were constant.

The experiment was repeated using $3cm^3$, $2cm^3$ and $1cm^3$ of (PGR), but keeping the [CTAB]/[PGR] ratio at 2.6.

2.4.2.2 Results and Discussion.

The Cr-PGR-CTAB system had its wavelength of maximum absorption at 572 nm. A plot of the absorbance against the concentration of chromium in Cr-PGR-CTAB at the λ_{max} is shown in fig. 2.10. Similarly as in the Cr-PGR system, there is no λ_{max} for the solutions below 500ppm of Cr^{3+}, hence there is no linear relationship between concentration and absorbance. The absorbance values are much lower for this system than for the Cr-PGR system, section 2.2.3. Consequently the extinction coefficient is much lower for the Cr-PGR-CTAB than for the Cr-PGR system. However there was a bathochromic shift of about 58nm in the λ_{max} of Cr-PGR as (CTAB) was added. The low extinction coefficients probably suggest that this is a rather insensitive method for the determination of chromium, though the bathochromic shift might be an asset in identification of Cr^{3+} in the presence of (PGR) and (CTAB), especially in the presence of some other metals. The extinction coefficients are shown in table 2.5.

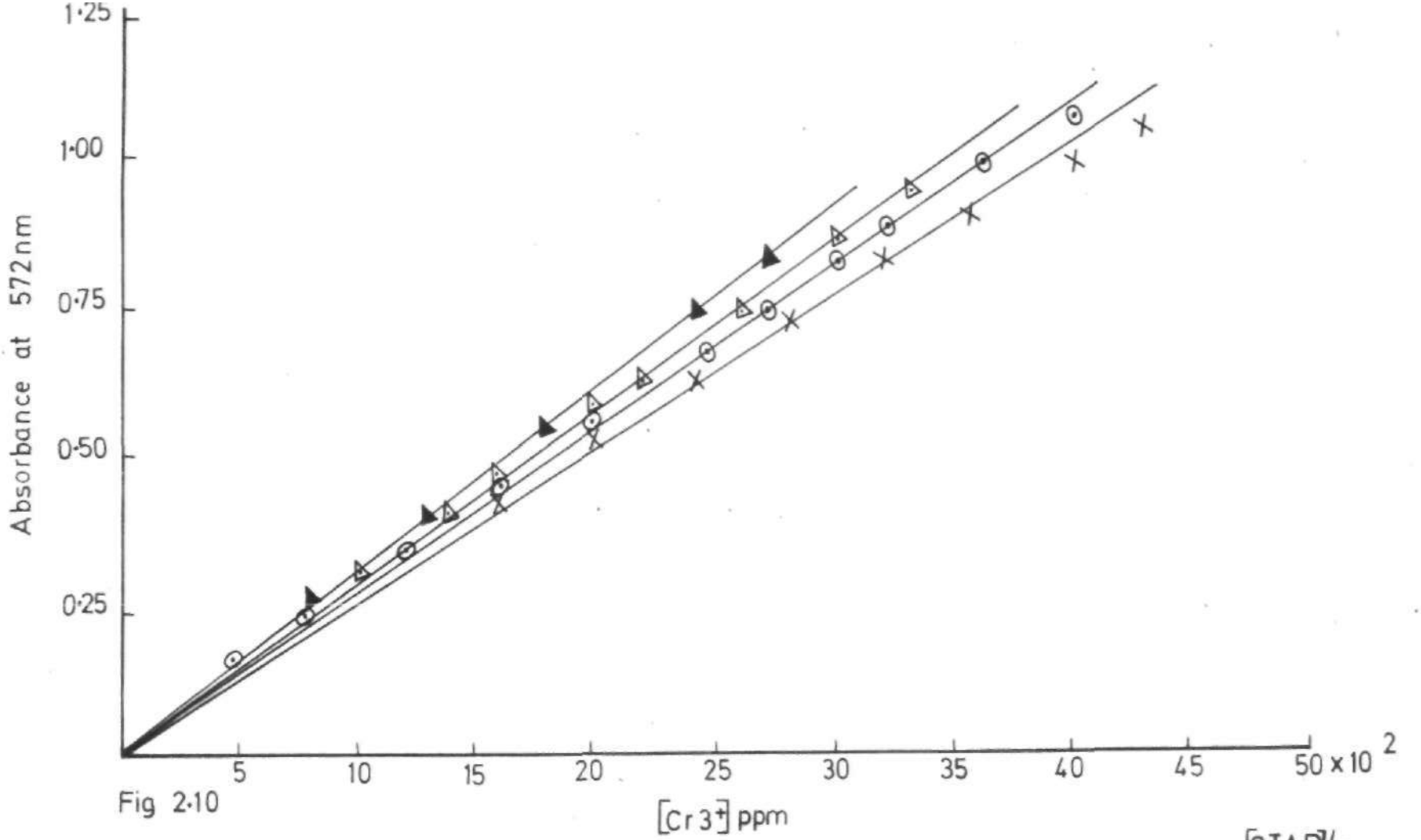


Fig 2·10

Calibration curve for Cr^{3+} at 572nm using different [PGR] but keeping [CTAB]/[PGR] at 2·6

(X) [PGR] = 8×10^{-6} M
(⊙) [PGR] = $1{\cdot}6 \times 10^{-5}$ M
(△) [PGR] = $2{\cdot}4 \times 10^{-5}$ M
(▲) [PGR] = $3{\cdot}2 \times 10^{-5}$ M

Concentration of (PGR) x 10^5M	Extinction coefficient $l.mole^{-1}$ cm^{-1}
0.8	13.50
1.6	14.20
2.4	14.75
3.2	15.53

Table 2.5 Extinction coefficient of Cr^{3+} for different (PGR) concentrations in the presence of (CTAB).

2.5 INTERFERENCE STUDY

The selectivity of the methods described in sections 2.4.1 and 2.4.2 for zinc and chromium respectively was investigated by separate determination of 6.10 x 10^{-6}M zinc and 1.92 x 10^{-2}M chromium each in the presence of Al, Cd, Co, Cu, Fe, Mg or Ni. The effect of the chloride anion was tested on zinc by using analytical grade zinc chloride. Similarly the effect of the nitrate anion was tested on chromium using chromium nitrate.

2.5.1 Zinc interference study.

The absorbance of 6.10 x 10^{-6}M zinc as zinc nitrate in the Zn - PGR - CTAB system was determined at 560nm using the method described in 2.4.1.1. This was repeated in the presence of Al, Cd, Co, Cr, Cu, Fe, Mg or Ni, as interfering ions taken one at a time in varying molar concentrations relative to zinc.

The change in the absorbance of Zn - PGR - CTAB due to the presence of each of these metals was determined and taken as a measure of interference. It was expressed as a percentage of the absorbance due to the pure Zn-PGR-CTAB system alone. The results are shown in table 2.6.

Ion added	$\frac{\{M^{n+}\}}{\{Zn^{2+}\}}$	Absorbance	Interference %
Zn - PGR - CTAB system alone		0.045	-
Cu^{2+}	1	0.035	-22.22
Co^{2+}	1	0.097	115.93
Fe^{3+}	1	0.063	40.63
Ni^{2+}	1	0.097	115.93
Al^{3+}	1	0.077	71.11
Cr^{3+}	1	0.026	-43.33
Mg^{2+}	1	0.123	174.22
Cd^{2+}	1	0.076	68.88
Cl^{-}(as $ZnCl_2$)	1	0.085	89.33

Table 2.6 Interference (%) of some ions in the determination of zinc using (PGR) and (CTAB) as reagents.

The results show that all these metals interfere seriously in the determination of zinc. No attempts were made in the present study to mask these interfering ions. In the case of chloride ions which had

very serious interference, the method described in 2.4.1.1 was repeated using analytical grade zinc chloride instead of the nitrate. The results are shown in table 2.7.

System	λmax (nm)	Extinction coefficient $l.mole^{-1}\ cm^{-1} \times 10^{-3}$
$Zn(NO_3)_2$/PGR	520	10.78
$Zn(NO_3)_2$/PGR/CTAB	560	4.94
$ZnCl_2$/PGR	522	10.95
$ZnCl_2$/PGR/CTAB	580	10.32

Table 2.7 Extinction coefficient and λ_{max} of the chloride compared with the nitrate salts of zinc.

From table 2.7, the extinction coefficient for the chloride salt is higher than that of the nitrate salt both in the presence and absence of CTAB. This might be due to the fact that, in the competition for PGR^- ions by Zn^{2+} ion, the later, from the $ZnCl_2$ interacted more with PGR^- ions than the Zn^{2+} ions from $Zn(NO_3)_2$ since the anionic size of nitrate is bigger than that of the chloride and could produce a steric effect. In the presence of (CTAB) this is even more prominent.

2.5.2 Chromium interference study.

The absorbance of 1.92×10^{-2}M chromium in the Cr - PGR - CTAB system was determined at 572nm using the method described in 2.4.2.1. This was repeated in the presence of some metal ions in varying molar concentrations relative to chromium.

The change in absorbance of Cr - PGR - CTAB system due to the presence of each one of these foreign ions was determined and taken as a measure of the interference and expressed as the percentage of the absorbance due to pure Cr - PGR - CTAB system alone. The results are presented in table 2.8.

Ion added	$\frac{\{Mn^+\}}{\{Cr^{3+}\}}$	Absorbance at 572nm	Interference (%)
Cr-PGR-CTAB system alone	-	0.295	-
Cd^{2+}	1	0.328	11.19
Co^{2+}	1	0.333	12.88
Fe^{3+}	1	0.298	1.02
Fe^{3+}	2	0.256	-13.02
Al^{3+}	1	0.353	19.66
Cu^{2+}	1	0.305	3.39
Cu^{2+}	2	0.336	13.97
Mg^{2+}	1	0.306	3.97
Mg^{2+}	2	0.360	22.17
Zn^{2+}	1	0.236	-19.72
Ni^{2+}	1	0.392	32.88
No_3^-(as $Cr(NO_3)_3$)	1	0.520	76.21

Table 2.8 Interference (%) of some ions in the determination of chromium using (PGR) and (CTAB) as reagents.

The results show that iron(III) has little interference and copper causes some interference while all the other ions interfere seriously in the determination of chromium by the method described in 2.4.2. In the case of nitrate that had serious interference, the method described in 2.4.2 was repeated using analytical grade chromium nitrate instead of the chloride. The results are shown in table 2.9.

System	λmax (nm)	Extinction coefficient $l.mole^{-1}\ cm^{-1}$
$CrCl_3$/PGR	414	18.2
$CrCl_3$/PGR/CTAB	572	14.2
$Cr(NO_3)_3$/PGR	574	15.43
$Cr(NO_3)_3$/PGR/CTAB	574	14.26

Table 2.9 Extinction coefficient and λ_{max} of the chloride compared with the nitrate salts of chromium.

From table 2.9, in the presence of (CTAB), there is not much difference between the results obtained for chloride and the nitrate salts. However in the absence of (CTAB) the chloride salt had a higher (ε) probably because there was more interaction between Cr^{3+} ion of $CrCl_3$ and PGR^- than for the Cr^{3+} of $Cr(NO_3)_3$ because of steric effect that might be produced by the nitrate anion.

CHAPTER 3

3.1 STUDY OF CATECHOL VIOLET

3.1.1 Reagents and solutions.

(i) Catechol violet (CV) ($C_{19}H_{14}O_7S$), (4×10^{-4}M).

0.01544g of catechol violet was dissolved in distilled deionized water and made up to $100cm^3$ in a standard volumetric flask.

(ii) Sodium hydroxide 10^{-2}M.

This was prepared as in section 2.1.1.

(iii) Hydrocholric acid 10^{-2}M.

This was prepared as in section 2.1.1.

3.1.1.2 Apparatus.

(i) All absorbance measurements were made with a Unicam SP 1750B spectrophotometer with digital readout and 10mm quartz cells.

(ii) pH values were determined with PYE Unicam PW 9418 Philips pH meter.

3.1.2 Potentiometric titration of aqueous solution of catechol violet with sodium hydroxide and hydrochloric acid.

3.1.2.1 Method.

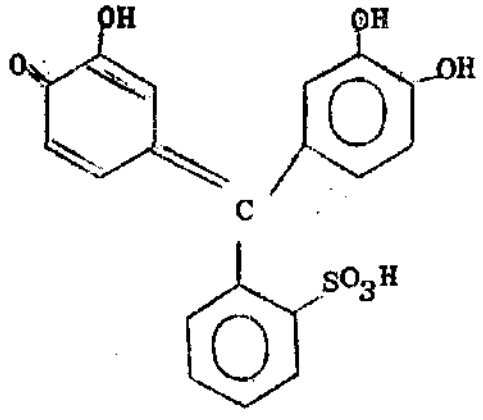
$2cm^3$ of the stock catechol violet solution (4×10^{-4}M) was accurately pipetted into a $50cm^3$ volumetric flask and made to the mark with distilled deionized water.

This solution was poured into a clean $100cm^3$ beaker and titrated with $10^{-2}M$ sodium hydroxide from a burette. The pH of the solution was taken after each addition of the alkali. The process was repeated using $10^{-2}M$ hydrochloric acid.

A plot of pH against the equivalents of sodium hydroxide or hydrochloric acid gives the potentiometric titration curve in fig. 3.1.

3.1.2.2 Results and Discussion.

Aqueous (CV) solution is acidic as shown by the initial pH of 4.30 in water. The structural formula also shows that it is an acid.



Catechol violet is one of the triphenylmethane reagents. An aqueous solution of it is yellow. At a pH below 1.5, the colour is red, and between pH 2 and 6, it is yellow while at pH 7, it is violet. However above pH 10 the colour is blue. The colour change is ascribed

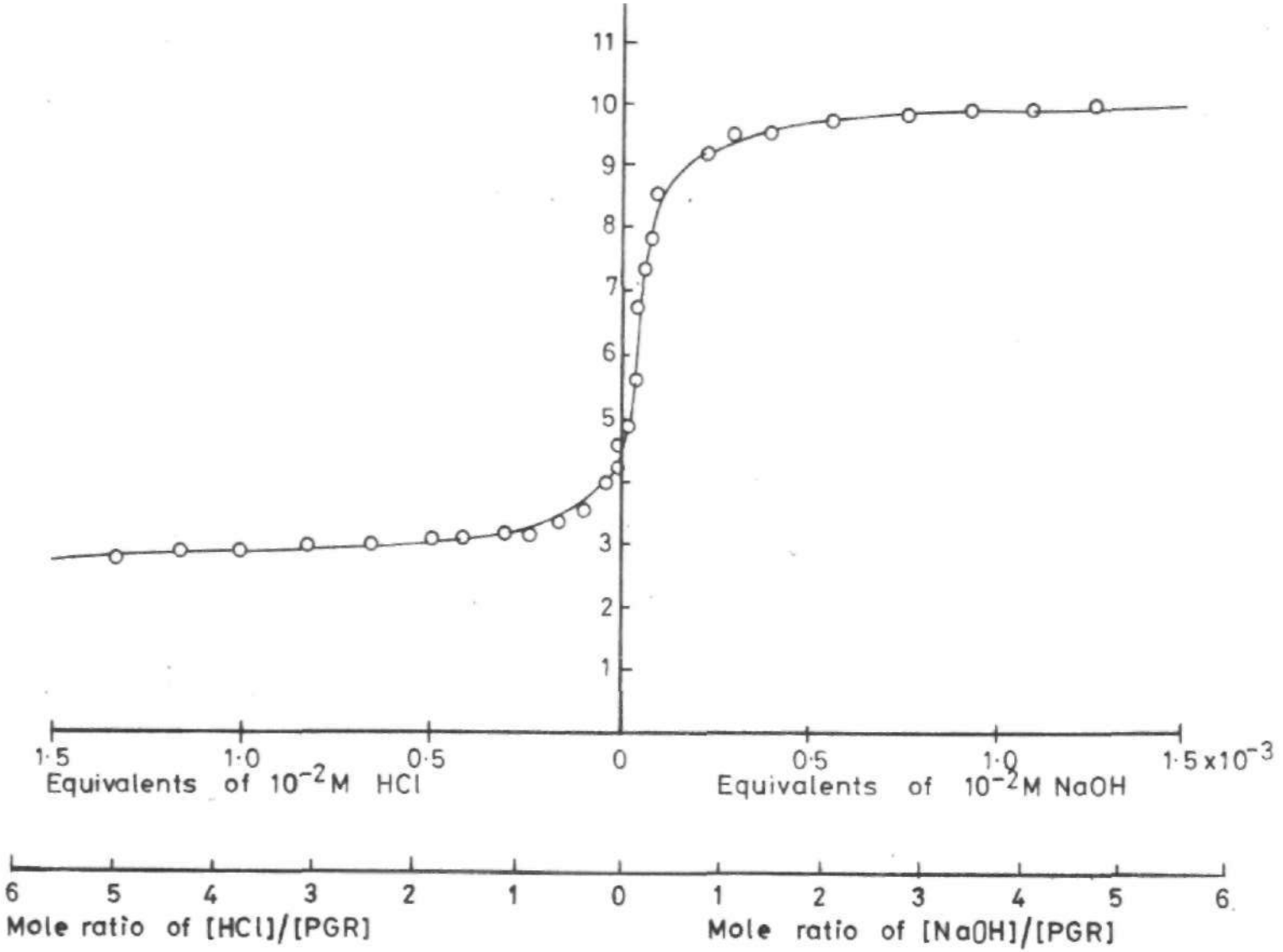
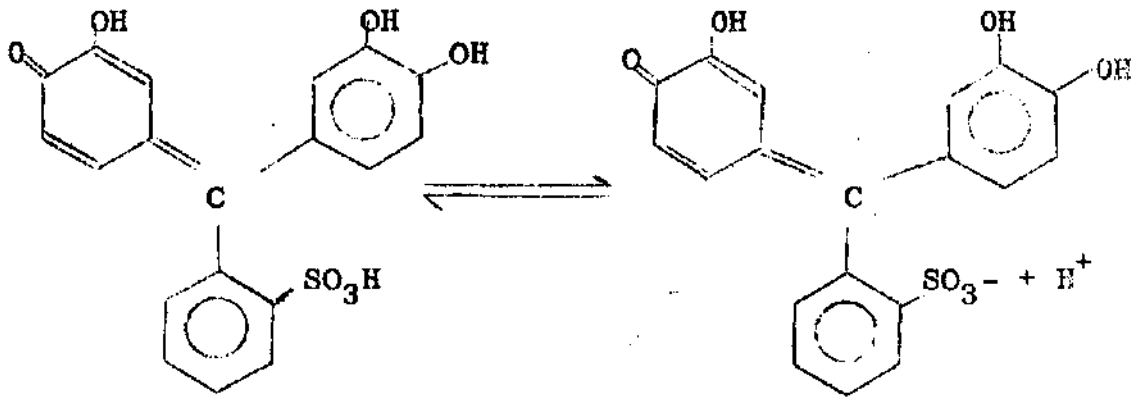


Fig. 3·1 Potentiometric titration of catechol violet solution with both sodium hydroxide and hydrochloric acid [PGR]=$1{\cdot}6 \times 10^{-5}$ M

to the progressive ionization of the hydroxyl groups. The blue strongly alkaline solutions are unstable and lose their colour fairly rapidly.



Catechol violet quickly releases its proton to a base as shown by the steep rise in pH on addition of sodium hydroxide.

Aqueous catechol violet appears to be well buffered against pH changes above about pH10.2. Around this region too, catechol violet would be anionic hence it forms coloured complexes (usually blue or green) with many divalent metals. The strongly alkaline solutions being unstable, lose their colour fairly rapidly probably due to aerial oxidation.

3.1.3 The dependence of the absorbance of aqueous solution of catechol violet on pH.

3.1.3.1 Method.

To $2cm^3$ of the $4 \times 10^{-4}M$ (CV) solution in different $50cm^3$ standard flasks was added sodium hydroxide ($10^{-2}M$) solution. The volumes of sodium hydroxide added were selected to give different values of pH of a

sufficient spread on finally diluting the (CV) solution to the $50cm^3$ mark with distilled deionized water. It was repeated using $10^{-2}M$ HCl.
The UV absorption characteristics of each solution as well as the pH were determined after 30 minutes of mixing the reagents.

3.1.3.2 Results and Discussion

A plot of the different absorbances against corresponding pH is shown in fig. 3.2. Similarly the λ_{max} values of the absorbances of the solutions against pH are plotted in fig. 3.3. The absorbance values of the solution at pH 10.5 is quite high and tends to increase at higher pH values. On fig. 3.3 in the alkaline region and above pH 10, the λ_{max} is fairly constant. The highly acidic range of the indicator was not investigated. Also from fig. 3.1, the alkaline range of the indicator is resistant to pH changes. The alkaline range was therefore chosen for the purpose of this work because of the reasonably high absorbance, the fairly constant λ_{max} and its resistance to pH changes.

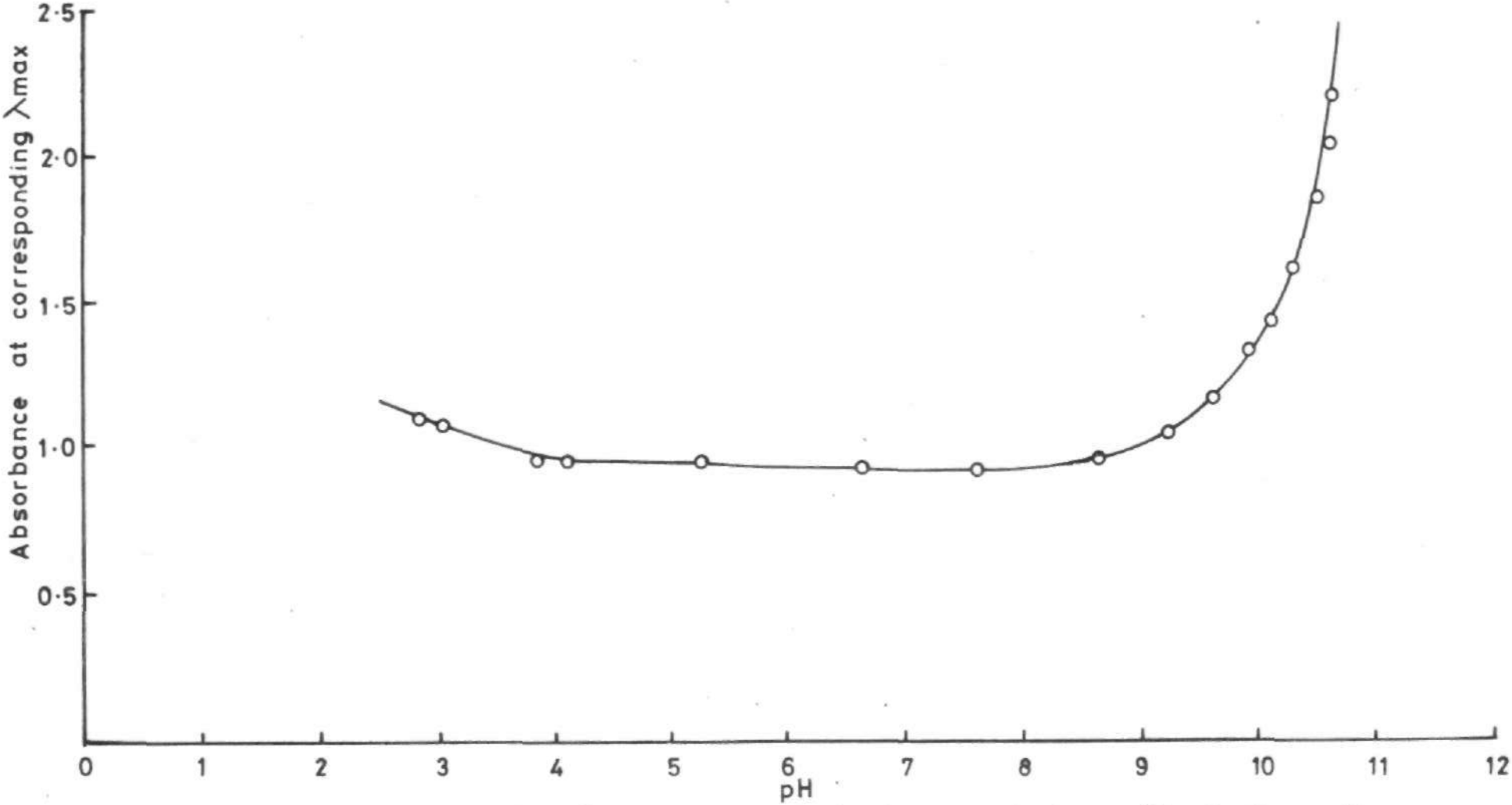


Fig. 3·2 Spectrophotometric titration of catechol violet solution with both sodium hydroxide and hydrochloric acid [CV]= $1{\cdot}6 \times 10^{-5}$ M

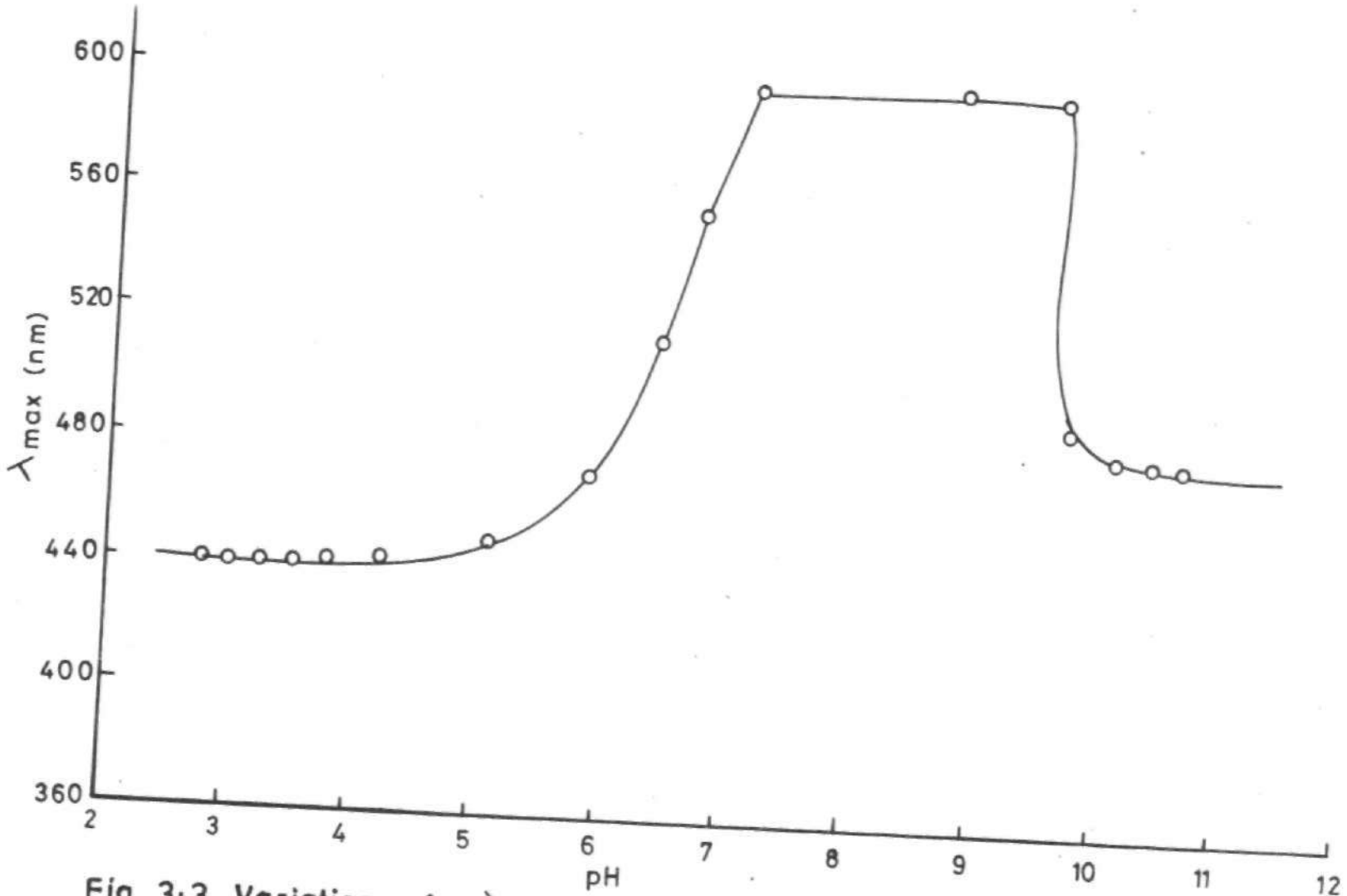


Fig. 3·3 Variation of λmax of aqueous catechol violet solution with pH [CV]= $1{\cdot}6 \times 10^{-5}$ M

3.1.4 The effect of concentration of $NaHCO_3$/NaOH buffer (pH 10.5) on the absorbance of catechol violet.

3.1.4.1 Reagents.

$NaHCO_3$/NaOH buffer (32) at pH 10.5 (2.5×10^{-2}M).

$500cm^3$ of 5×10^{-2}M $NaHCO_3$ {4.2g/l} and $178cm^3$ of 0.1M NaOH {4g/l} were mixed together and diluted with distilled deionized water to $1000cm^3$ in a standard volumetric flask.

3.1.4.2 Method.

$2cm^3$ of 4×10^{-4}M (CV) was accurately measured into a $50cm^3$ standard flask, $5cm^3$ of the 2.5×10^{-2}M carbonate buffer pH 10.5 was added and the mixture was made up to $50cm^3$ with distilled deionized water in a standard flask. Other similar solutions were prepared using the same volume ($2cm^3$) of 4×10^{-4}M (CV), but different volumes of the stock buffer solution.
The UV absorbance was taken at the wavelength of maximum absorbance after 20 minutes of mixing the reagents, when the absorbance characteristics were constant using 10mm cells and distilled deionized water as reference. The pH of each solution was also determined.

3.1.4.3 Results and Discussion

The table below shows the pH, the wavelength of maximum absorption and the absorbance for the solutions prepared.

Concentration of 2.5×10^{-2}M Carbonate buffer (cm^3)	pH	λ_{max} (nm)	Absorption at λ_{max}
5	10.10	482	0.144
10	10.30	478	0.152
20	10.40	478	0.162
30	10.50	476	0.166
40	10.50	476	0.168

Table 3.1 Dependence of pH and absorbance on concentration of $NaHCO_3/NaOH$

Aqueous alkaline (CV) pH 10.5 has a wavelength of maximum absorption at 476nm. From table 3.1 about $30cm^3$ of the $NaHCO_3/NaOH$ buffer was required to effectively buffer the reaction medium against pH changes. From the above results $25cm^3$ of buffer pH 10.5 was considered to be most suitable and was used in subsequent studies.

3.1.5 Investigation of Beer - Lambert law for aqueous catechol violet solution.

3.1.5.1 Method.

$0.50cm^3$ of (CV), 4×10^{-4}M solution was accurately measured into a $50cm^3$ standard flask. $25cm^3$ of buffer pH 10.5 was added and the mixture made up to $50cm^3$ with distilled deionized water. Other solution mixtures

were prepared with different volumes of (CV) and $25cm^3$ of the buffer. The UV absorbance at 476nm was recorded after 20 minutes of mixing the reagents, when the absorbance characteristics were constant.

3.1.5.2 Results and Discussion.

A plot of absorbance against concentration is shown in fig. 3.4. The absorption of the aqueous (CV) solution at pH 10.5 obeyed Beer-Lamberts law even at high concentrations of the indicator i.e. even up to $4.8 \times 10^{-5}M$ of the indicator. The extinction coefficient of (CV) was calculated from the graph to be 1.0×10^4 $l.mol^{-1}cm^{-1}$. For all subsequent work $2.5cm^3$ of the $4 \times 10^{-4}M$ stock ($2 \times 10^{-5}M$) of (CV) i.e. $2 \times 10^{-5}M$ experimental concentration was used.

3.2 INTERACTION OF CATECHOL VIOLET WITH METAL IONS (Cu^{2+} and Al^{3+})

2.1 Reagents.

Appropriate weights of the Analytical grade of the metallic salts, $Cu(NO_3)_2.3H_2O$ and $Al(NO_3)_3.9H_2O$, were dissolved in distilled deionized water in a $500cm^3$ standard flask and made to the mark. Appropriate volume of this stock solution (10^4ppm) or higher was accurately measured into a $100cm^3$ standard flask and made to the mark with water to obtain a 100ppm solution of M^{n+} which was used for the subsequent studies.

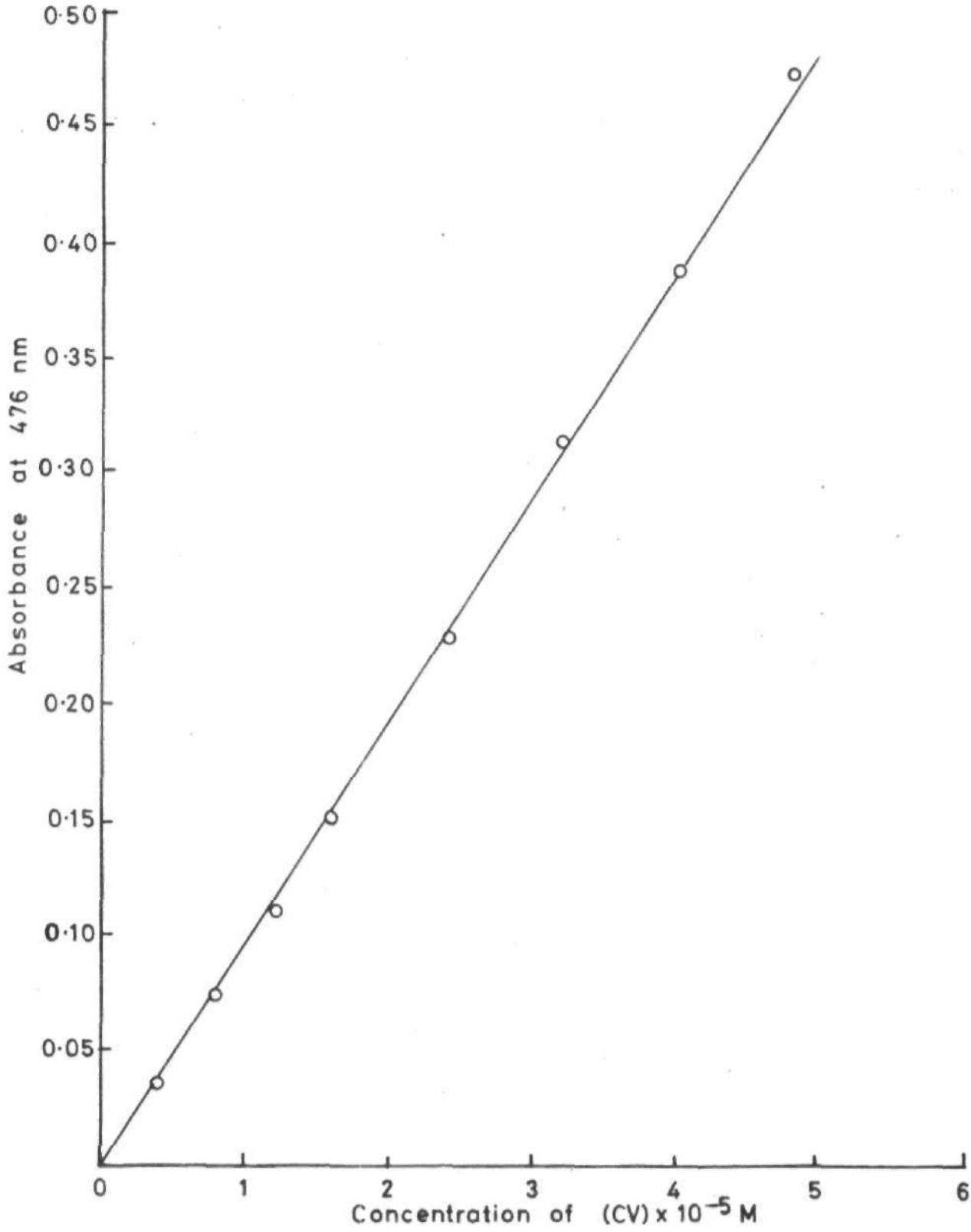


Fig. 3·4 Beer–Lambert's law calibration curve for catechol violet solution

3.2.2 Interaction of (CV) with Cu^{2+}.

3.2.2.1 Method.

$2cm^3$ aliquots of 4×10^{-4}M aqueous (CV) solution were accurately measured into different $50cm^3$ standard flasks. $25cm^3$ of the stock bicarbonate buffer pH 10.5 was added to each flask followed by different volumes of the 100ppm (1.57×10^{-3}M) Cu^{2+} solution. Each solution was made up to the mark with distilled deionized water. The wavelength of maximum absorbance and the corresponding absorbance value for each solution were determined using a blank solution not containing copper ions, but otherwise the same as the sample solution. The measurements were taken after 20 minutes of mixing the reagents when the absorbance characteristics were constant. The experiments were repeated using $1cm^3$, $3cm^3$, $4cm^3$ and $5cm^3$ of (CV).

3.2.2.2 Results and Discussion.

The aqueous Cu - CV system at pH 10.5 had its wavelength of maximum absorption at 610nm. The colours of the solutions range from light bluish green to greenish colour. A plot of the absorbance against concentration for the system at the λ_{max} is shown in fig 3.5. There is a linear relationship between concentration and absorbance at very low concentrations of the metal.

Table 3.2 shows the extinction coefficient of the complex formed.

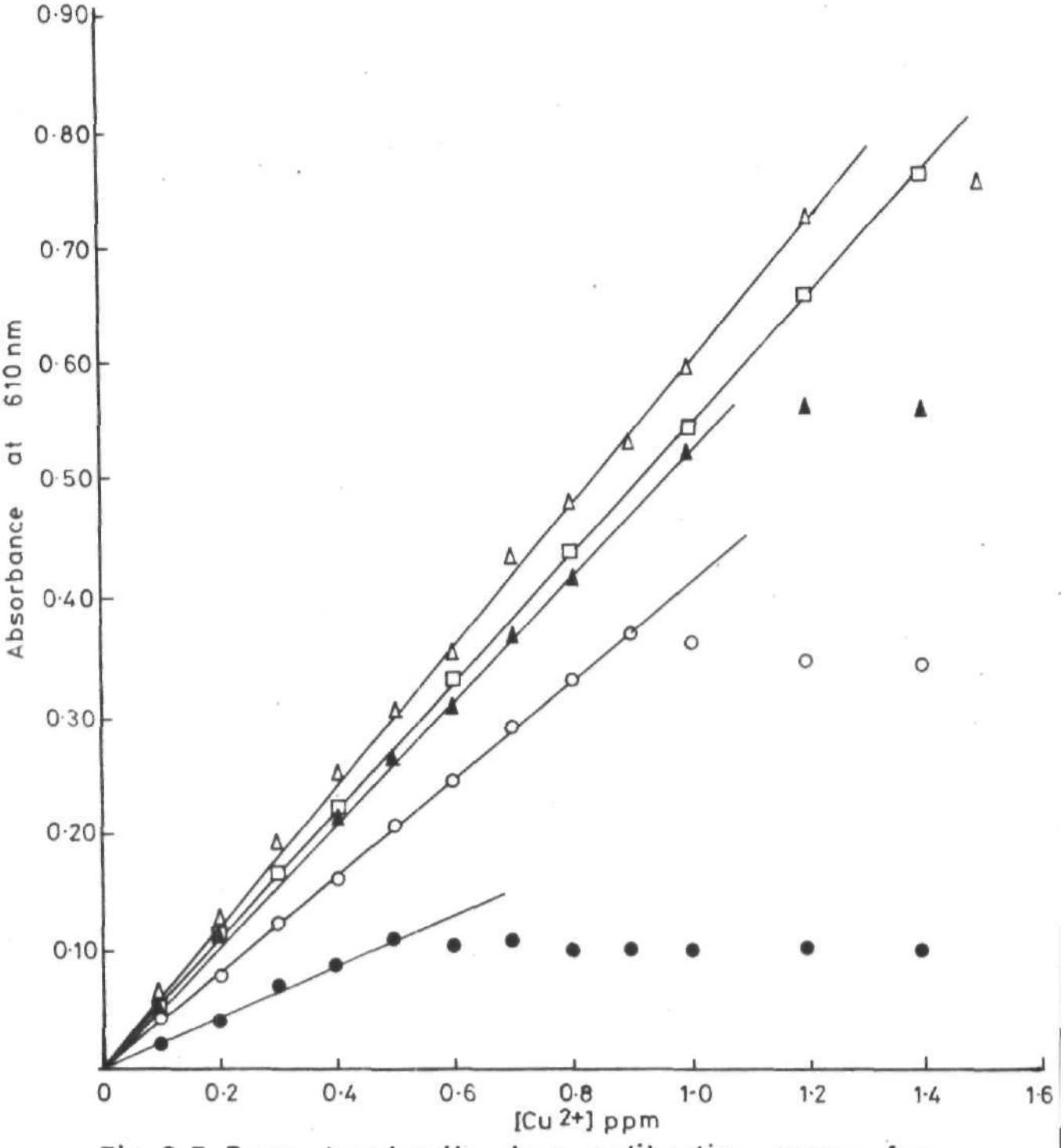


Fig. 3·5 Beer–Lambert's law calibration curve for CV–Cu^{2+} Complex

(●) [CV] = 8×10^{-6} M (▲) [CV] = $2{\cdot}4 \times 10^{-5}$ M (○) [CV] = $1{\cdot}6 \times 10^{-5}$ M

(△) [CV] = $3{\cdot}2 \times 10^{-5}$ M (□) [CV] = $4{\cdot}0 \times 10^{-5}$ M

Concentration of (CV) x 10^5M	Extinction coefficient $l.mole^{-1}.\ cm^{-1}$ x 10^{-4}
0.8	1.38
1.6	2.60
2.4	3.30
3.2	3.88
4.0	3.56

Table 3.2 Variation of extinction coefficient of Cu^{2+} in Cu - CV system with (CV) concentration.

A plot of the extinction coefficient against (CV) concentration, not shown, reveals that there is an increased sensitivity in determining aluminium until a maximum value is reached at 3.2 x 10^{-5}M of (CV).

3.2.3 Interaction of (CV) with Al^{3+}.

3.2.3.1 Method.

$2cm^3$ aliquots of 4 x 10^{-4}M aqueous (CV) solution were accurately measured into different $50cm^3$ standard volumetric flasks. $25cm^3$ of the stock bicarbonate buffer pH 10.5 was added to each flask followed by different volumes of the 100 ppm Al^{3+} solution. Each solution was made up to the mark with distilled deionized water.

The wavelength of maximum absorbance and the corresponding absorbance value for each solution were determined using a blank solution not containing any Al^{3+} ions, but otherwise the same as the sample solution. The measurements of the absorbance of the purple solutions were taken after 10 minutes of mixing the reagents when the absorbance characteristics were constant. This time of waiting prior to absorbance measurement was established in an auxiliary kinetic experiment. The experiments were repeated using $1cm^3$, $3cm^3$, $4cm^3$ and $5cm^3$ of (CV).

3.2.3.2 Results and Discussion.

The aqueous Al - CV system had its wavelength of maximum absorption at 578nm. The colour of the solution became increasingly purple as the concentration of Al^{3+} increased. A plot of the absorbance against concentration for the system at the λ_{max} is shown in fig. 3.6. All the plots show a linear increase between concentration and absorbance only at very low concentrations of aluminium ions. However at very low concentrations of aluminium ions when 8×10^{-6}M (CV) was used, there was no λ_{max}, and this is shown by dotted lines in fig. 3.6.

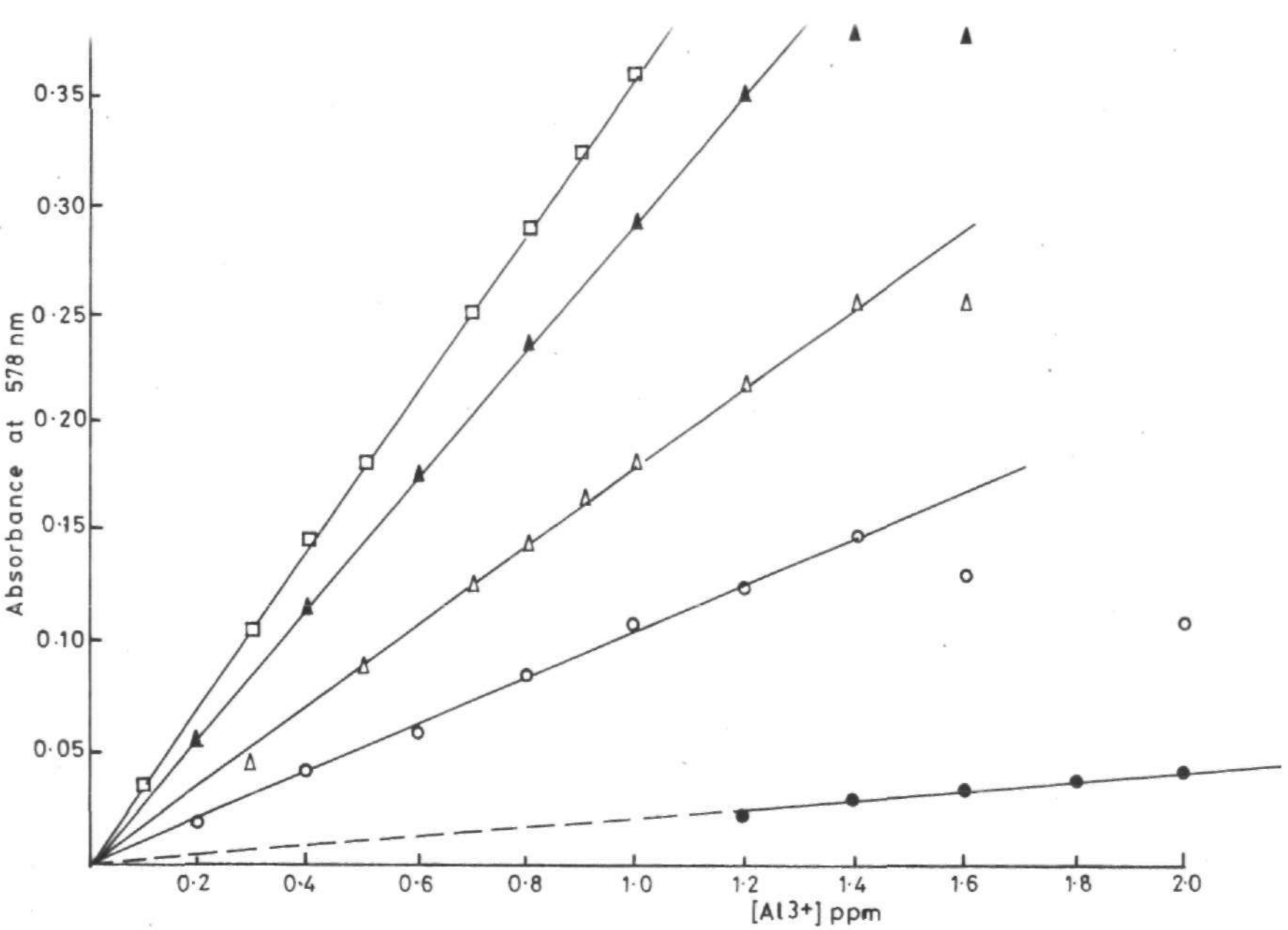


Fig. 3·6 Beer–Lambert's law calibration curve for CV–Al^{3+} complex

(●)[CV] = 8×10^{-6} M (Δ)[CV] = $2 \cdot 4 \times 10^{-5}$ M (□)[CV] = $4 \cdot 0 \times 10^{-5}$ M

(○)[CV] = $1 \cdot 6 \times 10^{-5}$ M (▲)[CV] = $3 \cdot 2 \times 10^{-5}$ M

Concentration of (CV) x 10^{5} M	Extinction coefficient $l.mole^{-1}\ cm^{-1} \times 10^{-3}$
0.8	0.54
1.6	2.85
2.4	4.82
3.2	7.97
4.0	9.89

Table 3.3 Variation of extinction coefficient of Al^{3+} in Al - CV system with (CV) concentration.

The increase in extinction coefficient with increase in the concentration of (CV) used table 3.3 shows that the system tends to be more sensitive for the determination of aluminium at higher concentrations of catechol violet. The concentration of (CV) required for optimum sensitivity appeared not much higher than 4.0×10^{-5}M however.

3.3 DETERMINATION AND MAXIMISING THE CONDITIONS FOR CATECHOL VIOLET (CV) AND CETYLTRIMETHYLAMMONIUM BROMIDE (CTAB) INTERACTIONS.

3.3.1 Method.

$3.5cm^3$ aliquots of 4×10^{-4}M aqueous (CV) solution were accurately measured into different $50cm^3$ standard flasks. $25cm^3$ of the stock $NaHCO_3/NaOH$ buffer pH 10.5 was measured into each flask. Different volumes of

4×10^{-4}M (CTAB) solution were added to each flask and the mixture made up to the $50cm^3$ mark with distilled deionized water.

The wavelength of maximum absorbance and the corresponding absorbance value for each solution were determined using the spectrophotometer, in 10mm quartz cells against a blank solution that did not contain any (CTAB). The UV absorption characteristics were measured after 20 minutes when the readings had become steady. The experiments were repeated using $2.5cm^3$, $1.5cm^3$ and $0.75cm^3$ of (CV).

3.3.2 Results and Discussion.

The aqueous CTAB - CV system at pH 10.5 had its wavelength of maximum absorption at 600nm. A plot of the absorbance against concentration for the system at the λ_{max} is shown in fig. 3.7. Each of the curves has a peak and the composition of the [CTAB]/[CV] at this peak is calculated by the mole ratio method.

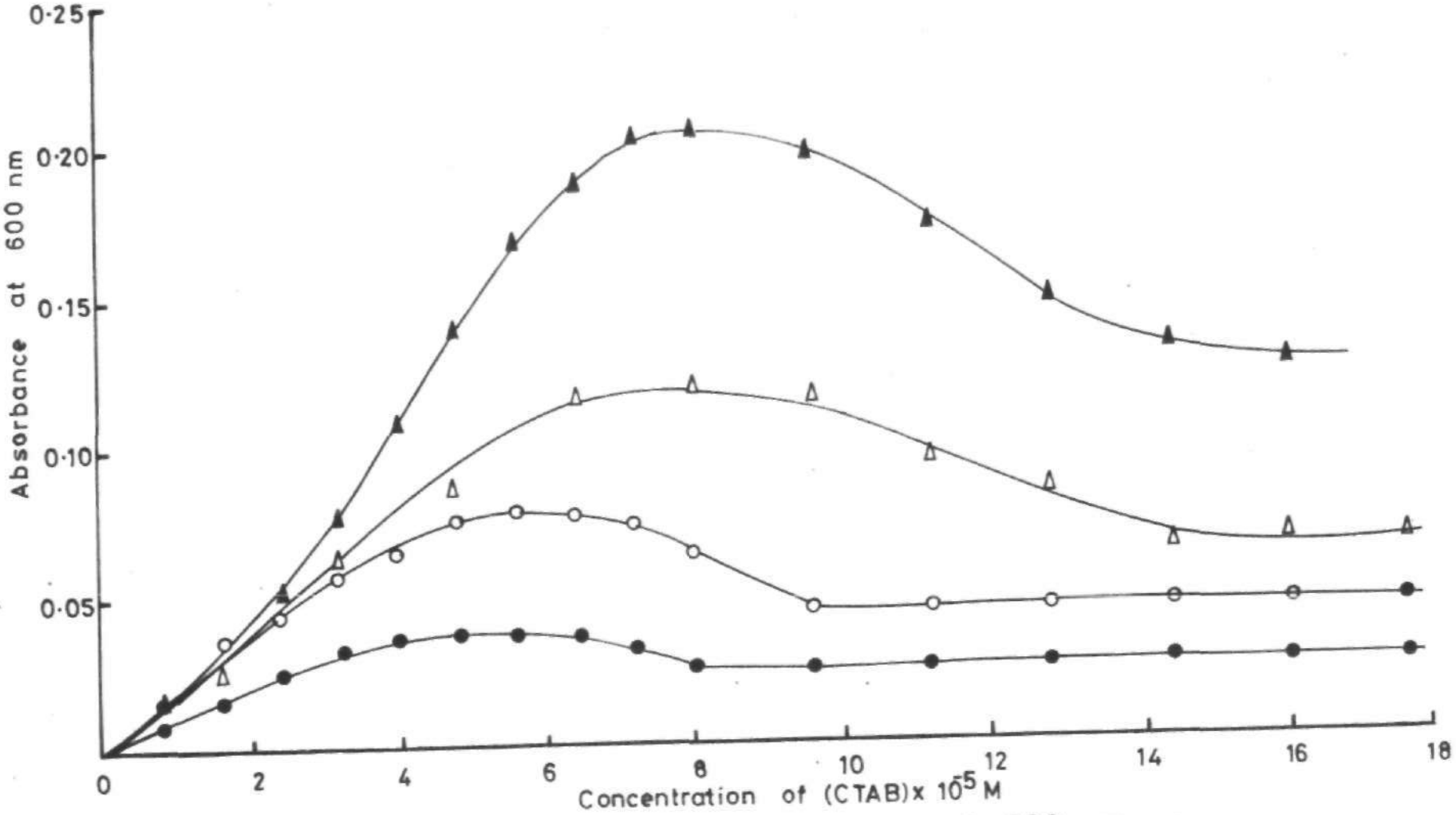


Fig. 3·7 Absorption spectra of CTAB/CV complex at 600 nm

(●) [CV] = 6×10^{-6} M (Δ) [CV] = 2×10^{-5} M (○) [CV] = $1{\cdot}5 \times 10^{-5}$ M (▲) [CV] = $2{\cdot}8 \times 10^{-5}$ M

Concentration of (CV) used x 10^5M	Concentration of (CTAB) at peak x 10^5M	Mole ratio of {CTAB}/{CV}
2.8	8.8	3.14
2.0	8.0	4.00
1.2	5.6	4.66
0.6	4.0	6.67

Table 3.4 Mole ratio of {CTAB}/{CV} at different {CV} concentrations in the CV - CTAB system.

Generally from fig. 3.7, it is seen that as the concentration of (CV) decreases the peak of the curve flattens out. Since it is difficult to clearly estimate the molar ratio of {CTAB}/{CV} which is required for specific interactions from table 3.4, a plot of the concentration of (CV) used against the concentration of (CTAB) at peak is recorded in fig. 3.8. From this plot, the mole ratio of {CTAB}/{CV} required for specific interaction is found to be three to one. Hence for all subsequent works on this system, the molar ratio of {CTAB}/{CV} was kept at three to one.

3.4 STUDY OF THE TERNARY SYSTEM M^{n+} - CV - CTAB. (M^{n+} = Cu^{2+} or Al^{3+})

3.4.1 The Cu - CV - CTAB system.

3.4.1.1 Method.

$5cm^3$ aliquots of 4×10^{-4}M aqueous (CV) solution were accurately measured into different $50cm^3$ standard flasks. $25cm^3$ of the stock bicarbonate buffer at pH 10.5

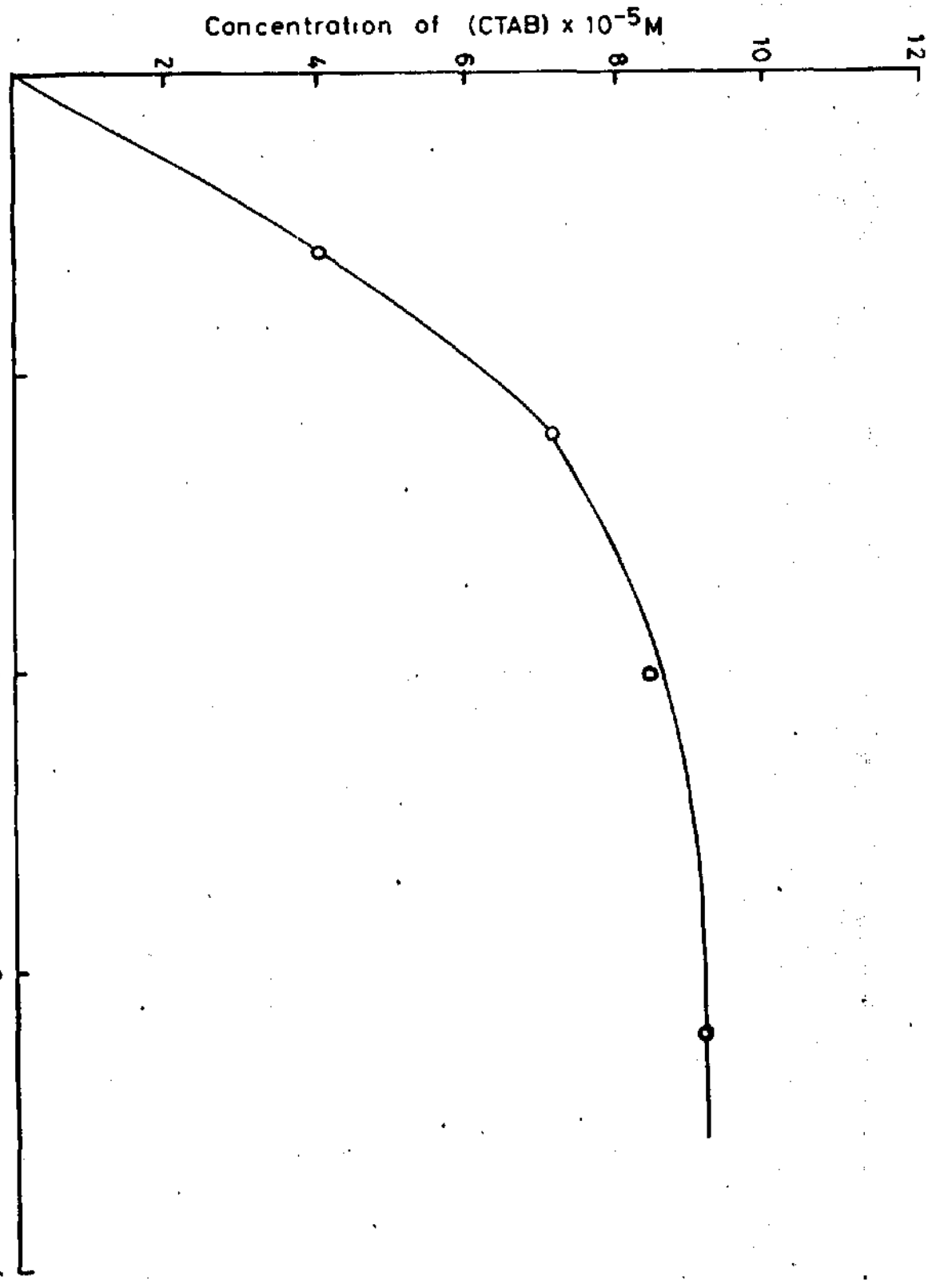


Fig. 3.8 Variation of [CTAB] concentration with [C

was added to each flask. $15cm^3$ of $4 \times 10^{-4}M$ (CTAB) solution was also added to each flask followed by different volumes of 100 ppm ($1.57 \times 10^{-3}M$) Cu^{2+} solution. Each flask was made up to the $50cm^3$ mark with distilled deionized water. The UV spectrum of the greenish solution was taken at the wavelength of maximum absorption using a reagent blank as reference, containing the same concentration of (CV), (CTAB) and buffer as in the experimental solution, 15 minutes after mixing the reagents when the absorbance characteristics were steady. The experiments were repeated using $4cm^3$, $3cm^3$ $2cm^3$ and $1cm^3$ of (CV), while the molar ratio of CTAB/CV was kept at three to one.

3.4.1.2 Results and Discussion.

Fig. 3.9 shows the UV spectra of $3.2 \times 10^{-5}M$ (CV) in the presence of $1.25 \times 10^{-5}M$ copper ions as well as the effect of the addition of $9.6 \times 10^{-5}M$ (CTAB) on the system. The binary complex had its λ_{max} at 610nm, while the ternary complex had its λ_{max} at 698nm. Hence there was a considerable bathochromic shift of 88nm on addition of (CTAB).

The plot of the absorbance against the concentration is shown fig. 3.10. It was found that the wavelength of maximum absorption increased from 670nm at low (CV) concentration to 698nm at higher (CV) concentrations.

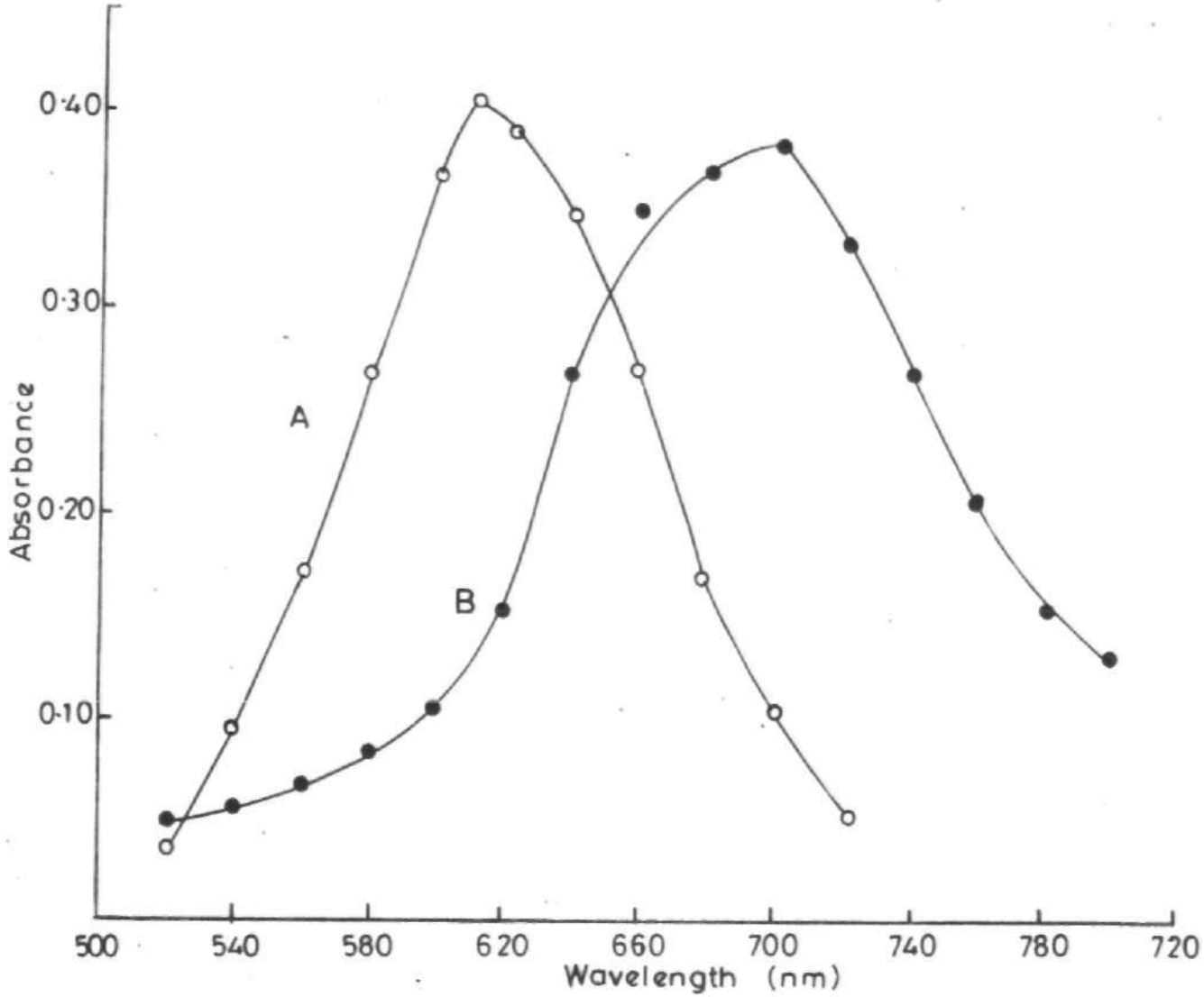


Fig.3·9 Absorption spectra of (A),CV−Cu^{2+} system
(B), Cu−CV−CTAB system

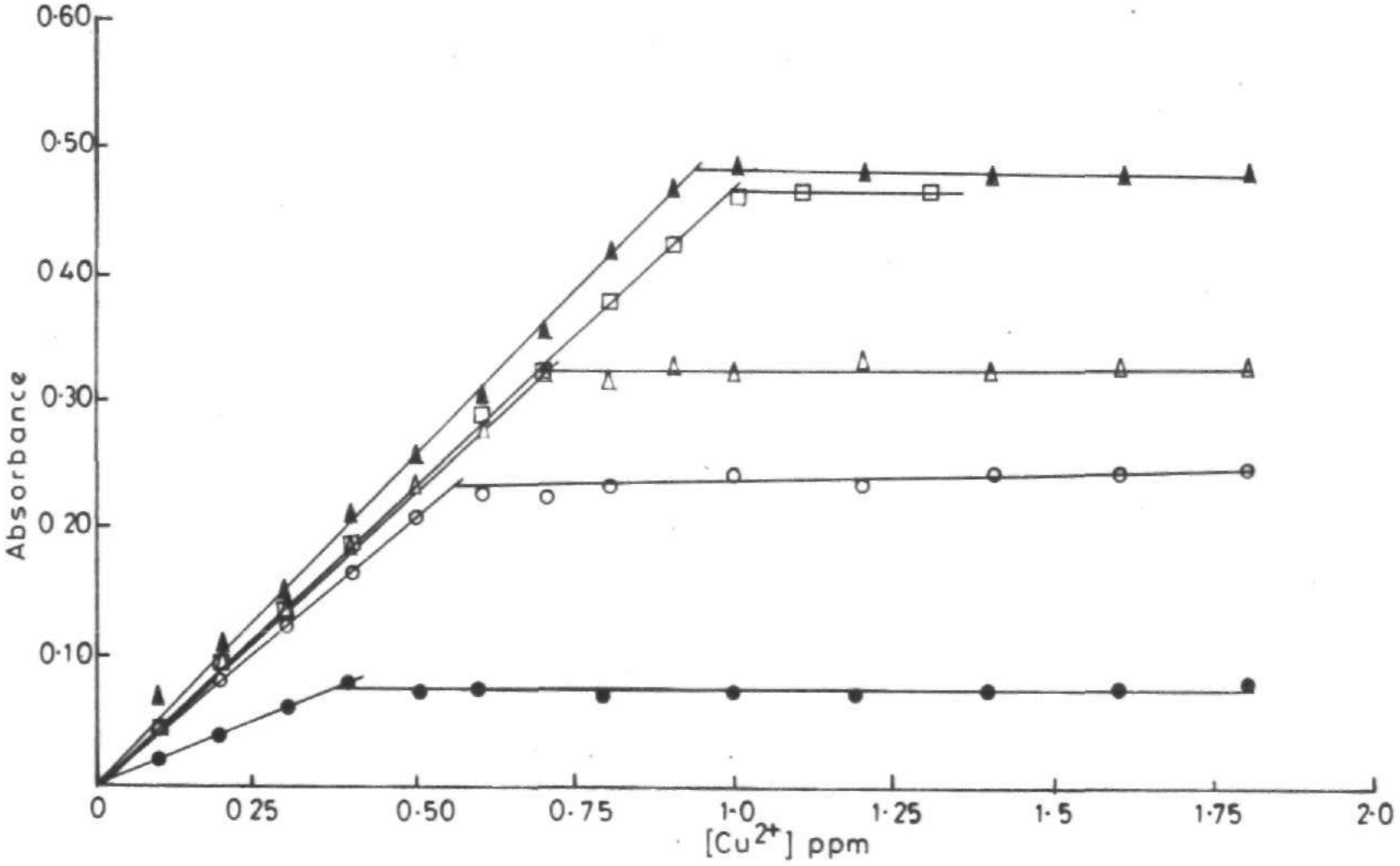


Fig. 3·10 Absorption spectra of Cu–Cv–CTAB Complex

(●) [Cv] = 8×10^{-6} M at 670 nm (▲) [CV] = $3{\cdot}2 \times 10^{-5}$ M at 698 nm

(○) [CV] = $1{\cdot}6 \times 10^{-5}$ M at 692 nm (□) [CV] = 4×10^{-5} M at 698 nm

(Δ) [CV] = $2{\cdot}4 \times 10^{-5}$ M at 698 nm

There is a linear relationship between absorbance and concentration only at very low concentrations of Cu^{2+}. The extinction coefficient of the ternary system (Cu - CV - CTAB) is given below.

Concentration of (CV) used x 10^{5}M	Extinction coefficient in $l.mole^{-1}$ cm^{-1} x 10^{-4}
0.8	1.27
1.6	2.65
2.4	2.89
3.2	3.00

Table 3.5 Variation of the extinction coefficient of Cu^{2+} in Cu - CV - CTAB with (CV) concentrations.

The results in table 3.5 show that the extinction coefficient for the system has a limiting value, thus showing a limit for the sensitivity of the method. Hence at about 3.2 x 10^{-5}M (CV) the method would have its highest sensitivity for the determination of copper.

Since each of the curves in fig. 3.10 has two segments, the molar composition of the ternary system can be deduced, because it is believed that the complex had a definite composition at the point of intersection of these lines.

Concentration of (CV) used x 10^5M	Concentration of Cu^{2+} at intercept x 10^5M	Molar ratio of (CV) to Cu^{2+}
0.8	0.63	1.27
1.6	0.85	1.90
2.4	1.10	2.18
3.2	1.57	2.03
4.0	1.60	2.50

Table 3.6 Molar ratio of {CV}/{Cu^{2+}} in the ternary system of Cu - CV - CTAB.

From an average of the values of the molar ratio for all the five (CV) concentrations or that of the middle three, assuming the first and last values are out the molar ratio of(CV)to Cu^{2+} is 2. However from section 3.3, the {CTAB}/{CV} ratio was established to be 3. Hence if is assummed that the presence of the metal ions did not affect the specific interaction between (CTAB) and (CV) or that of (CTAB) did not affect the specific interaction between M^{n+} and (CV) then the molar composition of the ternary system is derived as shown below.

	(CTAB)		(CV)		(Cu^{2+})
Mole ratios	6	to	2	to	1

The complex can then be written as either

$Cu\{CV_2(CTAB)_6\}$ or $Cu\{CV - (CTAB)_3)_2$.

3.4.2 The Al - CV - CTAB system.

3.4.2.1 Method.

$4cm^3$ aliquots of $4 \times 10^{-4}M$ aqueous (CV) solution were accurately measured into different $50cm^3$ standard flasks. $25cm^3$ of the bicarbonate buffer pH 10.5 was added to each flask. $8cm^3$ of $4 \times 10^{-4}M$ (CTAB) solution was also added to each flask followed by different volumes of 100 ppm Al^{3+} solution. Each flask was made up to the $50cm^3$ mark with distilled deionized water. The wavelength of maximum absorbance and the corresponding absorbance value for each solution were determined in the spectrophotometer against a blank solution that contained no Al^{3+} ions. The UV spectrum of each solution was taken 30 minutes after mixing the reagents when the absorbance characteristics were constant. The experiments were repeated using $3cm^3$, $2cm^3$ and $1cm^3$ (CV), keeping the [CTAB]/[CV] at 2, based on the results of an auxiliary study, not shown, from where the molar ratio of [CTAB]/[CV] required for specific interaction was calculated.

3.4.2.2 Results and Discussion.

The aqueous Al - CV - CTAB ternary system had a wavelength of maximum absorption between 690nm and 696nm. The colour of the solutions ranged from light green to deep green. A plot of the absorbance against

concentration for the system is shown in fig. 3.11. It obey Beer - Lambert's law only at very low concentrations of the metal. The extinction coefficients of the systems studied were calculated and are shown below.

Concentration of (CV) used x 10^{5}M	Extinction coefficient in $l.mole^{-1}$ cm^{-1} x 10^{-3}
0.8	7.90
1.6	13.50
2.4	21.58
3.2	35.97

Table 3.7 Extinction coefficients for Al^{3+} in the ternary system of Al - CV - CTAB.

In addition to a considerable bathochromic shift of about 118nm which the ternary system showed over the Al - CV binary system section 3.2.3.2, there was a considerable increase in the extinction coefficient when (CTAB) was added to the latter. This indicates a marked increase in the sensitivity of the method for aluminium determination when the surfactant (CTAB) is present.

Since each of the complete study has two segments, the molar composition of the Al - CV - CTAB system was deduced, on the assumption that the complex had a definite composition at the point of intersection of these segments.

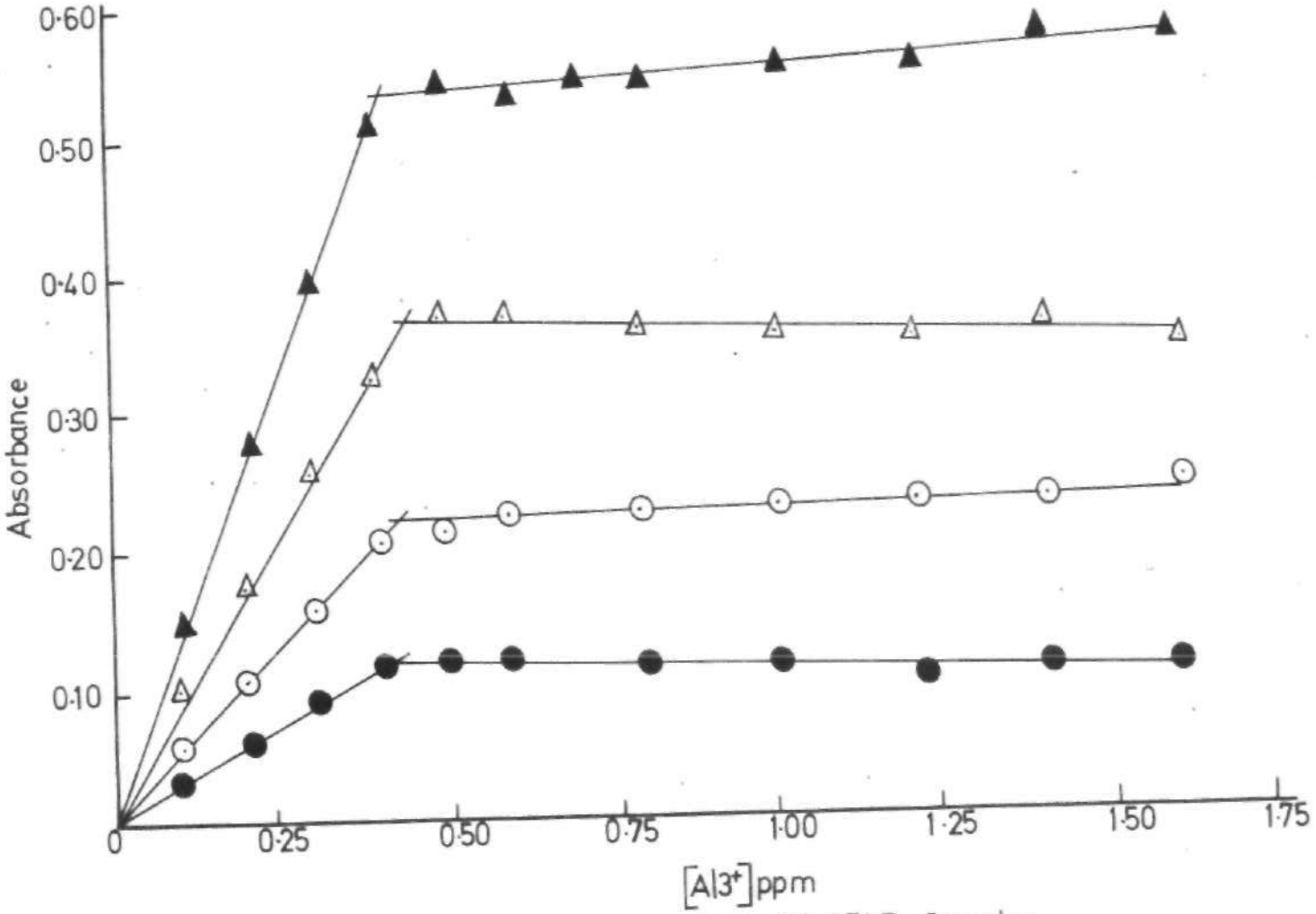


Fig 3.11 Absorption spectra of Al-CV-CTAB Complex

(●) [CV] = 8×10^{-6}M at 690nm (△) [CV] = 24×10^{-5}M at 696nm

(⊙) [CV] = 16×10^{-5}M at 692nm (▲) [CV] = 32×10^{-5}M at 696nm

Concentration of (CV) used x 10^5M	Concentration of Al^{3+} at intercept x 10^5M	Molar ratio of (CV) to Al^{3+}
0.8	1.48	0.54
1.6	1.56	1.03
2.4	1.63	1.47
3.2	1.48	2.16

Table 3.8 Mole ratio of $\{CV\}/\{Al^{3+}\}$ in the ternary system Al - CV - CTAB

From the linear graph of concentration of (CV) against mole ratio for the four concentrations of (CV), a slope of about 1.30 was obtained. Hence it was taken that the ratio of $\{CV\}/\{Al^{3+}\}^3$ was constant at 1.30. Having established that the {CTAB}/{CV} is 2, the molar composition of the ternary complex is derived as shown below, on making the assumption parallel to that in 3.4.1.2.

	(Al^{3+})		(CV)		(CTAB)
Mole ratio	1	to	1	to	2

The formula of the complex could then be written as $AlCV(CTAB)_2$.

3.5 INTERFERENCE STUDY.

3.5.1 Copper interference study.

The absorbance of 6.3 x 10^{-6}M copper as copper nitrate was determined at 690nm using the method

described in 3,4,1,1. This was repeated in the presence of Al, Cd, Co, Fe, Mg, Ni or Zn as interfering ions, taken one at a time in varying molar concentrations relative to copper. The effect of the chloride anion was tested on copper using the same concentration of copper chloride. The change in the absorbance of Cu - CV - CTAB due to the presence of each of these ions was determined and taken as a measure of interference. It was expressed as a percentage of the absorbance due to the pure Cu - CV - CTAB system alone. The results are shown in table 3.9.

Ion added	$\frac{[M^{n+}]}{[Cu^{2+}]}$	Absorbance at 690nm	Interference (%)
Cu^{2+} in Cu-CV-CTAB system		0.174	-
Co^{2+}	1	0.192	10.2
Fe^{3+}	1	0.208	19.3
Ni^{2+}	1	0.172	-1.07
Ni^{2+}	2	0.195	11.84
Al^{3+}	1	0.247	42.17
Cd^{2+}	1	0.175	1.08
Cd^{2+}	2	0.178	2.49
Cr^{3+}	1	0.185	6.5
Mg^{2+}	1	0.172	-1.14
Mg^{2+}	2	0.165	-5.17
Zn^{2+}	1	0.182	4.59
Cl^{-}(as $CuCl_2$)	1	0.130	-25.57

Table 3.9 Interference (%) of some ions in the determination of copper using (CV) and (CTAB) as reagents.

The results show that cobalt, iron(III), aluminium and chloride ions interfere seriously in the determination of copper. Nickel and chromium cause some interference while cadmium and magnesium cause very little or no interference. No attempts were made to mask these interfering ions. In the case of chloride ions which had very serious interference, the method described in 3.4.1.1 was repeated using analytical grade copper chloride instead of the nitrate. The results are shown in table 3.10.

System	λ_{max} (nm)	Extinction coefficient in $l.mol.^{-1}$ cm^{-1} x 10^{-4}
$Cu(NO_3)$/CV	610	2.69
$Cu(NO_3)_2$/CV/CTAB	692	2.65
$CuCl_2$/CV	610	1.50
$CuCl_2$/CV/CTAB	680	1.99

Table 3.10 Extinction coefficient and λ_{max} of the chloride compared with the nitrate salts of copper.

From table 3.10, both in the chloride and the nitrate salt, the effect of (CTAB) is almost negligible. However the (ε) values for the nitrate salt is higher than for the chloride salt. This could be due to a strong attraction between Cu^{2+} ion and Cl^- which is greater than between Cu^{2+} ion and NO_3^- ion. Hence in the nitrate salt, there is more Cu^{2+} to interact with CV^- ions; which consequently gives a bigger (ε).

3.5.2 Aluminium interference study.

The absorbance of 1.48×10^{-5}M aluminium as aluminium nitrate was determined at 692nm, using the method described in 3.4.2. The absorbance of the same concentration of aluminium in the presence of some metals - Cd, Co, Cr, Cu, Fe, Mg, Ni or Zn, and chloride ions in form of aluminium chloride, in varying molar concentrations relative to aluminium was determined. The change in absorbance was taken as a measure of interference and expressed in porcentage. The results are as shown in table 3.11.

Ion added	$\frac{\{M^{n+}\}}{\{Al^{3+}\}}$	Absorbance at 692nm	Interference (%)
Al^{3+} in Al-CV-CTAB system		0.182	-
Cu^{2+}	1	0.295	61.95
Fe^{3+}	1	0.239	31.3
Co^{2+}	1	0.207	13.6
Mg^{2+}	1	0.202	10.98
Cr^{3+}	1	0.126	-30.65
Cd^{2+}	1	0.278	52.22
Zn^{2+}	1	0.253	39.22
Ni^{2+}	1	0.193	6.28
Cl^{-}	1	0.253	39.22

Table 3.11 Interference (%) of some ions in the determination of aluminium using (CV) and (CTAB) as reagents.

The results show that nickel ions caused the least interference while chloride ions and those of the other metals cause serious interference in the determination of aluminium. In the case of the chloride ions, the method described in 3.4.2 was repeated using aluminium chloride instead of nitrate. The results are presented in table 3.12.

System	λ_{max} nm	Extinction coefficient $l.\ mole^{-1}\ cm^{-1} \times 10^{-3}$
$Al(NO_3)_3$/CV	578	2.85
$Al(NO_3)_3$/CV/CTAB	692	13.50
*$AlCl_3$/CV	-	-
$AlCl_3$/CV/CTAB	670	7.71

Table 3.12 Extinction coefficient and λ_{max} of the chloride compared with the nitrate salts of aluminium.

* No λ_{max}, hence no results.

The fact that there is no λ_{max} for $AlCl_3$/CV probably suggests that there was no specific interaction between Al^{3+} of $AlCl_3$ and CV^- ions. This could be due to the rather small ionic radius of Al^{3+} (0.50A). It is supposed that the Al^{3+} ions will strongly attract Cl^- ions than CV^- ions. However for the nitrate salt since the NO_3^- ion is larger than Cl^- ion, there will be a greater attraction between Al^{3+} and CV^- ions. This probably accounts for the bigger (ε) of the nitrate group in the presence of (CTAB) as seen in table 3.12.

CHAPTER 4

4.1 SUMMARY AND CONCLUSIONS.

In this study the interaction between zinc or chromium(III) ions and pyrogallol red (PGR) was investigated. Similarly the UV absorption characteristics of catechol violet (CV) and the metal-chelate binary complex of aluminium(III) or copper(II) was extensively studied. The addition of a relatively small amount of a cationic surfactant (CTAB) to the usually coloured binary system was thoroughly investigated especially the attendant selectivity and sensitivity of the micellar improved system.

The anionic chelometric dyes used in the course of this study reacted with the metal ions (in the absence of CTAB) to form water soluble binary metal-chelate complexes. These complexes absorb in the visible region, zinc (520nm), aluminium (578nm), copper (610nm) and chromium (414nm) with strong absorptions at pH 10.5. The addition of CTAB to these binary complexes had a dramatic effect, resulting in most cases to marked colour changes. Normally, the principal roles of (CTAB) are to

i. solubilize an otherwise insoluble reagent,

ii. produce a bathochromic shift, the advantage of which is to lessen or completely remove spectral overlap problems,

iii. cause a significant increase in the extinction coefficient which will improve the selectivity of the method.

However, in the studies reported in chapters two and three, since all the reagents were soluble (CTAB) did not act as a solubilizing agent. For the systems studied, the addition of (CTAB) led to a bathochromic shift of 40nm for zinc, 114nm for aluminium, 82nm for copper and 58nm for chromium. Similarly for some of the systems reported, the addition of (CTAB) produced on increase in the extinction coefficient, which showed that the ternary system was more sensitive, than the binary metal-indicator system for the determination of metal ions.

The experimental concentration of (CTAB) used throughout the study was greater than the critical micelle concentrations (the c.m.c. of (CTAB) is given as 6×10^{-6}M) (33). Therefore, since the experimental concentration of (CTAB) used was greater than the (c.m.c), it is assumed that micelle formation is apparent, though it is difficult to state categorically whether micelles or free ions were responsible for the reactions that occurred.

4.1.1 The pyrogallol red system.

From this study, it was established that there was a specific interaction between (PGR) and (CTAB) (λ_{max} at 550nm) which in turn had a definite interaction with either of Zn^{2+} or Cr^{3+}. Hence in addition to xylenol orange (21) methylthymol blue (22) which had been previously suggested for the determination of zinc, (PGR) is being proposed. The binary complex of Zn-PGR absorbs in the UV region in agreement with the work of Bailey, et al, (28) that put the λ_{max} of Bi(III) - XO at 550 ± 60nm. The addition of (CTAB) to the binary complex showed a bathochromic shift. The λ_{max} of the ternary Zn-PGR-CTAB system increased with increase in [PGR]. A bathochronic shift of 40nm was recorded for 8×10^{-6}M [PGR] while about 80nm was recorded when 3.2×10^{-5}M [PGR] was used. Similarly the extinction coefficient increased with [PGR]. However the concentration of (PGR) required for optimum sensitivity is 3.2×10^{-5}M. The limit of detection of zinc vary with [PGR] and again about 3.2×10^{-5}M (PGR) is required for maximum efficiency. Other than the relatively high absorbance recorded at high [PGR]. Only very low concentrations of zinc, below 6.1×10^{-6}M could be detected. Hence at high [PGR], the large bathochromic shift, the high absorbance as well as the increase in extinction coefficient suggest an enhanced sensitivity in the determination of zinc using this method.

Though the use of (CV) and xylenol orange (20) have been reported for the determination of chromium, (PGR) is proposed in this study. Even though a bathochromic shift of 58nm was obtained when (CTAB) was added to the binary system, the absorbances were rather low. This method can not be used to estimate chromium below 500 ppm. Since the extinction coefficient decreased on the addition of (CTAB), the method is regarded as less sensitive. However, it may be used to detect high concentrations of Cr^{3+}, up to say 5000 ppm.

4.1.2 The catechol violet system.

There was a specific interaction between (CV) and (CTAB) (λ_{max} at 600nm) which is turn had a definite interaction with either of aluminium or copper ions. In addition to the use of xylenol orange, pyrogallol red, methylthymol blue, already reported for the detection of aluminium, the use of catechol violet is proposed. The ternary system obeyed Beer's law only at very low concentrations up to about 0.4 ppm. There were increases in the bathochromic shift and absorbance which increased the sensitivity, selectivity and extinction coefficient several fold when (CTAB) was added to the binary Al-CV system e.g. a bathochromic of over 114nm was recorded when 3.2×10^{-5}M (CV) was used. Since the detection limit of Al^{3+} decreased with increase in [CV], only very low [CV] e.g. 1.6×10^{-5}M is recommended for the detection of aluminium. In the Al-CV binary system, up to say 1.4 ppm

of Al^{3+} could be detected while only about 0.4ppm of it could be detected in the ternary system.

In the Cu - CV system, the addition of (CTAB) caused a bathochromic shift of about 82nm. Increase in (CV) increased the detection limit of Cu^{2+}. The addition of (CTAB) to the binary system, did not lead to any appreciable increase in the absorbance or the extintion coefficient. Hence other than the advantage of the bathochromic shift obtained, the method is regarded as insensitive in terms of the detection limit of Cu^{2+} and extinction coefficient. The optimum [CV] for this system is 3.2×10^{-5}M for maximum sensitivity in Cu^{2+} determination.

4.2. RECOMMENDATIONS.

4.2.1 Details of the recommended method for a calibration curve for the determination of zinc and chromium.

Solution preparation:

(i) Pyrogallol red (PGR), ($C_{19}H_{12}O_8S$), (4×10^{-4}M)

0.01602g of pyrogallol red dissolved in distilled deionized water and made up to $100cm^3$ in a standard flask.

(ii) Aqueous solution of cetyltrimethylammonium bromide (CTAB), $[CH_3(CH_2)_{15}](CH_3)_3NBr$, 4×10^{-4}M.

0.14578g solid surfactant is dissolved in distilled deionized water in one litre standard flask and made to the mark.

(iii) $NaHCO_3/NaOH$ buffer solution, pH 10.5

To $500cm^3$ of $5 \times 10^{-2}M$ $NaHCO_3$ (4.2g/l) add $178cm^3$ of 0.10M(4g/l) sodium hydroxide and make up to one litre in a standard flask with distilled deionized water.

(iv) M^{n+} solution (Zn^{2+} or Cr^{3+})

Prepare 10^4ppm stock solution of each of $Zn(NO_3)_2.6H_2O$ and $CrCl_3.6H_2O$ in standard flasks with distilled deionized water ($CrCl_3.6H_2O$ is prefered to $Cr(NO_3)_3.9H_2O$ because it gives higher extinction coefficient). The solutions are standardized by suitable methods (15b) for $Zn(NO_3)_2.6H_2O$ and (15c) for $CrCl_3.6H_2O$.

Appropriate dilutions are made in case of zinc to get 100ppm, (secondary stock).

Method.

In to each of several $50cm^3$ very clean standard flasks, pipette $4cm^3$ of the stock indicator solution and $25cm^3$ of the $NaHCO_3/NaOH$ buffer solution of pH 10.5. This is followed by $10.5cm^3$ of (CTAB).

Then add aliquots of from $0.1cm^3$ to $1cm^3$ of 100 ppm zinc or from 2.5 to $20cm^3$ of 10^4ppm standardized chromium solution. Then make the mixture of solutions in each flask up to the mark with distilled deionized water.

Allow the chromium solution to stand for 15 minutes, while that of zinc as soon as it is prepared and measure the absorbance at 572nm for chromium and 600nm for zinc against a reagent blank with no M^{n+}. For the zinc salt the calibration curve should be linear up to 0.4 ppm, and give an extinction coefficient of 15.40×10^3 $l.mole^{-1}$ cm^{-1} while it should be linear for chromium salt between 1000 ppm and about 3500 ppm and with an extinction coefficient of 15.53.

4.2.2 Details of the recommended methods for a Calibration for the determination of aluminium and copper.

Solution preparation.

(i) Catechol violet (CV), ($C_{19}H_{14}O_7S$), 4×10^{-4}M

0.01544g of catechol violet dissolved in distilled deionized water and made up to $100cm^3$ in a standard flask.

(ii) M^{n+} solutions (Al^{3+} or Cu^{2+})

Stock metal ion solutions of approximately 10^4ppm $Al(NO_3)_3.9H_2O$ or $Cu(NO_3).3H_2O$ are prepared in distilled deionized water and standardised by suitable methods (15d) for aluminium and (15e) for copper. Appropriate dilutions to final experimental solutions are made from the standardised stock solution.

Method.

In to each of several $50cm^3$ very clean standard flasks, pipette $4cm^3$ of (CV) and $25cm^3$ of the buffer. This is followed by $12cm^3$ of (CTAB) for copper salt or $8cm^3$ (CTAB) for aluminium salts.
Then add aliquots of from $0.1cm^3$ to $1cm^3$ of standandised M^{n+} solution preferably in steps of $0.1cm^3$ increase. Then make the mixture of solution in each flask to the mark with distilled deionized water. Allow the aluminium salt solution to stand for 30 minutes, while that of copper should stand for 15 minutes. Measure the absorbance at 698nm for copper or 696nm for aluminium against a reagent blank containing no M^{n+}.

The calibration curve, should be linear up to 0.4 ppm for aluminium and up to 0.8 ppm for copper and give an extinction coefficient of 3.10×10^4 $l.mole^{-1}.cm^{-1}$ for copper and 39.97×10^3 $l.mole^{-1}.cm^{-1}$ for aluminium.

4.3 SUGGESTIONS FOR FURTHER INVESTIGATION.

1. The selectivity of most spectrophotometric methods is limited, especially because of interference. It is therefore necessary to mask the interfering ions by appropriate masking agents. It is not until this is done that the optimum sensitivity of the method for the determination of metals could be ascertained.

2. The common anions of interest in analysis of elements after digestion of sample are halides (Cl^-, Br^-, F^-) and the nitrate. Though in these studies, Cl^- had been selected as a representative member of the halide group with nitrate, it is necessary to find other arguments to justify the preference of nitrate or chloride salt of the metals for the calibration curves.

3. Although, in this study, the interference effect of Ca^{2+} or P is not reported, it is essential to check this aspect most especially since the elements are commonly found in food materials.

4. It might be necessary to repeat the studies reported in this dissertation using (CTAB) < (c.m.c) to know if and how micelle formation is relevant to the effectiveness of the determination of trace metals with (CTAB) especially in terms of the bathochromic shift and the extinction coefficient. A comparative study of spectral parameters e.g. λ_{max}, (ε) etc for the metal-chelate complexes formed in the absence and presence of micellar systems might also be drawn from such studies.
Also the possibility of determination of the stability constants of the binary and ternary complexes should be considered.

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