Spectrophotometric Determination of Thermodynamic Ionization Constants of some Organic Acids and their Metallic Complexes in Aqueous Medium

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SPECTROPHOTOMETRIC DETERMINATION OF THERMODYNAMIC IONIZATION CONSTANTS OF SOME ORGANIC ACIDS AND THEIR METALLIC COMPLEXES IN AQUEOUS MEDIUM

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SUPERVISOR'S CERTIFICATE

Certified that the research work described in the thesis entitled "Spectrophotometric determination of the thermodynamic ionization constants of some organic acids and their metallic complexes in aqueous medium" was carried out by Shri Ram Narayan Soni, M.Sc., under my guidance and supervision during the period January, 1964 to June, 1967.

S L Gupta

(S. L. GUPTA)

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RAM NARAYAN SONI

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P A R T I

GENERAL INTRODUCTION

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1 Ionization Constant

The term ionization constants means those constants which are used to measure the strength of acids and bases. They reveal the proportions of the different ionic species into which a substance is divided at any chosen pH. This kind of information is useful in many ways. For example, different ionic species have different ultra-violet spectra and significant spectrophotometry can be done only when this is kept in mind. The ionic species of a given substance differ in other physical properties also and in chemical and biological properties as well[1]. Ionization constants, by defining the pH range in which a substance is least ionized, indicate the conditions under which it can be isolated in maximal yield and this has great value in preparative chemistry. They are often used to help diagnose the structure of a newly isolated substance and can help to confirm the identity of two substances which have no melting point.

The determination of ionization constants by conductometry is the oldest method. It takes somewhat longer time than by potentiometry and is a less versatile method but it is specially useful for very weak acids. Most of the ionization constants determined before 1930 were found by conductometry, but many of these old values are inaccurate. Nevertheless the method is

capable of giving highly accurate values if sufficient care is taken.

The most convenient method for the determination of ionization constants is potentiometric titration. However, spectrophotometry is particularly suitable for sparingly soluble substances, and also for work at very high and very low pH values which are beyond the range of the glass electrode. It can be used only for substances which absorb ultra-violet or visible light and the relevant ionic species must show absorption maxima at different wavelengths. Spectrophotometry is related to potentiometry in that the spectra are determined in buffers whose pH values are determined by potentiometry. Whereas potentiometric determination of an ionization constant measures the hydrogen ions not bound by the unknown, the spectrophotometric method measures the spectral shift produced when the unknown binds hydrogen ions. Raman spectra and nuclear magnetic resonance permit the determination of the ionization constants of such strong acids as nitric and trifluoroacetic acids[2].

Another method is determination of the increase in aqueous solubility of unknown at various pH values[3]. This is not so accurate a method as conductometry, potentiometry and spectrophotometry but it is useful in those cases where a substance (i) is too insoluble in water for potentiometry and conductometry and (ii) has no useful ultra-violet spectra. The catalysis of hydrolysis of an ester, disaccharide or glucoside, as a measure of ionization constants, has only historical interest.

Of many weak electrolytes which have been studied by spectrophotometry, the early work of von Halban and Kortüm[4] on 2:4 dinitrophenol is a classical example. Their method consisted of measuring the absorptions of the indicator in excess alkali and in excess acid, and to compare with these absorptions obtained in water and in salt solutions. The ionization constants of phenols have been attempted by many workers[5-7]. Thus Bordwell and Cooper[8] have determined the ionization constant of cresol. Biggs and coworkers[9-11] have done a considerable work on the ionization constants of nitrophenols. The halogenated substituted phenols have been studied spectrophotometrically[12-13]. The ionization constants of cyano, formyl, methoxy carbonyl, methoxy and phenyl phenols have been investigated by various authors[14-18]. Ernst and Herring[19] have measured the thermodynamic ionization constants of m- and p-acetyl phenols without the explicit use of activity coefficients for the charged species spectrophotometrically. Bale and Monk[20] have obtained dissociation constants of chloroacetic and propionic acids in 20% ethanol using 2:4 dinitrophenol as a colour reference.

A new method has been derived for spectrophotometric determination of ionization constants of diprotic acids by Ernst and Menashi[21-22]. Thamer[23] has given two methods for determining ionization constants of dibasic acids applicable for any degree of overlaping of the ionization constants. A minimum amount of data is required in either method. Irving and coworkers[24] have determined ionization constants of dibasic

acids. The studies on acid-base equilibria in acetonitrile by spectrophotometry and conductometry have been made by Kolthoff, Bruckenstein and Chantooni[25] showing complete dissociation of perchloric acid. The spectra of p-iodobenzoic acid has been studied by Robinson and Ang[26] in which acid curve is only slightly displaced to longer wavelengths, but the accuracy of determination of ionization constant is lower than that for other acids investigated by spectrophotometric method.

Davis[27-28] et al. obtained ionization constants of some derivatives of picric acid on the assumption that the effects of substituents on the ionization constant of phenol are additive. Spectrophotometric measurements of several concentrations of 4-chloro-4'-aminodiphenyl sulphone at various known pH were made from which the value of ionization constant was determined[29]. They[30] also studied the ionization constants of 4-aminobenzophenone at several temperatures.

Bates and Hetzer[31] have calculated the thermodynamic functions for the ionization process of protonated acid form of 2-amino-2-(hydroxymethyl)-1-3-propanediol [tris-(hydroxymethyl)-aminomethane]. Derivatives of barbituric acid have been studied by many workers[32-33]. The ionization constant of triethanolammonium ion has been determined by Bates and Allen[34]. Muhummad[35-36] et al. have obtained the ionization constants of hydrogen peroxide and hydrogen sulphide.

Substitution groups can change the electron density on an acidic group by polar interaction. Many authors have attempted

to divide polar interactions into inductive effects, displacement of electrons along the molecular chain or ring and direct or electrostatic field effects which occur, at least in part, through the solvent[37-42]. The distinction is a fruitless one because there is no way to estimate one type of interaction independently of the other. It has often been assumed that the Kirkwood-Westheimer theory can be used to calculate the direct effect, but this view cannot be maintained[43]. Commonly, these changes in acid strength are treated by considering them as arising from the polar effect, the resonance effect, hydrogen bonding, and steric hindrance. Often more than one of these considerations plays a significant role in determining the acid strength of a molecule, and it is difficult to find examples which illustrate just one of them. Therefore, it is necessary to select the principal effect, even though other factors contribute to the change in acid strength.

The effects of substituents can also be treated by a "Linear Free Energy" relationship. The most generally used special form of this expression is the modified Hammett equation - $\Delta pK_a = \rho\sigma$ where the substitution constant 'σ' measures the ability of the substituent to either withdraw electrons from the ring or donate them to it by induction and resonance. It depends primarily on the nature of substituent group and secondarily on the position of the substitution because resonance is more important at the para position than at the meta position. It is assumed to be independent of temperature and solvent.

'ρ' is the reaction constant which is the same for all substituents but depends on the solvent, temperature and nature of of the acid group.

The Hammett equation is a landmark in the development of physical organic chemistry. With it one can store and correlate a large quantity of equilibrium and rate data. The sign and magnitude of 'ρ' have proved useful in characterizing the nature of reactions and in speculating on their mechanisms.

A change in temperature causes a shift in the equilibrium point which is of both theoretical and practical interest. The change in enthalpy, entropy and heat capacity associated with an acid-base reaction can be found from the variation from its equilibrium constant with temperature. These thermodynamic properties afford interesting insights into acid-base behaviour, particularly with regard to solution effects. Acid-base equilibria are also disturbed by addition or removal of species foreign to the equilibria. The nature of the solvent, for example, is changed when methanol is added to an aqueous solution of a weak acid. The medium can also be changed by addition of a foreign solute, such as sodium chloride.

2 Complex

The study of complexes has been one of the major areas of research in inorganic chemistry for many years. Amongst other methods, spectrophotometry is of tremendous importance in the study of complexes. Two problems have received considerable

attention; the determination of equilibrium constants, and the determination of the stoichiometry of the complexes. The spectrophotometric method is particularly powerful, since it does not require that the complex be capable of separate existence. Evidence for the formation of quite unstable complexes can be obtained, and their stoichiometry, their free energies, and even their enthalpies and entropies of formation can be determined.

The empirical method of determining complex stoichiometry is widely used in investigating molecular complexes, where 1:1 ratios are by far the most common. In the field of ionic complexes, however, much higher ratios are usually encountered, and more systematic methods of determination of complex stoichiometry have been developed. The best known of these is Job's method of continuous variation[44]. This method has largely been designed for convenience in use and accordingly is based on spectrophotometric analysis of mixtures in the ratio of x:(1-x) volumes of equimolar solutions of concentration M of the two components A and B of the complex. Although Job stated that the method was applicable only when a single complex was formed between A and B, a method has been proposed which is applicable if a series of complexes is formed[45]. This method, however, has not proved very reliable and has not found wide application. The method can also be used for stability constant determination for certain limited systems containing one complex species[46]. A critical study of the application of this method was published recently by Asmus[47-48].

The molar-ratio method[49] is very similar to the method of continuous variation. The difference lies in the fact that the total analytical concentration of metal or ligand is held constant rather than the sum of the metal and ligand concentration. This method can also be used for finding out stability constant of the complex provided instability constant of the complex is not too large. The slope-ratio method[50] is most valuable for weak complexes, since the absorbance measurements used with this method involve only solutions containing a large excess of the metal and solutions containing a large excess of ligand, However, the method is applicable only when one complex species is formed and Beer's law is followed.

If one or more coloured complexes are formed in a system, then the optical density of the solution changes with a change in the addend concentration. It is impossible to find the equilibrium concentrations of complexes directly by measurement of optical density of the solution, since it is necessary to know the molecular extinction coefficients of each complex formed in the system. If only one coloured compound is formed in solution, the calculation of equilibrium constants is comparatively simple[44,49,51]. However, considerable difficulties arise when several complexes are formed in the system. The calculation of stability constants with stepwise complex formation from a study of physico-chemical properties of solutions (including optical density) was examined by Yatsimirskii[52] and Bjerrum[53].

Lot of work has been done on the complexes between various ligands and metal ions. 2:4 Dihydroxybenzoic; 2-hydroxy-3-

naphthoic and 3:5 dinitrosalicylic acids are colorimetric reagents used for the estimation of cations. Tanabe and Hata[54] studied the colour reactions of various acids with cobalt and copper in presence of 2-3 drops of 28% ammonia. 2:4 Dihydroxybenzoic acid also gives colour reaction with chlorine and o-toluidine[55]. The complexes of this acid with calcium, iron, aluminium have been studied gravimetrically by various authors[56-58]. Srivastava et al.[59-60] studied complexes of titanium and tungston with 3:5 dinitrosalicylic acid which is used in analysis of sugar, gravimetrially. The studies on stability of complexes of trivalent metal ions with 3:5 dinitrosalicylic acid have also been made by Kuznetsov and Basargincow[61] potentiometrically.

3 Complexes between surface-active substances

The polarographic method first described by Heyrovsky in 1922 consists in recording current vs. voltage curve using a dropping mercury electrode. Alternating current polarography refers to the technique in which a small alternating potential or sinusoidal form is superposed on to the direct potential, under polarographic conditions, and the resulting alternating current is measured. The term "a.c. polarography" is used in connection with study of electron transfer reactions. The same experimental technique can also be used to study the behaviour of surface-active substances which produce capacity changes at the interface even in absence of electron transfer. The study of surfactants by this method has been termed "Tensammetry".

Very little data are available in literature on electrode processes in presence of adsorbed film, studied by a.c. polarography. Breyer and Hacobian[62] observed that when a mixture of two surface-active substances was present in a solution of an indifferent supporting electrolyte, only tensammetric wave was obtained, corresponding to that substance whose peak potential, 'E_s', occurred at more negative potential. They also found[63] that certain depolarizers freely penetrate surface films and yield good a.c. waves even after addition of surface-active substance such as p-nitrophenol in presence of octyl alcohol. Gupta and Sharma[64] also investigated the influence of tensammetric waves on one another by a.c. polarography and found that in most of the cases studied, the influence of more cathodic tensammetric peak on less cathodic peak is due to greater adsorbility of the surface-active substance corresponding to more cathodic peak and consequently forming a unimolecular film on the electrode surface. In some cases the influence is due to some interaction between two surface-active substances to form a complex which is more surface-active than the individual surfactants.

The author successfully applied tensammetry for the study of the complexes between surface-active substances. He has also confirmed such complexes by electrical conductivity and infra-red spectrophotometry.

4 Proposed work by the candidate

The present work deals with the detailed and systematic studies of determining thermodynamic ionization constants of

2-hydroxy-3-naphthoic acid, 2:4 dihydroxy benzoic acid, 3:5 dinitrosalicylic acid and 3:5 dinitrobenzoic acid spectrophotometrically on which no data are available in literature. The ionization constants of these acids have been determined at various temperatures and the thermodynamic functions like change of free energy, enthalpy, entropy and heat capacity for ionization process are calculated and equations relating these thermodynamic functions with absolute temperature given. The ionization constants of these acids have also been obtained in different methanol-water mixtures.

Thermodynamic ionization constants of ortho, meta and para toluic acids and p-fluorobenzoic acid along with their thermodynamic functions at various temperatures have been determined with special reference to their structural influence on ionization constant.

The water soluble coloured and colourless complexes formed by the interactions of 2-hydroxy-3-naphthoic acid, 2:4 dihydroxybenzoic acid, and 3:5 dinitrosalicylic acid with some di and trivalent metal ions,on which no data are available in literature, have been studied spectrophotometrically. The composition of the complexes thus formed are established using Job's method of continuous variation, slope-ratio method and molar-ratio method and confirmed conductometrically. The instability constants of the complexes at various ionic strength and at different temperatures have been obtained and the values of ΔF, ΔH and ΔS calculated. The probable structure of these complexes has also been proposed.

Attempts have also been made to study complexes between surface-active substances, viz., complexes of pyridine with o-cresol and n-amylalcohol in aqueous medium, by a.c. polarography and their confirmation by conductometry and infra-red spectrophotometry.

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P A R T II

TECHNIQUE AND RESULTS

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Technique

The absorbance measurements were made by manually operated Hilger Uvispeck spectrophotometer (Model H700-308 of Hilger & Watts. Ltd., London) using 1 cm. matched silica cells. The cell compartment was equipped with a jacket through which water could be circulated from a thermostat (Townson & Mercer). The thermostat was maintained at the desired temperature between 10 to 60°C. It was seen that the temperature of flowing water remained constant with an accuracy of ± 0.1°C.

A direct reading pH meter (Philips PR 9400) was used for pH measurements which could read with an accuracy of ± 0.01. Conductivity meter (type LRB, Wissenschaftlich - Technische Werkstatten, Germany) with a titration cell (LTI), which had a thermostatic jacket for temperature stability, was used for conductance measurements.

There are many methods available for the determination of the electrical double layer capacity. The bridge method[1] adopted by Grahame is undoubtedly the most precise but it is very laborious. On the other hand, the a.c. polarographic technique developed by Breyer and Gutman[2] and modified by Doss and

Kalyanasundaram[3] as well as by Doss and Gupta[4] is shown to be very convenient for such investigation. This technique essentially consists in applying to a d.m.e., an a.c. ripple of low amplitude over the d.c. potentials and measuring the a.c. component of the pulsating current by measuring the a.c. voltage drop across the resister put in series with the d.m.e. This is done by feeding the voltage to an amplifier (Brüel and Kjaer, vacuum tube voltmeter, type 2407, Copenhagen (least count 0.2 mV and maximum amplification 60 db) and applying the amplified and rectified current into a galvanometer. The voltage drop resister consists of a resistance box, the magnitude of resistance necessary for producing a particular voltage drop being measured for calculating the current passing. This has rendered the measuring the system independent of the frequency of the ripple[3].

The infra-red spectra in the O-H stretching region were studied by employing Carl-Zeiss UR 10 spectrometer with lithium fluoride optics and in the overtone region with a Cary-14R spectrophotometer with variable temperature cells.

Results

Spectrophotometric determination of the thermodynamic ionization constants of some organic acids in aqueous medium and related thermodynamic functions.

This work deals with the spectrophotometric determination of the thermodynamic ionization constants of 2-hydroxy-3-naphthoic acid, 2:4 dihydroxybenzoic acid and 3:5 dinitrosalicylic acid and their confirmation with potentiometric method. The thermodynamic

ionization constants of 3:5 dinitrobenzoic acid, ortho, meta, para toluic acids and p-fluorobenzoic acid have also been determined in aqueous medium spectrophotometrically and results are shown as a function of absolute temperature by the equation $pK_a = A/T + B + CT$. In case of 2-hydroxy-3-naphthoic acid, ortho, meta, para toluic acids p-fluorobenzoic acid and 3:5 dinitrobenzlic acid, the ionization constants decrease with increase of temperature showing that ionization process in each case is exothermic and have large negative heats of ionization. The ionization processes of 2:4 dihydroxybenzoic acid and 3:5 dinitrosalicylic acid are endothermic and have large positive heats of ionization. The thermodynamic functions like change in free energy, enthalpy, entropy and heat capacity for all the acids have been calculated from the temperature coefficients and equations relating these thermodynamic functions with absolute temperature given. All the thermodynamic functions except ΔS for 2:4 dihydroxybenzoic acid and 3:5 dinitrosalicylic acid show increase in magnitude (with sign) with increase in temperature. Their limits of deviation between observed and calculated values are given.

The pK_a values for all the acids increase with increase of ionic strength and can be related by equation $pK_a = A + BI$ up to an ionic strength of 0.1. The ionization constant of each acid has been obtained in various methanol-water mixtures. It was found that the values of ionization constants for all acids decrease up rapidly up to a concentration of 40% methanol in the mixture but concentrations greater than this produce slow

decrease in the value of ionization constant. The decrease of ionization constant with increase of methanol composition in the mixture is related to the dielectric constant of the medium which decreases with the increase of methanol percentage. The decrease in the extent of solvation of the ionic species by increasing concentration of methanol may also have some influence in decreasing ionization constant. The medium effect has been expressed by Born's equation. Assuming ions to be rigid spheres and the radius of hydronium ion which is associated with the ions of the acid to be approximated by that of the water molecules, the estimated radius of each acid ion has been calculated.

The change in acid strength with the change of molecular structure has been explained on the basis of I and T effects. The observation that the substituent group fluoro has little effect is due to the fact that -I and +T properties oppose each other and -I effect predominates over +T effect whereas the large effect of methyl group is due to the fact that +I and +T effects are in the same direction. In the para position the I effect should be smaller than in meta position because of the increased distance. Thus the strength of benzoic acid is decreased by a methyl group in the para position even more than in the meta position. In almost every set of isomers the ortho is the strongest acid, and even when a substituent has both +I and +T properties, the resultant acid is stronger than benzoic acid.

The effect of substituents has been treated by modified

Hammett equation. The plot of pK_a of substituted benzoic acids against substitution constants gives a straight line and from the slope of this straight line, the value of reaction constant has been calculated to be 1.01 which agrees well with the literature value of 1.0.

Spectrophotometric and conductometric studies of the complexes of 2-hydroxy-3-naphthoic acid in aqueous medium.

This work deals with detailed and systematic studies of the interactions of 2-hydroxy-3-naphthoic acid with uranyl, iron aluminium and beryllium ions in aqueous medium.

The following are the main results obtained as a result of these investigations:-

1. The orange-coloured water soluble complex formed by the interaction of uranyl ion and 2-hydroxy-3-naphthoic acid has been studied spectrophotometrically in aqueous medium. It has an absorption maximum at 450 mμ and a flat region thereafter. The optimum pH range is 4.5 to 4.8 and it is stable towards time. The formula of the complex, established spectrophotometrically and conductometrically is UO_2R. The molecular extinction coefficient is 4.16×10^2. The instability constant of the complex has been determined for different ionic strengths and temperatures. The value of ΔH and ΔS are found to be -5.104 k.cal/mole and 37.2 ± 0.2 e.u. respectively. The probable structure of the complex is also suggested.

2. Ferric ion forms a blue, water soluble 1:1 complex with 2-hydroxy-3-naphthoic acid with maximum absorbance at 570 mμ.

The pH range of constant maximum absorbance is 2.3 to 3.1. The molecular extinction coefficient of the complex is 2.30×10^3. The dissociation constant of the complex has been obtained for various ionic strengths and temperatures, and the values of ΔH and ΔS have been calculated.

3. The colourless complex formed by 2-hydroxy-3-naphthoic acid with aluminium has been studied in aqueous solutions of different ionic strengths and at different temperatures spectrophotometrically. The molecular composition has been determined by Job's method of continued variation and is found to be AlR. The values of ΔH and ΔS are found to (-9.45 ± 0.15) k. cal/mole and (52.2 ± 1.5) e.u. The probable structure of the complex is also suggested.

4. Spectrophotometric method has been employed to study the colourless complex formed by beryllium with 2-hydroxy-3-naphthoic acid in aqueous solutions of different ionic strengths and at various temperatures. The molecular composition has been determined by Job's method of continued variation and is found to be BeR. The probable structure of the complex is also suggested conductometrically.

Spectrophotometric and conductometric studies of complexes of 2:4 dihydroxybenzoic acid in aqueous medium

This work deals with the detailed and systematic studies on coloured complexes of 2:4 dihydroxybenzoic acid with cupric ions in acidic medium and in presence of ammonia. The colourless complexes of this acid with Al^{+3} and Be^{+2} ions have been

studied spectrophotometrically. Polarographic method has also been applied to confirm the complexes of 2:4 dihydroxybenzoic acid with Fe^{+3} and Cu^{+2} ions. The following are the results obtained in this investigation.

1. The reddish violet complex formed by 2:4 dihydroxybenzoic acid with cupric ions in presence of ammonia has been studied in aqueous solutions of different ionic strengths and at different temperatures. It has an absorption maximum at 490 mμ. The optimum pH range is 10.0 to 11.0. The molecular composition of the complex has been determined by Job's method of continued variation, slope-ratio method and molar-ratio method and is found to be 1:1. The molecular extinction coefficient of the complex is 1.53×10^3. The values of ΔH and ΔS are found to be -2.30 k.cal/mole and 28.4 e.u. respectively. The probable structure of the complex is suggested.

2. Cupric ion forms a green, water soluble complex with 2:4 dihydroxybenzoic acid with maximum absorption at 390 mμ in acidic medium. The complex is stable to wide temperature variation and at the pH range of 5.0 to 6.0. The molecular extinction coefficient is 0.54×10^2. The formula of the complex, established spectrophotometrically and conductometrically, is CuR. The instability constant of the complex has been determined at various ionic strengths and at different temperatures and the values of ΔH and ΔS given. The probable structure of the complex is also suggested.

3. The colourless complex formed by 2:4 dihydroxybenzoic acid with aluminium has been studied in aqueous studies of

different ionic strengths and at different temperatures spectrophotometrically. The molecular composition has been determined by Job's method of continued variation and is found to be A1R. The quantities ΔH and ΔS have been calculated from the temperature coefficient of the instability constant. The probable structure of the complex is also suggested.

4. The colourless complex formed by the interaction of beryllium with 2:4 dihydroxybenzoic acid has been studied spectrophotometrically in aqueous solutions of different ionic strengths and at different temperatures. The molecular composition of the complex has been determined by Job's method of continued variation and molar-ratio method and is found to be 1:1. The values of ΔH and ΔS are calculated to be-(1.49±0.2) k.cal/mole and (24.7 ± 1.5) e.u. The probable structure of the complex is also suggested.

5. Complexes of cupric and ferric ions with 2:4 dihydroxybenzoic acid in aqueous medium have been studied successfully by a.c. polarography. The results obtained are in good agreement with the values obtained by spectrophotometric method except for the dissociation constant for the complex between ferric ion and the acid.

Spectrophotometric studies on the composition and stability constant of the complex between 3:5 dinitrosalicylic acid and ferric ions in aqueous medium

The composition of orange coloured water soluble complex formed by 3:5 dinitrosalicylic acid with ferric ions has been studies by Job's method of continued variation, slope-ratio

method and molar-ratio method spectrophotometrically. It has an absorption maximum at 450 mμ. The optimum pH range is 2.7 to 3.2. The molecular extinction coefficient of the complex is 2.10×10^3. The values of ΔH and ΔS are found to be -7.38 k.cal and 49.2 e.u. respectively.

Studies on the complexes of pyridine with o-cresol and n-amyl alcohol in aqueous medium by Tensammetry and Infra-red spectrophotometry.

1. By tensammetry, the ratios of o-cresol to pyridine and n-amyl alcohol to pyridine in the complex are found to be 1:1 and 1:3 respectively, the same ratios of the surfactants in the complexes found conductometrically. It has been shown that n-amyl alcohol forms micelles in aqueous solution at concentrations greater than 0.25 per cent. It is concluded that tensammetry can be successfully applied for the investigation of the composition of the complexes between surface-active substances.

2. Infra-red measurements show the strong interactions between o-cresol and n-amyl alcohol with pyridine. The average 1:1 equilibrium constant for o-cresol and pyridine complex at 25°C is about $21^{lm^{-1}}$. The $\Delta\upsilon_{OH}$ is about 500 cm^{-1}. The 1:1 equilibrium constant for n-amyl alcohol and pyridine complex is approximately 1 liter per mole and the frequency shift of the O-H stretching bond is about 420 cm^{-1}. Apparently the enthalpy of formation of the hydrogen bond is of the order of 4 k.cal/mole.

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P A R T III

CHAPTER I TO CHAPTER V

CHAPTER I

SPECTROPHOTOMETRIC DETERMINATION OF THE THERMODYNAMIC IONIZATION CONSTANTS OF SOME ORGANIC ACIDS

PAPER No. 1

SPECTROPHOTOMETRIC DETERMINATION OF THE THERMODYNAMIC IONIZATION CONSTANT OF 2-HYDROXY-3- NAPHTHOIC ACID IN WATER FROM 10 TO 50° AND RELATED THERMODYNAMIC QUANTITIES

SPECTROPHOTOMETRIC DETERMINATION OF THE THERMODYNAMIC IONIZATION CONSTANT OF 2-HYDROXY-3-NAPHTHOIC ACID IN WATER FROM 10 TO 50° AND RELATED THERMODYNAMIC QUANTITIES

The thermodynamic ionization constant (K_a) of 2-hydroxy-3-naphthoic acid in aqueous solution from 10 to 50° is derived from the measurements of the absorption spectrum of the acid in different buffer solutions. The results are given as a function of temperature (T) in °K by an equation $pK_a = 1548.611/T - 8.68660 + 0.0243121\ T$. The thermodynamic quantities like changes of free energy (ΔF), enthalpy (ΔH) entropy (ΔS), and heat capacity (ΔCp) for the dissociation process are calculated from the temperature coefficient of the dissociation constant. The equations relating these thermodynamic functions with absolute temperature are also given. The "pK_a" of the acid increases linearly with increase in ionic strength and can be expressed by the equation $pK_a = 3.6990 + 3.3733\ I$ up to an ionic strength (I) of 0.10. The values of "K_a" have also been obtained for various methanol-water mixtures.

2-Hydroxy-3-naphthoic acid forms coloured complexes with Fe^{+3} and UO_2^{+2} ions in aqueous solution[1]. This communication

reports the determination of thermodynamic ionization constant of the above acid in aqueous solution spectrophotometrically and its confirmation by potentiometric method. These studies have also been extended to the determination of "K_a" at different temperatures and the related thermodynamic quantities like change in free energy, entropy, etc., on which no data are available in literature. The effect of ionic strength has been studied and the values of K_a have also been determined in various methanol-water mixtures.

EXPERIMENTAL

2-Hydroxy-3-naphthoic acid was B.D.H., L.R. quality and was recrystallised before use. Sodium perchlorate (E.Merck) was used for maintaining ionic strength. Sodium acetate, potassium hydroxide, acetic acid (B.D.H., A.R.) and formic acid (May & Baker) were used for preparing buffer solutions. Methanol was of B.D.H., A.R. quality and was redistilled in an all glass fractionating system and the middle one-third of the distillate was used for experiments. All the solutions were prepared in conductivity water. The technique and details have been described earlier.

RESULTS AND DISCUSSION

Fig. 1 gives the absorption spectrum of 2.0×10^{-4} M of 2-hydroxy-3-naphthoic acid in aqueous medium. Curve 1, refers to the acid standard and curve 2 to the base standard. The

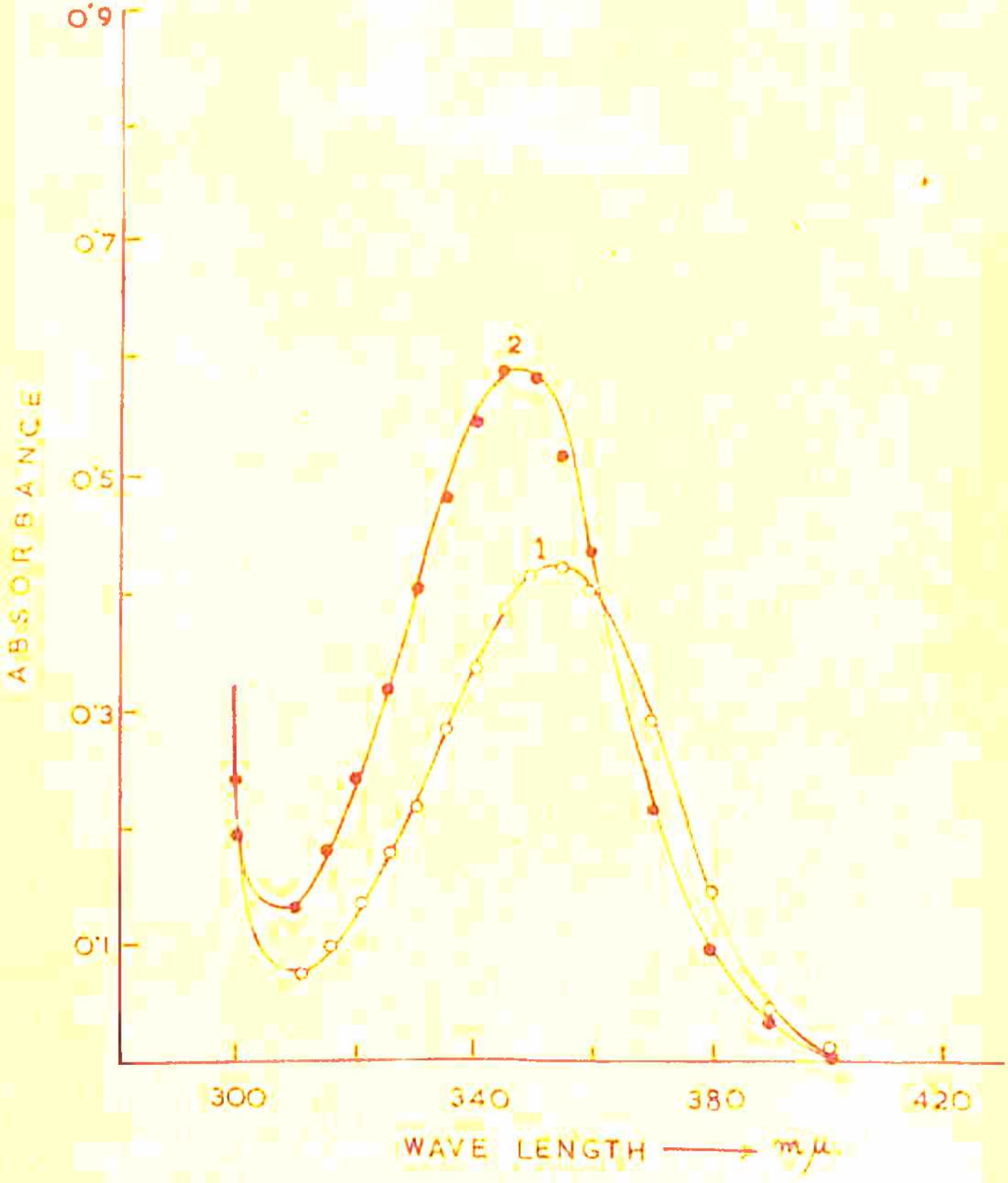

FIG. 1

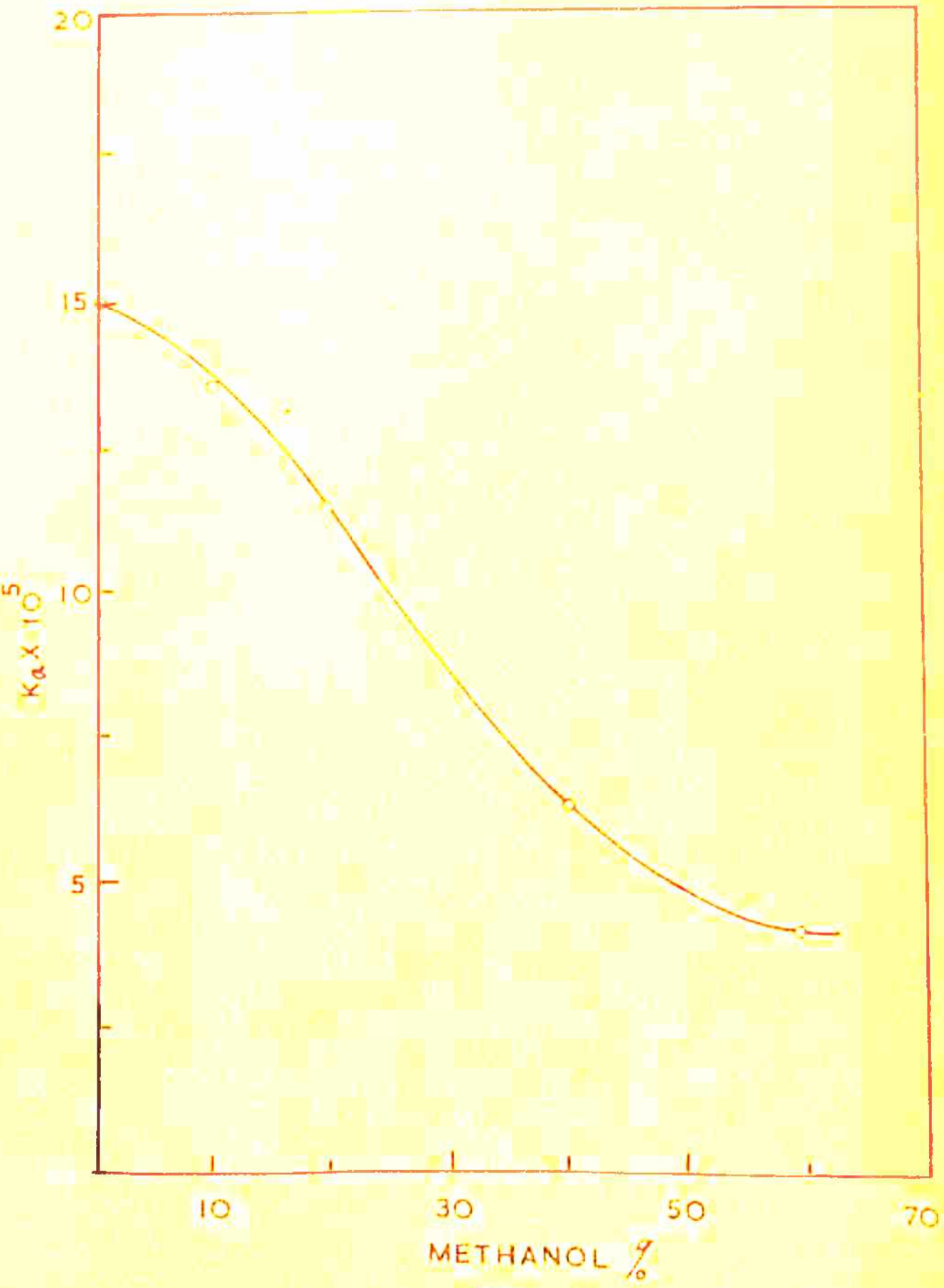

FIG. 2

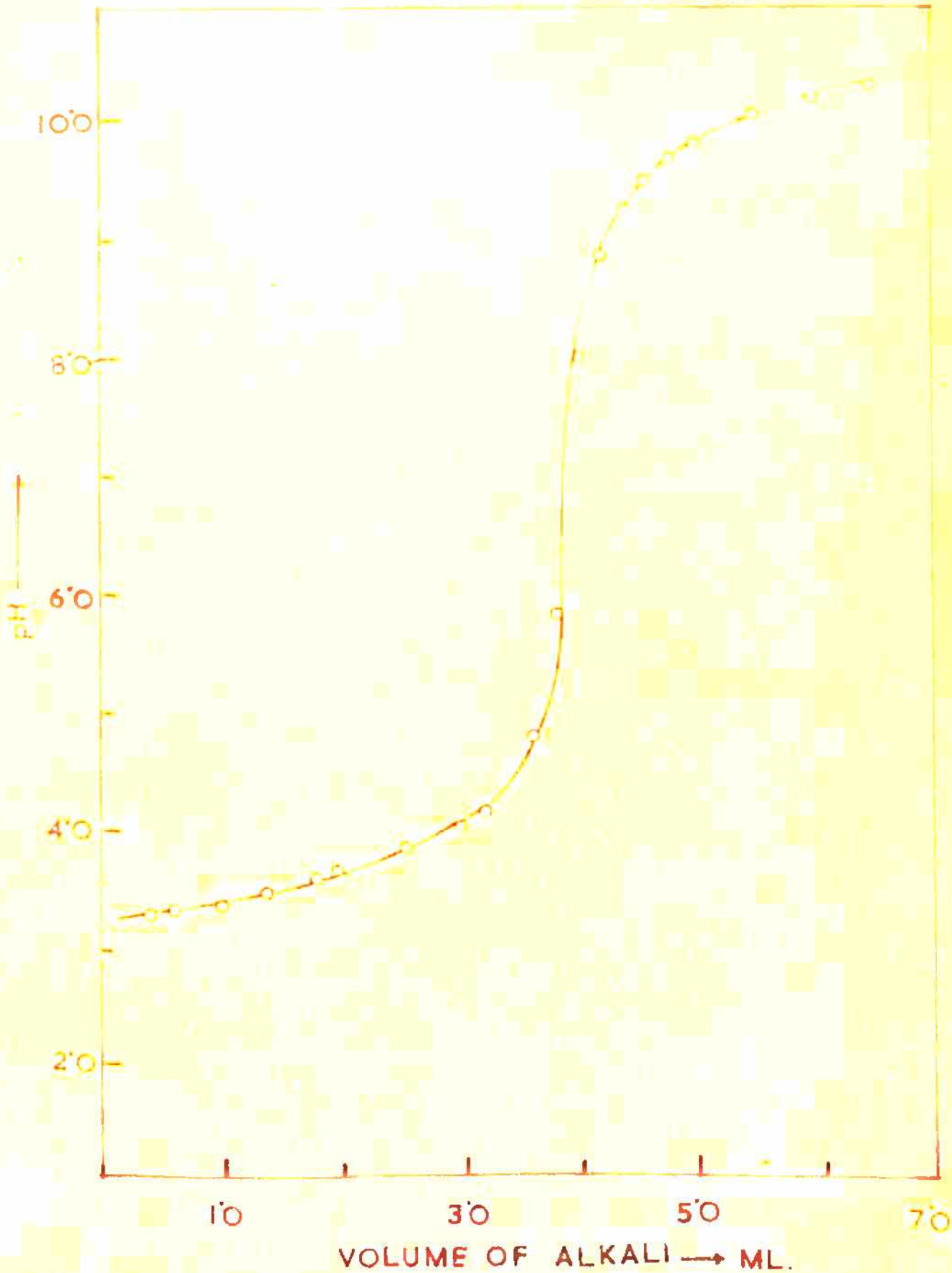

FIG. 3

LEGEND OF FIGURES

Fig. 1: Absorption spectrum of 2-hydroxy-3-naphthoic acid in aqueous medium ($C = 2.0 \times 10^{-4}$ mole/l).

Curve 1: Acid standard (0.1 M HCl)

Curve 2: Base standard (0.1 M NaOH)

Fig. 2: Thermodynamic ionization constant of the acid in various methanol-water mixtures.

Fig. 3: Thermodynamic ionization constant of the acid by potentiometric method.

measurements have been made at wavelength of 340 mμ, at which different ionic forms of the acid have maximum absorption difference. Two sets of buffer solution (i) sodium acetate and acetic acid (ii) formic acid and potassium hydroxide, were used. The ionization constant K_a is given by the equation -

$$pK_c = pH + \log \frac{b-e}{e-a} \qquad \ldots \quad (i)$$

where pH is that of the buffer solution of the acid having absorption "e" and "a" and "b" are the absorbances of the same concentration of the acid in (0.1 M) acid and (0.1 M) base respectively. Further, the value of the thermodynamic ionization constant (K_a) may be calculated by the equation[2] -

$$pK_a = pK_c + \frac{I^{1/2}}{1 + I^{1/2}} \qquad \ldots \quad (ii)$$

where "I" is the ionic strength of the buffer solution.

Table I gives the calculated values of pK_a using two different sets of buffer solutions. It is seen that in both the cases the pK_a values were found to be constant within the limits of ± 0.04 unit of pK_a. Further, the values of pK_a at various ionic strengths of the buffer solution were determined and it can be seen from Table II that "pK_a" increases with increase in ionic strength. This increase in pK_a with ionic strength is linear up to a ionic strength of 0.1 and could be expressed by the equation -

$$pK_a = 3.6990 + 3.37330\ I \qquad \ldots \quad (iii)$$

Table I

Ionization constant of 2-hydroxy-3-naphthoic acid in aqueous medium.

Concn. of acid = 2.0×10^{-4}M; λ = 340 mμ; Temp. = 30°.

'b' (in 0.1 M NaOH) = 0.535; 'a' (in 0.1 M HCl) = 0.319

Sl. No.	Buffer	pH	e.	pK_c	pK_a
1.	Formic acid and Potassium hydroxide	3.25	0.378	3.68	3.78
		3.45	0.401	3.66	3.75
		3.50	0.407	3.66	3.76
		3.55	0.408	3.69	3.79
2.	Sodium acetate and acetic acid	3.25	0.379	3.66	3.72
		3.30	0.384	3.65	3.72
		3.40	0.392	3.68	3.75

Average value of pK_a = 3.75

Table II

Effect of ionic strength on the ionization of 2-hydroxy-3-naphthoic acid in aqueous medium

Ionic strength	pK_a(Obs.)	pK_a(Calc.)*
0.01	3.75	3.74
0.03	3.80	3.80
0.06	3.91	3.90
0.09	4.00	4.00
0.11	4.10	4.07
0.21	4.19	4.40

* $pK_a = 3.6990 + 3.3733\ I$

where I has the usual significance. The calculated values of pK_a by the equation are shown in the third column of Table II showing good agreement with the observed values. The increase in pK_a with increase of ionic strength is due to the lowering of activity coefficient of the ionic species with increase of ionic strength.

Table III records the values of pK_a at different temperatures. The results in this table show that pK_a increases with increase in temperature and corresponding values could be expressed by the equation -

$$pK_a = A/T - B + C\,T \qquad \ldots \quad (iv)$$

where A, B and C are constants with following values -

$$A = 1548.611; \quad B = 8.68660 \quad \text{and} \quad C = 2.43121 \times 10^{-2}$$

The calculated values of pK_a from the above equation are recorded in the third column which agree with the observed values, (second solumn) in Table III. The fact that the enthalpy change (ΔH) is negative (vide Table IV) indicates that the dissociation of the acid in aqueous solution is exothermic process. The value of K_a, therefore decreases with increase of temperature. The decrease of K_a with increase of temperature may also be related to the dielectric constant of the medium which decreases with increase of temperature[3].

From Eq.(iv) are obtained the values of the change of free energy (ΔF), heat content (ΔH), entropy (ΔS), and heat capacity (ΔCp) of the dissociation of 2-hydroxy-3-naphthoic acid. These

are recorded in Table IV. All the thermodynamic functions shown in this table increase in magnitude (with sign) linearly with of temperature. These relations can be expressed by the equations:

$$\Delta F = 29433.0 - 164.67\ T + 0.46250\ T^2\ j.mole^{-1} \quad \ldots \quad (v)$$

$$\Delta H = -0.12396\ T^2\ j.mole^{-1}. \quad \ldots \quad (vi)$$

$$\Delta S = -30.368 - 0.26475\ T^2\ j.deg^{-1}.mole^{-1} \quad \ldots \quad (viii)$$

$$\Delta Cp = -0.26425\ T\ \ j.deg^{-1}.mole^{-1}. \quad \ldots \quad (viii)$$

These equations are valid from T = 283.16 °K to 323.16 °K. The limits of deviations between the observed and the calculated values of these thermodynamic functions are as follows:-

$\Delta F = \pm 20.j.mole^{-1}$;

$\Delta H = \pm 3.0\ j.mole^{-1}$;

$\Delta S = \pm 0.3\ j.deg^{-1}.mole^{-1}$;

$\Delta Cp = \pm 0.02\ j.deg^{-1}.mole^{-1}$.

Fig. 2 shows the nature of the curve obtained by plotting "K_a" vs. different compositions of the methanol-water mixture. The value of K_a decreases rapidly up to a concentration of 40% methanol in the mixture but concentrations greater than this produce slow decrease in value of K_a. This is related to the decrease of the dielectric constant of the medium by increasing the percentage of methanol in the mixture. The decrease in the extent of solvation of ionic species by increasing the concen-

Table III

Determination of ionization constant of 2-hydroxy-3-naphthoic acid in aqueous medium at different temperatures.

Temp.°K	pK_a(Obs.)	pK_a(Calc.)*
283.16	3.67	3.67
293.16	3.73	3.72
303.16	3.79	3.79
313.16	3.86	3.87
323.16	3.96	3.96

* $pK_a = 1548.611/T - 8.68660 + 0.0243121\ T$.

Table IV

Thermodynamic functions for the ionization of 2-hydroxy-3-naphthoic acid in aqueous medium from 10 to 50°.

Temp. °K.	ΔF ($j.mole^{-1}$)	ΔH ($j.mole^{-1}$)	ΔS ($j.deg^{-1}.mole^{-1}$)	ΔCp ($j.deg^{-1}.mole^{-1}$)
283.16	19886	- 9938	- 105.3	- 74.8
293.16	20959	-10652	- 107.8	- 77.5
303.16	22016	-11392	- 110.2	- 80.1
313.16	23161	-12155	- 112.8	- 82.7
323.16	24517	-12944	- 115.9	- 85.4

tration of methanol in mixture may also have some influence in decreasing the value of K_a.

Attempts have also been made to calculate thermodynamic ionization constant of 2-hydroxy-3-naphthoic acid by titrating 40 ml. of 10^{-3}M acid with 10^{-2}M alkali potentiometrically (Fig. 3). The value of pK_a was found to be 3.74 which agrees with the value of 3.75 obtained spectrophotometrically.

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PAPER NO. 2

THERMODYNAMIC IONIZATION CONSTANTS OF 2:4 DIHYDROXYBENZOIC ACID AND RELATED THERMODYNAMIC FUNCTIONS IN AQUEOUS MEDIUM FROM SPECTROPHOTOMETRIC MEASUREMENTS

THERMODYNAMIC IONIZATION CONSTANTS OF 2:4 DIHYDROXYBENZOIC ACID AND RELATED THERMODYNAMIC FUNCTIONS IN AQUEOUS MEDIUM FROM SPECTROPHOTOMETRIC MEASUREMENTS

The thermodynamic ionization constants of 2:4 dihydroxybenzoic acid in aqueous solution are determined by spectrophotometric measurements. The results are shown as a function of temperature (T) in degrees kelvin by equations -

$$pK_1^T = -5.6987 \times 10^2/T + 8.2464 - 0.010083\ T \quad \text{and}$$

$$pK_2^T = 86.224/T + 9.0440 - 0.0014476\ T.$$

The thermodynamic quantities like change of free energy (ΔF), enthalpy (ΔH), entropy (ΔS) and heat capacity (ΔCp) for both the ionization processes are calculated. The equations relating these thermodynamic quantities with absolute temperature are given. The thermodynamic ionization constants in various methanol-water mixtures have also been obtained and the radius of the acid ion has been calculated.

2:4 Dihydroxybenzoic acid is an analytical reagent for the determination of various bivalent and trivalent metal ions. Gupta et al.[1,2,3] reported the complexes of 2:4 dihydroxybenzoic

acid with Cu^{+2}, Fe^{+3} and Al^{+3}, etc. The first ionization constant of this acid has been determined by various authors[4,5,6]. As no data are available in literature about the ionization constant at various temperatures and in various methanol-water mixtures, the author has undertaken this study to calculate the thermodynamic functions from spectrophotometric measurements.

EXPERIMENTAL

A recrystallised B.D.H., L.R. sample of 2:4 dihydroxybenzoic acid was used for preparing standard solution. Chloroacetic acid, formic acid, potassium hydroxide, borax, boric acid, potassium dihydrogen phosphate and disodium hydrogen phosphate were of B.D.H., AnalaR quality, used for preparing buffer solutions. Potassium chloride (B.D.H., A.R.) was used for varying ionic strength.

Methanol was of B.D.H., AnalaR quality and was redistilled in all glass fractionating system and the middle one-third of the distillate was used for the experiments. All the solutions were prepared in conductivity water. The technique and other details have been described earlier.

RESULTS AND DISCUSSION

The absorption curves of 2:4 dihydroxybenzoic acid in aqueous solutions are recorded in the region 230-310 mμ. The results of these measurements are shown in Fig. 1. The absorption curves of the solutions containing same concentration of

2:4 dihydroxybenzoic acid at different pH values were obtained and it was interesting to note that in the wavelength range of 260 to 270 mμ, absorption of the solutions were decreased from pH 1.0 to 6.5 and there was sudden increase in the absorption after 6.5 pH. The analytical wavelengths have been selected such that the difference between the absorbances of various species was as great as possible and only a small variation of absorbance occurred when the wavelength was changed. To meet this condition, wavelengths from 260 to 270 mμ were in good agreement for determining the ionization constants. Solutions of 8.0×10^{-5}M of 2:4 dihydroxybenzoic acid were used in this investigation, so that the optical densities lay in the most sensitive range of the instrument. The pK^T values were calculated in the same way as described earlier[7].

Two sets of buffer solutions of constant ionic strength[8] (i) chloroacetic acid and potassium hydroxide and (ii) formic acid and potassium hydroxide were used to calculate first ionization constant of the acid. Boric acid and sodium borate buffer was used for the determination of second ionization constant. The measurements of optical density at different wavelengths and at different pH values gave consistant values of ionization constants. These are recorded in the Tables, I, II and III.

The ionization constants of 2:4 dihydroxybenzoic acid were calculated at various ionic strengths (vide table IV). It was observed that pK^T values increase with increase of ionic strength and this was due to the lowering of the activity

Table I

First ionization constant of 2:4 dihydroxybenzoic acid in aqueous medium.

Concn. of the acid = 8.0×10^{-5}M. Temp. = 30°

λmu	258	260	262	265
"a" =	0.896	0.827	0.735	0.550
"b" =	0.285	0.215	0.168	0.137

Buffer system : Formic acid - potassium hydroxide

Molarity acid	Molarity base	Absorbance "e" Wave-length - mu				pK1			
		258	260	262	265	258	260	262	265
0.0413	0.0093	.602	.530	.461	.345	3.33	3.33	3.33	3.29
0.0349	0.0094	.565	.498	.426	.323	3.33	3.33	3.32	3.31
0.0303	0.0095	.534	.462	.399	.305	3.34	3.33	3.33	3.34
0.0281	0.0096	.509	.453	.379	.297	3.31	3.35	3.32	3.35
0.0214	0.0097	.446	.377	.321	.238	3.35	3.35	3.36	3.31
0.0186	0.0098	.433	.355	.307	.227	3.35	3.30	3.36	3.30

Average value = 3.33

Table II

Buffer system : Chloroacetic acid - potassium hydroxide

0.0162	0.0089	.664	.607	.513	.398	3.31	3.33	3.29	3.33
0.0139	0.0093	.620	.527	.450	.347	3.38	3.32	3.29	3.31
0.0125	0.0095	.545	.463	.398	.301	3.36	3.33	3.34	3.33
0.0118	0.0095	.510	.450	.366	.284	3.36	3.30	3.32	3.30

Average value = 3.33

Table III

Second dissociation constant of 2:4 dihydroxybenzoic acid in aqueous medium

Concn. of the acid = 8.0×10^{-5} M Temp. = 30°

λ mμ = 260 262 265 268 270

"a" = 0.215 0.168 0.137 0.140 0.150

"b" = 0.810 0.903 1.018 1.091 1.106

Buffer system: Sodium borate and boric acid.

Molarity $Na_2B_4O_7$	Molarity H_3BO_3	Absorbance "e" Wave-length - mμ					pK_2^T Wave-length - mμ				
		260	262	265	268	270	260	262	265	268	270
0.005	0.0264	0.462	0.475	0.507	0.524	0.541	8.89	8.89	8.90	8.91	8.90
0.005	0.0198	0.509	0.513	0.533	0.562	0.582	8.86	8.90	8.94	8.94	8.93
0.005	0.0166	0.524	0.539	0.572	0.605	0.625	8.86	8.89	8.90	8.91	8.90
0.005	0.0139	0.538	0.553	0.593	0.638	0.658	8.87	8.90	8.91	8.90	8.90
0.005	0.0112	0.558	0.583	0.636	0.682	0.684	8.92	8.84	8.93	8.89	8.95
0.005	0.0069	0.580	0.614	0.672	0.726	0.747	8.92	8.91	8.90	8.89	8.88

Average value = 8.90

Table IV

Effect of ionic strength on the ionization of 2:4 dihydroxybenzoic acid in aqueous medium

Temp. = 30°C

Ionic strength	pK_1^T	pK_2^T
0.01	3.33	8.91
0.02	3.35	8.92
0.06	3.39	8.95
0.11	3.43	9.00
0.16	3.46	9.02
0.21	3.48	9.05

Table V.

Thermodynamic ionization constants of 2:4 dihydroxybenzoic acid at different temperatures.

Temp. °K	pK_1^T (Obs.)	pK_1^T (Calc.)*	pK_2^T (Obs.)	pK_2^T (Calc.)+
283.16	3.38	3.38	8.94	8.94
293.16	3.35	3.35	8.91	8.91
303.16	3.31	3.31	8.89	8.89
313.16	3.27	3.27	8.87	8.87
323.16	3.22	3.22	8.84	8.84
333.16	3.18	3.18	8.82	8.82

* $pK_1^T = -5.6987 \times 10^2/T + 8.2464 - 0.010083\ T.$

+ $pK_2^T = 86.224/T + 9.0440 - 0.0014476\ T.$

coefficient of the ionic species with increase in ionic strength. The values of pK_1^T and pK_2^T can thus be computed by extrapolation of the curves to zero ionic strength.

The values of the thermodynamic ionization constants were determined at different temperatures. These are recorded in Table V. The results show that both pK_1^T and pK_2^T decrease with increase of temperature and corresponding values can be expressed by the equations -

$$pK_1^T = -5.6987 \times 10^2/T + 8.2464 - 0.010083\ T \quad \text{and}$$

$$pK_2^T = 86.224/T + 9.0440 - 0.0014476\ T.$$

The values of pK_1^T and pK_2^T calculated from above equations are recorded in these tables which agree well with the observed values. The fact that the enthalpy change (ΔH) is positive indicates that ionization of the acid in aqueous medium is endothermic process. Therefore, the ionization constants increase with the increase of temperature.

The thermodynamic functions like change of free energy (ΔF), enthalpy (ΔH), entorpy (ΔS) and heat capacity (ΔCp) are calculated for the ionization processes. These are recorded in Tables VI and VII. Thermodynamic functions can be expressed by these equations. (For the first ionization process.)

$$\Delta F = -20182 + 216.79\ T - 285.33 \times 10^{-3}\ T^2$$

$$\Delta H = 27.40 + 0.080505\ T^2$$

$$\Delta S = -82.019 + 0.14194\ T \quad \text{and} \quad \Delta Cp = 0.14194\ T.$$

Table VI

Thermodynamic functions for the first ionization of 2:4 dihydroxybenzoic acid at various temperatures in aqueous medium.

Temp.°K	ΔF ($j \cdot mole^{-1}$)	ΔH ($j.mole^{-1}$)	ΔS ($j\text{-}deg^{-1}.mole^{-1}$)	ΔCp ($j.deg^{-1}\ mole^{-1}$)
283.16	18326	6482	- 41.8	40.2
293.16	18788	6948	- 40.4	41.6
303.16	19216	7431	- 38.9	43.0
313.16	19609	7929	- 37.3	44.4
323.16	19914	8443	- 35.8	45.9
333.16	20273	8963	- 34.7	47.3

Table VII

Thermodynamic functions for second ionization of 2:4 dihydroxybenzoic acid at various temperatures in aqueous medium.

Temp.°K	ΔF ($j.mole^{-1}$)	ΔH ($j.mole^{-1}$)	ΔS ($j.deg^{-1}.mole^{-1}$)	ΔCp ($j.deg^{-1}.mole^{-1}$)
283.16	48478	3626	- 158.4	25.6
293.16	50026	3887	- 157.4	26.5
303.16	51666	4157	- 156.7	27.4
313.16	53179	4435	- 155.6	28.3
323.16	54710	4723	- 154.7	29.2
333.16	56284	5019	- 153.9	29.8

The limits of deviation between the observed and calculated values are as follows:-

$\Delta F = \pm 56$ j.mole^{-1};

$\Delta H = \pm 13$ j.mole^{-1};

$\Delta S = \pm 0.28$ j.deg^{-1}.mole^{-1};

$\Delta Cp = \pm 0.02$ j.deg^{-1}.mole^{-1}.

The thermodynamic quantities for the second ionization process can be expressed by following equations:-

$\Delta F = -6.043 \times 10^3 + 2.235 \times 10^2 T - 0.010933\ T^2$

$\Delta H = 0.04522\ T^2$

$\Delta S = -1.8398 \times 10^2 + 0.09040\ T$

$\Delta Cp = 0.0904\ T$ and

the limits of deviations are -

$\Delta F = \pm 56$ j.mole^{-1};

$\Delta H = \pm 4$ j.mole^{-1};

$\Delta S = \pm 0.4$ j.deg^{-1}.mole^{-1};

$\Delta Cp = \pm 0.02$ j.deg^{-1}.mole^{-1}.

The ionization constants of 2:4 dihydroxybenzoic acid have also been calculated in various methanol-water mixtures. Fig. 2 shows the nature of the curves obtained by plotting K_1^T and K_2^T against the compositions of methanol-water mixtures.

It is seen that both K_1^T and K_2^T decrease rapidly up to a concentration of about 40% methanol in the mixture but concentrations greater than this produce slow decrease in the values of ionization constants. This is related to the decrease of dielectric constant of the medium by increasing the percentage of methanol in the mixtures.

Further, if the ions of 2:4 dihydroxybenzoic acid are regarded as rigid spheres having a mean radius r, the medium effect can be expressed by Born's equation

$$-\log \frac{{}_sK^T}{{}_wK^T} = \frac{e^2}{rkT\ 2.303} \left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right)$$

Where ${}_sK^T$ and ${}_wK^T$ are thermodynamic ionization constants of the acid in mixture and water respectively, 'e' the proton charge, 'k' the Boltzmann constant, 'ϵ_s' and 'ϵ_w' are the dielectric constants of the mixture and water respectively. Curves 1 and 2 (Fig.3) show the dependence of the medium effect on the reciprocal of the dielectric constant and curves 3 and 4 show its dependence on the mole fraction of methanol in the mixtures. Thus we obtain straight lines and equations for curves 1 and 2 are -

$$-\log \frac{{}_sK_1^T}{{}_wK_1^T} = -2.876 + \frac{219.0}{\epsilon_s} \quad \text{and}$$

$$-\log \frac{{}_sK_2^T}{{}_wK_2^T} = -2.347 + \frac{251.2}{\epsilon_s} .$$

From the slopes of the straight lines, the mean radii of ions

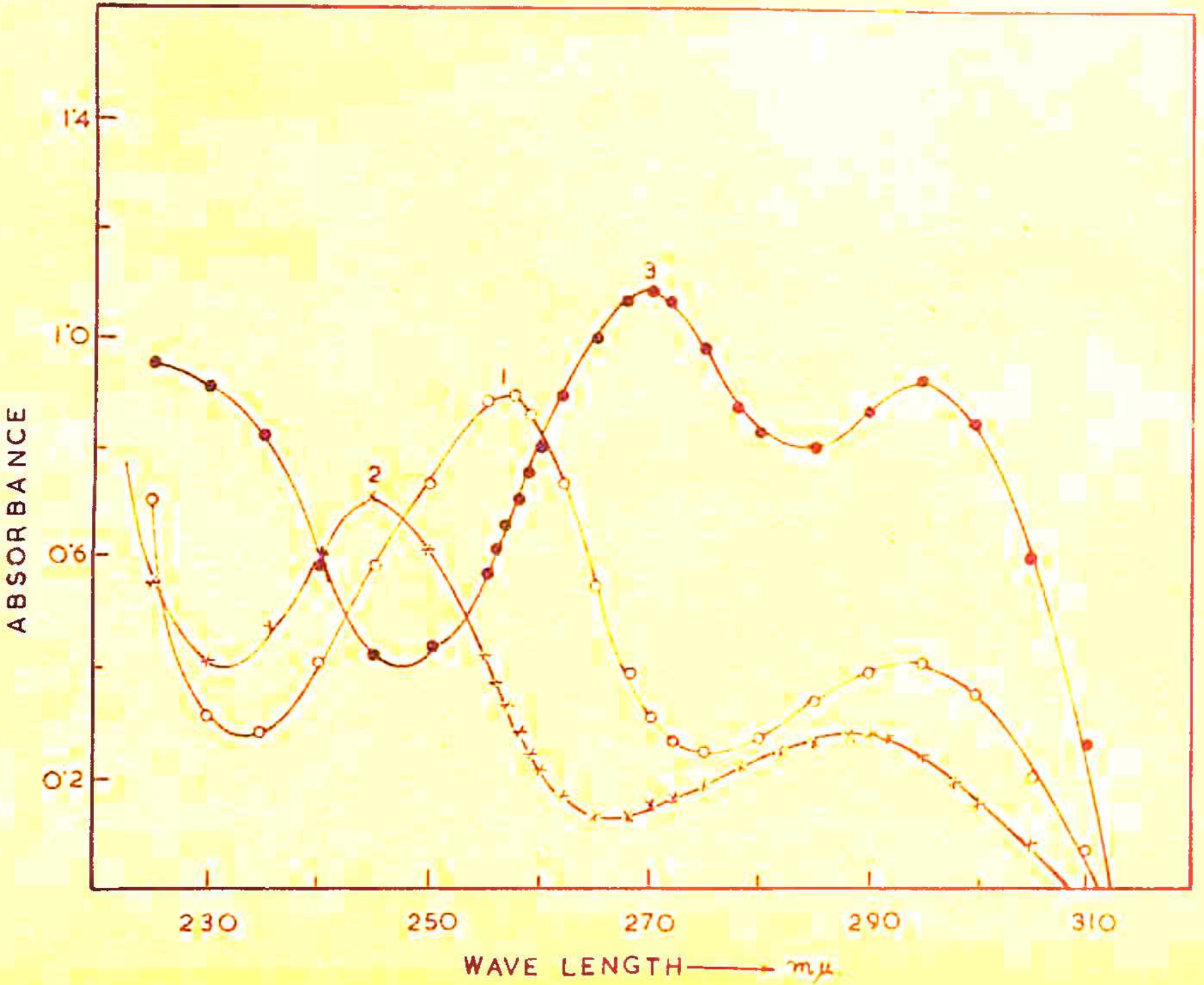

FIG. 1

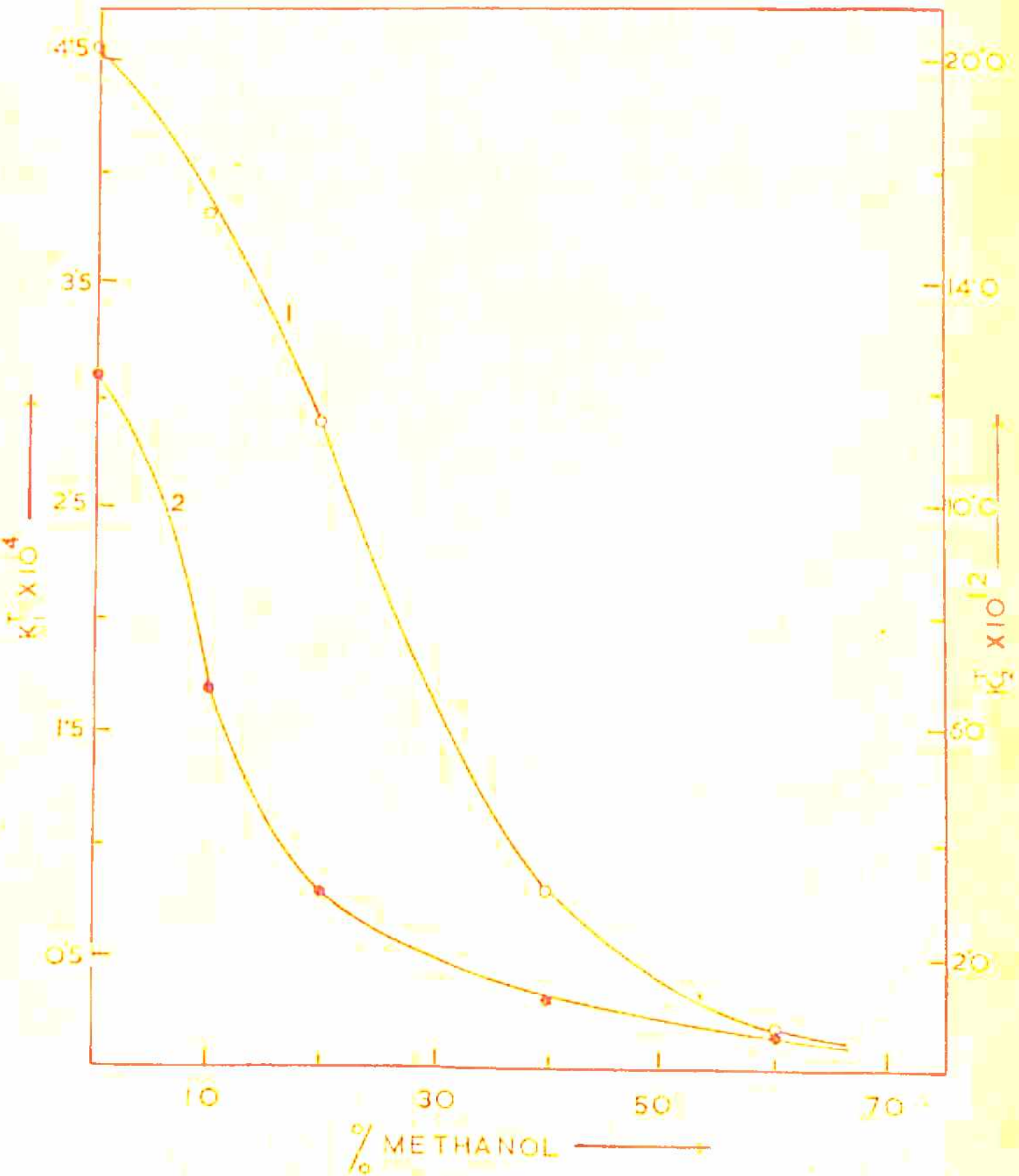
4·5
3·5
2·5
1·5
0·5
$K_1^T \times 10^4$
20·0
14·0
10·0
6·0
2·0
$K_2^T \times 10^{12}$
1
2
10
30
50
70
% METHANOL

FIG. 2

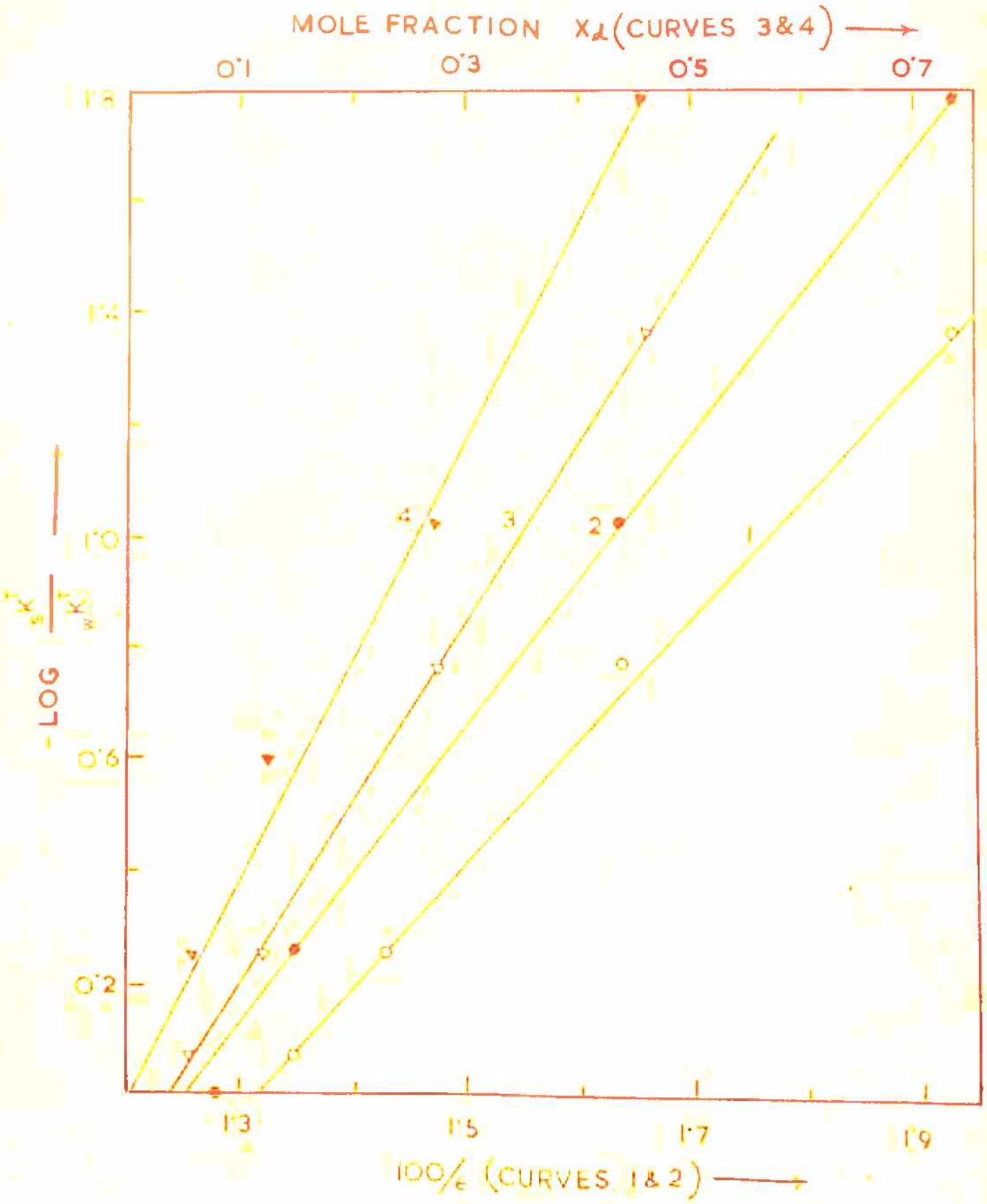
MOLE FRACTION X_d (CURVES 3&4) ⟶
0·1
0·3
0·5
0·7
1·8
1·4
1·0
0·6
0·2
$-\log \frac{K_s^T}{K_w^T}$
1·3
1·5
1·7
1·9
100/ε (CURVES 1&2) ⟶
1
2
3
4

FIG. 3

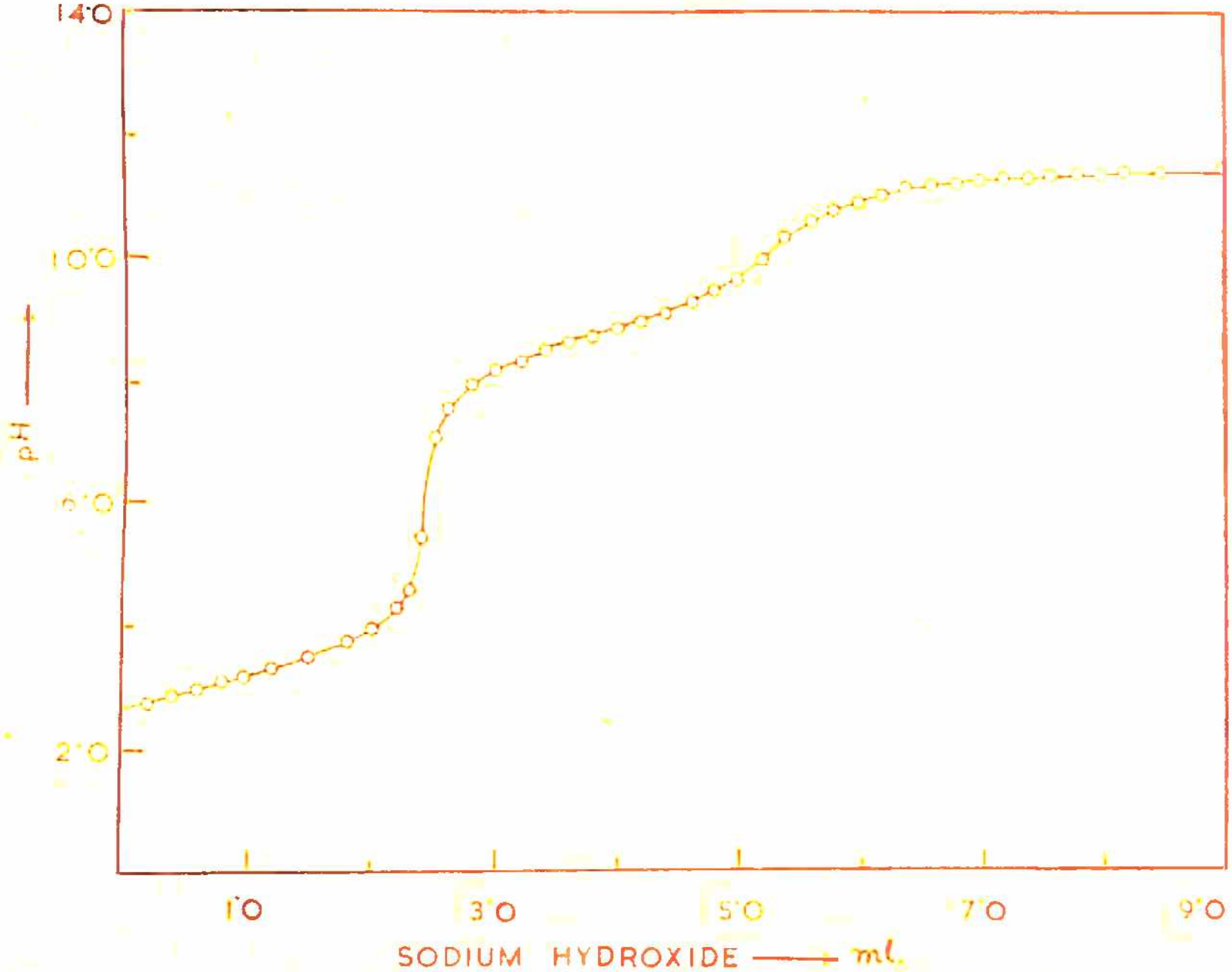

FIG. 4

LEGEND OF FIGURES

Fig. 1: Absorption curves of aqueous solutions of 2:4 dihydroxybenzoic acid (C = 8.0×10^{-5} mole/l).

Curve 1: 4-5 M HCl

Curve 2: pH = 6.5

Curve 3: pH $\approx$ 13

Fig. 2: Ionization constants of 2:4 dihydroxybenzoic acid in various methanol-water mixtures.

Fig. 3: Dependence of the medium effect on the reciprocal of dielectric constant and on the mole fraction of methanol.

Fig. 4: Ionization constants of 2:4 dihydroxybenzoic acid by potentiometric method.

are calculated. Further, the radius of the hydronium ion may be approximated by that of water molecule, 1.4 Å, the radii of acid ions have been calculated to be 0.89 and 0.73 Å.

The pK^T values thus obtained spectrophotometrically are further confirmed by Fig. 4 which gives the potentiometric titration curve of 2:4 dihydroxybenzoic acid with sodium hydroxide. From this curve the value of pK_1^T and pK_2^T are 3.31 and 8.92 at 30°C.

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PAPER No. 3

SPECTROPHOTOMETRIC DETERMINATION OF THE THERMODYNAMIC IONIZATION CONSTANT OF 3:5 DINITROSALICYLIC ACID IN AQUEOUS MEDIUM FROM 10° TO 60° AND RELATED THERMODYNAMIC FUNCTIONS

SPECTROPHOTOMETRIC DETERMINATION OF THE THERMODYNAMIC IONIZATION CONSTANT OF 3:5 DINITROSALICYLIC ACID IN AQUEOUS MEDIUM FROM 10° TO 60° AND RELATED THERMODYNAMIC FUNCTIONS

The second ionization constant of 3:5 dinitrosaliclic acid in aqueous medium has been determined by spectrophotometric method. Measurements have been made at several temperatures and results are shown as a function of absolute temperature by equation -

$$pK_2^T = -841.44/T + 14.2414 - 0.013675\ T.$$

From these, the free energy, heat content, entropy and heat capacity changes accompanying the dissociation have been calculated. The equations relating these thermodynamic functions with absolute temperature are also given. The values of pK_2^T increase linearly with increase in ionic strength and can be expressed by the equation $pK_2^T = 7.3120 + 1.830\ I$ up to an ionic strength (I) of 0.1. The values of pK_2^T have also been obtained for various methanol-water mixtures and mean radius of the ions has been calculated.

3:5 Dinitrosalicylic acid gives colour reactions with various substances. The first ionization constant of this

acid has been calculated conductometrically by Bray et al.[1] This acid forms complexes with Titanium[2] and Tungston[3]. Amino-cobalt complexes of 3:5 dinitrosalicylic acid have been studied by Giorgio[4]. Gupta and Soni[5] have made extensive study on the complex between Fe^{+3} ions and 3:5 dinitrosalicylic acid. However, the present investigation gives the results obtained in the determination of the second thermodynamic ionization constant and related thermodynamic functions spectrophotometrically on which no data are available.

EXPERIMENTAL

3:5 Dinitrosalicylic acid (B.D.H., L.R.) was used for preparing standard solution. Potassium hydrogen phosphate and disodium hydrogen phosphate were of B.D.H. AnalaR quality and used for buffer solutions. Sodium perchlorate (E. Merck) was used for varying ionic strength.

Methanol was of B.D.H.; AnalaR quality and was redistilled in all glass fractionating system and the middle one-third of the distillate was used for the experiments. All the solutions were prepared in conductivity water. The technique and other details have been described earlier.

RESULTS AND DISCUSSION

The absorption spectra of 3:5 dinitrosalicylic acid at various stages of the dissociation at known hydrogen ion concentrations are shown in Fig. 1. The spectra exhibit a

sharp isobestic point at 344 mμ in addition to two well defined bands, one in the 250-340 mμ region and the other in 350-460 mμ. The intensity of long wave band increases with the increase of pH until it reaches a maximum value at pH ≈ 13 when the acid is in the ionic form. It, therefore, indicates that in the region of 400-430 mμ, the only light absorbing species is the doubly ionized form of the acid. Since the second ionization constant of 3:5 dinitrosalicylic acid as calculated by pH measurements was 7.30, the buffer consisting of potassium dihydrogen phosphate and disodium hydrogen phosphate, was prepared for various pH values according to Perrin[6]. The amounts of each species of the partially dissociated 3:5 dinitrosalicylic acid are proportional to their absorbance values. The pK_2^T values were calculated in the same way as described in our earlier paper[7]. The measurements of absorbance at different wave lengths and at different pH values gave consistant values of ionization constant. These are recorded in Table I. However, the first ionization constant of 3:5 dinitrosalicylic acid is difficult to be determined from spectrophotometric measurements.

The second ionization constant of 3:5 dinitrosalicylic acid were calculated at various ionic strengths. It is seen that pK_2^T increases with increase of ionic strength. This increase in pK_2^T with ionic strength is linear and could be expressed by the equation -

$$pK_2^T = 7.3120 + 1.830\ I$$

up to an ionic strength of 0.1, where I has the usual signifi-

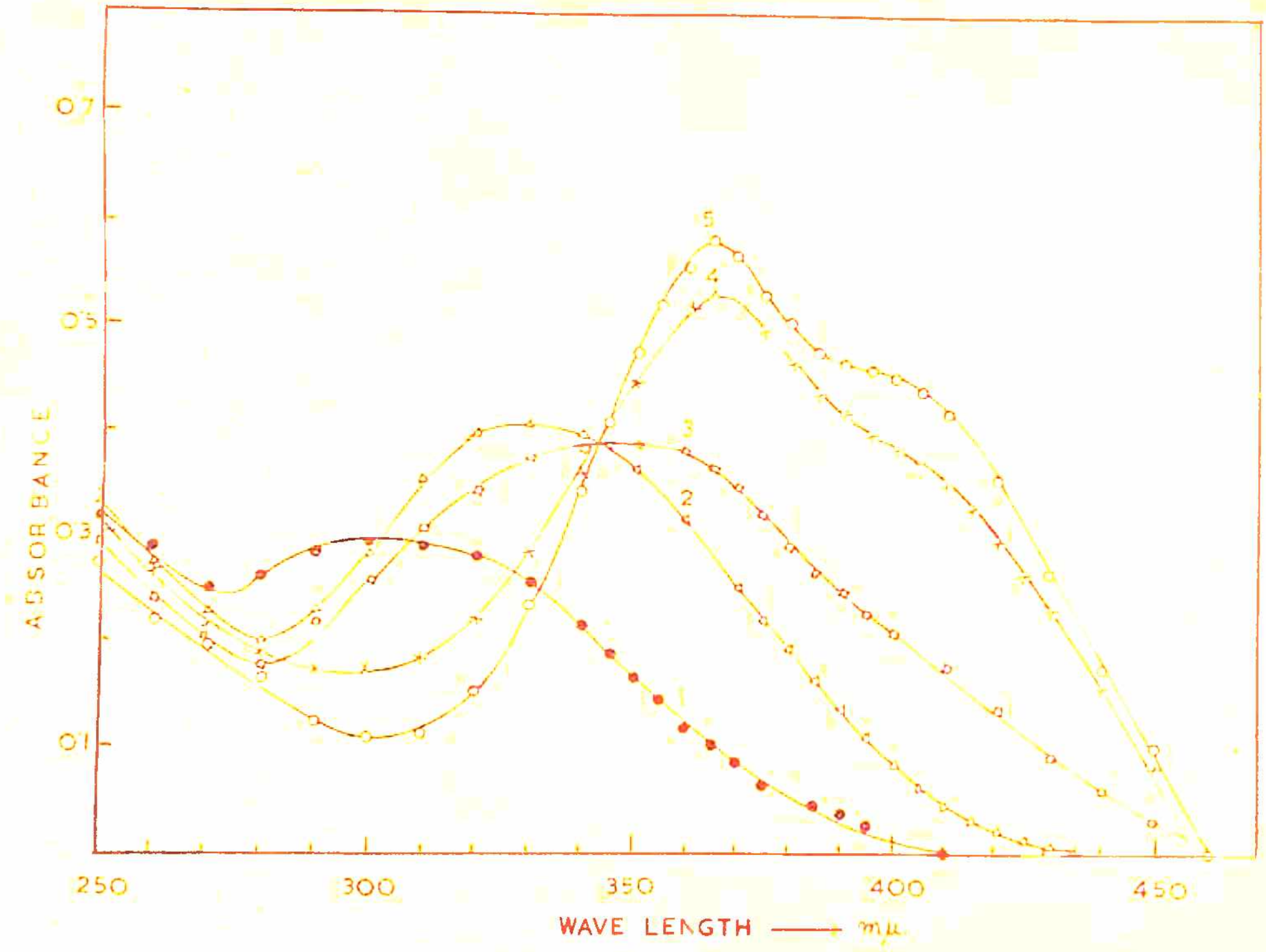
0·7
0·5
0·3
0·1
ABSORBANCE
5
4
3
2
1
250
300
350
400
450
WAVE LENGTH ——→ mμ

FIG. 1

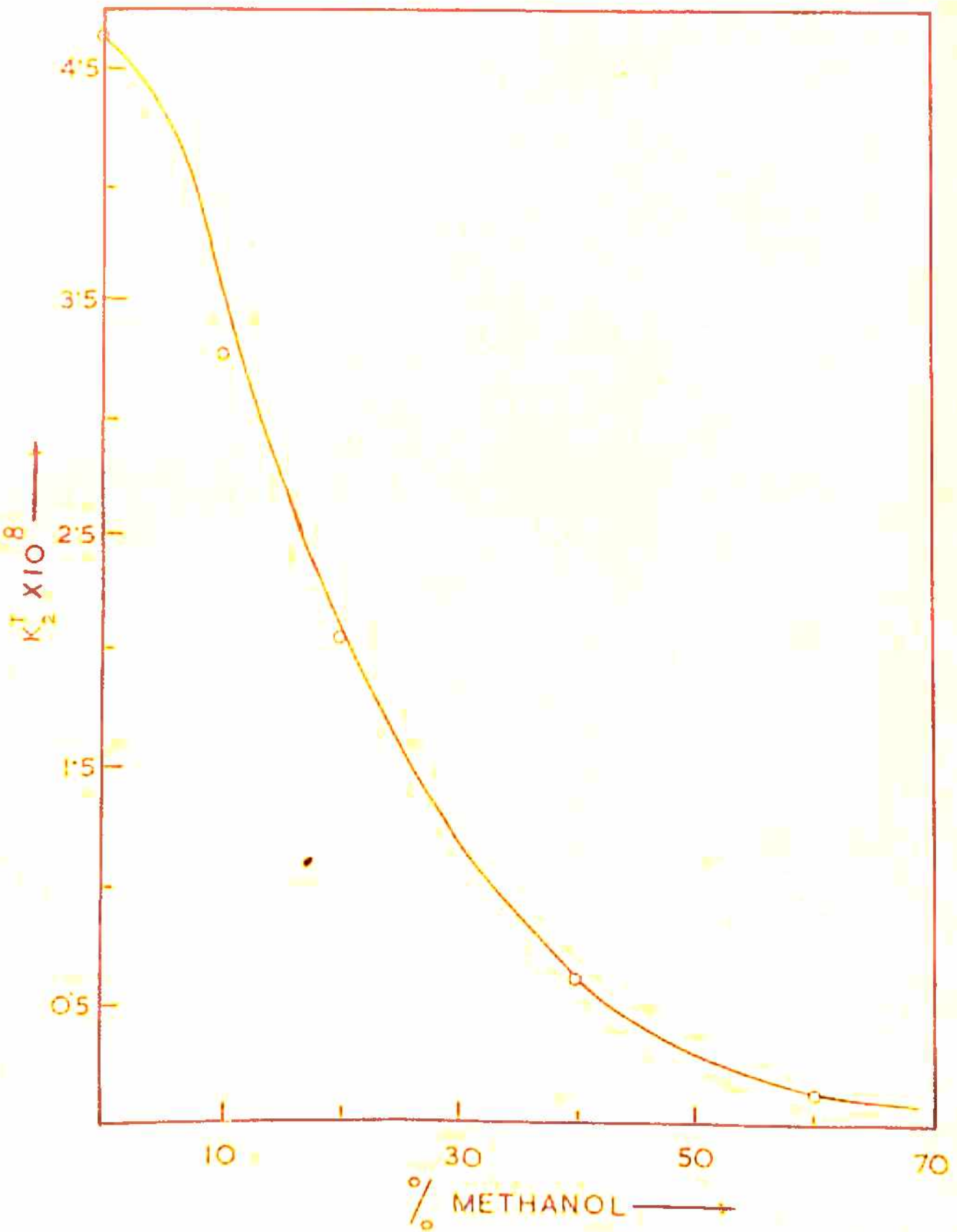

FIG. 2

MOLE FRACTION x_2 (CURVE 2)
0·1
0·3
0·5
0·7
1·8
1·4
1·0
0·6
0·2
2
1
LOG $\frac{K_s}{K_w}$
1·3
1·5
1·7
1·9
100/ϵ (CURVE 1)

FIG. 3

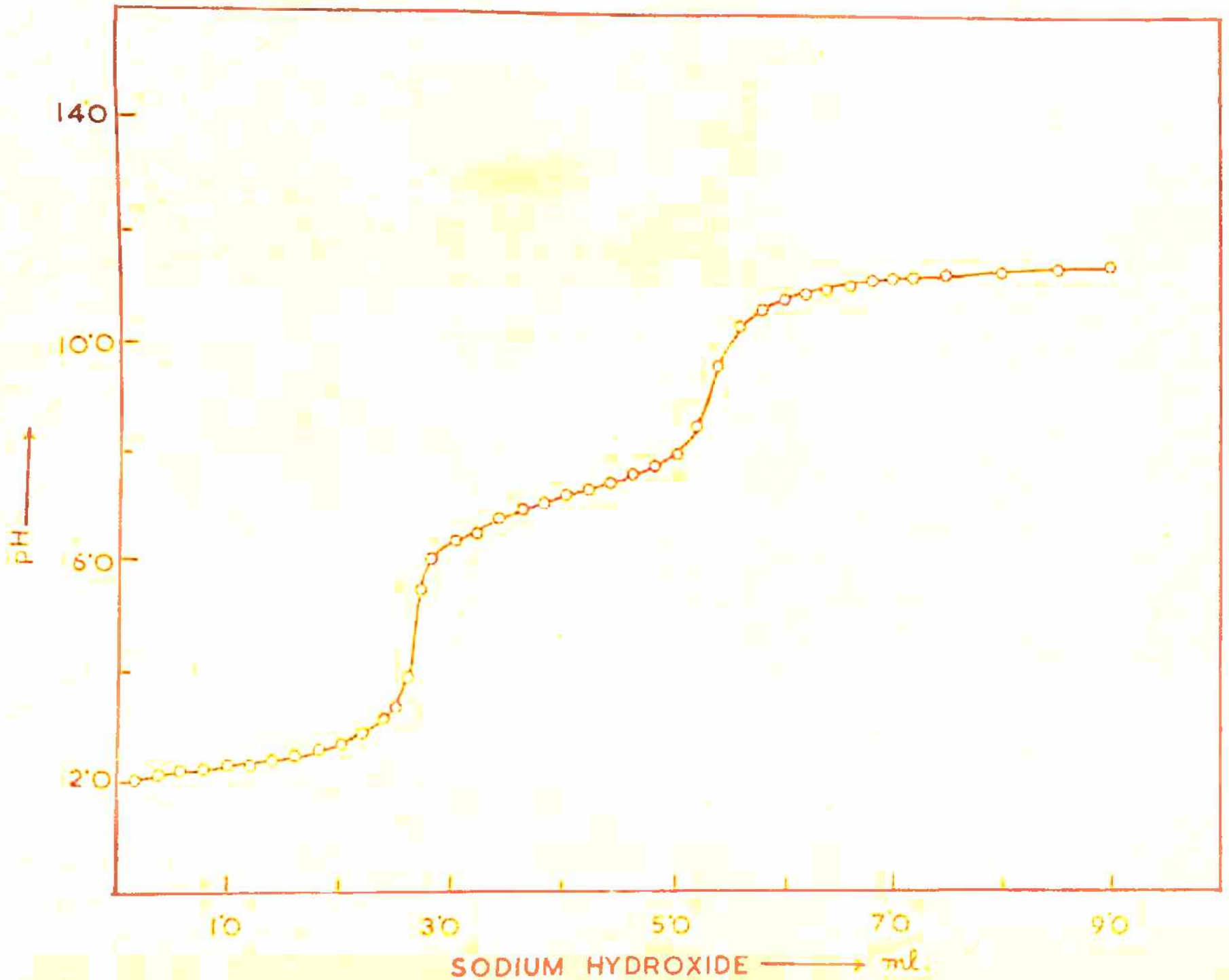

FIG. 4

LEGEND OF FIGURES

Fig. 1: Absorption spectra of 3:5 dinitrosalicylic acid in aqueous medium (Concn = 4.0×10^{-5} mole/l).

Curve 1: 4-5 M HCl

Curve 2: pH = 2

Curve 3 : pH = 7.1

Curve 4: pH = 8

Curve 5: pH ≈ 12.

Fig. 2: Ionization constant of 3:5 dinitrosalicylic acid in various methanol-water mixtures.

Fig. 3: Dependence of the medium effect on the reciprocal of dielectric constant and on the mole fraction of methanol.

Fig. 4: Potentiometric titration of 3:5 dinitrosalicylic acid against sodium hydroxide.

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cance. The calculated values of pK_2^T by the equation are shown in the third column showing good agreement with the values of pK_2^T obtained in the second column of Table II. The increase in pK_2^T with increase of ionic strength is due to the lowering of activity coefficient of the ionic species with increase of ionic strength.

Table III gives the values of pK_2^T at different temperatures. It is interesting to note that pK_2^T decreases with increase of temperature and corresponding values can be expressed by the equation -

$$pK_2^T = -841.44/T + 14.2414 - 0.013675\ T$$

The values of pK_2^T calculated from above equation are recorded in the third column which agree well with the observed values (second column) in Table III. The fact that the enthalpy change is positive (Vide Table III) indicates that ionization of the acid in aqueous medium is endothermic process. The temperature coefficient of this process is -0.00523.

The thermodynamic functions like change of free energy (ΔF), enthalpy (ΔH), entropy (ΔS) and heat capacity (ΔCp) accompanying the ionization are calculated. These are recorded in Table IV. The changes of these functions with temperature can be expressed by the equations -

$$\Delta F = -37329 + 412.752\ T - 491.752 \times 10^{-3}\ T^2$$

$$\Delta H = 0.10011\ T^2$$

$$\Delta S = -169.519 + 0.1984\ T \text{ and}$$

$$\Delta Cp = 0.1984\ T$$

Table I

Second ionization constant of 3:5 dinitrosalicylic acid in aqueous medium.

Concn. = 4.0×10^{-5} M Temp. = 30°.

λ mu =	410	420	430
"a" =	0.031	0.013	0.0044
"b" =	0.420	0.356	0.266

Buffer system : Potassium dihydrogen phosphate - disodium hydrogen phosphate.

Molarity KH_2PO_4	Molarity Na_2HPO_2	Absorbance 'e' Wave-length-mμ 410	420	430	pK_2^T 410	420	430
0.002568	0.002478	0.186	0.147	0.108	7.33	7.34	7.33
0.001946	0.002685	0.214	0.173	0.125	7.35	7.35	7.36
0.001308	0.002897	0.260	0.211	0.154	7.34	7.36	7.37
0.000958	0.003013	0.292	0.238	0.180	7.34	7.35	7.33

Average value = 7.34.

Table II

Effect of ionic strength on the second ionization constant of 3:5 dinitrosalicylic acid in aqueous medium.

Temp. = 30°.

Ionic strength	pK_2^T(Obs.)	pK_2^T(Calc.)*
0.01	7.32	7.33
0.03	7.37	7.37
0.06	7.43	7.42
0.09	7.48	7.48
0.10	7.49	7.49
0.15	7.52	7.59
0.20	7.56	7.68

* $pK_2^T = 7.3120 + 1.830\ I.$

Table III

Second ionization constant of 3:5 dinitrosalicylic acid in aqueous medium at different temperatures.

Temp.	pK_2^T(Obs.)	pK_2^T(Calc.)*
283.16 °K	7.40	7.40
293.16	7.36	7.36
303.16	7.33	7.32
313.16	7.27	7.26
323.16	7.21	7.22
333.16	7.15	7.16

* $pK_2^T = -841.44/T + 14.2414 - 0.013675\ T.$

Table IV

Thermodynamic functions for second ionization of 3:5 dinitrosalicylic acid at various temperatures in aqueous medium

Temp. °K	Δ F (j.mole^{-1})	Δ H (j.mole^{-1})	Δ S (j.deg^{-1}.mole^{-1})	Δ Cp (j.deg^{-1}.mole^{-1})
283.16	41023	8029	- 113.3	56.2
293.16	41328	8606	- 111.6	58.2
303.16	42617	9204	- 110.2	60.1
313.16	43626	9822	- 107.9	63.0
323.16	44584	10458	- 105.6	64.1
333.16	45571	11114	- 103.4	66.1

These equations are valid from T = 283.16°K to 333.16°K. The limits of deviations between the observed and the calculated values of these functions are as follows -

$\Delta F = \pm 88$ j.mole^{-1}; $\Delta H = \pm 4$ j.mole^{-1};

$\Delta S = \pm 0.8$ j.deg^{-1}.mole^{-1}; and $\Delta C_p = \pm 0.02$ j.deg^{-1}.mole^{-1}.

The ionization constants of the acid have also been determined for various methanol-water mixtures. Fig. 2 shows the nature of the curve obtained by plotting "K_2^T" against composition of the methanol-water mixtures. The value of "K_2^T" decreases rapidly up to a concentrations of 40% methanol in the mixture but concentrations greater than this produces slow decreases in the value of K_2^T. This is related to the decrease of dielectric constant of the medium by increasing the percentage of methanol.

This result has been treated in terms of the Born equation-

$$-\log \frac{{}_sK_2^T}{{}_wK_2^T} = \frac{e^2}{rkT \ln 10} \left(\frac{1}{\epsilon_s} \quad \frac{1}{\epsilon_w}\right)$$

where the symbols have usual significance. In order to measure the acid strength with respect to water, a plot of -

$$-\log \frac{{}_sK_2^T}{{}_wK_2^T}$$

against reciprocal of the dielectric constant gave a straight line having an equation -

$$-\log \frac{{}_sK_2^T}{{}_wK_2^T} = -2.9684 + \frac{231.8}{\epsilon_s} .$$

Curves 1 & 2, Fig. 3 indicate the dependence of the medium effect on the reciprocal of dielectric constant and on the mole fraction of methanol. From the above equation the radius of 3:5 dinitrosalicylic acid ion is calculated to be 0.82 Å.

Further, the value of pK_2^T has been confirmed by potentiometric method. The titration of 3:5 dinitrosalicylic acid against sodium hydroxide gave two inflexion points (Fig. 4) and the value of pK_2^T has been calculated to be 7.32 at 30°C.

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PAPER No. 4

SPECTROPHOTOMETRIC DETERMINATION OF THE THERMODYNAMIC IONIZATION CONSTANTS OF SOME SUBSTITUTED BENZOIC ACIDS WITH SPECIAL REFERENCE TO THEIR STRUCTURAL INFLUENCE

SPECTROPHOTOMETRIC DETERMINATION OF THE THERMODYNAMIC IONIZATION CONSTANTS OF SOME SUBSTITUTED BENZOIC ACIDS WITH SPECIAL REFERENCE TO THEIR STRUCTURAL INFLUENCE

The thermodynamic ionization constants of ortho, meta, para methyl and para fluoro substituted benzoic acids from 10 to 60° have been determined in aqueous solution spectrophotometrically in different buffer solutions. The results are given as a function of temperature. The thermodynamic functions like change of free energy (ΔF), enthalpy (ΔH), entropy (ΔS) and heat capacity (ΔCp) for each ionization process are calculated from the temperature coefficient. The ionization constants for each acid have also been obtained for various methanol-water mixtures. The structural effects on the ionization constants of these acids have been discussed.

Dippy[1,2,3] et al. have done a considerable amount of work on the ionization constants of mono-carboxylic acids. They have determined the thermodynamic ionization constants of substituted benzoic acids conductometrically[4]. The present work provides the thermodynamic ionization constants of ortho,

meta, para methyl and para fluoro substituted benzoic acids from spectrophotometric measurements on which no data are available in literature. These studies have further been extended for the determination of the ionization constants at different temperatures and in various methanol-water mixtures.

EXPERIMENTAL

Recrystallised samples of ortho, meta, para methyl and para fluoro substituted benzoic acids (B.D.H., L.R.) were used for preparing stock solutions. Succinic acid, formic acid and potassium hydroxide were of B.D.H. AnalaR quality and used to prepare Buffer solutions. Methanol (B.D.H., A.R.) distilled in all glass fractionating system and the middle one-third of the distillate was used for the experiments. The other chemicals used for preparing acid and base standards were of B.D.H., AnalaR quality. All the solutions and subsequent dilutions were made with conductivity water. The technique and other details have been described earlier.

RESULTS AND DISCUSSION

The absorption curves of these acids were measured as a function of pH over the range 220-280 mμ. The spectra are shown in Figures 1,2,3, & 4. The optimum concentration of each acid has been choosen such that the highest concentration at which an accurate measurement can be made of the species with the higher absorbance. It was observed that the spectra are

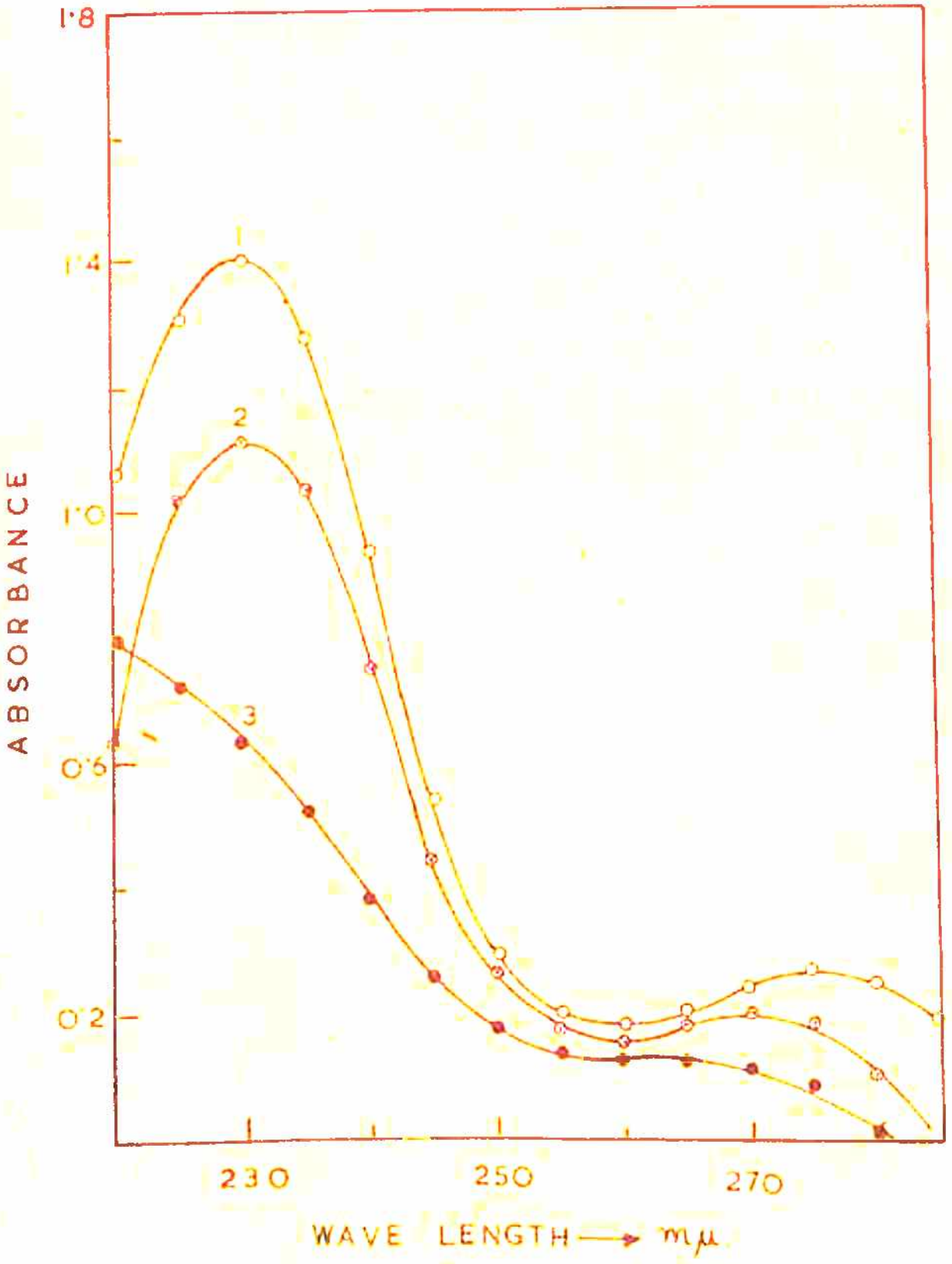

FIG. 1

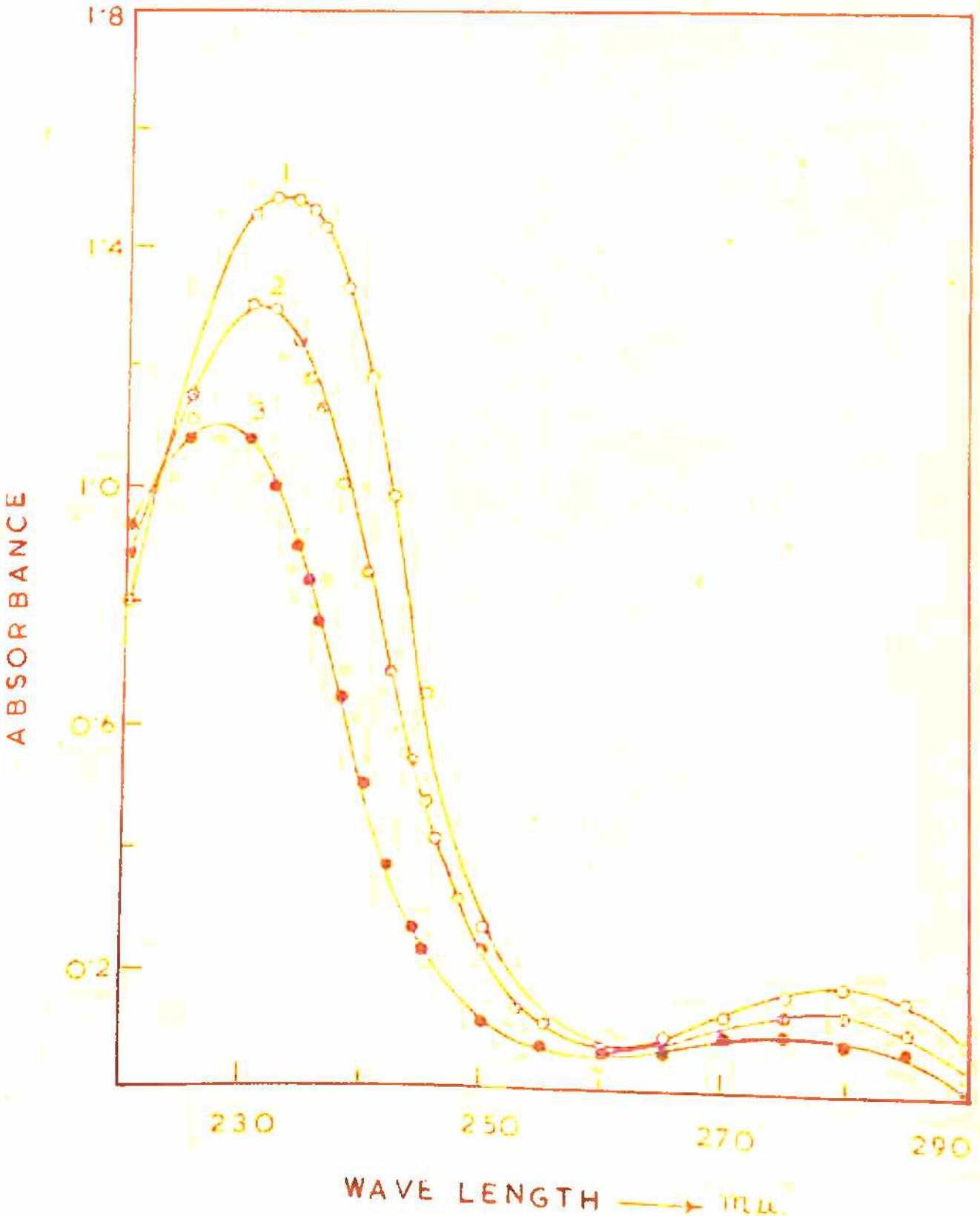

FIG. 2

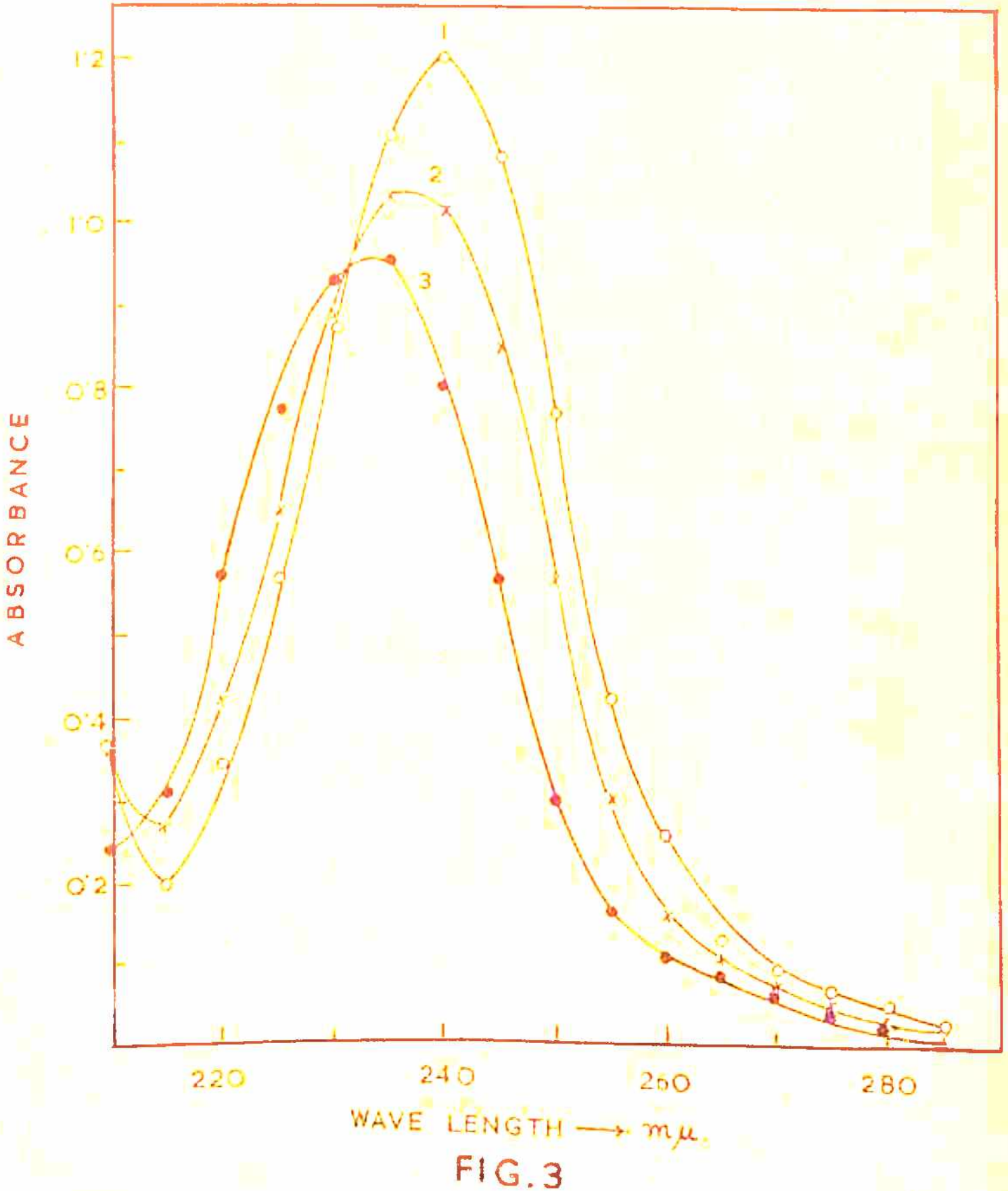

FIG. 3

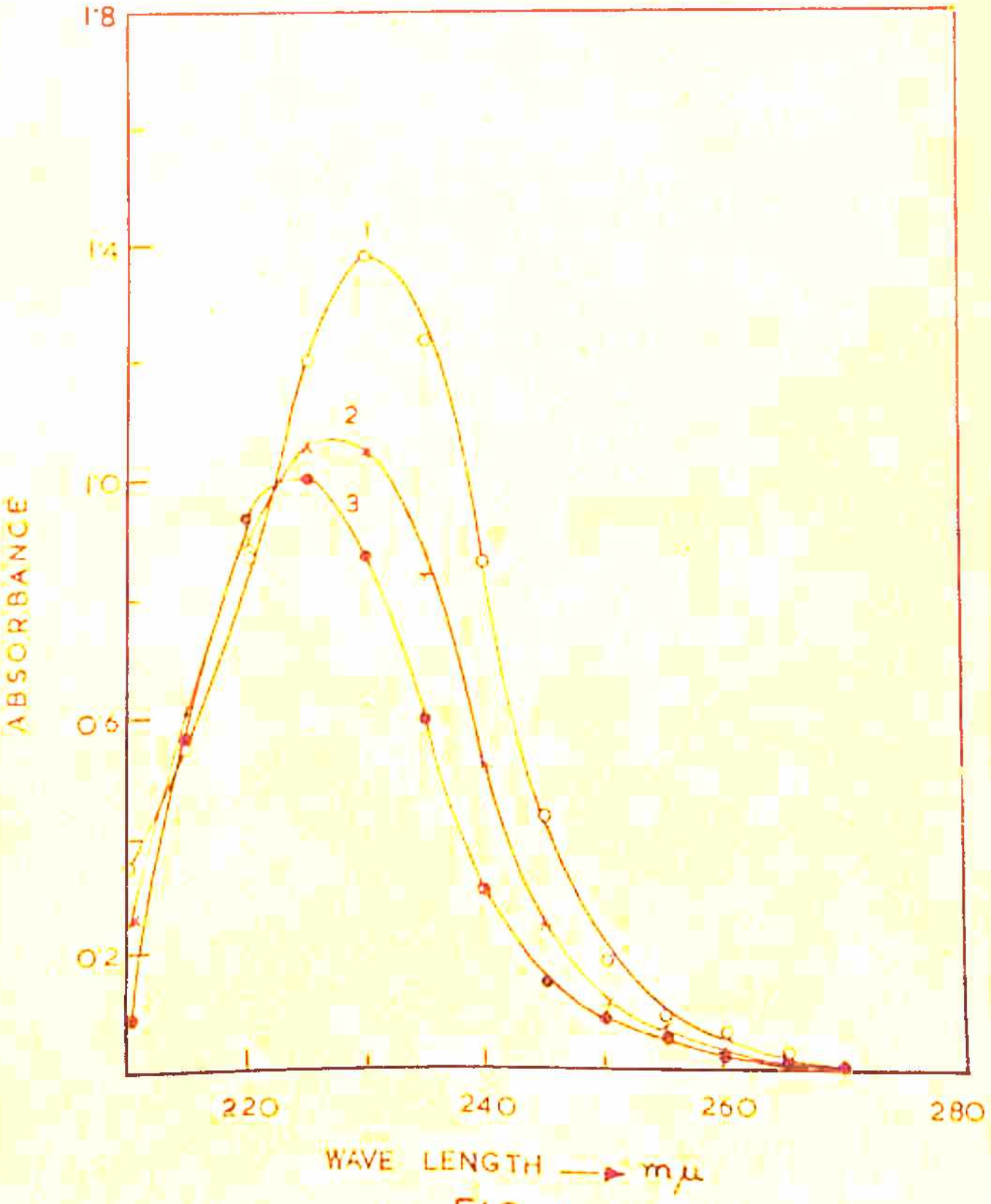

FIG. 4

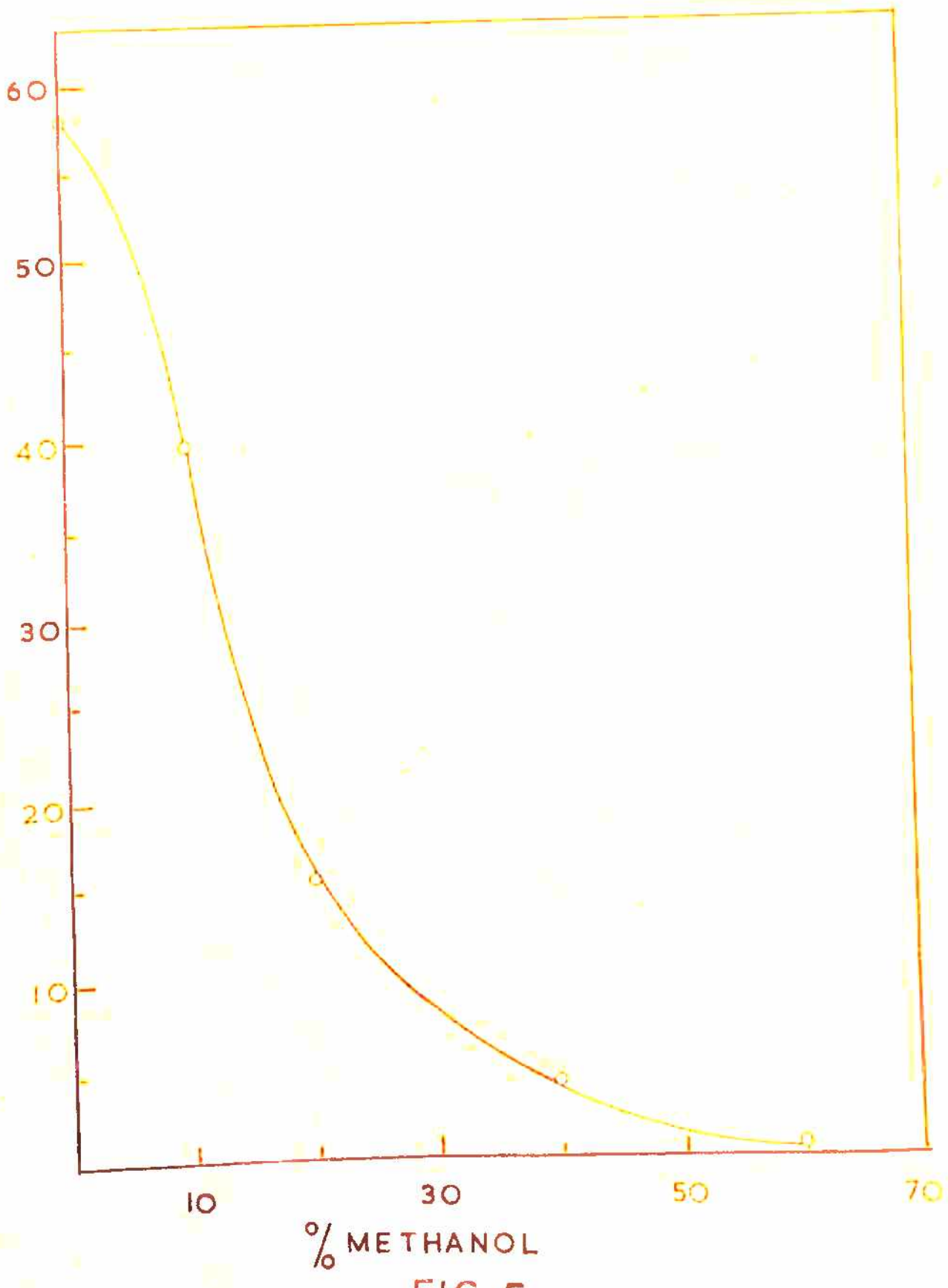

FIG. 5

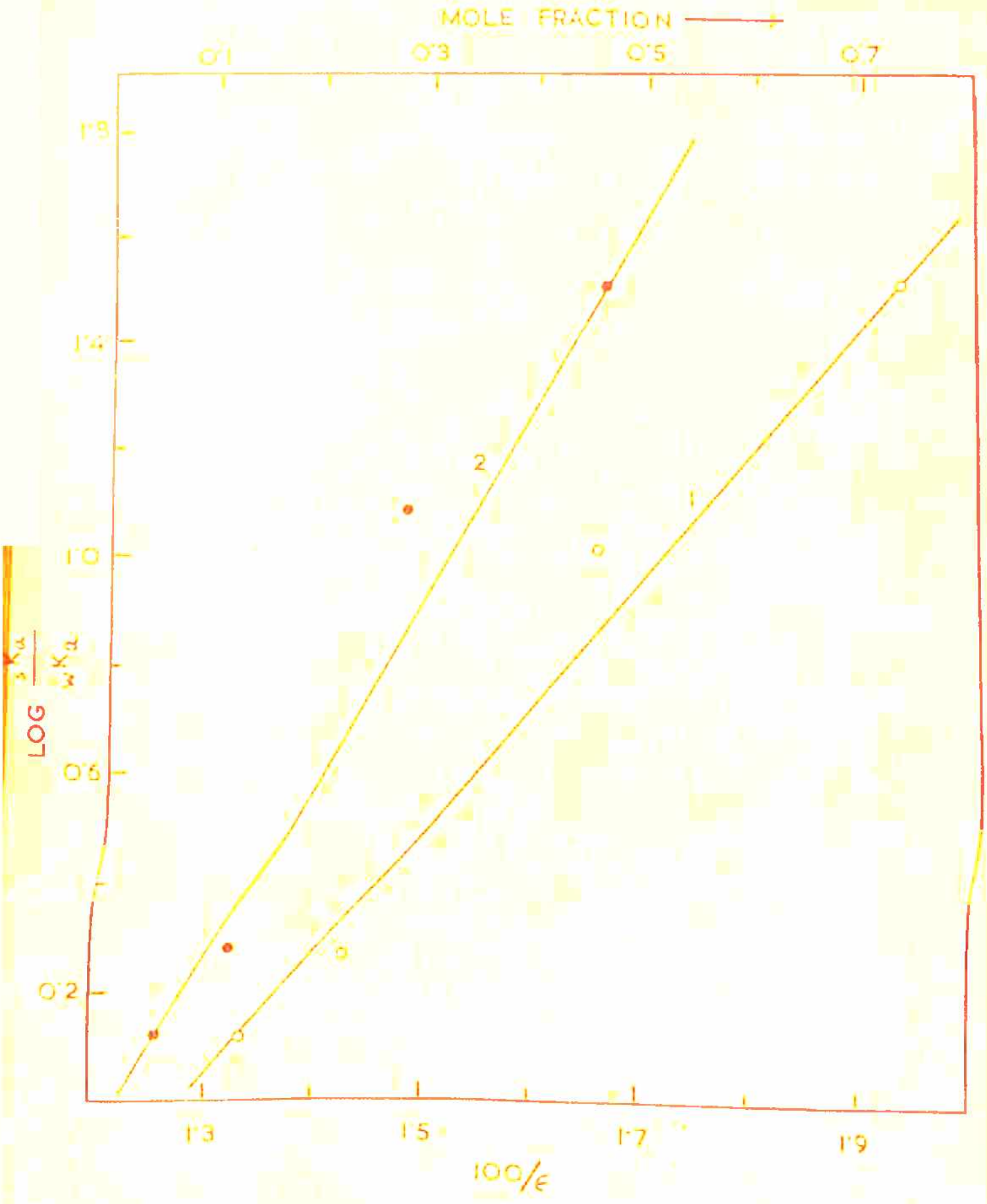
MOLE FRACTION
0·1
0·3
0·5
0·7
1·8
1·4
1·0
0·6
0·2
LOG $\frac{K_{a_1}}{K_{a_2}}$
2
1
0
1·3
1·5
1·7
1·9
100/ε

FIG. 6

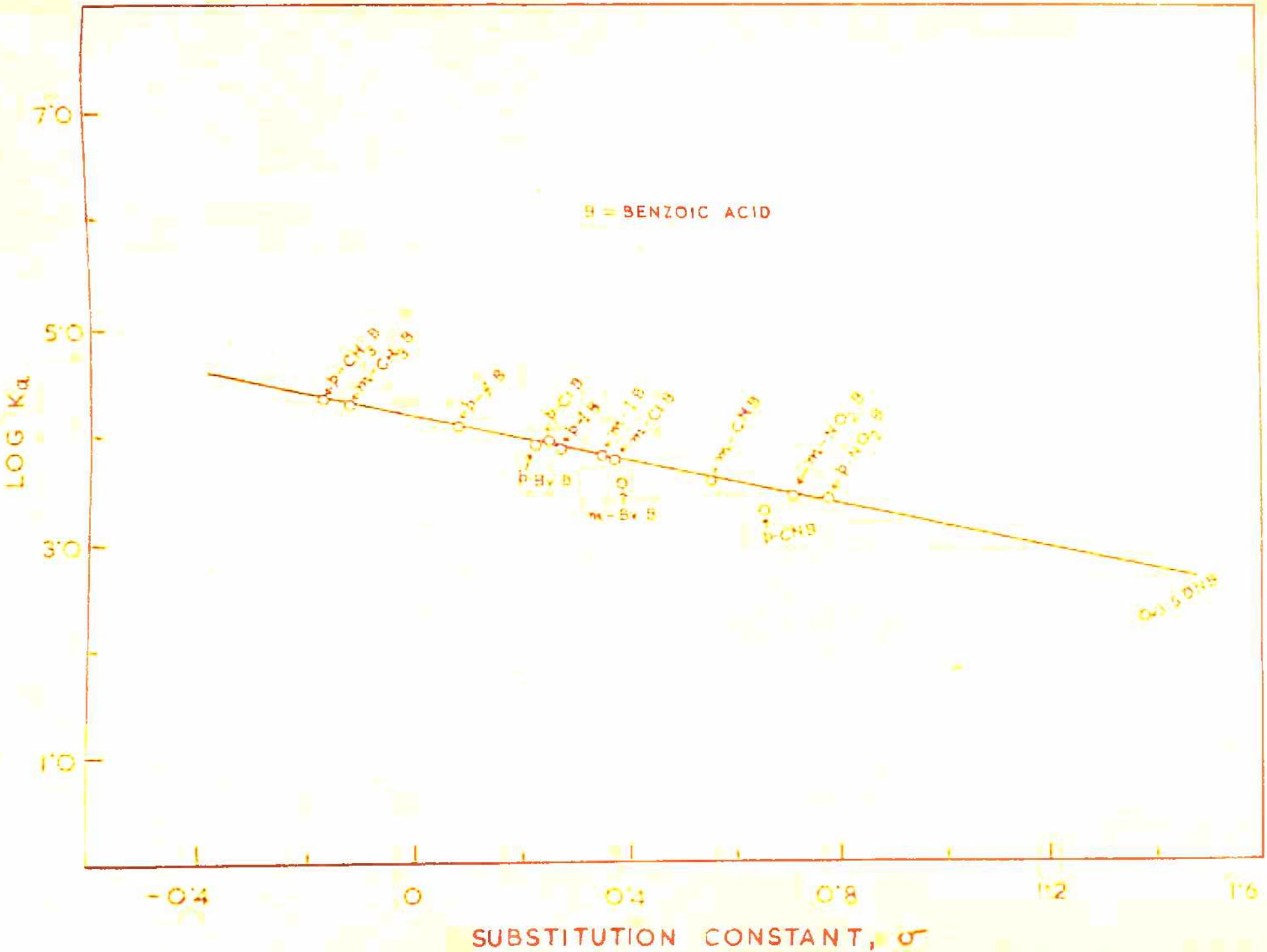
H = BENZOIC ACID
LOG Ka
7·0
5·0
3·0
1·0
-0·4
0
0·4
0·8
1·2
1·6
SUBSTITUTION CONSTANT, σ

FIG. 7

LEGEND OF FIGURES

Fig. 1: Absorption curves of aqueous solutions of o-toluic acid ($C = 8.0 \times 10^{-3}$ mole/l)

Curves 1-3: Acid, buffer and base standards respectively.

Fig. 2: Absorption curves of aqueous solutions of m-toluic acid ($C = 1.6 \times 10^{-4}$ mole/l).

Curves 1-3: Acid, buffer and base standards respectively.

Fig. 3: Absorption curves of aqueous solutions of p-toluic acid ($C = 8.0 \times 10^{-5}$ mole/l).

Curves 1-3: Acid, buffer and base standards respectively.

Fig. 4: Absorption curves of aqueous solutions of p-fluorobenzoic acid ($C = 1.20 \times 10^{-4}$ mole/l).

Curves 1-3: Acid, buffer and base standards respectively.

Fig. 5: Ionization constant of p-toluic acid in various methanol-water mixtures.

Fig. 6: Dependence of the medium effect on the reciprocal of dielectric constant and on fraction of methanol.

Fig. 7: Applicability of Hammett Equation.

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very much similar to each other. In view of the similarity of the spectra of these acids it is clear that the same criteria of choice of wavelength and experimental procedure hold. Wavelengths have been selected such that the difference between optical densities of undissociated and ionized species were large enough for the determination of the ionization constants.

The thermodynamic ionization constants have been calculated in a similar way as described in earlier paper[5]. Two sets of buffer solutions of constant ionic strength[6], (i) formic acid and potassium hydroxide (ii) succinic acid and potassium hydroxide were prepared. Measurements of optical density at various wavelengths and at different pH values gave consistant values of pK_a. These are recorded in Tables I,II,III & IV.

Further, the ionization constants have been obtained at various ionic strengths. It was found that the ionization constants of these acids decrease with increase of ionic strength. The decrease of ionization constant with ionic strength is linear up to an ionic strength of 0.1 and can be expressed by a general equation $pK_a = A + BI$, where A and B are constants and I is the ionic strength. The decrease of ionization constant with increase of ionic strength is due to lowering of activity coefficient of the ionic species. Thus the values of pK_a can be computed by extrapolation of curves to zero ionic strength. The results are given in Table V.

The values of thermodynamic ionization constants were

Table I

Ionization constant of o-toluic acid in aqueous medium

Concn. of the acid = 8.0×10^{-5} M Temp. = 20°C

λ_{mu} =	225	230	235	240
"a" =	1.301	1.403	1.274	0.932
"b" =	0.719	0.644	0.526	0.379

Buffer system: Formic acid - potassium hydroxide

		Absorbance "e"				pK_a			
		Wave-length - mu							
Molarity acid	Molarity base	225	230	235	240	225	230	235	240
0.01805	0.00982	1.023	1.071	0.903	0.654	3.93	4.00	3.91	3.90
0.01360	0.00992	0.900	0.903	0.782	0.564	3.90	3.96	3.96	3.95
0.01180	0.00995	0.839	0.790	0.672	0.482	3.94	3.94	3.93	3.91
0.01150	0.00996	0.824	0.787	0.670	0.481	3.96	3.96	3.97	3.96
0.01120	0.00999	0.775	0.721	0.600	0.432	3.83	3.95	3.93	3.93
0.01050	0.00999	0.754	0.688	0.570	0.413	3.96	3.94	3.95	3.96

Average value = 3.95

Buffer system: Succinic acid - potassium hydroxide

0.05497	0.00962	1.125	1.177	1.055	0.870	3.96	3.97	3.98	3.98
0.02329	0.00965	0.951	0.975	0.845	0.614	3.92	3.98	3.97	3.97
0.01643	0.00950	0.880	0.866	0.742	0.536	3.93	3.96	3.96	3.95
0.01302	0.00925	0.836	0.790	0.684	0.498	3.95	4.02	3.98	3.97
0.01012	0.00895	0.785	0.740	0.620	0.446	3.92	3.96	3.96	3.88

Average value = 3.96

Table II

Ionization constant of m-toluic acid in aqueous medium.

Concn. of the acid = 1.6×10^{-4} M Temp. = 30°C

λ mμ	235	238	240	242
"a"	1.468	1.332	1.180	0.981
"b"	0.842	0.648	0.500	0.365

Buffer system: Formic acid - Potassium hydroxide

Molarity acid	Molarity base	Absorbance "e" Wave-length - mμ 235	238	240	242	pK_a 235	238	240	242
0.01722	0.00982	1.284	1.131	0.979	0.807	4.33	4.33	4.33	4.35
0.01503	0.00989	1.237	1.068	0.924	0.752	4.33	4.30	4.32	4.33
0.01360	0.00992	1.184	1.009	0.857	0.690	4.33	4.30	4.29	4.30
0.01230	0.00994	1.114	0.932	0.777	0.625	4.33	4.30	4.27	4.32
0.01205	0.00995	1.086	0.921	0.764	0.609	4.31	4.32	4.30	4.30
0.01120	0.00999	0.959	0.796	0.648	0.502	4.36	4.34	4.33	4.35

Average value = 4.31

Buffer system: Succinic acid - potassium hydroxide.

0.04142	0.00960	1.352	1.204	1.055	0.870	4.28	4.19	4.32	4.30
0.03184	0.00963	1.289	1.137	0.979	0.812	4.29	4.30	4.28	4.33
0.02150	0.00958	1.222	1.055	0.903	0.737	4.33	4.32	4.31	4.33
0.01750	0.00950	1.167	1.004	0.842	0.674	4.33	4.33	4.30	4.30
0.01106	0.00907	1.018	0.836	0.684	0.530	4.29	4.28	4.27	4.26
0.00918	0.00889	0.975	0.788	0.640	0.488	4.33	4.30	4.31	4.29

Average value = 4.31

Table III

Ionization constant of p-toluic acid in aqueous medium

Concn. of the acid = 8.0×10^{-5} M Temp. = 20°C

λ mμ	=	245	250	255
"a"	=	1.078	0.759	0.418
"b"	=	0.529	0.283	0.155

Buffer system : Formic acid - potassium hydroxide.

Molarity acid	Molarity base	Absorbance "e" Wavelength mμ 245	250	255	pK_a 245	250	255
0.01722	0.00982	0.913	0.616	0.334	4.32	4.32	4.38
0.01321	0.00993	0.812	0.530	0.293	4.33	4.33	4.34
0.01230	0.00995	0.735	0.462	0.250	4.33	4.33	4.30
0.01175	0.00995	0.684	0.420	0.231	4.35	4.30	4.31
0.00605	0.00998	0.557	0.304	0.169	4.34	4.25	4.35

Average value = 4.33

Buffer system: Succinic acid - Potassium hydroxide

0.03693	0.00962	0.959	0.658	0.361	4.35	4.36	4.36
0.02712	0.00962	0.899	0.607	0.329	4.32	4.33	4.29
0.00215	0.00958	0.854	0.561	0.310	4.32	4.31	4.30
0.01373	0.00933	0.742	0.466	0.253	4.30	4.29	4.27
0.01106	0.00908	0.690	0.420	0.233	4.32	4.30	4.32
0.00918	0.00889	0.646	0.379	0.215	4.33	4.30	4.37

Average value = 4.32

Table IV

Ionization constant of p-fluorobenzoic acid in aqueous medium

Concn. of the acid = 1.20×10^{-4} M Temp. = 30°C

$\lambda_{m\mu}$ =	230	235	240
"a" =	1.382	1.238	0.857
"b" =	0.870	0.594	0.301

Buffer system: Formic acid - Potassium hydroxide.

Molarity acid	Molarity base	Absorbance "e" Wavelength mμ 230	235	240	pK_a 230	235	240
0.02588	0.00965	1.268	1.102	0.745	4.14	4.17	4.20
0.01913	0.00980	1.215	1.018	0.674	4.16	4.16	4.16
0.01722	0.00982	1.200	1.000	0.654	4.21	4.18	4.19
0.01229	0.00995	1.041	0.810	0.486	4.15	4.15	4.15
0.00390	0.00980	0.921	0.652	0.348	4.19	4.15	4.11

Average value = 4.16

Buffer system: Succinic acid - Potassium hydroxide

0.04950	0.00960	1.229	1.086	0.726	4.10	4.21	4.21
0.03439	0.00963	1.190	1.027	0.636	4.10	4.16	4.03
0.02510	0.00961	1.137	0.947	0.604	4.10	4.13	4.13
0.01861	0.00951	1.089	0.883	0.548	4.12	4.17	4.15
0.01298	0.00927	1.018	0.788	0.448	4.28	4.18	4.10
0.00106	0.00901	0.975	0.726	0.411	4.11	4.16	4.10

Average value = 4.13

Table V

Effect of ionic strength on the ionization constants of substituted benzoic acids in aqueous medium

Temp. = 20°C

Ionic Strength (I)	pK_a							
	o-toluic acid		m-toluic acid		p-toluic acid		p-fluorobenzoic acid	
	(Obs.)	(Calc)	(obs)	(calc)	(Obs)	(Calc)	(obs)	(Calc)
0.01	3.95	3.95	4.31	4.30	4.32	4.33	4.08	4.08
0.03	3.98	3.98	4.35	4.34	4.35	4.35	4.16	4.15
0.06	4.03	4.04	4.40	4.39	4.37	4.37	4.25	4.25
0.11	4.09	4.10	4.49	4.49	4.40	4.40	4.40	4.40
0.21	4.16	4.23	4.52	4.65	4.44	4.46	4.45	4.77

o-Toluic acid $pK_a = 3.9530 + 0.905713\ I$

m-Toluic acid $pK_a = 4.2860 + 1.8200\ I$

p-Toluic acid $pK_a = 4.3300 + 0.63975\ I$

p-Fluorobenzoic acid $pK_a = 4.0500 + 3.3130\ I$

determined at various temperatures. The results show that pK_a values for all these acids increase with the increase of temperature and corresponding values can be expressed by an equation:-

$$pK_a = A/T + B + CT,$$

where A, B and C are constants. The pK_a values calculated from respective equations are in good agreement with the observed values. These are given in Table VI. The fact that the enthalpy change (ΔH) is negative indicates that ionization process in each case is exothermic. Therefore, the values of pK_a increase with the increase of temperature. The temperature coefficients of ortho, meta, para methyl and para fluoro substituted benzoic acids are 0.0039, 0.00447, 0.00459 and 0.00952 respectively which are very similar to those of carboxylic acids.

The thermodynamic functions like change of free energy, enthalpy, entropy and heat capacity associated with each ionization process are calculated. These are recorded in Tables VII, VIII, IX & X. All the thermodynamic functions shown in these tables increase in magnitude (with sign) with increase of temperature. These relations could be expressed by general equations -

$$\Delta F = A + BT + CT^2$$

$$\Delta H = A + BT^2$$

$$\Delta S = A + BT$$

$$\Delta Cp = AT.$$

Table VI

Thermodynamic ionization constants of substituted benzoic acids in aqueous medium at different temperatures.

Temp.°K	pK_a							
	o-toluic acid		m-toluic acid		p-toluic acid		p-fluorobenzoic acid	
	(Obs)	(Calc)	(Obs)	(Calc)	(Obs)	(Calc)	(Obs)	(Calc)
283.16	3.93	3.93	4.22	4.22	4.29	4.29	4.02	4.02
293.16	3.97	3.97	4.27	4.27	4.34	4.33	4.06	4.06
303.16	4.00	4.00	4.32	4.32	4.37	4.37	4.12	4.13
313.16	4.05	4.05	4.37	4.37	4.41	4.42	4.23	4.24
323.16	4.08	4.09	4.41	4.41	4.47	4.46	4.35	4.35
333.16	4.12	4.12	4.44	4.44	4.52	4.51	4.50	4.49

o-Toluic acid $pK_a = -120.911/T + 3.60549 + 0.0026466\ T$

m-Toluic acid $pK_a = -531.45/T + 6.4292 - 0.001166\ T$

p-Toluic acid $pK_a = 73.035/T + 2.5642 + 0.0051762\ T$

p-fluorobenzoic acid $pK_a = 3636.1/T - 22.4250 + 0.048059\ T$

Table VII

Thermodynamic functions for the ionization of o-toluic acid in aqueous medium from 10 to 60°C

Temp.	ΔF ($j\text{-}mole^{-1}$)	ΔH ($j\text{-}mole^{-1}$)	ΔS ($j\text{-}deg^{-1}.mole^{-1}$)	ΔCp ($j.deg^{-1}.mole^{-1}$)
283.16°K	21302	-6021	-96.5	- 42.3
293.16	22328	-6454	- 98.2	- 44.0
303.16	23258	-6902	- 99.5	- 45.5
313.16	24281	-7364	-101.1	- 47.0
323.16	25699	-7842	-103.8	- 48.5
333.16	26315	-8335	-104.0	- 50.0

$$\Delta F = 645.4 + 49.730\ T + 0.08200\ T^2\ j.mole^{-1}.$$

$$\Delta H = 0.075086\ T^2\ j.mole^{-1}.$$

$$\Delta S = -54.181 - 0.15012\ T\ j.deg^{-1}.mole^{-1}.$$

$$\Delta Cp = -0.15012\ T\ j.deg^{-1}.mole^{-1}.$$

Table VIII

Thermodynamic functions for the ionization of m-toluic acid in aqueous medium from 10 to 60°C.

Temp.	ΔF (j-mole^{-1})	ΔH (j-mole^{-1})	ΔS (j-deg^{-1}.mole^{-1})	ΔC_p (j.deg^{-1}.mole^{-1})
283.16°K	22898	-6862	- 105.1	- 48.5
293.16	23987	-7355	- 106.9	- 50.2
303.16	25116	-7866	- 108.8	- 51.9
313.16	26192	-8393	- 110.4	- 53.6
323.16	27313	-8938	- 112.2	- 55.3
333.16	28367	-9499	- 113.6	- 57.0

$$\Delta F = -12843.1 + 140.562\ T - 0.05066\ T^2 \quad j.mole^{-1}$$

$$\Delta H = -1.0 - 0.085570\ T^2 \quad j.mole^{-1}.$$

$$\Delta S = -56.623 - 0.17120\ T \quad j.deg^{-1}.mole^{-1}.$$

$$\Delta Cp = -0.17120\ T \quad j.deg^{-1}.mole^{-1}.$$

Table IX

Thermodynamic functions for the ionization of o-toluic acid in aqueous medium from 10 to 60°C

Temp.°K	ΔF (j.mole^{-1})	ΔH (j.mole^{-1})	ΔS (j.deg^{-1}.mole^{-1})	ΔCp (j.deg^{-1}.mole^{-1})
283.16	23253	-7043	- 107.0	- 49.8
293.16	24347	-7549	- 108.8	- 51.5
303.16	25399	-8073	- 110.4	- 53.3
313.16	26475	-8615	- 112.0	- 55.0
323.16	27764	-9147	- 114.3	- 56.8
333.16	28822	-9750	- 115.8	- 58.6

$$\Delta F = 4545.0 + 27.560\ T + 0.1360\ T^2 \quad j.mole^{-1}$$

$$\Delta H = -0.087847\ T^2\ j.mole^{-1}$$

$$\Delta S = -57.210 - 0.17580\ T\ j.\ deg^{-1}.mole^{-1}.$$

$$\Delta Cp = -0.17580\ T\ \ j.deg^{-1}.mole^{-1}.$$

Table X

Thermodynamic functions for the dissociation of p-fluorobenzoic acid in aqueous medium from 10 to 60°C.

Temp.°K	ΔF ($j.mole^{-1}$)	ΔH ($j.mole^{-1}$)	ΔS ($j.deg^{-1}.mole^{-1}$)	ΔCp ($j.deg^{-1}.mole^{-1}$)
283.16	21804	-14604	- 125.0	- 125.7
293.16	22736	-15608	- 131.0	- 130.2
303.16	23940	-16746	- 134.2	- 134.6
313.16	25386	-17868	- 138.1	- 139.0
323.16	26666	-19028	- 141.4	- 143.5
333.16	28689	-20222	- 146.8	- 147.9

$$\Delta F = 79683 - 494.65\ T + 1.0250\ T^2\ j.mole^{-1}.$$

$$\Delta H = -13.00 - 0.18231\ T^2\ j.mole^{-1}.$$

$$\Delta S = 0.670 - 0.4440\ T\ \ j.deg^{-1}.mole^{-1}.$$

$$\Delta Cp = -0.4440\ T\ \ j.deg^{-1}.mole^{-1}.$$

These equations are valid from T = 283.16 to 333.16 ^{o}K. The limits of deviations between the observed and calculated values are summarised in Table XI.

Table XII records the ionization constants of these acids in various methanol-water mixtures. It has been found that the values of ionization constant for all acids decrease rapidly up to a concentration of 40% methanol in the mixture but concentrations greater than this produce slow decrease in the value of ionization constant. Fig. 5 gives the typical curve obtained by plotting ionization constant against compositions of methanol water mixtures. The decrease of ionization constant with increase of methanol composition in the mixtures is related to the dielectric constant of the medium which decreases with the increase of methanol percentage. The decrease in the extent of solvation of the ionic species by increasing concentration of methanol may also have some influence in decreasing ionization constant[7].

Again, if the ions are regarded as rigid spheres having a mean radius r, the medium effect can be expressed by Born's equation -

$$-\log \frac{{}_{s}K_{a}}{{}_{w}K_{a}} = \frac{e^2}{rkT\ \ln 10}\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right)$$

Where ${}_{s}K_{a}$ and ${}_{w}K_{a}$ are the thermodynamic ionization constants of acid in mixture and water respectively, "e" the proton change, "k" the Boltzman constant, "ϵ_s" and "ϵ_w" are the dielectric constants of mixture and water respectively. Curves 1 and 2

Table XI

Deviation of thermodynamic functions of substituted benzoic acids.

Acid	ΔF $j.mole^{-1}$	ΔH $j.mole^{-1}$	ΔS $j.deg^{-1}.mole^{-1}$	ΔCp $j.deg^{-1}.mole^{-1}$.
o-toluic acid	± 52	± 2	± 0.5	± 0.2
m-toluic acid	± 27	± 2	± 0.2	± 0.3
p-toluic acid	± 35	± 2	± 0.3	± 0.3
p-fluorobenzoic acid	± 85	±13	± 0.5	± 0.2

Table XII

Ionization constants of substituted benzoic acids in methanol-water mixtures.

Methanol (%)	Ionization constant x 10^6			
	o-toluic acid	m-toulic acid	p-toluic acid	p-fluoro-benzoic acid
10	82.3	34.0	39.8	56.0
20	36.2	16.8	15.5	38.6
40	6.2	3.22	4.11	7.49
60	1.5	1.10	0.56	2.46

Fig. 6 represent the typical curves relating the dependence of the medium effect on the reciprocal of the dielectric constant and on the mole fraction of methanol respecitvely for p-fluorobenzoic acid. Hence from the slopes of the straight lines thus plotted for each acid, the mean radius of ions is calculated. The radius of the hydronium ion which is associated with the ions of the acid may be approximated by that of the water molecule, 1.4 Å, therefore, the estimated radii of ortho, meta, para methyl and p-fluoro substituted benzoic acids are 0.58, 0.88, 0.65 and 0.79 Å respectively.

A change in the molecular structure which alters the strength of the bond between the acid hydrogen and the atom to which it is bonded alters the strength of the acid. Commonly, these changes in acid strength are treated by considering them as arising from the polar effect, the resonance effect, hydrogen bonding and steric hindrance. Often more than one of these considerations plays a significant role in determining the acid strength of a molecule. Therefore, it is necessary to select the principal effect even though other factors contribute to the change in acid strength.

Comparing the pK_a values of p-fluoro and p-methyl benzoic acids, we can examine the effect of substituent groups fluoro, and methyl in the para position of the parent acid (benzoic acid). It can be seen that pK_a value of p-fluorobenzoic acid (4.10) is slightly less than that of benzoic acid (4.18) whereas the pK_a value of p-methyl benzoic acid (4.35) is more than that of benzoic acid. This can be explained on the basis of

-I and +T properties of the substituent fluoro group and +I and +T effects of methyl group. The observation that the substituent group fluoro has little effect is due to the fact that -I and +T properties oppose each other and -I effect predominates over +T effect whereas the large effect of methyl group is due to the fact that +I and +T effects are in the same direction.

In the para position the I effect should be smaller than in meta position because of the increased distance. However, the para position is capable of falicitating tautomerism and hence almost every substituent placed in this position is capable of exterting T effect. If the sign of both I and T is the same, the effect is increased. Thus methyl group has +I and +T properties and hence the strength of benzoic acid is decreased by a methyl group in the para position even more than in the meta position.

The ortho position is the most complicated of all. In almost every set of isomers the ortho is the strongest acid, and even when a substituent has both +I and +T properties, the resultant acid is stronger than benzoic acid as can be seen from the pK_a values of ortho methyl benzoic acid (3.98) and benzoic acid (4.18).

It can be seen from Tables VII,VIII,IX & X that although the values of change in free energies are not much different for methyl substituted benzoic acids as that of para fluoro benzoic acid, whereas the heats of ionizations (with negative sign) are much higher for p-fluorobenzoic acid as compared to

methyl substituted benzoic acids. This may be due to the dependence of ΔH on proton affinity of the base conjugate to the acid. However ΔS and ΔCp do not depend on proton affinity and it is difficult to explain particularly large value of ΔCp of p-fluorobenzoic acid as compared to methyl substituted benzoic acids.

The effects of substituents can also be treated by a "Linear Free Energy" relationship (Hammett equation). The most generally used equation for such studies is the modified Hammett equation -

$$pK_a = \rho\sigma$$

Where the substituent constant 'σ' measures the ability of the substituent to either withdraw electrons from the ring or donate them to it by induction or resonance. Substituents that have more electron withdrawing power than hydrogen have positive substituent constants, i.e., the substituted acid is stronger than the unsubstituted and pK_a is positive. Those with less electron withdrawing power than hydrogen have negative sigma values. It depends primarily on the nature of the substituent and secondarily on the position of the substitution because resonance is more important at the para position that at the meta position. It is assumed to be indpendent of temperature, solvent and the nature of the acid group. The reaction constant 'ρ' expresses the sensitivity of the acidic group to inductive and resonance effects and as the distance between substituent and acid group increases the reaction constant

decreases. When the acid can conjugate with the ring the reaction constant is larger than when conjugation is impossible. It is the same for all substituents but depends on the solvent, temperature and the acid group.

Figure 7 gives the straight line plot of pK_a of substituted benzoic acids against substituent constants. In plotting this curve we have taken literature values of thermodynamic ionization comstants of substituted benzoic acids except for meta, para methyl and para fluoro benzoic acids determined by us spectrophotometrically. This shows that they follow the Hammett's rule. The slope of the straight line gives the value of ρ, the reaction constant which comes out to be 1.01 in good agreement with the literature value of 1.0.

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PAPER No. 5

SPECTROPHOTOMETRIC DETERMINATION OF THE THERMODYNAMIC IONIZATION CONSTANT OF 3:5 DINITROBENZOIC ACID IN WATER FROM 10° TO 50° AND RELATED THERMODYNAMIC QUANTITIES

(Jour. Indian Chem. Soc., 1965, 42, 377.)

[Jour. Indian Chem. Soc., Vol. 42, No. 6, 1965]

Spectrophotometric Determination of the Thermodynamic Ionisation Constant of 3,5-Dinitrobenzoic Acid in Water from 10° to 50° and Related Thermodynamic Quantities

S. L. Gupta and R. N. Soni

The thermodynamic ionisation constant (K_a) of 3,5-dinitrobenzoic acid in water from 10° to 50° has been investigated spectrophotometrically. The results are shown as a function of temperature (T) in °K by $pK_a = -1147.0/T + 6.9381 - 9.933 \times 10^{-4} T$. The changes of free energy ($\triangle F$), enthalpy ($\triangle H$), entropy ($\triangle S$), and heat capacity ($\triangle C_p$) for the dissociation process have been calculated from the temperature coefficient of the dissociation constant. The equations relating these thermodynamic functions with absolute temperature are also given. The 'pK_a' of the acid increases linearly with increase in ionic strength of the buffer solution and can be related by the equation $pK_a = 2.0297\ I + 2.9255$ up to an ionic strength (I) of 0.1. The values of K_a have also been found out for various methanol-water mixtures.

In a previous communication, Gupta *et al*[1]. reported the determination at 303.45°K of the thermodynamic ionisation constant (K_a) of 3,5-dinitrobenzoic acid in water, which is in use to characterise the alcohols. These studies have now been extended to the determination of 'K_a' at different temperatures in the range of 283.16° to 323.16° K and of the related thermodynamic quantities like change in free energy, entropy, etc. on which no data exist in the literature. The effect of ionic strength has been studied and the value of K_a has also been determined in various methanol-water mixtures.

EXPERIMENTAL

A recrystallised B D H. sample of 3, 5-dinitrobenzoic acid was used. Methanol was of B. D. H., A R quality and was redistilled in an all-glass fractionating system and the middle one-third of the distillate was used for experiments. Potassium chloride (B.D.H., A. R.) was used for maintaining different ionic strengths. The other chemicals used for preparing acid standard, base standard, and buffer solutions were of AnalaR quality of B. D. H. Conductivity water was used for preparing solutions.

A Hilger Uvispec spectrophotometer, model H700.308, having 1 cm effective light path, was used for studying the absorption spectra over a temperature range of 10° to 50°. The cell compartment was fitted with a jacket through which water could be circulated from a thermostat (Townson and Mercer Ltd., England). A thermometer, inserted into the cell compartment and allowed to come to temperature equilibrium, showed a variation of less than 0.1° over periods of time much longer than those needed to make measurements of optical density. Absorption of the acid was determined in (*a*) 0.1*M*-HCl, (*b*) a buffer containing sodium acetate (1.25 ml of 0.1*M*) and acetic acid (23.75 ml of 0.1*M*), and (*c*) 0.1*M*-NaOH. Beckman *p*H-meter (model H2) was used for *p*H measurements.

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CHAPTER II

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES ON COMPLEXES OF 2-HYDROXY-3-NAPHTHOIC ACID IN AQUEOUS MEDIUM

PAPER No. 6

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES OF THE COMPLEX BETWEEN UO_2^{+2} AND 2-HYDROXY-3-NAPHTHOIC ACID IN AQUEOUS MEDIUM

(Jour. Indian Chem. Soc., 1966, 43, 311.)

PAPER No. 7

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES OF THE COMPLEX BETWEEN Fe^{+3} AND 2-HYDROXY-3-NAPHTHOIC ACID IN AQUEOUS MEDIUM.

(Jour. Indian Chem. Soc., 1966, 43, 473)

[Jour. Indian Chem. Soc., Vol. 43, No. 7, 1966]

Spectrophotometric and Conductometric Studies of the Complex between Fe(III) Ion and 2-Hydroxy-3-naphthoic Acid in Aqueous Medium

S. L. Gupta and R. N. Soni

Fe^{3+} ion forms a blue, water-soluble complex with 2-hydroxy-3-naphthoic acid with maximum absorbance at 570 mμ. The *p*H range of constant maximum absorbance is between 2·3 and 4·1. The molecular extinction coefficient is 2.30×10^3. The formula of the complex, established spectrophotometrically and conductometrically is FeR (R = reagent). The dissociation constant of the complex, as calculated from Job's method and mole-ratio method at 30°, is 0.804×10^{-5} and 0.981×10^{-5}, respectively, whereas the free energy of formation of the complex is −6.945 kcal./mole at 30° from the latter method.

2-Hydroxy-3-naphthoic acid forms a blue water-soluble complex with Fe^{3+} in acidic medium. The complex is formed almost instantaneously and the colour intensity remains unaltered even after 12 hours at the room temperature. The complex shows maximum absorbance at 570 mμ where the absorption by the reagent is negligible.

As no data are available in the literature on the above complex, the nature and composition of the complex have been determined spectrophotometrically, using Job's method of continued variations[1], slope-ratio method[2], and mole-ratio method[3]. The formula of the complex has been confirmed by conductometric studies. The dissociation constant of the complex has also been determined.

EXPERIMENTAL

A pure solution of ferric chloride was prepared from ferrous ammonium sulphate[4] (B.D.H., A.R.) and the iron content was estimated by the oxide method before preparing the standard solutions. 2-Hydroxy-3-naphthoic acid (R) was a B.D.H. pure sample and was recrystallised before use. Hydrochloric acid and sodium acetate used were of B.D.H. AnalaR quality.

Absorbance measurements were made by a Hilger Uvispec spectrophotometer (Model H700-308 of Hilger Watts Ltd., London) using 1 cm effective light path. Conductometric measurements were made, using a conductivity meter (type LBR, manufactured by Wissenschafflich-Technische Werkstatten, Germany) and *p*H by a Beckman *p*H-meter (Model H2). All the experiments were done at a constant temperature of 30°±0.1°.

1. *Ann. Chim.*, 1928, *x*, **9**, 113.
2. Harvey and Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.
3. Yoe and Jones, *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 111.
4. Vogel, "A Text Book of Quantitative Inorganic Analysis", Longmans Green & Co. Ltd., 3rd ed., 1962, p. 470.

EXTENSION OF THE WORK

This study has further been extended for the determination of instability constants at different ionic strengths and at various temperatures. The instability constant of the complex (K_{in}) have been calculated at various ionic strength as mentioned earlier and are reported in Table I.

The instability constants of the complex at a constant ionic strength have also been obtained at different temperatures. The results are recorded in Table II. The logarithm of the instability constants have been plotted against 1/T (Fig. 5) and from the slope of the straight line thus obtained, ΔH has been found to be -4.09 k.cal/mole. Assuming this to be constant over the range of experimental temperatures, the value of ΔS has been calculated as 35.5 e.u. The probable structure of the complex may be assigned as:-

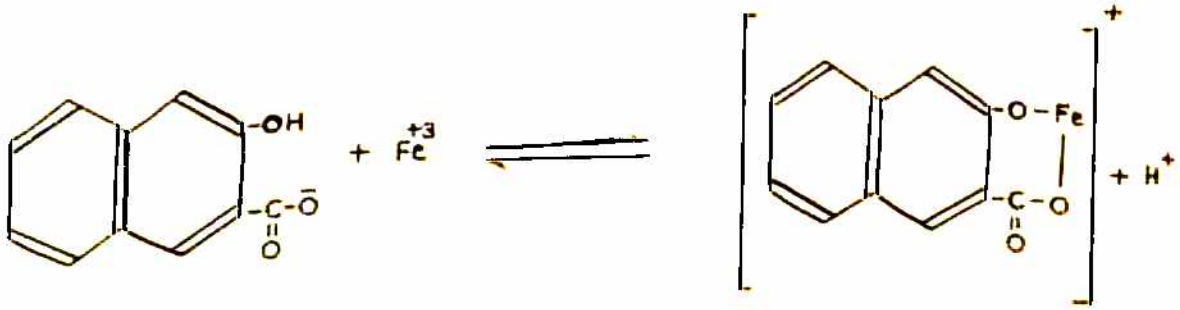

Table I

Effect of ionic strength on instability constant of the complex between Fe^{+3} ion and 2-hydroxy-3-naphthoic acid in aqueous medium.

λ = 570 mu; pH = 2.6; Temp. = 30°C

Ionic strength	Instability constant
0.02	1.04×10^{-5}
0.05	1.08×10^{-5}
0.08	1.17×10^{-5}
0.10	1.36×10^{-5}
0.15	1.48×10^{-5}
0.20	1.67×10^{-5}

Table II

Instability constant of the complex at different temperatures.

Ionic strength = 0.02; λ = 570 mu; pH = 2.6

Temp.	Instability constant
283.16°K	1.43×10^{-5}
293.16	1.25×10^{-5}
303.16	1.04×10^{-5}
313.16	8.45×10^{-6}
323.16	6.87×10^{-6}
333.16	5.61×10^{-6}

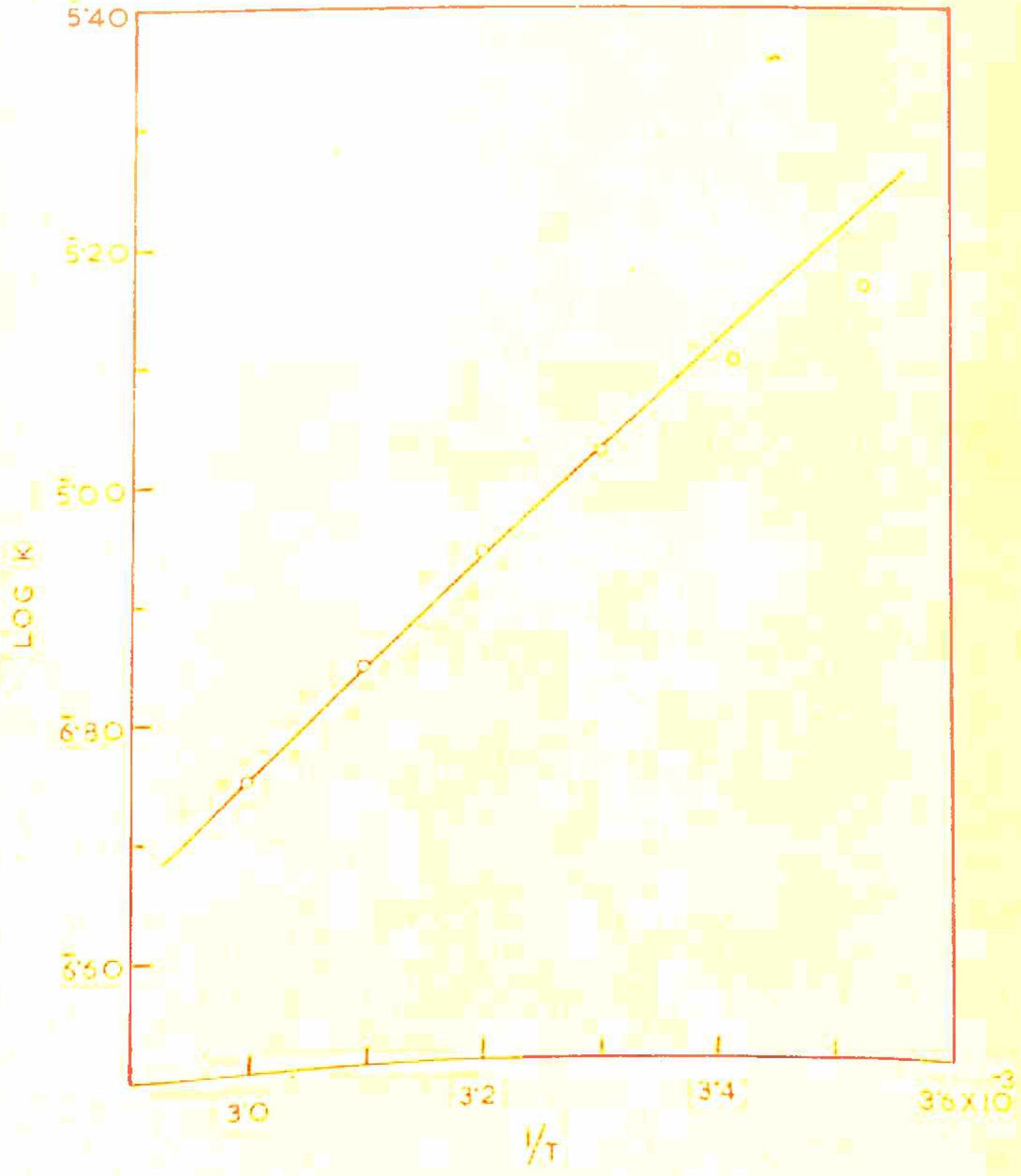

FIG. 5

PAPER No. 8

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES OF THE COMPLEX BETWEEN ALUMINIUM AND 2-HYDROXY-3-NAPHTHOIC ACID IN AQUEOUS MEDIUM

(Jour. Indian Chem. Soc., 1967, 44, 195)

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES OF THE COMPLEX BETWEEN ALUMINIUM AND 2-HYDROXY-3-NAPHTHOIC ACID IN AQUEOUS MEDIUM

The colourless complex formed by 2-hydroxy-3-naphthoic acid with aluminium has been studied in aqueous solutions of different ionic strengths and at different temperatures spectrophotometrically. The molecular composition has been determined by Job's method of continued variation and is found to be AlR (R = Reagent). The values of ΔH and ΔS are found to be - (7.45 ± 0.15) k.cal/mole and (52.2 ± 1.5) e.u. respectively. The probable structure of the complex is suggested.

The blue coloured water soluble complex formed by 2-hydroxy-3-naphthoic acid with Fe^{+3} ion has been investigated by Gupta and Soni[1]. It is seen that aluminium forms a colourless complex with 2-hydroxy-3-naphthoic acid in aqueous medium. The present investigation, therefore, gives the results obtained in the study of the complex between aluminium and 2-hydroxy-3-naphthoic acid in aqueous medium on which no data are available in literature. The molecular composition of the complex has been determined by Job's method of continued variation[2]. The

instability constant of the complex has been determined at various ionic strengths and at various temperatures.

EXPERIMENTAL

Aluminium perchlorate was prepared by heating pure aluminium chloride (E. Merck) with concentrated perchloric acid (E. Merck) until the solution no longer gave a test for chloride ion. It was diluted to required volume and sufficient perchloric acid was added to prevent hydrolysis. The aluminium content was estimated as oxide[3].

2-Hydroxy-3-naphthoic acid was B.D.H., L.R. sample and was recrystallised before use. Sodium perchlorate (E.Merck) was used to adjust the ionic strength. Hydrochloric acid and sodium hydroxide used were of AnalaR quality of B.D.H.

Absorbance measurements were made by Hilger Uvispec spectrophotometer (Model H 700-308 of Hilger Watts Ltd., London) using one cm. effective light path. The cell compartment was fitted with jacket through which water could be circulated from a thermostat (Townson and Mercer Ltd., England). A thermometer inserted into the cell compartment and allowed to come to temperature equilibrium showed a variation of less than 0.1°C over period of time much longer than those needed to make measurement of optical density.

Conductometric measurements were made using conductivity meter (LBR of Wissenschaftlich Technische Werkstatten, Germany). The titrations were carried out in a titration cell (type LTI)

which had a thermostatic jacket for temperature stability. The pH measurements were made by Beckman pH meter (Model H2). All the solutions and subsequent dilutions were made with conductivity water.

RESULTS AND DISCUSSION

2-Hydroxy-3-naphthoic acid (pH 4.0) absorbs strongly in ultraviolet with an absorption maximum at 345 mμ, whereas aluminium perchlorate is transparent round this wavelength. The addition of aluminium perchlorate shifts the absorption maximum of 2-hydroxy-3-naphthoic acid from 345 mμ to 350 mμ indicating complex formation between aluminium and 2-hydroxy-3-naphthoic acid. This shift was found from pH 2.5 to 5.0. Investigation above pH 5.0 could not be carried out because of precipitation of aluminium presumably as hydroxide. Hence the pH of 4.0 was selected for subsequent studies.

Composition of the complex: Fig. 1 gives the molecular composition of the complex at pH 4.0 using Job's method of continued variation. The optical density measurements were made at 340, 355 and 360 mμ keeping total molarity of 8.0×10^{-4}M. The quantity, $\bar{D}$ (the difference between the total optical density of the solution and that which is shown by the acid solution alone if no reaction occurs at the same pH), was plotted against $[Al^{+3}]/[Al^{+3}]+[HOC_{10}H_6CO_2H]$. At 355 and 360 mμ the complex has a higher absorption than that of free complexing agent and at 340 mμ the complexing agent has higher absorption than that of the complex. As such $\bar{D}$ at 355 and 360 mμ passes through

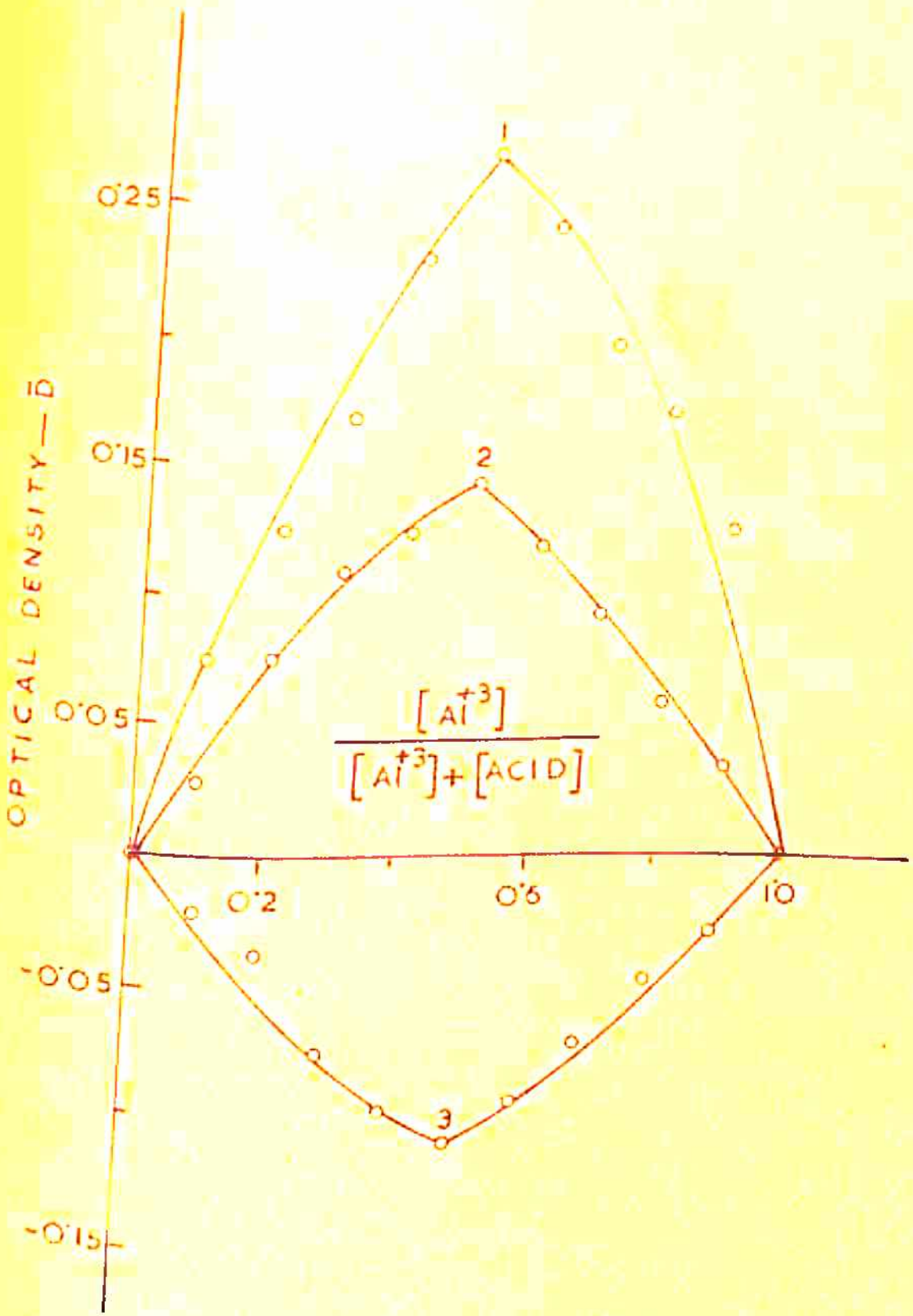
OPTICAL DENSITY — D
0·25
0·15
0·05
-0·05
-0·15
0·2
0·6
1·0
1
2
3
$\frac{[Al^{+3}]}{[Al^{+3}]+[ACID]}$

FIG. 1

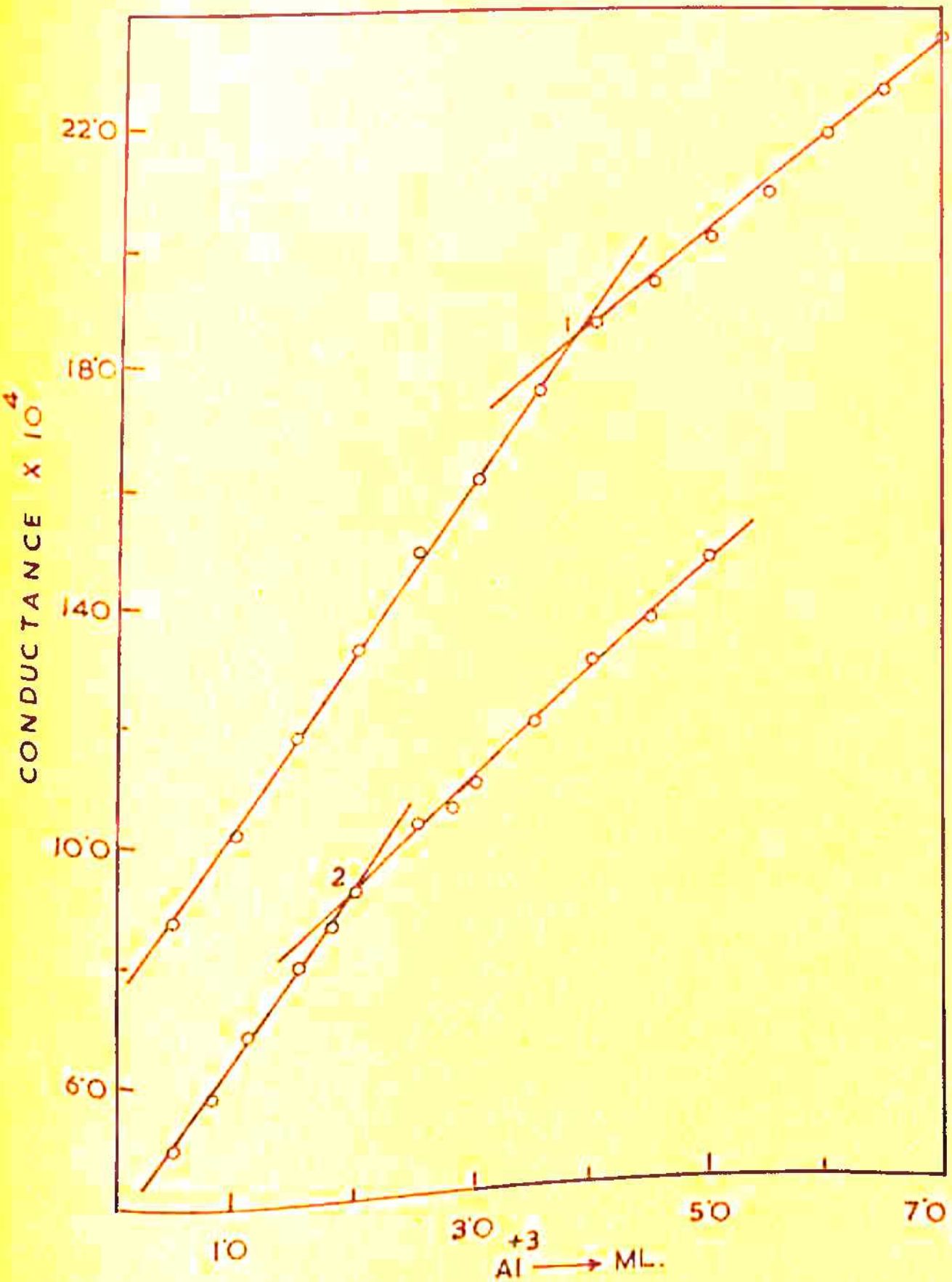

FIG. 2


Al^{+3} → ML.
1·0
3·0
5·0
7·0
3·2
3·0
2·8
pH
6·0
5·0
4·0
CONDUCTANCE X 10^{4}
3
2
1
SODIUM HYDROXIDE - ML.

FIG. 3

LEGEND OF FIGURES

Fig. 1: Job's method of continued variation.

Total molarity = 8.0×10^{-4}M; pH = 4.0.

Curves 1-3: 360, 355 and 340 mμ respectively.

Fig. 2: Complex by conductivity method.

Curve 1: 40 ml. of 1.0×10^{-3}M vs.

1.0×10^{-2}M Al^{+3} solution

Curve 2: 40 ml. of 5.0×10^{-4}M vs.

1.0×10^{-2}M Al^{+3} solution

Fig. 3: Structure of the complex.

Curve 1: 1:1, Curve 2: 1:2.

Mixtures of metal and ligand, titrated with

0.01 M NaOH.

Curve 3: 25 ml. of 1.0×10^{-3}M acid titrated with

1.0×10^{-2}M Al^{+3} solution.

maximum and that at 340 mμ passes though a minimum. The maximum at 0.5 indicates the formation of 1:1 complex.

Molecular Extinction Coefficient: The molecular extinction coefficient of the complex was calculated from the optical density of the solutions containing aluminium and 2-hydroxy-3-naphthoic acid in which the metal ion was in excess so that the concentration of the complex could be taken to be equal to that of the ligand. The average value of extinction coefficient of the complex at 340, 355 and 360 mμ is (1589 ± 4), (2457 ± 3) and (2580 ± 3) respectively whereas for the ligand it has been found to be (2132 ± 5), (1855 ± 2) and (1459 ± 3) at the above wavelengths respectively.

Instability constant: The instability constant of the complex

$$K_{in} = \frac{\{[Al^{+3}]_{Total} - [Complex]\}\{[Acid]_{Total} - [Complex]\}}{[Complex]}$$

has been calculated. The concentration of the complex is calculated from the optical density of the solution containing aluminium and the ligand using expression.

$$\text{Optical density} = \epsilon_2[Complex]1 + \epsilon_1\{[Acid] - [Complex]\}1.$$

whereas ϵ_2 and ϵ_1 are the molecular extinction coefficients of the complex and the ligand respectively and 1, the cell width.

At pH 4.0, the instability constant has been determined at different ionic strengths (vide Table I). Further the instability constant was determined at different temperatures. The results are recorded in Table II. The logarithm of the instability

Table I

Effect of ionic strength on the instability constant of the complex

λ = 355 mμ; pH = 4.0; Cell width = 1 cm.; Temp. = 20°

Ionic Strength	Instability Constant
0.02	(2.80 ± 0.09) x 10^{-5}
0.06	(4.16 ± 0.20) x 10^{-5}
0.09	(5.45 ± 0.15) x 10^{-5}
0.11	(6.72 ± 0.04) x 10^{-5}
0.16	(8,45 ± 0.15) x 10^{-5}
0.21	(1.08 ± 0.24) x 10^{-4}

Table II

Instability constant of the complex at different temperatures.

Ionic strength = 0.02; λ = 355 mμ; pH = 4.0

Temp.°K	Instability Constant
293.16	(2.80 ± 0.09) x 10^{-5}
303.16	(1.69 ± 0.16) x 10-5
313.16	(1.26 ± 0.23) x 10^{-5}
323.16	(6.59 ± 0.24) x 10^{-6}
333.16	(3.79 ± 0.37) x 10^{-6}

constants have been plotted against 1/T which is linear and from the slope of the straight line, ΔH has been found to be -(9.45 ± 0.15) k.cal/mole. Assuming this to be constant over the range of experimental temperatures, ΔS of the reaction has also been calculated and is (52.2 ± 1.5) e.u.

Conductometric studies: Curves 1 and 2, Fig. 2 give the titration curves of 40 ml. of 1 x 10^{-3}M and 5.0 x 10^{-4}M acid with 1 x 10^{-2}M solution of aluminium perchlorate respectively. From these curves also the ratio of the reagent to aluminium is found to be 1:1 which confirms the composition of the complex as obtained spectrophotometrically.

Structure of the Complex: Curve 3, Fig. 3 shows that the pH of 2-hydroxy-3-naphthoic acid (25 ml. of 10^{-3}M pH = 3.15) is gradually decreased by the addition of aluminium perchlorate solution (10^{-2}M pH = 3.50) and becomes constant at 2.90 when one equivalent of aluminium perchlorate (2.5 ml.) was added. This evidently shows an increase in the H^+ ion concentration in the mixture. This is only possible when hydroxyl hydrogen of the 2-hydroxy-3-naphthoic acid is replaced by aluminium. This is in accordance with the view advanced by Owens and Yoe[4] in the structure of Be-phenoxyquinizarin sulphate (1:1) complex.

Effect of addition of Sodium hydroxide solution: Two sets of solutions were prepared by mixing 10^{-3}M aluminium perchlorate with 10^{-3}M sodium salt of 2-hydroxy-3-naphthoic acid in the ratio of 1:1 and 1:2 respectively. The total volume in each case being kept constant by the addition of conductivity water and the solutions were allowed to stand for half an hour for

attaining equilibrium. Varying amounts of 10^{-2}M sodium hydroxide solutions were added to both samples and conductance values were noted down as usual. The observed data were plotted against the ml. of alkali added. It was interesting to note that in both the cases, conductance curves 1 and 2, Fig. 3 exhibited only one break corresponding to one equivalent of alkali added. Since the sodium salt of the acid was added, the only proton which could be replaced as a result of chelation was the hydroxyl hydrogen. The break at one equivalent of sodium hydroxide in both the cases, therefore, suggested that only 1:1 complex is formed in the system. On the basis of the above experimental observations the structure of the complex can be assigned as below:

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4. Yoe and Owens, Anal. Chem., 1959, 31, 384.

PAPER No. 9

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES ON THE INTERACTION OF BERYLLIUM WITH 2-HYDROXY-3-NAPHTHOIC ACID IN AQUEOUS MEDIUM

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES ON THE INTERACTION OF BERYLLIUM WITH 2-HYDROXY-3-NAPHTHOIC ACID IN AQUEOUS MEDIUM

Spectrophotometric method has been employed to study the colourless complex formed by the interaction of beryllium with 2-hydroxy-3-naphthoic acid in aqueous solutions of different ionic strengths and at various temperatures. The molecular composition of the complex has been determined by Job's method of continued variation and is found to be BeR (R = Reagent). The probable structure of the complex is also suggested.

2-Hydroxy-3-naphthoic acid forms a number of complexes. The coloured complexes formed by 2-hydroxy-3-naphthoic acid with Fe^{+3} and UO_2^{+2} [1,2] have been studied. Recently Gupta and Soni[3] investigated a colourless complex between 2-hydroxy-3-naphthoic acid with aluminium. In course of our investigation it has been found that it also forms a colourless complex with beryllium. The present study therefore gives the molecular composition of the complex and instability constants at different ionic strengths and at different temperatures.

EXPERIMENTAL

2-Hydroxy-3-naphthoic acid was B.D.H.,L.R. sample and was recrystallised before use. Beryllium perchlorate was prepared by heating beryllium chloride (E. Merck) with concentrated perchloric acid until the solution no longer gave a test for chloride ion. It was diluted to required volume and sufficient perchloric acid was added to prevent hydrolysis. The beryllium content was estimated gravimetrically. All other chemicals used were of B.D.H. AnalaR quality.

Absorbance, conductance and pH measurements were made in a similar manner as described in our earlier paper[3]. All the solutions and subsequent dilution were made with conductivity water.

RESULTS AND DISCUSSION

2-Hydroxy-3-naphthoic acid absorbs strongly ultra-violet region with an absorption maximum at 345 mμ whereas beryllium perchlorate is transparent round this wavelength. Addition of beryllium perchlorate to reagent shifts the absorption maximum of 2-hydroxy-3-naphthoic acid from 345 to 360 mμ, indicating the formation of the complex. The shift was found from pH 2.5 to 5.5. Investigations above 5.5. pH could not be made because of precipitation. Hence pH 4.5 was selected for subsequent studies.

COMPOSITION OF THE COMPLEX

Job's Method - In this method various solutions were prepared keeping total molarity of 8.0×10^{-4}M. The quantity $\bar{D}$ - (the difference between the total optical density of the solution and that which is shown by the acid solution alone if no reaction occurs at the same pH) was plotted against $[Be^{+2}]/[Be^{+2}]+[Acid]$ at 340, 355 and 360 mμ. The maximum at 0.5 in all the cases indicates the formation of 1:1 complex.

Molecular extinction coefficients and instability constants

The molecular extinction coefficients of complex and acid and instability constants have been calculated in a similar way as described earlier[3]. The values of molecular extinction coefficients of complex and that of the acid at 360 mμ and at 4.5 pH are (2345 ± 3) and (1585 ± 3) respectively.

Table I records the instability constant of the complex at various ionic strengths. It was found that the instability constant increases with the increase of ionic strength. The ionic atmospheres about the complex ions are denser in the salt solution and the screening effect reduces their rate of recombination[4]. The instability constant has been determined at different temperatures (vide Table II). The decrease in the instability constant is due to the decrease of dielectric constant of water with increase of temperature, and the plot of logarithm of the instability constant against 1/T gave a straight line. From the slope of the straight line, the values of ΔH was

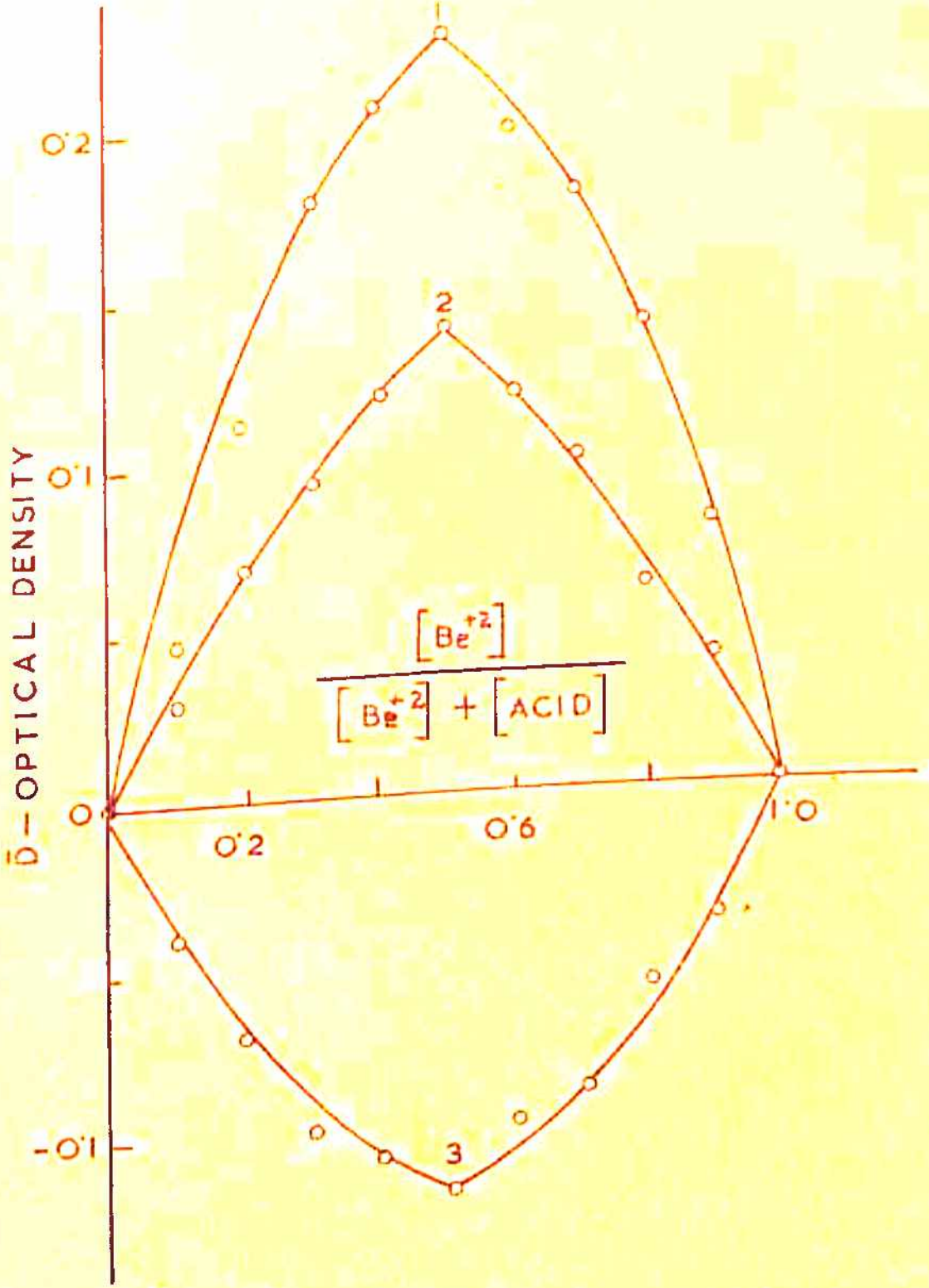


FIG. 1

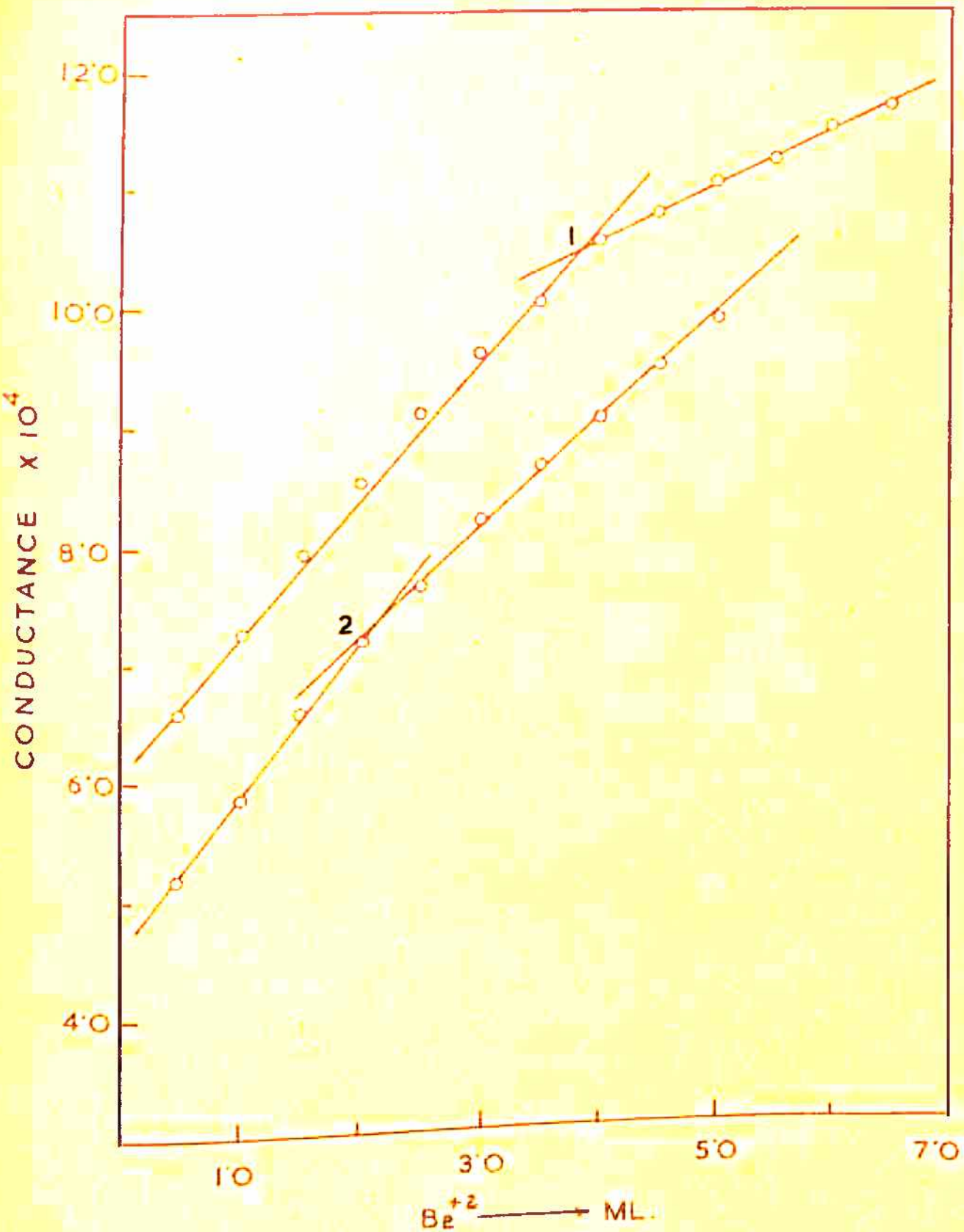


FIG. 2

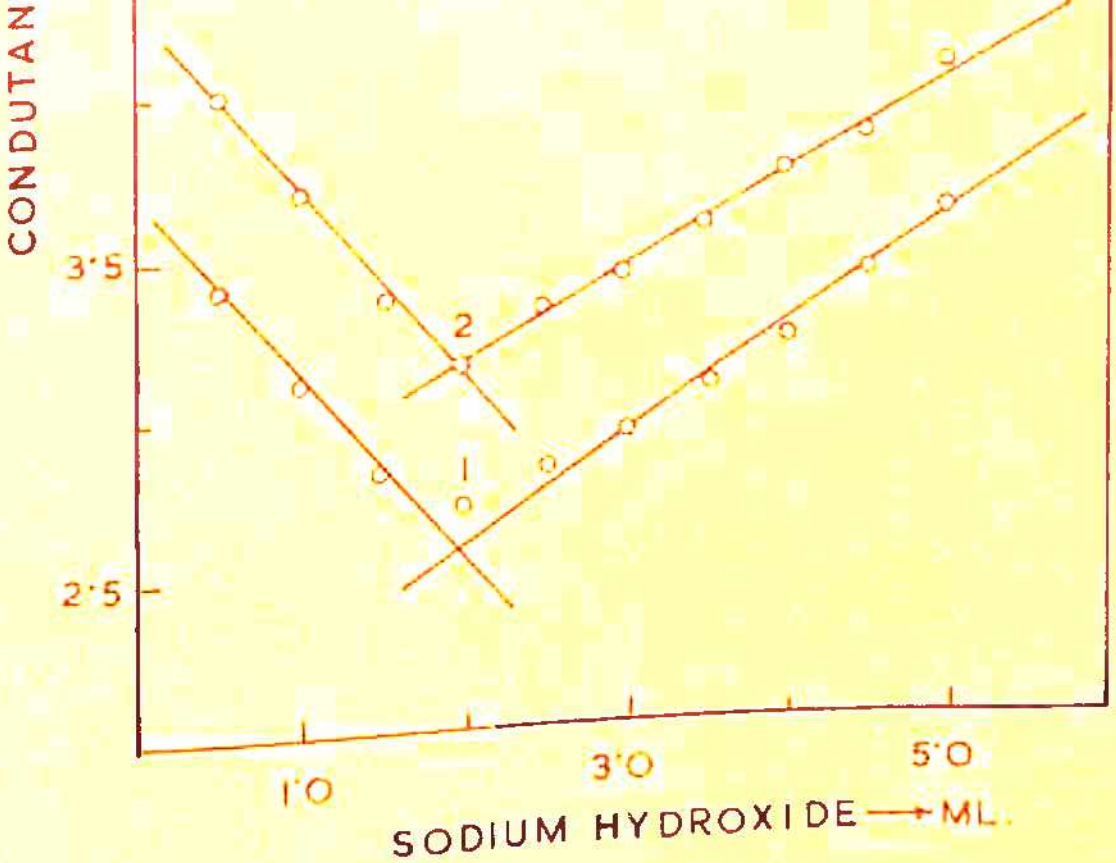
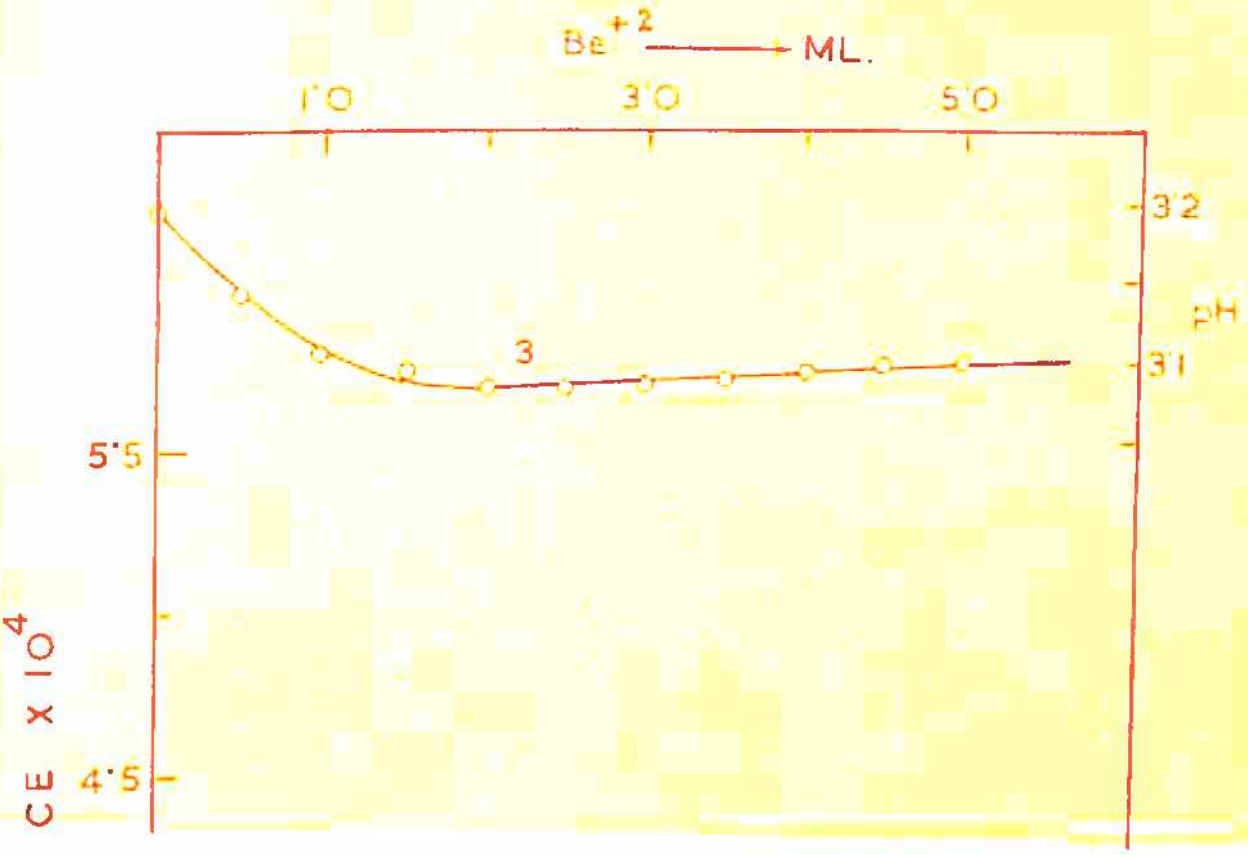


FIG. 3


Be+2 → ML.
1·0
3·0
5·0
3·2
3·1
pH
3
5·5
4·5
CE x 10^4

LEGEND OF FIGURES

Fig. 1: Job's method of continued variation.

Total molarity = 8.0×10^{-4}M; pH = 4.5.

Curves 1-3: 360, 355 and 340 mμ respectively.

Fig. 2: Complex by conductivity method.

Curve 1: 40 ml. of 1.0×10^{-3}M vs. 1.0×10^{-2}M Be^{+2} solution.

Curve 2: 40 ml. of 5.0×10^{-4}M vs. 1.0×10^{-2}M Be^{+2} solution.

Fig. 3: Structure of the complex.

Curve 1: 1:1,

Curve 2: 1:2 mixtures of metal and ligand titrated with 0.01 M NaOH.

Curve 3: 20 ml. of 10^{-3}M acid titrated with 1.0×10^{-2}M Be^{+2} solution.

Table I

Effect of ionic strength on the instability constant of the Complex between Be^{+2} and 2-hydroxy-3-naphthoic acid.

λ = 360 mμ; pH = 4.5; Cell width = 1 cm., Temp. = 30°C

Ionic Strength	Instability Constant
0.01	$(3.01 \pm 0.02) \times 10^{-5}$
0.02	$(4.10 \pm 0.10) \times 10^{-5}$
0.05	$(4.80 \pm 0.30) \times 10^{-5}$
0.08	$(5.70 \pm 0.30) \times 10^{-5}$
0.10	$(6.45 \pm 0.20) \times 10^{-5}$
0.15	$(7.31 \pm 0.30) \times 10^{-5}$
0.20	$(8.15 \pm 0.10) \times 10^{-5}$

Table II

Instability constant of the complex at different temperatures

Ionic strength = 0.01; λ = 360 mμ; pH = 4.5

Temp. °K	Instability Constant
283.16	$(4.10 \pm 0.08) \times 10^{-5}$
293.16	$(3.58 \pm 0.02) \times 10^{-5}$
303.16	$(3.02 \pm 0.02) \times 10^{-5}$
313.16	$(2.39 \pm 0.15) \times 10^{-5}$
323.16	$(1.91 \pm 0.08) \times 10^{-5}$
333.16	$(1.65 \pm 0.08) \times 10^{-5}$

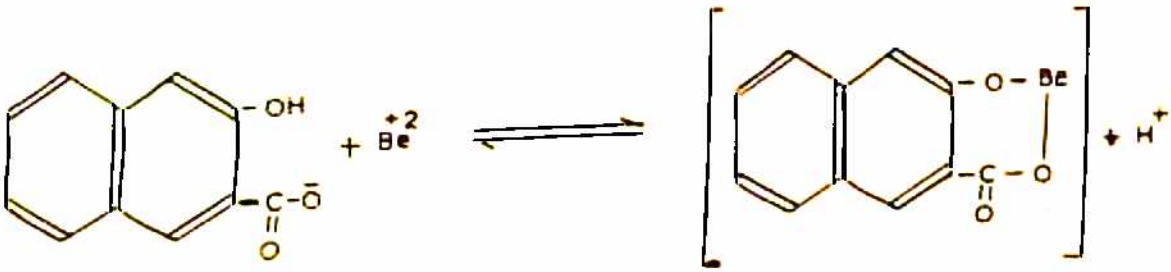
found to be -(3.67 ± 0.5) k.cal/mole. Assuming this to be constant over the range of experimental temperatures, the value of ΔS has been calculated to be (32.8 ± 2.0) e.u.

Conductometric studies - The molecular composition of the complex has also been confirmed by conductometric measurements. Curves 1 and 2, Fig. 2 give conductometric titrations of 40 ml. of 1.0 x 10^{-3}M and 0.5 x 10^{-3}M of the reagent with 1 x 10^{-2}M beryllium perchlorate solution which shows the formation of 1:1 complex.

Structure of the complex - Curve 3, Fig. 3, shows that the pH of 2-hydroxy-3-naphthoic acid (20 ml. of 10^{-3}M; pH 3.2) is gradually decreased by the addition of beryllium perchlorate (10^{-2}M; pH = 3.70) and became constant at 3.10 when one equivalent of beryllium perchlorate was added. This shows that there is an increase of hydrogen ion concentration. This is only possible when hydroxyl hydrogen of the 2-hydroxy-3-naphthoic acid is replaced by beryllium.

Further, two sets of solutions were prepared by mixing sodium salt of 2-hydroxy-3-naphthoic acid and beryllium perchlorate in the ratio of 1:1 and 1:2 respectively. The total volume in each case being kept constant by the addition of conductivity water. These solutions were titrated with sodium hydroxide solution. It was observed that in both the cases conductance curves 1 and 2 (Fig. 3) exhibited only one break at one equivalent of sodium hydroxide added. Since sodium salt of the acid was used, the only proton which could be replaced

as a result of chelation was hydroxyl hydrogen of 2-hydroxy-3-naphthoic acid, thus suggesting the formation of 1:1 complex. On the basis of the above experimental observations, the structure of the complex can be assigned as -



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4. P. Debye, Trans. Electrochem. Soc., 1942, 82, 265.

CHAPTER III

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES ON THE COMPLEXES OF 2:4 DIHYDROXYBENZOIC ACID IN AQUEOUS MEDIUM

PAPER No. 10

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES OF THE COMPLEX OF Cu^{+2} ION AND 2:4 DIHYDROXYBENZOIC ACID IN AQUEOUS MEDIUM

(Jour. Indian Chem. Soc., 1966,43,331.)

Jour. Indian Chem. Soc., Vol. 43, No. 5, 1966]

Spectrophotometric and Conductometric Studies of the Complex of Cu^{2+} Ion and 2,4-Dihydroxybenzoic Acid in Aqueous Medium

S. L. Gupta, R. N. Soni, and J. N. Jaitly

Cu^{2+} ion forms a green, water-soluble complex with 2,4-dihydroxybenzoic acid with maximum absorption at 390 mμ in acidic medium. The complex is stable to wide temperature variation and at the pH range of 5.0 to 6.0. The molecular extinction coefficient is 0.54×10^4. The formula of the complex, established spectrophotometrically and conductometrically, is CuR (R = reagent). The dissociation constant of the complex and its free energy of formation from Job's method are 1.995×10^{-3} and -3.71 kcal./mole at 30°, respectively. The probable structure of the complex is also suggested.

Tanabe and Hata[1] studied the colour reaction of 2,4-dihydroxybenzoic acid with Cu^{2+} ion and found a green colour to develop in presence of 1 to 2 drops of 28% NH_4OH, changing to reddish violet after 2 to 3 min. In a systematic study of the reaction between 2,4-dihydroxybenzoic acid and Cu^{2+} ion, we find that a green-coloured, water-soluble complex is formed instantaneously at the *p*H range of 5.0 to 6.0 and a reddish violet complex at the *p*H range of 9 to 11; the latter is not instantaneous and takes some hours. In view of the paucity of data about the nature and composition of these complexes, an investigation was undertaken to study the complexes spectrophotometrically using the same methods as described in another communication[2]. Formation of the green coloured, water-soluble complex between 2,4-dihydroxybenzoic acid and Cu^{2+} in acidic medium is instantaneous. Its intensity remains constant even up to 24 hours and is stable to wide temperature variation. The complex shows the maximum absorbance at 390 mμ where the absorbance by the reagent and the metal is very small. The details of the reddish violet complex will be reported in a subsequent communication.

EXPERIMENTAL

A pure sample of $CuSO_4.5H_2O$ (B.D.H., A.R.) was used for preparing standard solutions. 2,4-Dihydroxybenzoic acid (R) was B.D.H., L.R. sample and was recrystallised before use. HCl, NaOH, and sodium acetate used were of B.D.H. AnalaR quality.

Measurements of absorbance and conductance were made in the same way as described previously[2]. Measurements of *p*H were made with a Beckman *p*H meter (Model H 2). All the experiments were made at a constant temperature of 30°±0.1°.

1. *Ann. Rep. Fac. Pharm. Kanazawa Univ.*, 1956, **6**, 7; *Chem. Abs.*, 1957, **51**, 2458°.
2. Gupta and Soni, this *issue*, p. 311.

EXTENSION OF THE WORK

This study has further been extended for the determination of instability constants at different ionic strengths and at various temperatures. The instability constant of the complex (K_{in}) have been calculated at various ionic strengths as mentioned earlier and are reported in Table I.

The instability constants of the complex at a constant ionic strength have also been obtained at different temperatures. The results are recorded in Table II. The logarithm of the instability constants have been plotted against 1/T (Fig. 5) and from the slope of the straight line thus obtained, Δn has been found to be -1.5 k.cal/mole. Assuming this to be constant over the range of experimental temperature, the value of ΔS has been calculated as 17.7 e.u.

Table I

Effect of ionic strength on the instability constant of the complex between Cu^{+2} ion and 2:4 dihydroxybenzoic acid in acidic medium.

λ = 390 mμ; pH = 5.5 Temp. = 30°C

Ionic strength	Instability constant
0.01	1.88×10^{-3}
0.02	2.05×10^{-3}
0.03	2.16×10^{-3}
0.05	2.31×10^{-3}
0.08	2.57×10^{-3}
0.10	2.81×10^{-3}
2.15	3.04×10^{-3}
0.20	3.20×10^{-3}

Table II

Instability constant of the complex at different temperatures

Ionic strength = 0.01; λ = 390mμ; pH = 5.5

Temp.°K	Instability constant
283.16	1.94×10^{-3}
293.16	1.88×10^{-3}
303.16	1.70×10^{-3}
313.16	1.58×10^{-3}
323.16	1.47×10^{-3}
333.16	1.36×10^{-3}

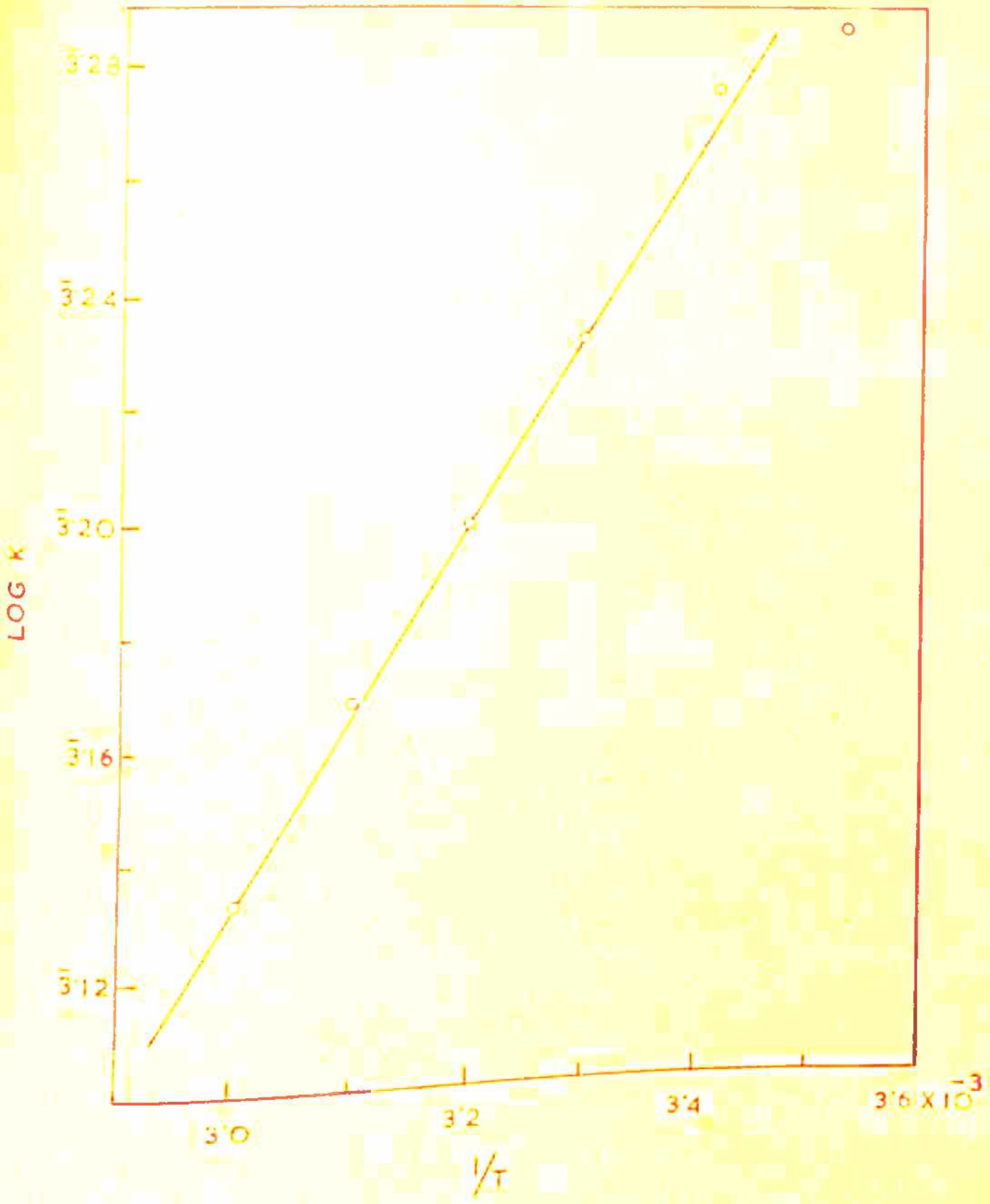


FIG. 5

PAPER No. 11

SPECTROPHOTOMETRIC STUDIES OF THE COMPLEX BETWEEN Cu^{+2} AND 2:4 DIHYDROXYBENZOIC ACID IN PRESENCE OF AMMONIA

(Jour. Inst.Chem., In press.)

SPECTROPHOTOMETRIC STUDIES OF THE COMPLEX BETWEEN Cu^{+2} AND 2:4 DIHYDROXYBENZOIC ACID IN PRESENCE OF AMMONIA

The reddish violet complex formed by 2:4 dihydroxybenzoic acid with cupric ion in presence of ammonia has been studied in aqueous solutions of different ionic strengths and at different temperatures spectrophotometrically. It has an absorption maximum at 490 mμ. The optimum pH range is 10.0 to 11.0. The molecular composition of the complex has been determined by Job's method of continued variation, slope-ratio method, molar-ratio method and is found to be CuR (R = Reagent). The molecular extinction coefficient of the complex is 1.53×10^3. The values of ΔH and ΔS are found to be -2.30 k.cal per mole and 28.4 e.u. respectively.

Tanabe and Hata[1] studied the colour reaction of 2:4 dihydroxybenzoic acid with cupric ion in presence of 1 to 2 drops of 28% ammonia. They found that a green colour is first developed which changes to reddish violet after sometime. In a previous communication Gupta et al.[2] studied green water soluble complex formed by 2:4 dihydroxybenzoic acid with cupric ions in acidic medium. The present communication gives the nature and composition of the complexformed (spectrophotometrically) using Job's method of continued variation[3], slope-ratio method[4] and molar-ratio method[5] in presence of ammonia. The instability constant

of the complex has been determined at different ionic strengths and at different temperatures.

EXPERIMENTAL

A standard solution of copper was made from $CuSO_4.5H_2O$ (B.D.H., A.R.). 2:4 Dihydroxybenzoic acid (R) was B.D.H., L.R. sample and was recrystallised before use. Ammonia solution was of B.D.H.; L.R. quality. Potassium chloride (B.D.H.,A.R.) was used for adjusting ionic strengths. The technique and other details have been described earlier.

RESULTS AND DISCUSSION

Spectral studies - Equal volumes of copper sulphate solution ($M \times 10^{-3}$) and the reagent ($M \times 10^{-3}$) were taken in 25 ml. flask. Suitable quantity of 25% ammonia solution was added so that the pH after dilution was 10.5. The development of the colour was slow and takes about 24 hours for complete reaction. The complex so formed showed maximum absorption at 490 mμ. The absorption due to 2:4 dihydroxybenzoic acid and copper sulphate is negligible at this wave-length. The corresponding wave-length of 490 mμ was thus used for subsequent work.

Effect of pH - Solutions containing the same concentration of copper sulphate and the reagent were prepared at different pH values by the addition of ammonia and absorbance noted at 490 mμ. It was found that the complex was stable between the pH range 10.0 to 11.0 and hence a pH of 10.5 was selected for subsequent studies.

Composition of the Complex

Job's Method - A series of solutions was prepared from copper sulphate and the reagent ($M \times 10^{-3}$) in which the ratios of copper to reagent varied from 1:11 to 11:1. The pH was kept at 10.5 by adding suitable quantity of ammonia. The absorbance was made at 490 mμ after 24 hours. Curves 1, 2 and 3, Fig. 1 were obtained using total molarity of 2.4×10^{-3}, 1.2×10^{-3} and 6.0×10^{-4}M respectively. The maximum at 6:6 indicates the formation of complex containing copper and the reagent in the ratio of 1:1.

Slope-ratio Method - The concentration of variable component was varied from 4.0×10^{-5}M to 2.4×10^{-4}M in presence of excess concentration of 4.0×10^{-4}M of the constant component. The pH of solutions was maintained at 10.5 and absorbance measurements were taken at 490 mμ after 24 hours. Fig. 2 shows the absorbance plotted against the concentration of the variable component at 490 mμ. The slopes of two straight lines provide the copper : reagent ratio as 1:1.

Molar-ratio Method - A series of solutions was prepared from 2.0×10^{-4}M of acid and varying amounts of copper sulphate solution were added such that mole ratio of reagent to copper was from 1:Q2 to 1:7. Fig. 3 shows a break at a ratio of one mole of reagent to one mole of copper.

Molecular Extinction coefficient and instability constant

Using optical densities of solutions containing large excess of 2:4 dihydroxybenzoic acid so that as a first approxi-

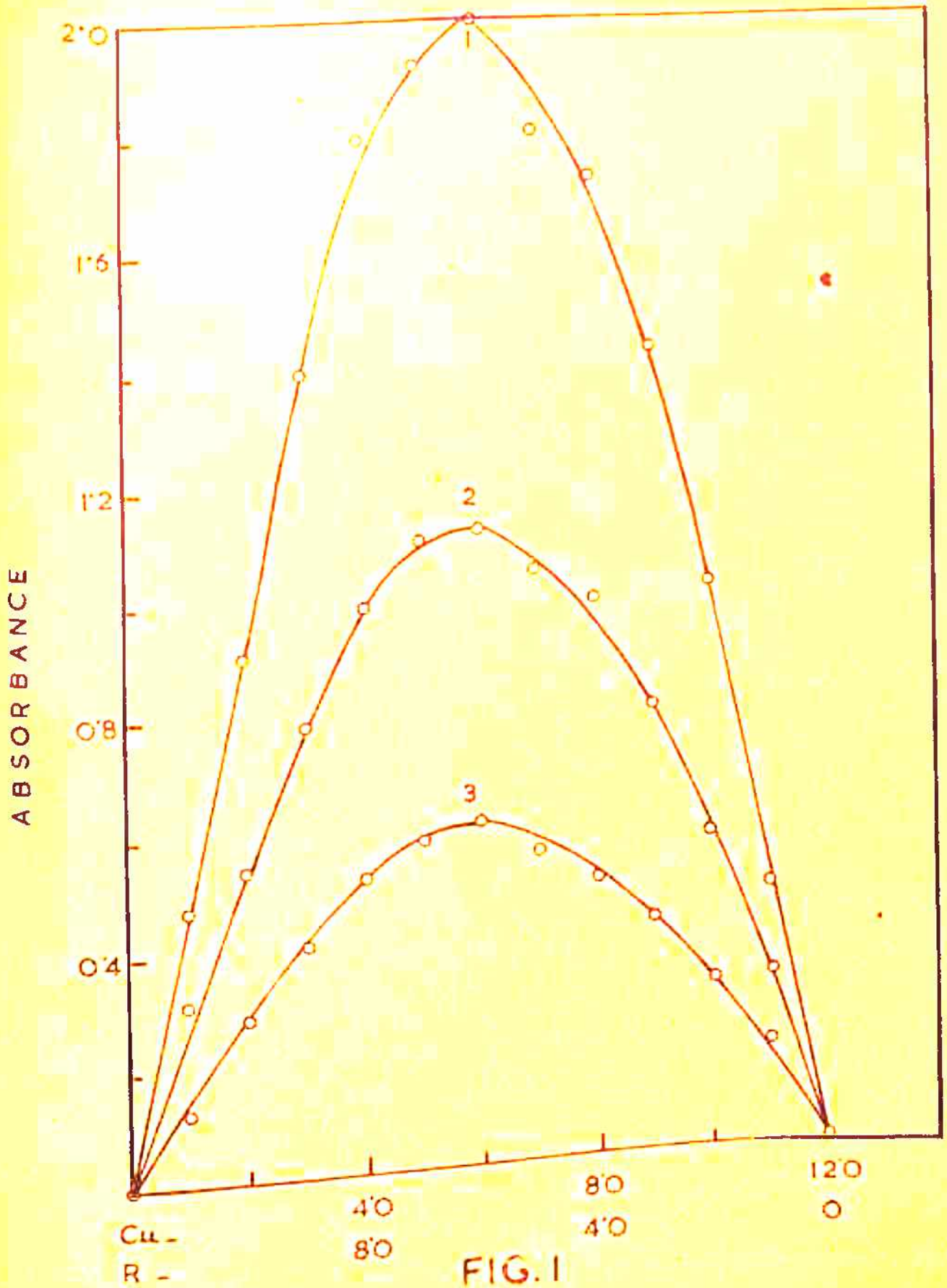


FIG. 1

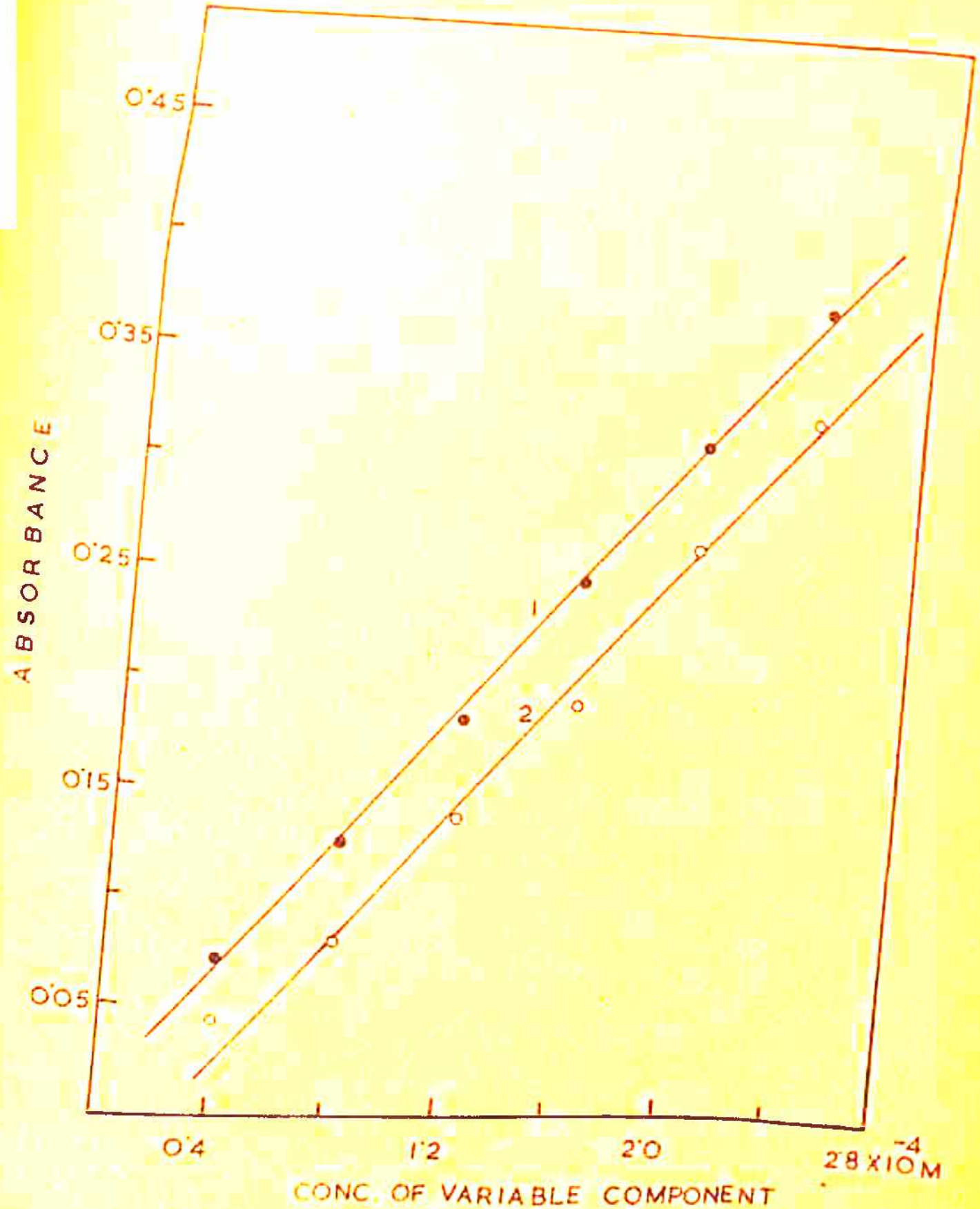

0·45
0·35
0·25
0·15
0·05
ABSORBANCE
1
2
0·4
1·2
2·0
2·8 X 10⁻⁴ M
CONC. OF VARIABLE COMPONENT

FIG. 2

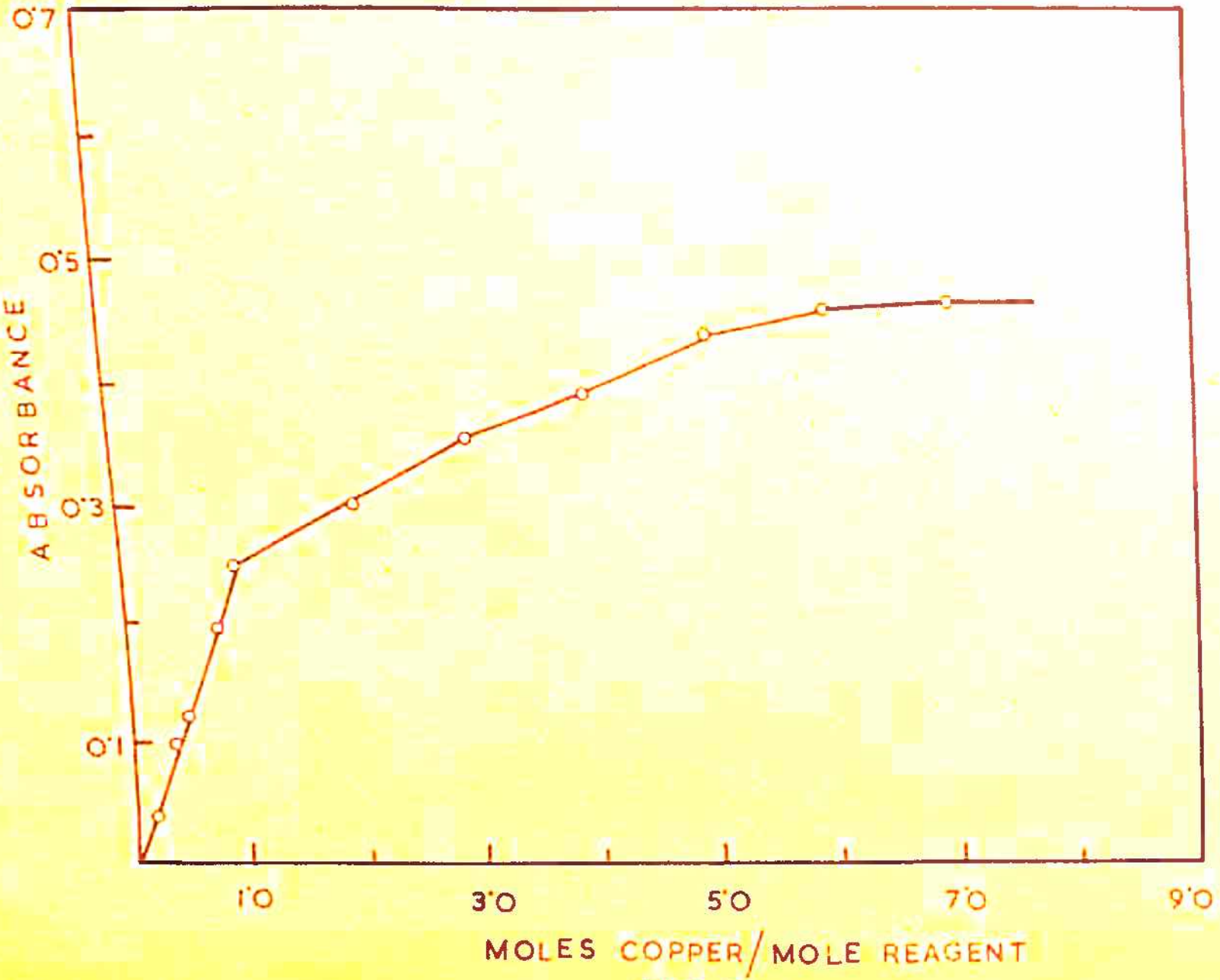

0·7
0·5
0·3
0·1
ABSORBANCE
1·0
3·0
5·0
7·0
9·0
MOLES COPPER/MOLE REAGENT

FIG. 3

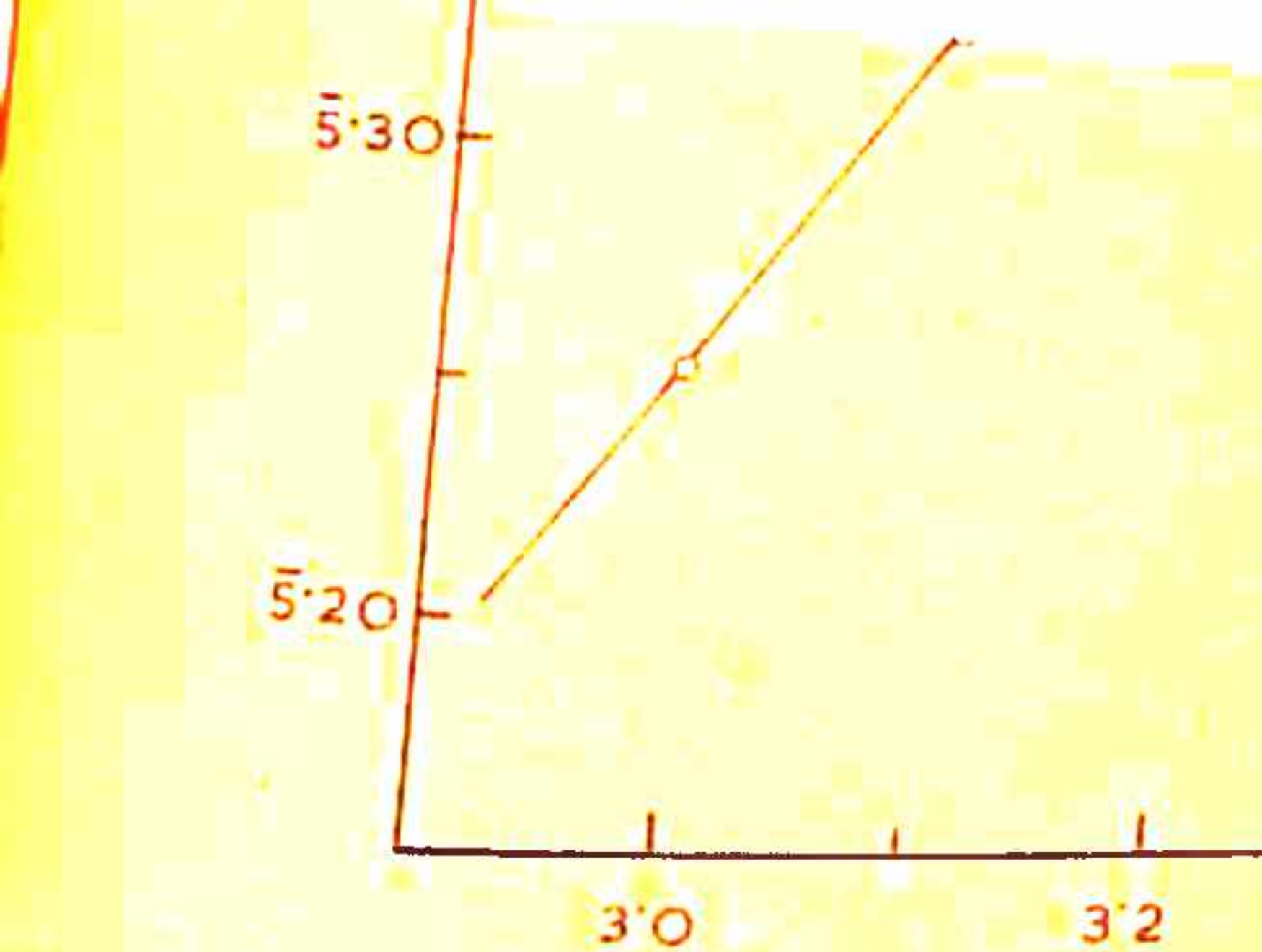


FIG. 4

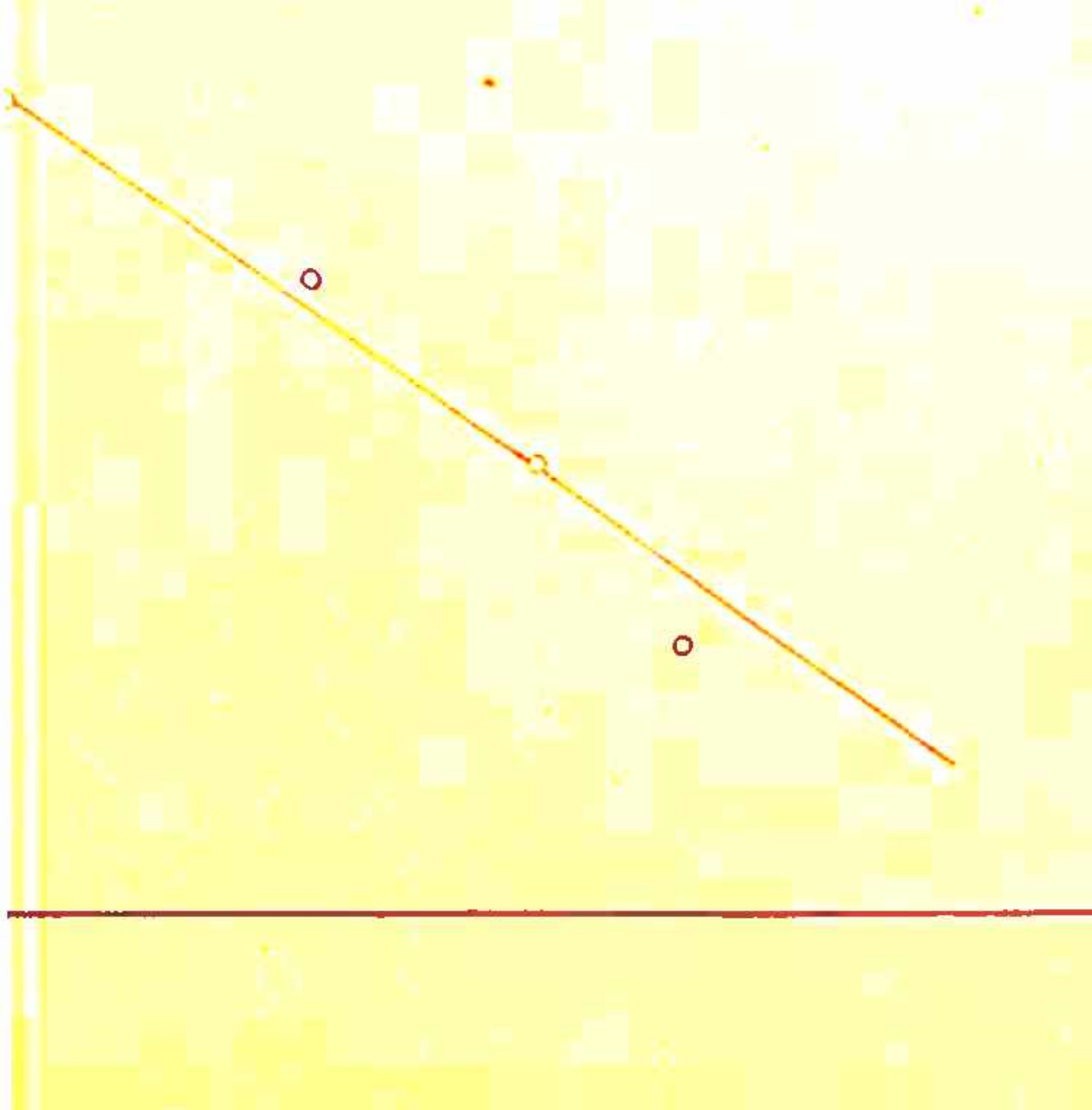

3·4 x 10⁻³

LOG K

$\bar{5}.40$

$\bar{5}.50$

$\bar{5}.60$



LEGEND OF THE FIGURES

Fig. 1: Job's method of continued variation.

Curve 1. Total Molarity 2.4×10^{-3}M

Curve 2. Total Molarity 1.2×10^{-3}M

Curve 3. Total Molarity 6.0×10^{-4}M

Fig. 2: Slope-ratio method.

Curve 1. Copper varying

Curve 2. Reagent varying

Fig. 3: Molar-ratio method.

Fig. 4: Variation of log K with 1/T.

---

mation the concentration of the complex may be taken to be equal to that of copper ions added, the molecular extinction coefficient of the complex is found to be 1.53×10^3. The instability constant of the complex

$$K_{in} = \frac{\{[Cu^{+2}]_{Total} - [Complex]\}\{[Acid]_{Total} - [Complex]\}}{[Complex]}$$

has been calculated where the concentration of the complex is obtained from the extinction coefficient of the complex. The instability constants of the complex at pH 10.5 have been determined at ionic strengths 0.01, 0.02, 0.05, 0.08, 0.10, 0.15 and 0.20 (vide Table I).

The instability constant of the complex at a constant ionic strength of 0.01 has also been determined at different temperatures. The results are recorded in Table II. Further, the logarithm of the instability constants have been plotted against 1/T (Fig. 4). From the slope of the straight line, ΔH has been found to be -2.30 k.cal per mole. Assuming this to be constant over the range of experimental temperatures, ΔS of the reaction has also been calculated and is 28.4 e.u.

Proposed Structures of the Complex

Cupric ion forms a complex with ammonia with a structure $Cu(NH_3)_4^{+2}$. Since at higher pH, the carboxylic and phenolic groups of 2:4 dihydroxybenzoic acid are largely dissociated[6], therefore, two ammonia groups of $Cu(NH_3)_4^{+2}$ are replaced with 2:4 dihydroxybenzoic acid forming a neutral chelate as mentioned below, This

Table I

Effect of ionic strength on the instability constant of the complex

pH = 10.5; λ = 490 mμ; Temp. = 20°.

Ionic Strength	Instability Constant
0.01	3.06×10^{-5}
0.02	6.57×10^{-5}
0.05	1.04×10^{-4}
0.08	1.49×10^{-4}
0.10	1.81×10^{-4}
0.15	2.38×10^{-4}
0.20	2.86×10^{-4}

Table II

Instability constant of the complex at different temperatures

Ionic strength = 0.01; pH = 10.5; λ = 490 mμ.

Temp.°K	Instability Constant
293.16	3.06×10^{-5}
303.16	2.90×10^{-5}
313.16	2.54×10^{-5}
323.16	2.18×10^{-5}
333.16	1.80×10^{-5}

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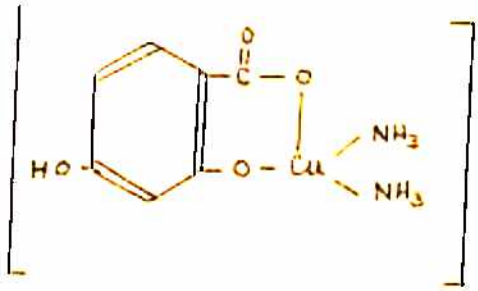
is in accord with the normal co-ordination number of four for the copper.



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PAPER No. 12

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES OF THE COMPLEX BETWEEN ALUMINIUM AND 2:4 DIHYDROXYBENZOIC ACID IN AQUEOUS MEDIUM

(Jour. B.I.T.S., In press.)

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES OF THE COMPLEX BETWEEN ALUMINIUM AND 2:4 DIHYDROXYBENZOIC ACID IN AQUEOUS MEDIUM

The colourless complex formed by 2:4 dihydroxybenzoic acid with aluminium has been studied in aqueous solutions of different ionic strengths and at different temperatures spectrophotometrically. The molecular composition has been determined by Job's method of continued variation and is found to be AlR (R = Reagent). The quantities ΔH and ΔS, have been calculated from the temperature coefficient of the instability constant. The probable structure of the complex is also suggested.

In course of our investigations on complexes formed by 2:4 dihydroxybenzoic acid with various bivalent and trivalent metal ions, it has been found that aluminium forms a colourless complex with 2:4 dihydroxybenzoic acid. As there are no data available in literature about the stability constant and the thermodynamic functions regarding this complex, the present investigation, therefore, gives the results obtained in such studies spectrophotometrically.

EXPERIMENTAL

2:4 Dihydroxybenzoic acid was B.D.H., L.R. sample and was recrystallised before preparing the standard solution. Aluminium perchlorate was prepared by heating pure aluminium chloride (E. Merck) with concentrated perchloric acid (E. Merck) until the solution no longer gave a test for chloride ion. It was diluted to required volume and sufficient perchloric acid was added to prevent hydrolysis. The aluminium content was estimated as oxide[1].

Ionic strength of solutions was adjusted by sodium-perchlorate (E. Merck). Hydrochloric acid and sodium hydroxide used were of AnalaR quality of B.D.H. The technique and other details have been described earlier[2].

RESULTS AND DISCUSSION

2:4 Dihydroxybenzoic acid (pH = 4.5) absorbs strongly in ultra-violet with an absorption maximum at 290 mμ, whereas aluminium perchlorate is transparent round this wavelength. Addition of aluminium perchlorate to the 2:4 dihydroxybenzoic acid solution causes the shift in the absorption maximum to higher wavelengths 295 mμ, suggesting complex formation between aluminium and 2:4 dihydroxybenzoic acid. This shift was found from pH 3.0 to 5.0. Investigation above pH 5.0 could not be made because of precipitation of aluminium presumably as hydroxide. Hence the pH of 4.5 was selected for subsequent studies.

1. Composition of the Complex

The molecular composition of the complex at pH 4.5 was determined by Job's method[3]. The optical density measurements were made at the total molarity of 4.0×10^{-4} M at the wavelengths 295, 300 and 305 mμ. The quantity, $\bar{D}$ (the difference between total optical density of the solution and that which is shown by the acid solution alone if no reaction occurs at the same pH) was plotted against $[Al^{3+}]/[Al^{3+}] + [Acid]$. Fig. 1 shows the maximum in all the three curves at 0.5, indicating the formation of the 1:1 complex.

2. Molecular Extinction Coefficient

The molecular extinction coefficient of the complex was calculated by the method outlined in our earlier communication[4]. The average value of extinction coefficient of the complex at 305 mμ is (4528 ± 10) whereas for the ligand it has been found to be(1101 ± 3) at pH 4.5.

3. Instability constant

The instability constant of the complex

$$K_{in} = \frac{\{[Al^{+3}]_{Total} - [Complex]\}\{[Acid]_{Total} - [Complex]\}}{[Complex]}$$

has been calculated. The concentration of the complex is calculated from the optical density of the solution containing aluminium and the ligand using expression

$$\text{Optical density} = \epsilon_2[Complex]\,l + \epsilon_1\{[Acid] - [Complex]\}\,l$$

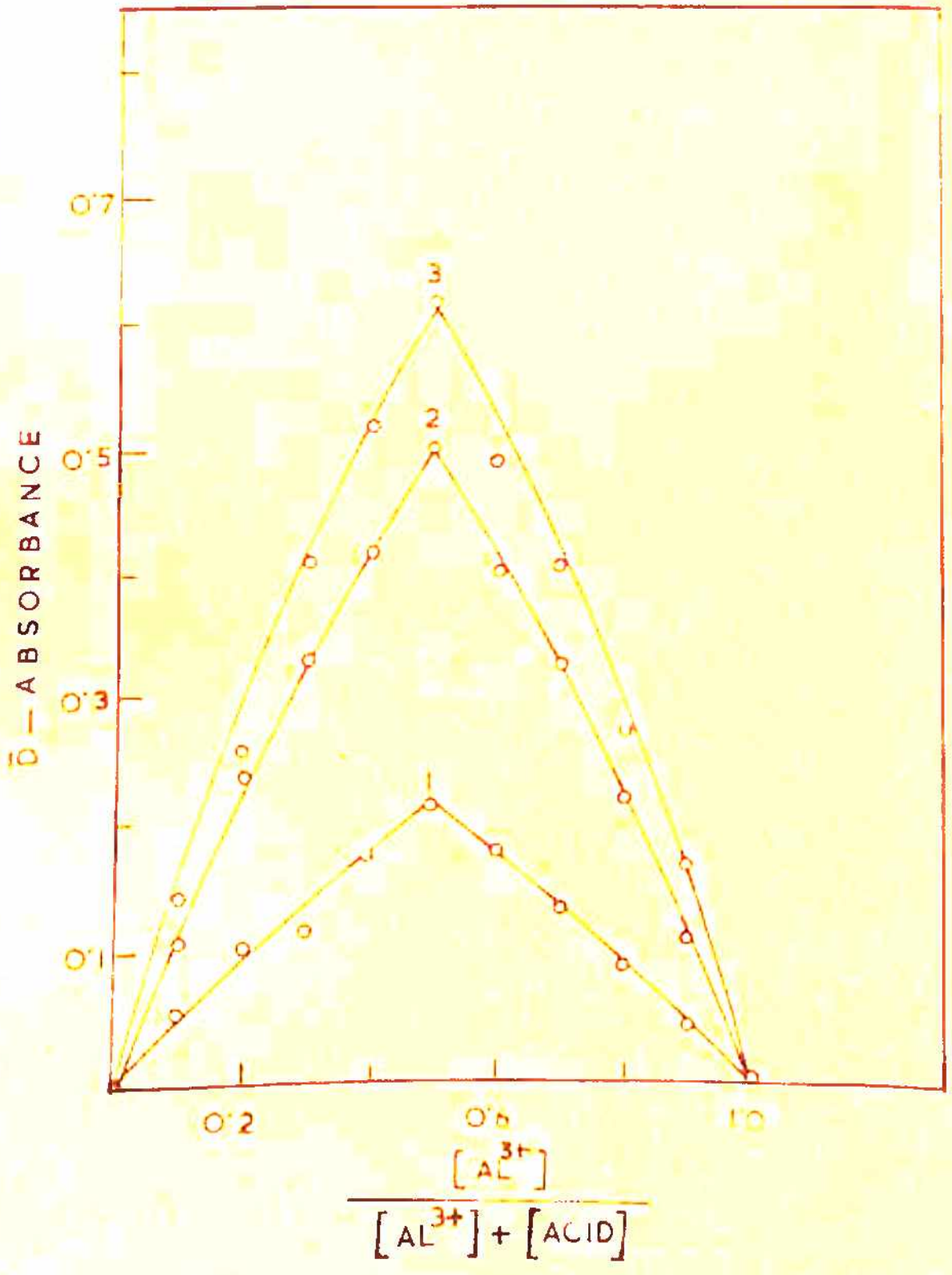

FIG. 1

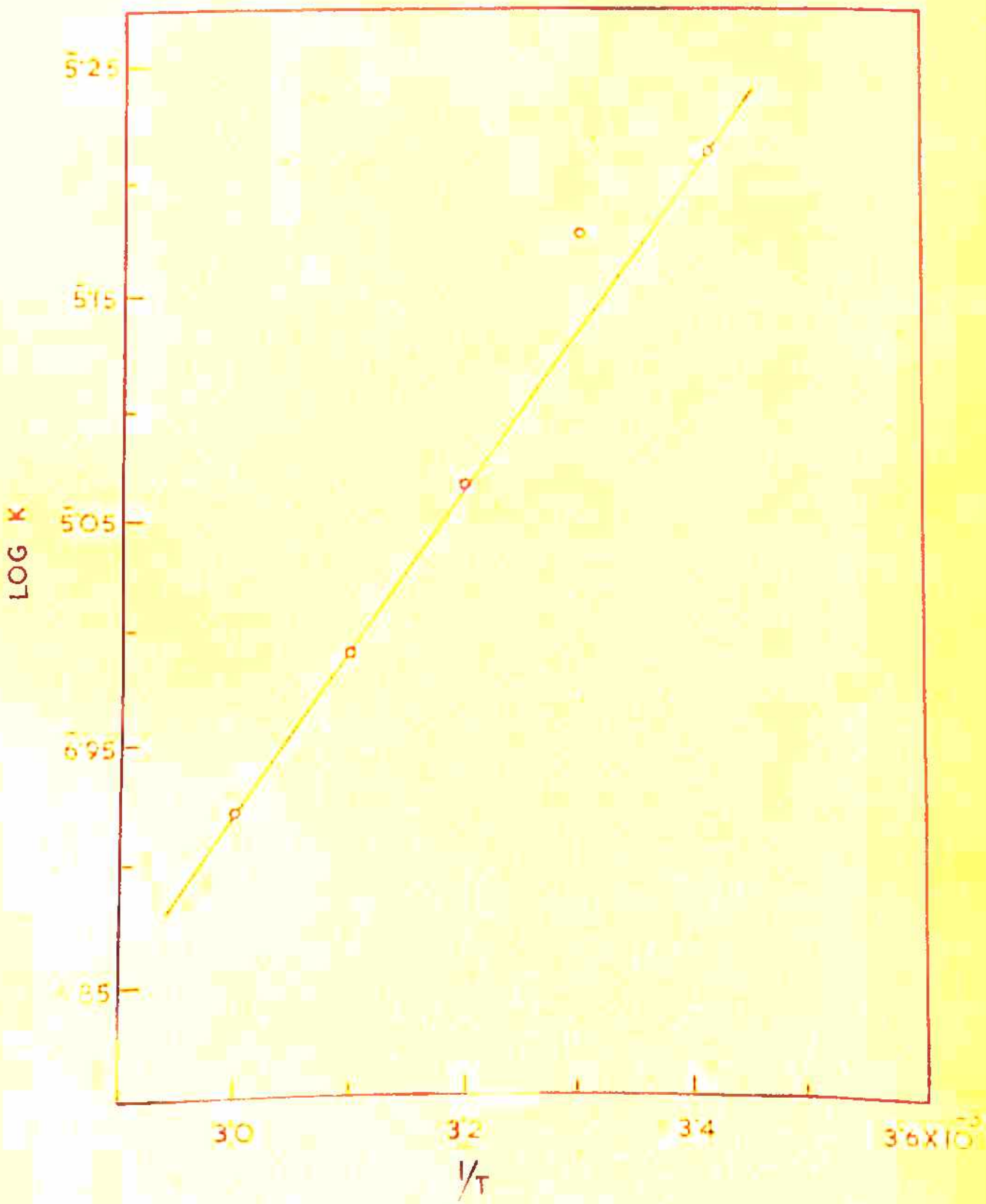

FIG. 2

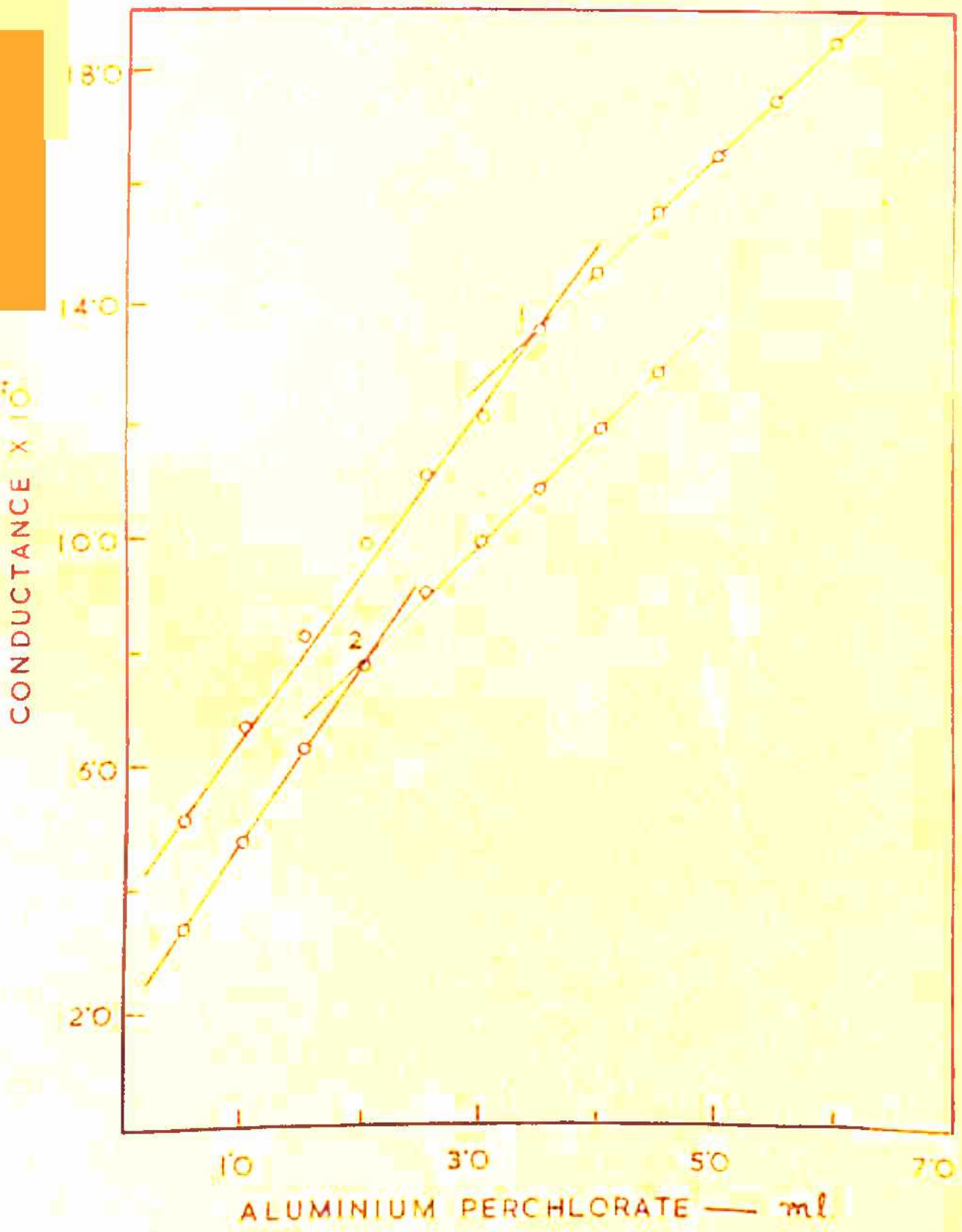
18·0
14·0
10·0
6·0
2·0
CONDUCTANCE X 10
1
2
1·0
3·0
5·0
7·0
ALUMINIUM PERCHLORATE — ml

FIG. 3

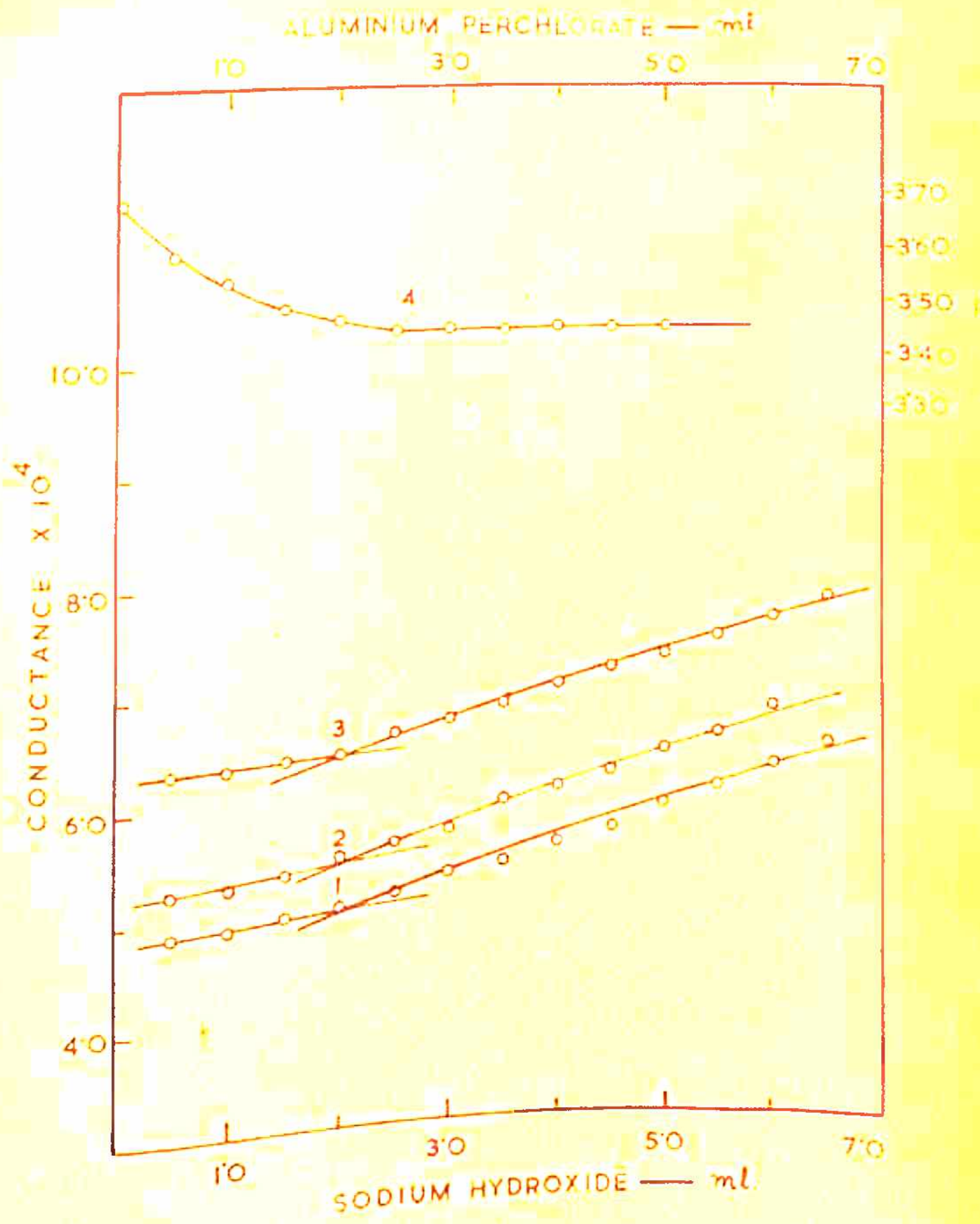
ALUMINIUM PERCHLORATE — ml
1·0
3·0
5·0
7·0
3·70
3·60
3·50
3·40
3·30
pH
10·0
8·0
6·0
4·0
CONDUCTANCE X 10⁴
4
3
2
1
1·0
3·0
5·0
7·0
SODIUM HYDROXIDE — ml.

FIG. 4

LEGEND OF FIGURES.

Fig. 1: Job's method of continued variation.
Total molarity 4.0×10^{-4}M, pH = 4.5.
Curves 1-3. 295, 300 and 305 mμ respectively.

Fig. 2: Variation of log K with 1/T.
Curve 1: 40 ml. of 1×10^{-3}M vs.
1.0×10^{-2}M Al^{+3} solution
Curve 2: 40 ml. of 5.0×10^{-4}M vs.
1.0×10^{-2}M Al^{+3} solution.

Fig. 4: Structure of the complex.
Curve 1: 1:1,
Curve 2: 1:2,
Curve 3: 1:3 mixtures of metal and ligand,
titrated with 10^{-2}M sodium hydroxide
Curve 4: 25 ml. of 1.0×10^{-3}M acid
titrated with 1.0×10^{-2}M Al^{+3} solution.

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whereas ϵ_2 and ϵ_1 are the molecular extinction coefficients of the complex and the ligand respectively, and l, the cell width.

The instability constant of the complex at 305 mμ has been determined at different ionic strengths. The results obtained are recorded in Table I. Further the instability constant was determined at different temperatures (Vide Table II,). The logarithm of the instability constants have been plotted against 1/T which is linear (Fig. 2) and from the slope of the straight line, ΔH has been found to be $-(3.3 \pm 0.50)$ k.cal/mole. Assuming this to be constant over the range of experimental temperatures, ΔS of the complex has also been calculated, i.e., (33.0 ± 2.0) e.u.

4. Conductometric Studies

Curves 1 and 2, Fig. 3 give the titration curves of 40 ml. of 1×10^{-3} M and 5.0×10^{-4} M acid with 1×10^{-2} M solution of aluminium perchlorate respectively. From these curves also the ratio of the reagent to aluminium is found to be 1:1 which confirms the composition of the complex as obtained spectrophotometrically.

5. Structure of the complex

Three sets of solutions were prepared by mixing 10^{-3}M aluminium perchlorate with 10^{-3}M sodium salt of 2:4 dihydroxy-benzoic acid in the ratio of 1:1, 1:2 and 1:3 respectively. The total volume in each case being kept constant by the addition of conductivity water and the solutions were allowed to

Table I

Effect of ionic strength on the instability constant of the complex

λ = 305 mμ; pH = 4.5; Cell width = 1 cm.; Temp. = 30°

Ionic Strength	Instability Constant
0.01	$(1.41 \pm 0.05) \times 10^{-5}$
0.02	$(1.56 \pm 0.03) \times 10^{-5}$
0.05	$(1.81 \pm 0.01) \times 10^{-5}$
0.08	$(2.13 \pm 0.04) \times 10^{-5}$
0.10	$(2.47 \pm 0.08) \times 10^{-5}$
0.15	$(2.93 \pm 0.15) \times 10^{-5}$
0.20	$(3.51 \pm 0.20) \times 10^{-5}$

Table II

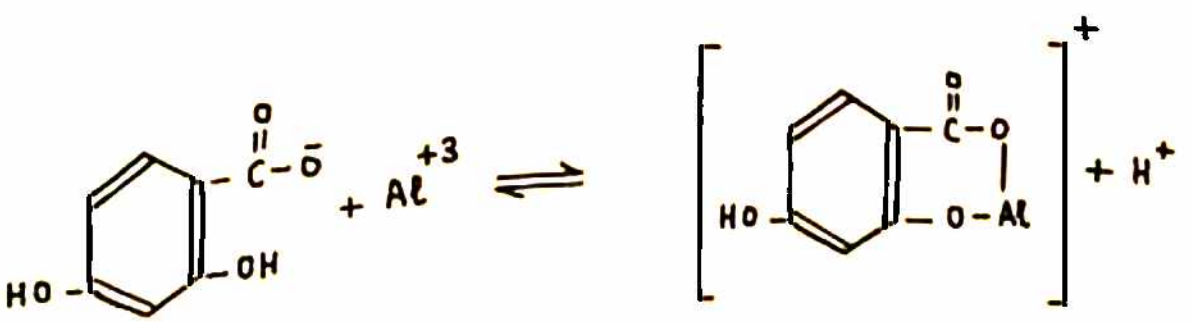
Instability Constant of the complex at different temperatures

Ionic strength = 0.01; λ = 305 mμ; pH = 4.5

Temp.	Instability Constant
293.16°K	$(1.65 \pm 0.06) \times 10^{-5}$
303.16	$(1.50 \pm 0.04) \times 10^{-5}$
313.16	$(1.16 \pm 0.03) \times 10^{-5}$
323.16	$(9.71 \pm 0.10) \times 10^{-6}$
333.16	$(8.33 \pm 0.30) \times 10^{-6}$

stand for half an hour for attaining equilibrium. Varying amounts of 10^{-2}M sodium hydroxide solutions were added to three samples and conductance values were noted down as usual. The observed data were plotted against the ml. of alkali added. It was found that in all the cases, conductance curves 1, 2 and 3 Fig. 4, exhibited only one break corresponding to one equivalent of alkali used. Since the sodium salt of the acid was used, the only proton which could be replaced as a result of chelation was the hydroxyl hydrogen. The break at one equivalent of sodium hydroxide in all the cases, therefore, suggested only 1:1 complex in the system.

Curve 4 Fig. 4 shows that the pH of 2:4 dihydroxybenzoic acid (25 ml. of 10^{-3}M, pH = 3.70) is gradually decreased by the addition of aluminium perchlorate solution (10^{-2}M, pH=3.50) and becomes constant at 3.45 when one equivalent of aluminium perchlorate solution (2.5 ml) was added. This evidently shows an increase in H^+ ion concentration in the mixture. This is only possible when hydroxyl hydrogen of 2:4 dihydroxybenzoic acid is replaced by aluminium. On the basis of the above experimental observations, the structure of the complex can be assigned as below:



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PAPER No. 13

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES OF THE COMPLEX BETWEEN BERYLLIUM AND 2:4 DIHYDROXYBENZOIC ACID IN AQUEOUS MEDIUM

SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES OF THE COMPLEX BETWEEN BERYLLIUM AND 2:4 DIHYDROXYBENZOIC ACID IN AQUEOUS MEDIUM

The colourless complex formed by the interaction of beryllium with 2:4 dihydroxybenzoic acid has been studied spectrophotometrically in aqueous solutions of various ionic strengths and at different temperatures. The molecular composition of the complex has been determined by Job's method of continued variation and Molar-ratio method and is found to be 1:1. The values of ΔH and ΔS are calculated to be $-(1.49 \pm 0.2)$ k.cal/mole and (24.7 ± 1.5) e.u. respectively. The probable structure of the complex is also suggested.

2:4 Dihydroxybenzoic acid forms a number of complexes with various metal ions. Complexes of 2:4 dihydroxybenzoic acid with Cu^{+2}, Fe^{+3}, Al^{+3} have been studied by Gupta et al.[1,2,3]. In course of our investigation on its complexes it was found that beryllium also forms a colourless complex. This paper, therefore, gives the results obtained in this study in aqueous medium on which no data are available in literature. The molecular composition of the complex has been determined by Job's method of continued variation[4] and molar-ratio method[5].

EXPERIMENTAL

Beryllium perchlorate was prepared by heating beryllium chloride (E. Merck) with concentrated perchloric acid (E.Merck) until the solution no longer gave a test for chloride ion. It was diluted to required volume and sufficient perchloric acid was added to prevent hydrolysis. The beryllium content was estimated gravimetrically.

2:4 Dihydroxybenzoic acid was B.D.H., L.R. sample and recrystallised before use. Sodium perchlorate was used to maintain the ionic strength. Other chemicals were of AnalaR quality of B.D.H. The technique and other details have been described earlier.

RESULTS AND DISCUSSION

2:4 Dihydroxybenzoic acid (pH = 5.0) absorbs strongly in ultra-violet region with an absorption maximum at 290 mμ, whereas beryllium perchlorate is transparent round this wavelength. Addition of beryllium perchlorate to 2:4 dihydroxybenzoic acid solution causes the shift in the absorption maximum to higher wavelength 300 mμ suggesting interaction between beryllium and 2:4 dihydroxybenzoic acid. This shift was found from 3.0 to 5.5 pH. Investigations above 5.5 could not be made because of precipitation of beryllium presumably as hydroxide. Hence the pH of 5.0 was selected for subsequent studies.

Composition of the Complex

Job's Method - A series of solutions was prepared from beryllium perchlorate and acid. The optical density measurements were made

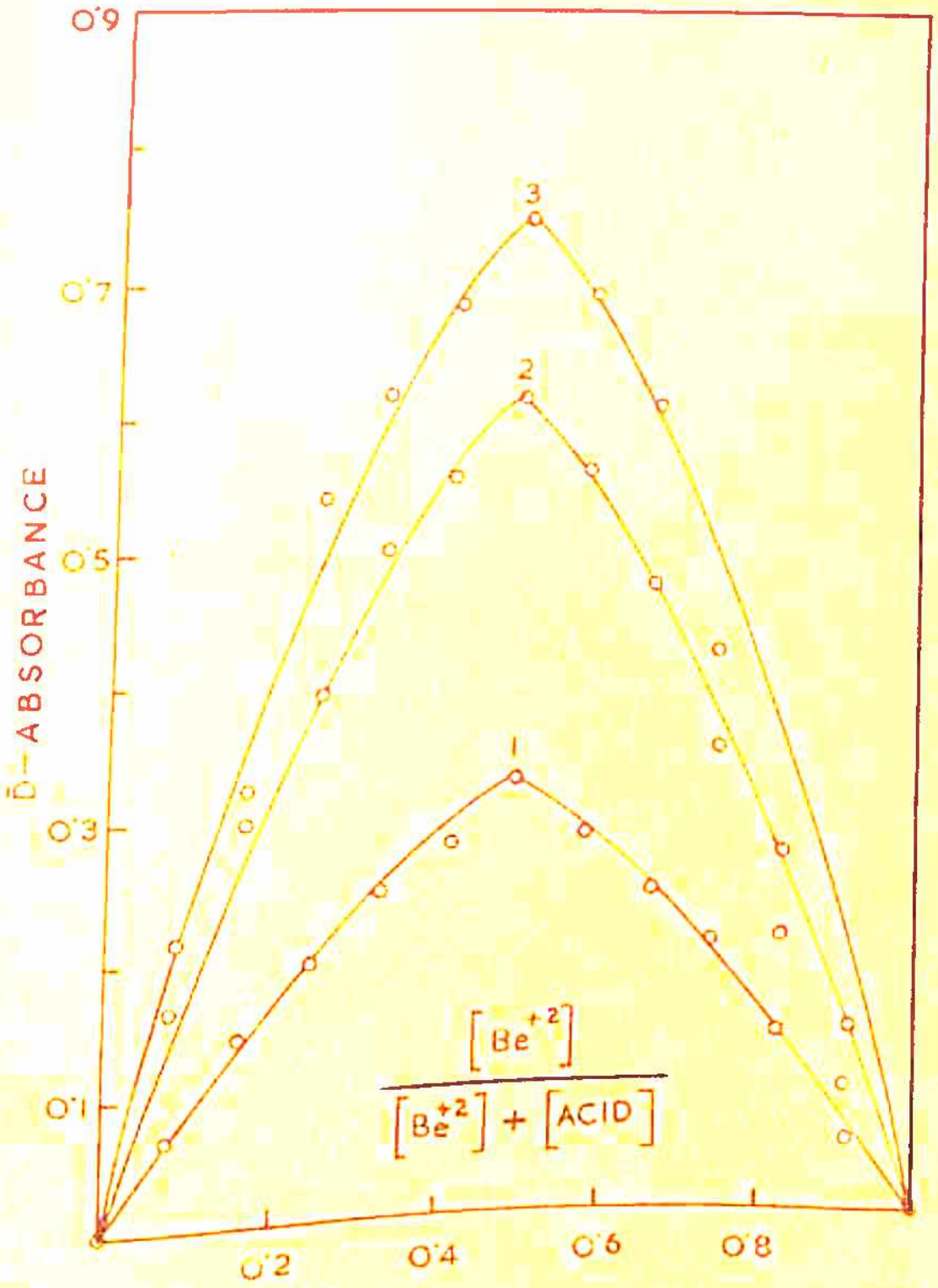


FIG. 1

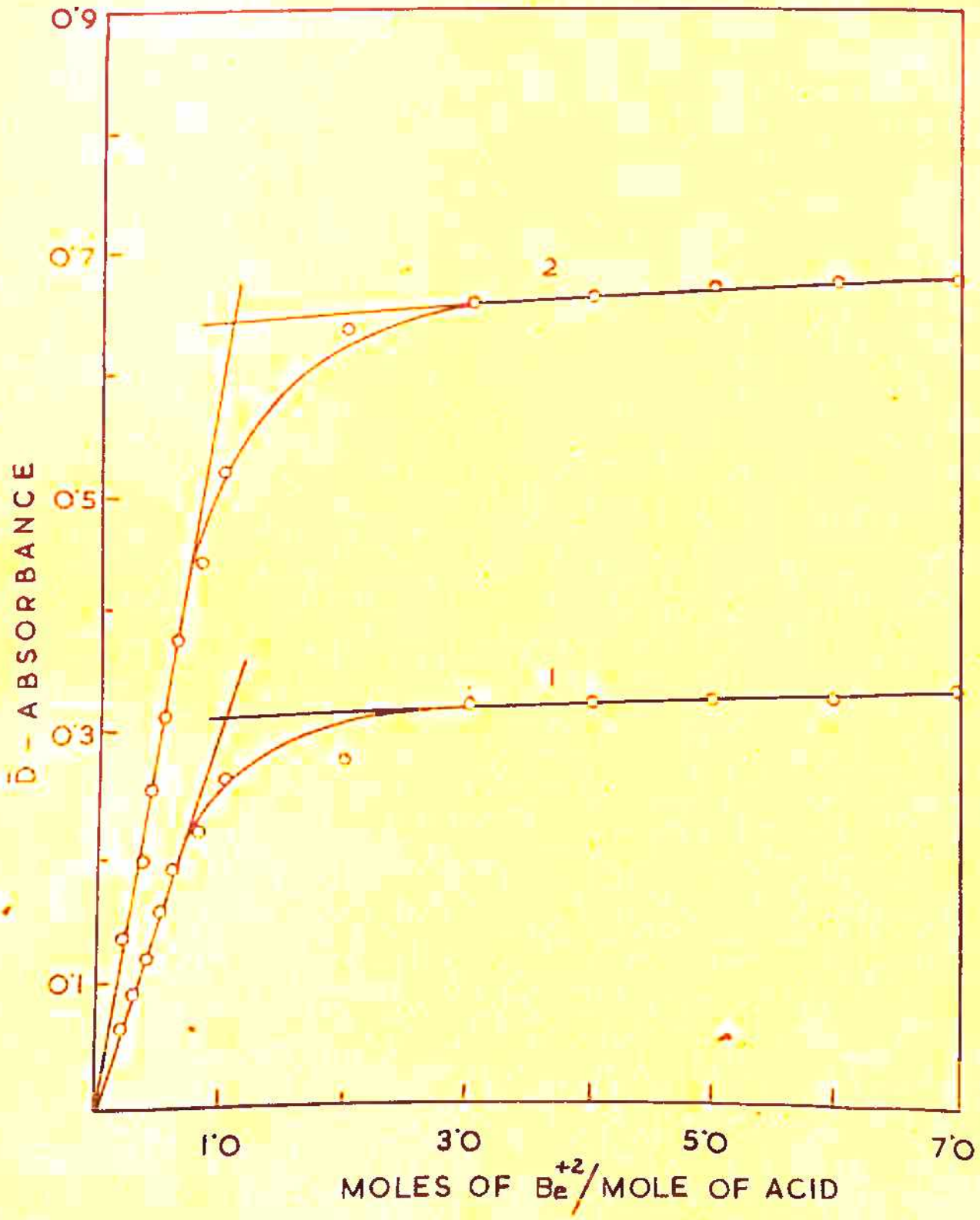

0·9
0·7
0·5
0·3
0·1
D - ABSORBANCE
2
1
1·0
3·0
5·0
7·0
MOLES OF Be+2/MOLE OF ACID

FIG. 2

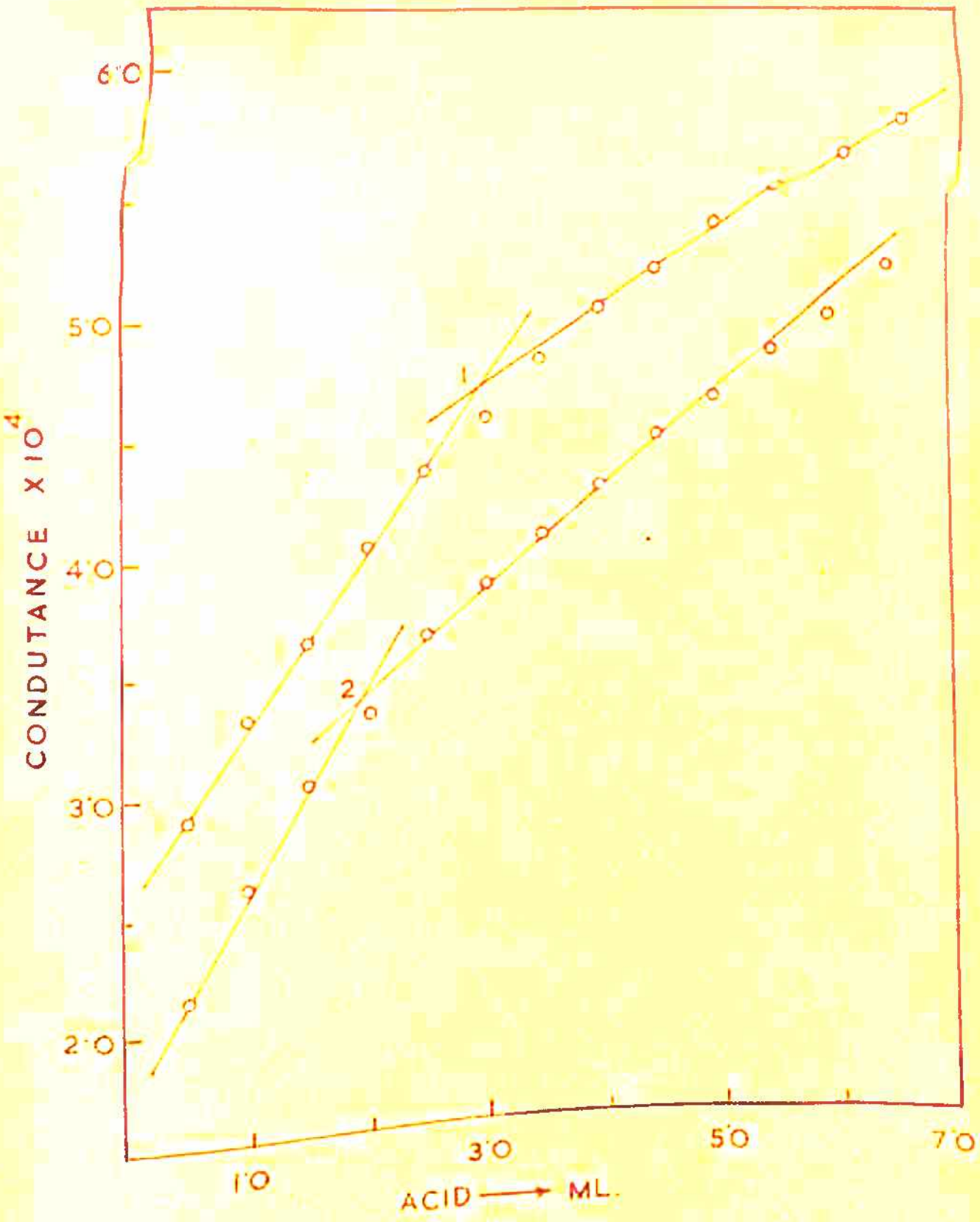


FIG. 3

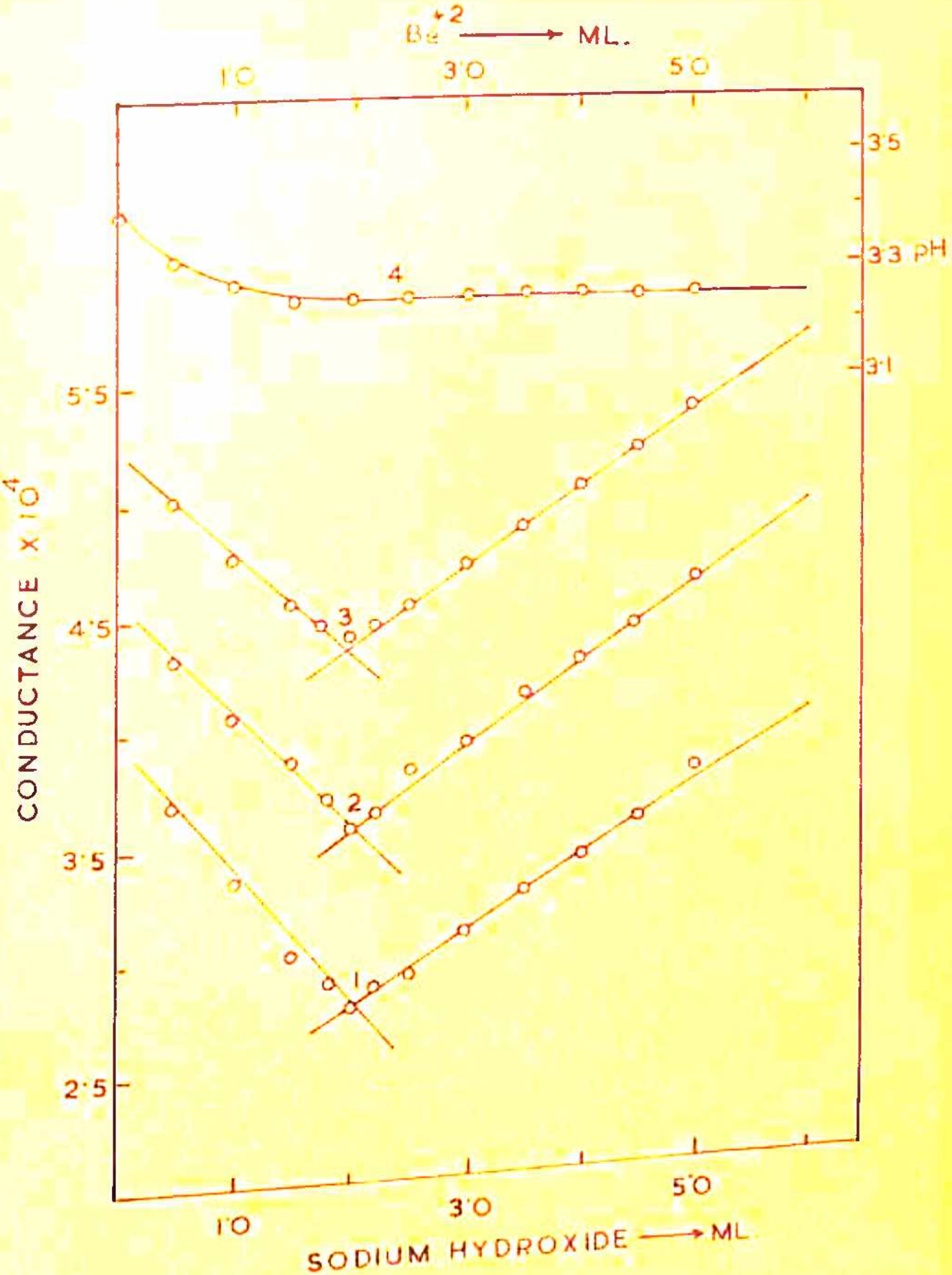

Be^{+2} ⟶ ML.
1·0
3·0
5·0
3·5
3·3 pH
3·1
4
3
2
1
5·5
4·5
3·5
2·5
CONDUCTANCE X 10^{-4}
1·0
3·0
5·0
SODIUM HYDROXIDE ⟶ ML.

FIG. 4

LEGEND OF FIGURES

Fig. 1: Job's method of continued variation.
Total molarity = 4.8×10^{-4}M; pH = 5.0

Curves 1-3:- 295, 300 and 305 mμ respectively.

Fig. 2: Molar-ratio method.

Curves 1-2:- 295 and 300 mμ respectively.

Fig. 3: Complex by conductivity method.

Curve 1:- 40 ml. of 7.5×10^{-4}M Be^{+2} vs.
1.0×10^{-2}M acid solution.

Curve 2:- 40 ml. of 5.0×10^{-4}M Be^{+2} vs.
1.0×10^{-2}M acid solution.

Fig. 4: Structure of the complex.

Curve 1:- 1:1, Curve 2: 1:2, Curve 3: 1:3 mixtures of metal and ligand titrated with 1.0×10^{-2}M NaOH.

Curve 4:- 20 ml. of 10^{-3}M acid vs.
1.0×10^{-2}M Be^{+2} solution.

---

at total molarity of 4.8×10^{-4}M at the wavelength 295, 300 and 305 mμ. The difference between total optical density of the solution and that which is shown by the acid solution alone if no reaction occurs at the same pH was plotted against $[Be^{+2}]/[Be^{+2}]+[Acid]$. Fig. 1 shows, the maximum in all the three curves at 0.5, formation of 1:1 complex.

Molar-ratio Method - A series of solutions was prepared from acid in which varying amounts of beryllium were added such that the molar-ratio of reagent to beryllium was varied from 1:0.2 to 1:7. Curves at 295 and 300 mμ (Fig. 2) show breaks at one mole of the reagent to one mole of beryllium.

Molecular extinction coefficient and instability constant

The molecular extinction coefficients of the complex and acid were calculated in the same way as described in our earlier communication[3]. The average values of extinction coefficients of complex and the acid at 300 mμ and at pH 5.0 are (6950 ± 13) and (2461 ± 10) respectively.

The instability constants of the complex at pH 5.0 were determined at various ionic strengths. These are recorded in Table I. It was observed that the addition of a neutral salt increases the extent of dissociation of the complex. The ionic atmospheres about the complex ions are denser in the salt solution. They screen the interaction between the ions of the complex and reduce their rate of recombination[6]. The instability constant was determined at different temperatures (Vide Table II). The

Table I

Effect of ionic strength on the instability constant of the complex between Be^{+2} and 2:4 dihydroxybenzoic acid.

λ = 300 mμ; pH = 5.0; Cell width = 1 cm; Temp.30°.

Ionic Strength	Instability constant
0.01	$(4.68 \pm 0.15) \times 10^{-5}$
0.02	$(5.21 \pm 0.20) \times 10^{-5}$
0.05	$(5.64 \pm 0.12) \times 10^{-5}$
0.08	$(5.94 \pm 0.05) \times 10^{-5}$
0.10	$(6.33 \pm 0.20) \times 10^{-5}$
0.15	$(6.94 \pm 0.15) \times 10^{-5}$
0.20	$(7.27 \pm 0.15) \times 10^{-5}$

Table II

Instability constant of the complex at different temperatures

Ionic strength = 0.01; pH = 5.0; λ = 300 mμ.

Temp. °K	Instability constant
283.16	$(5.26 \pm 0.05) \times 10^{-5}$
293.16	$(4.84 \pm 0.06) \times 10^{-5}$
303.16	$(4.68 \pm 0.15) \times 10^{-5}$
313.16	$(4.30 \pm 0.02) \times 10^{-5}$
323.16	$(3.88 \pm 0.02) \times 10^{-5}$
333.16	$(3.56 \pm 0.20) \times 10^{-5}$

---

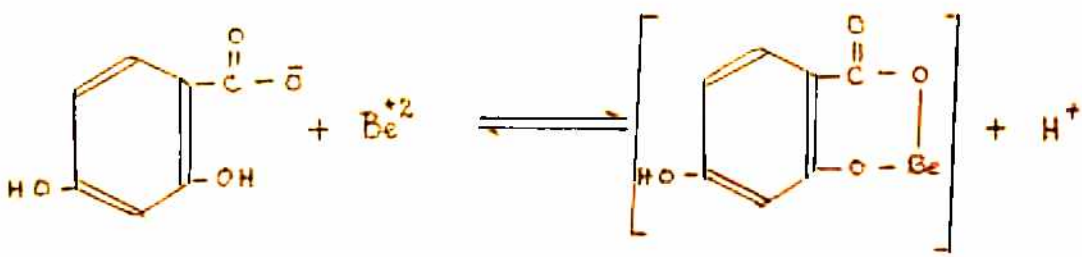
logarithm of the instability constants have been plotted against 1/T which gives linear curve and from the slope of the straight line ΔH has been found to be $-(1.49 \pm 0.2)$ k.cal/mole. Assuming this to be constant over the range of experimental temperatures, ΔS of the complex has been calculated and is (24.7 ± 1.5) e.u.

Conductometric studies - Curves 1 and 2, Fig. 2 give the conductometric titration (40 ml. of 7.5×10^{-4} M and 5.0×10^{-4} M beryllium solution with 1.0×10^{-2}M solution of 2:4 dihydroxybenzoic acid respectively). From these curves also the ratio of beryllium to acid is found to be 1:1.

Structure of the complex- Curve 4, Fig. 4 shows that the pH of 2:4 dihydroxybenzoic acid (20 ml. of 10^{-3} M; pH = 3.40) is gradually decreased by the addition of beryllium perchlorate (10^{-2}M; pH = 3.70) and became constant at 3.25 when one equivalent of beryllium perchlorate was added. Thus there is an increase in the hydrogen ion concentration. This is only possible when hydroxyl hydrogen of 2:4 dihydroxybenzoic acid is replaced by beryllium.

Further three sets of solutions were prepared by mixing beryllium perchlorate and sodium salt of the acid in the ratios of 1:1, 1:2 and 1:3 respectively. The total volume in each case being kept constant by the addition of conductivity water and the solutions were allowed to stand for half an hour for attaining equilibrium. These solutions were titrated with sodium hydroxide solution and conductance values were plotted against the volume of alkali added. It was observed that in all the cases conductance

curves 1, 2 and 3, Fig. 4 exhibited only one break at one equivalent of alkali added. Since sodium salt of the acid was used, the only proton which could be replaced as a result of chelation was the hydroxyl hydrogen. The break at one equivalent in all the cases, therefore, suggested 1:1 complex found in the system. On the basis of the above experimental observations, the structure of the complex may be assigned as



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PAPER No. 14

A.C. POLAROGRAPHIC STUDIES OF THE COMPLEXES OF Cu^{+2} AND Fe^{+3} IONS WITH 2:4 DIHYDROXY-BENZOIC ACID IN AQUEOUS MEDIUM

(Jour. Indian Chem.Soc., 1965, 42, 384)

CHAPTER IV

SPECTROPHOTOMETRIC STUDIES ON COMPLEX OF 3:5 DINITROSALICYLIC ACID

PAPER No. 15

SPECTROPHOTOMETRIC STUDIES ON THE COMPOSITION AND STABILITY OF THE COMPLEX BETWEEN 3:5 DINITROSALICYLIC ACID AND Fe^{+3} IONS IN AQUEOUS MEDIUM

(Jour. Inst. Chem., In press.)

SPECTROPHOTOMETRIC STUDIES ON THE COMPOSITION AND STABILITY OF THE COMPLEX BETWEEN 3:5 DINITROSALICYLIC ACID AND Fe^{+3} IONS IN AQUEOUS MEDIUM

The composition of orange coloured water soluble complex formed by 3:5 dinitrosalicylic acid with Fe^{+3} ion has been studied by Job's method of continued variation, slope-ratio method and molar-ratio method spectrophotometrically. The coloure produced is almost instantaneous and stable towards time. It has an absorption maximum at 450 mμ. The optimum pH range is 2.7 to 3.2. The molecular extinction coefficient of the complex is 2.106×10^3. The instability constants of the complex have been given for different ionic strengths and at different temperatures. The values of ΔH and ΔS are found to be -7.38 k.cal/mole and 49.2 e.u. respectively.

Srivastava et al.[1,2] studied the reaction of titanium and tungsten with 3:5 dinitrosalicylic acid. We have seen that Fe^{+3} ions also react with this acid and form a water soluble orange coloured complex. As no data are available in literature regarding the composition and stability of Fe-3:5 dinitrosali-

cylate complex, this investigation, therefore, gives the results obtained in such study.

EXPERIMENTAL

3:5 Dinitrosalicylic acid was B.D.H., L.R. sample and was recrystallised before use. A pure solution of ferric chloride was prepared from ferrous ammonium sulphate[3] (B.D.H., A.R.) and the iron content was estimated by oxide method before preparing the standard solution. Potassium chloride (B.D.H., A.R.) was used for adjusting the ionic strength. Sodium acetate, hydrochloric acid and sodium hydroxide used were of B.D.H. AnalaR quality. The technique and other details have been described earlier.

RESULTS AND DISCUSSION

(i) Spectral studies - 3:5 Dinitrosalicylic acid ($M \times 10^{-3}$) and ferric chloride solution ($M \times 10^{-3}$) were taken in the ratio of 1:1, 1:2 and 1:3. Suitable quantities of 1.0 M sodium acetate and 1.0 M HCl solutions were added and absorptions were recorded at different wavelengths. The complex showed the maximum absorption at 450 mμ in all the cases, thus indicating the formation of the complex[4]. The absorbance due to 3:5 dinitrosalicylic acid and ferric chloride is very small at this wavelength. The corresponding wavelength of 450 mμ was thus used for subsequent work.

(ii) Effect of pH - Solutions containing the same concentration

of 3:5 dinitrosalicylic acid and ferric chloride were prepared at different pH values and absorbance noted at 450 mμ. It was found that the complex was stable between the pH range of 2.7 to 3.2 and hence a pH of 3.0 was selected for subsequent studies.

(iii) Effect of temperature - Mixtures were heated on water bath to 85°C, cooled to room temperature and absorbance was measured after making up the volume. There was no difference in the absorbance of the sample and that prepared at room temperature. The complex was stable over a wide range of temperature variations.

COMPOSITION OF THE COMPLEX

(i) Job's method of continued variation - A series of solutions was prepared from 10^{-3}M ferric chloride and the acid in which the ratio of ferric to acid varied from 1:9 to 9:1. The pH was kept at 3.0 by addition of suitable quantities of sodium acetate and hydrochloric acid. The difference of absorbance was plotted against the ratio $[Fe^{+3}] / [Fe^{+3}] + [Acid]$. Curves 1, 2 and 3 Fig. 1 were obtained using total molarity 1×10^{-3}M, 5.0×10^{-4}M and 2.5×10^{-4}M respectively. The maximum at 0.5 in all the cases indicates the formation of the complex containing ferric and the acid in the ratio 1:1.

(ii) Slope-ratio method - The concentration of variable component was varied from 2.5×10^{-5}M to 1.5×10^{-4}M in presence of excess concentration of 1×10^{-3}M of the constant component (curves 1

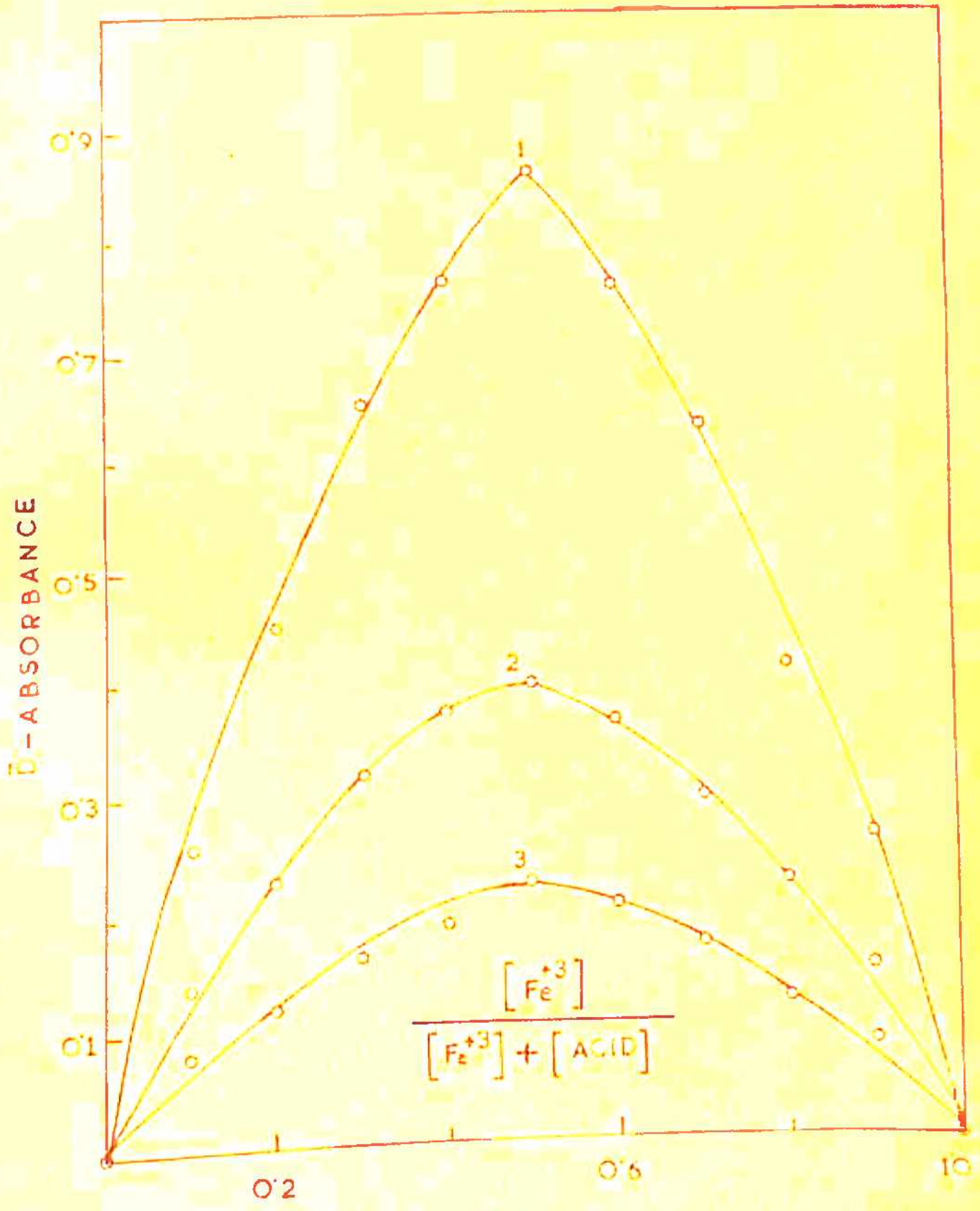


FIG. 1

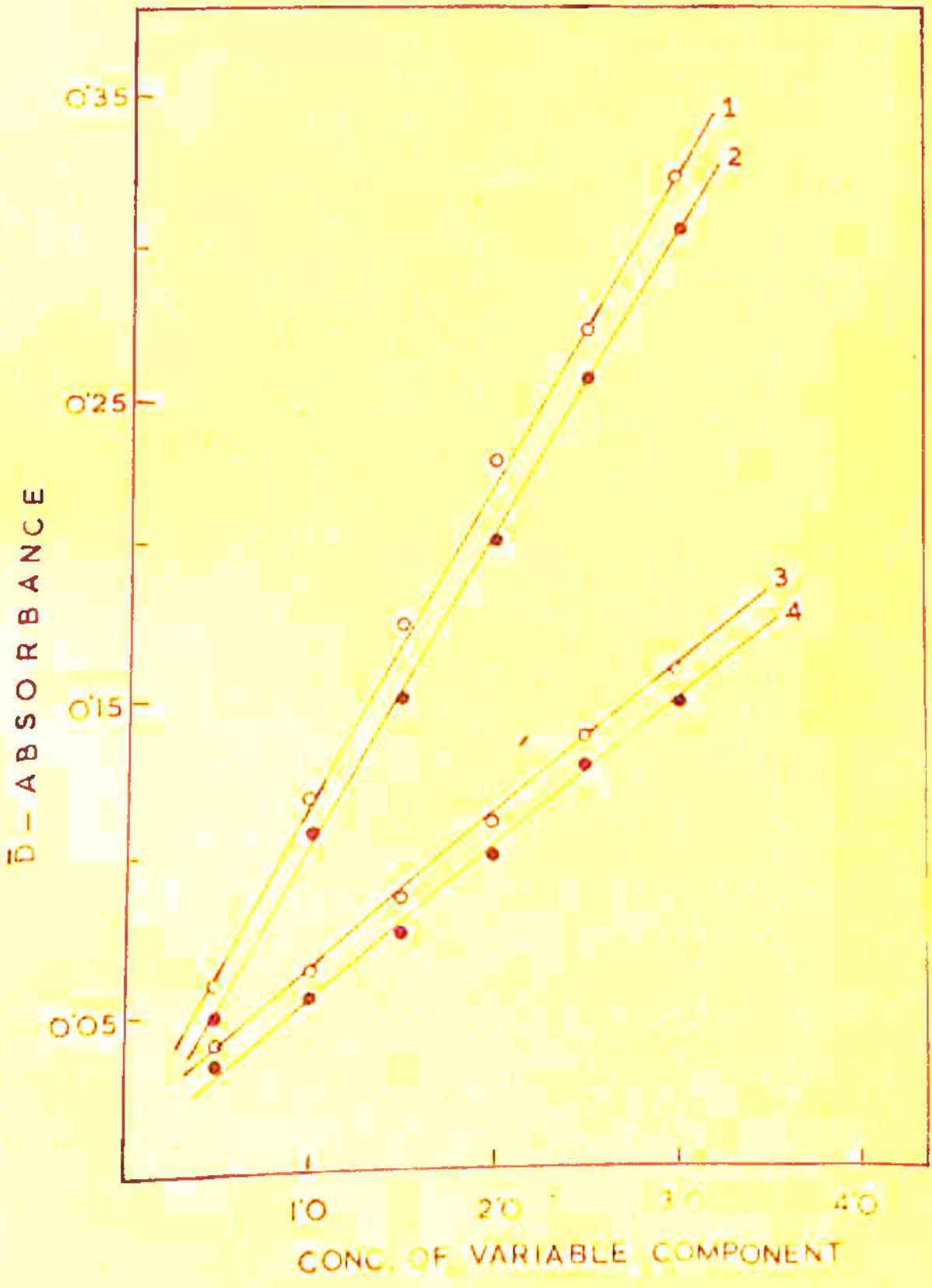
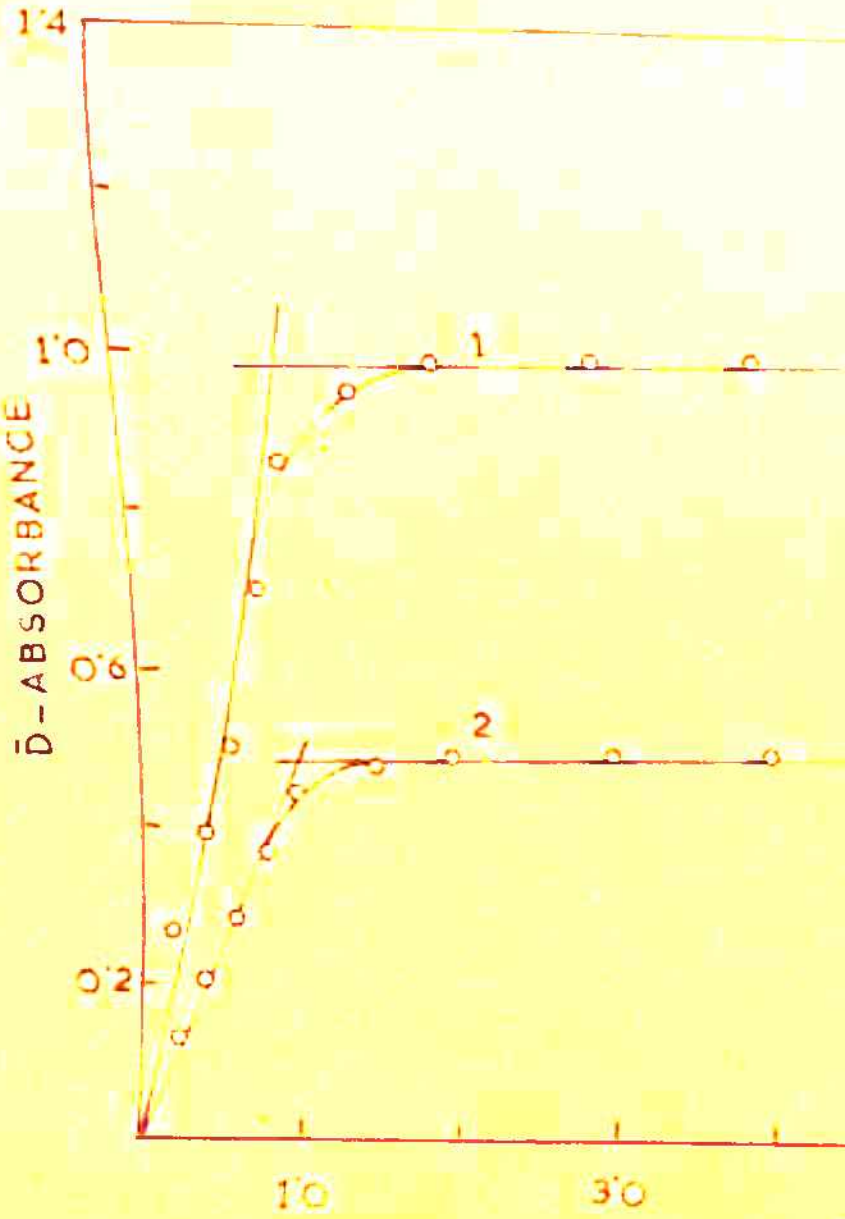
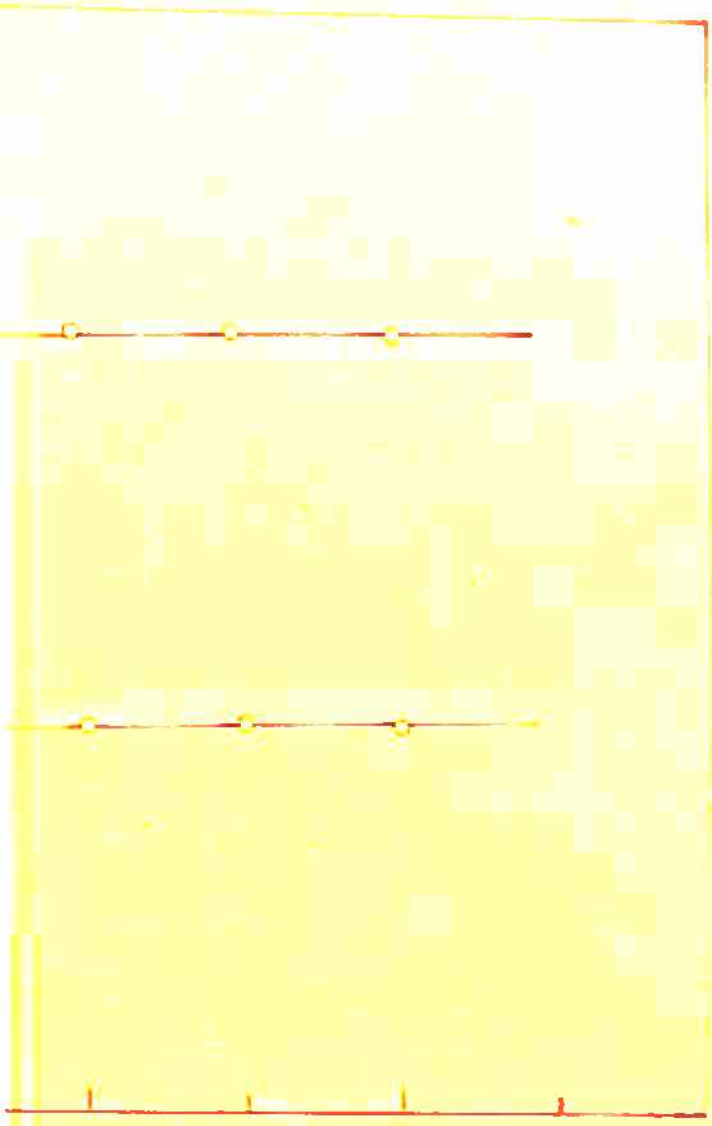

0·35
0·25
0·15
0·05
D – ABSORBANCE
1
2
3
4
1·0
2·0
3·0
4·0
CONC. OF VARIABLE COMPONENT

FIG. 2



FIG


5·0
7·0
MOLE ACID

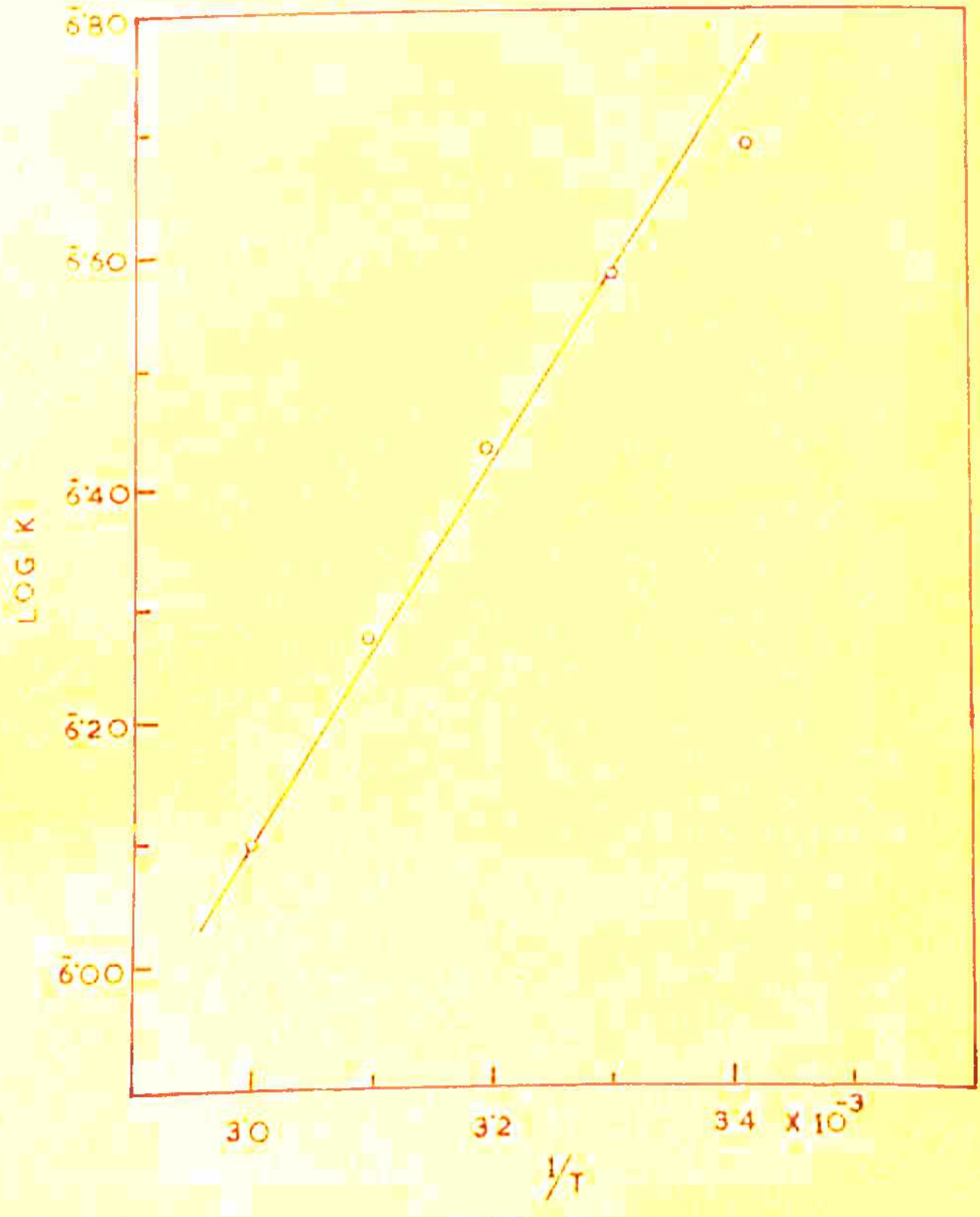

$\bar{5}\cdot80$
$\bar{5}\cdot60$
$\bar{6}\cdot40$
$\bar{6}\cdot20$
$\bar{6}\cdot00$
LOG K
3·0
3·2
3·4 X 10^{-3}
1/T

FIG. 4

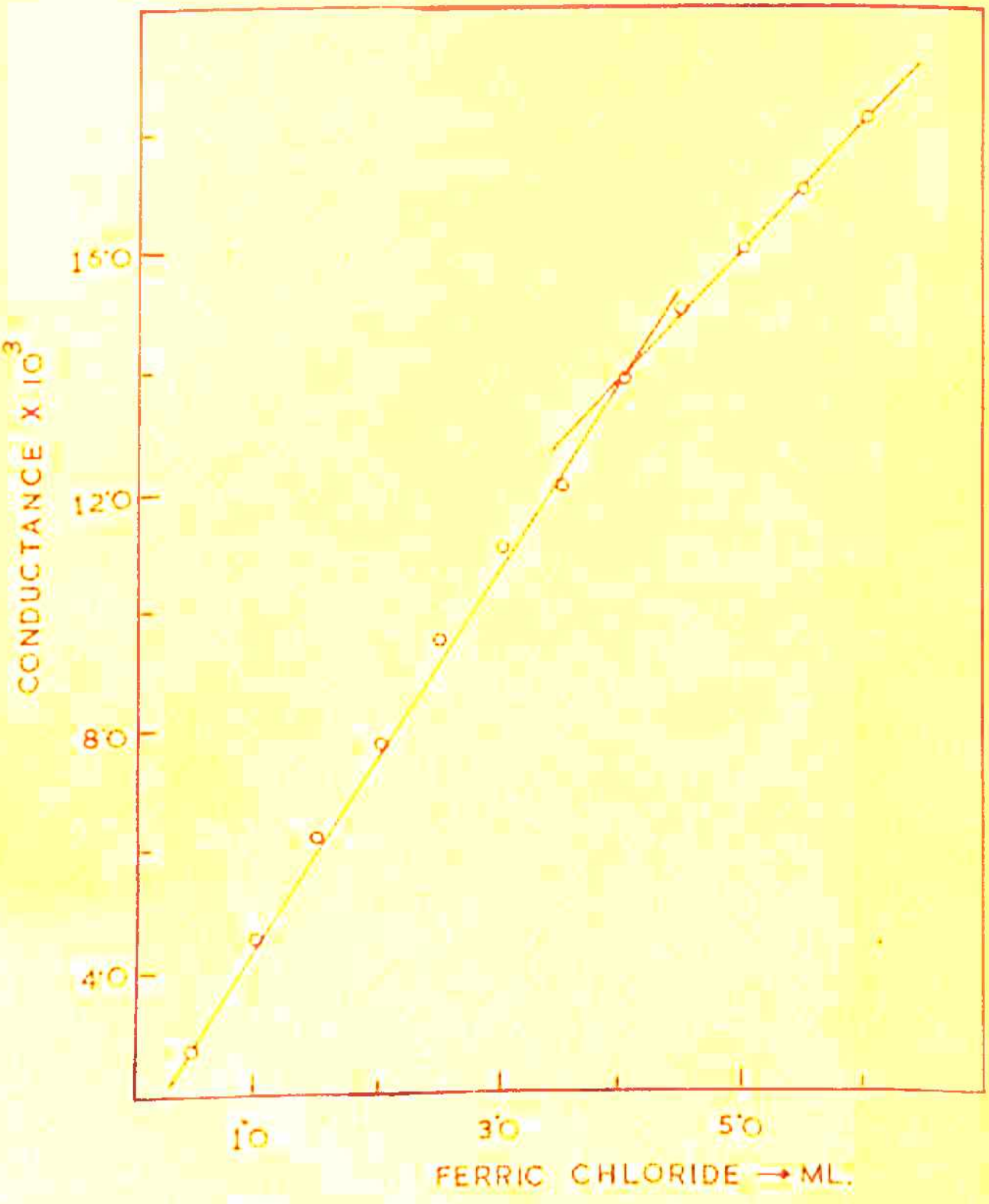


FIG. 5

LEGEND OF FIGURES

Fig. 1: Job's method of continued variation.

Curve 1: Total molarity 1.0×10^{-3}M.

Curve 2: Total molarity 5.0×10^{-4}M.

Curve 3: Total molarity 2.5×10^{-4}M.

Fig. 2: Slope-ratio method.

Curves 1 & 3: Fe^{+3} varying.

Curves 2 & 4: Reagent varying.

Fig. 3: Molar-ratio method.

Curve 1: 5.0×10^{-4}M concn.

Curve 2: 2.5×10^{-4}M concn.

Fig. 4: Variation of log K with 1/T.

Fig. 5: Conductivity method.

40 ml. of 1.0×10^{-3}M acid vs.

1.0×10^{-2}M ferric chloride solution.

and 2 Fig. 2). The pH of solutions was maintained at 3.0. The difference of absorbance at 450 mμ was plotted against the concentration of variable component. The slopes of two straight lines provide the ratio of the ferric and acid as 1:1. The same ratio is also obtained by varying the concentration of variable component from 1.25×10^{-5}M to 7.5×10^{-5}M in presence of excess concentration of 0.5×10^{-3}M of constant component. (Curves 3 and 4 Fig. 2.)

(iii) Molar-ratio method - A series of solutions was prepared from 5.0×10^{-4}M and 2.5×10^{-4}M of the acid at pH 3.0 as described earlier and varying amounts of ferric solution were added such that the mole ratio of acid to ferric was from 1:0.2 to 1:7. Curves 1 and 2 Fig. 3 show breaks at a ratio of one mole of acid to one mole of ferric ion.

Molecular extinction coefficient and instability constant

Using optical densities of solutions containing large excess of acid so that as a first approximation the concentration of the complex may be taken to be equal to that of ferric ions added, the molecular extinction coefficient of the complex is found to be 2.106×10^{3}. The instability constant of the complex (K_{in}) has been calculated where the concentration of the complex is obtained from the extinction coefficient of the complex. The instability constant of the complex at pH 3.0 have been determined at various ionic strengths (vide Table I).

The instability constants of the complex at a constant

Table I

Effect of ionic strength on the instability constant of the complex between Fe^{+3} ion and 3:5 dinitrosalicylic acid in aqueous medium.

pH = 3.0; λ = 450 mμ; Temp. = 30°C

Ionic strength (I)	Instability constant
0.01	3.77×10^{-6}
0.02	5.76×10^{-6}
0.05	8.49×10^{-6}
0.08	1.13×10^{-5}
0.10	1.45×10^{-5}
0.15	2.18×10^{-5}
0.20	3.00×10^{-5}

Table II

Instability constant of the complex at different temperatures

Ionic strength = 0.01; pH = 3.0; λ = 450 mμ

Temp. °K	Instability constant
293.16	4.84×10^{-6}
303.16	3.77×10^{-6}
313.16	2.67×10^{-6}
323.16	1.87×10^{-6}
333.16	1.25×10^{-6}

ionic strength of 0.01, have also been determined at different temperatures. The results are recorded in Table II. Further the logarithm of the instability constants have been plotted against 1/T (Fig. 4). From the slope of the straight line ΔH has been found to be -7.38 k.cal/mole. Assuming this to be constant over the range of experimental temperatures, ΔS of the reaction has also been calculated and is 49.2 e.u.

Attempt has also been made to calculate instability constant by molar ratio method. The dissociation of the complex may be written as

FeR^{+}	$\rightleftharpoons$ Fe^{+3}	+ R^{-}	
C	0	0	Initial concentration
$C(1-\alpha)$	αC	αC	Final concentration

where C is the concentration of the complex and α is the degree of dissociation. The instability constant K, is given by the equation :-

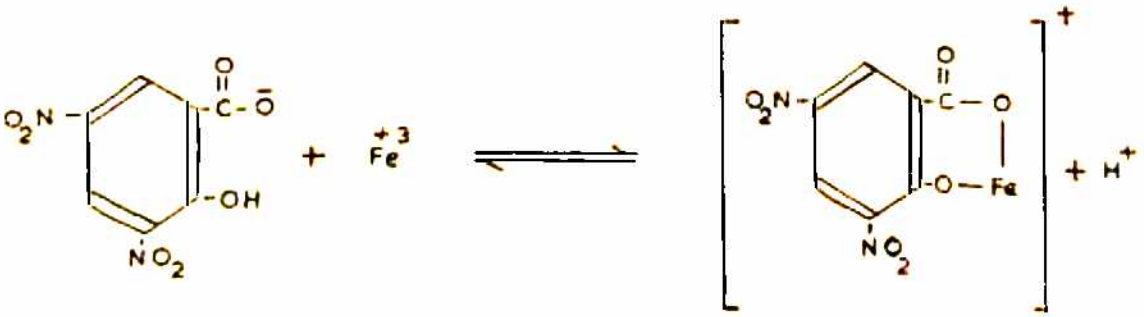
$$K = \frac{\alpha C \times \alpha C}{(1-\alpha)C} = \frac{\alpha^2 C}{(1-\alpha)}$$

From curve 2, Fig. 3:-

$$\alpha = \frac{E_m - E_s}{E_m} = \frac{0.495 - 0.441}{0.495} = 0.110$$

where the terms have their usual significance. Since the concentration of the complex is 2.5×10^{-4}M, by substituting these values in the above equation, the value of K at 30°C comes to 4.11×10^{-6}.

Conductometric studies - The composition of the complex is also confirmed by conductometric measurements. Fig. 5 shows the titration curve of 40 ml. of 1 x 10^{-3} M of the reagent against 1 x 10^{-2} M solution of ferric chloride. The break indicates the ratio of reagent to ferric ion as 1:1. The probable structure of the chelate may be as follows:



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CHAPTER V

COMPLEXES BETWEEN SURFACE ACTIVE SUBSTANCES

PAPER No. 16

STUDIES ON THE COMPLEXES OF PYRIDINE WITH o-CRESOL AND n-AMYL ALCOHOL IN AQUEOUS MEDIUM BY TENSAMMETRY

(Electrochim Acta., 1965, 10, 549.)

PAPER No. 17

INFRA-RED STUDIES ON COMPLEXES OF PYRIDINE WITH o-CRESOL AND n-AMYL ALCOHOL

INFRA-RED STUDIES ON COMPLEXES OF PYRIDINE WITH o-CRESOL AND n-AMYL ALCOHOL

Infra-red measurements show the strong interactions between o-cresol and n-amyl alcohol with pyridine. The average 1:1 equilibrium constant for o-cresol and pyridine complex at 25°C is about 21 lm^{-1}. The $\Delta\nu_{OH}$ is about 500 cm^{-1}. The 1:1 equilibrium constant for n-amyl alcohol and pyridine complex is approximately 1 liter per mole and the frequency shift of the O-H stretching bond is about 420 cm^{-1}. Apparently the enthalpy of formation of the hydrogen bond is of the order of 4 k.cal/mole.

Since earlier studies indicated that there was an appreciable interaction of pyridine with phenol as well as amyl alcohol, it was considered interesting to examine quantitatively the nature of these interactions. There are several reports in literature where hydrogen bonded interaction of amines with hydrolylic compounds are being investigated employing infra-red spectrophotometry[1,2,3]. The present work gives the results of infra-red spectroscopic studies on 1:1 hydrogen bonded complexes between pyridine and o-cresol as well as n-amyl alcohol.

EXPERIMENTAL

All the compounds and solvents employed were commercially available and were purified before use. The infra-red spectra in the O-H stretching region were studied by employing Carl-Zeiss UR 10 spectrometer with lithium fluoride optics and in the overtone region with a Cary-14R spectrophotometer.

The equilibrium constants were evaluated from the extinction of the free OH fundamental of the first OH overtone (at monomeric concentration of the acceptor) with varying concentrations of donors. The expression employed for the evaluation of the equilibrium constants were similar to that of Becker[4]

$$K = (D_A - D_{DA})/[D_{DA}(C_D - C_{DA})],$$

where D_A is the optical density of the OH band due to the acceptor (proton donor) at monomeric concentration ($\sim$ 0.007M and 0.02M for phenol and alcohols respectively) D_{DA} the optical density of the OH band of a solution containing the donor and acceptor, C_D the molar concentration of the donor (which is always taken in excess) and C_{DA} the concentration of the donor involved in the formation of the hydrogen bonded complex. In practice, C_{DA} is ignored in view of the large C_D. This equation was employed for the determination of equilibrium constants of 1:1 complex formation. The uncertainty in the infra-red frequency shifts $\Delta\nu_{OH}$ of the OH stretching band due to hydrogen bonding was $\pm$ 5 cm^{-1}.

RESULTS AND DISCUSSION

In Fig. 1 the effect of adding pyridine (0.27 M) on the free OH stretching band of o-cresol (0.01 M) in carbon tetrachloride solution is illustrated. It can be seen that the intensity of free OH band increases appreciably on addition of pyridine indicating that there is appreciable interaction.

The 1:1 equilibrium constant data for hydrogen bonded interaction between o-cresol and pyridine are given below:

Temp. 25°C

Pyr.	0.027 M	Pyr.	0.13 M
o-Cresol	0.012 M	o-Cresol	0.007 M
K =	20.5 lm^{-1}	K =	22.6 lm^{-1}.

The average 1:1 equilibrium constant at 25°C is about 21 lm^{-1}. The corresponding value of pyridine phenol system is 42 lm^{-1}. This is understable since o-cresol is a weak acid than phenol. The $\Delta\nu_{OH}$ in the o-cresol pyridine system is 500 cm^{-1}, a value comparable to that found in phenol pyridine system. Apparently the enthalpies of formation of hydrogen bonding complexes are nearly the same (about 6.0 k.cal/mole) in these systems. The large $\Delta\nu_{OH}$ (and therefore ΔH^{o}) clearly indicates that the strong hydrogen bonds are formed between o-cresol and pyridine.

The 1:1 equilibrium constant for the interaction of n-amyl alcohol with the pyridine was found to be approximately 1 lm^{-1} at about 25°C. This value is comparable with the equilibrium constant for the propanol-amine system. The $\Delta\nu_{OH}$ for the

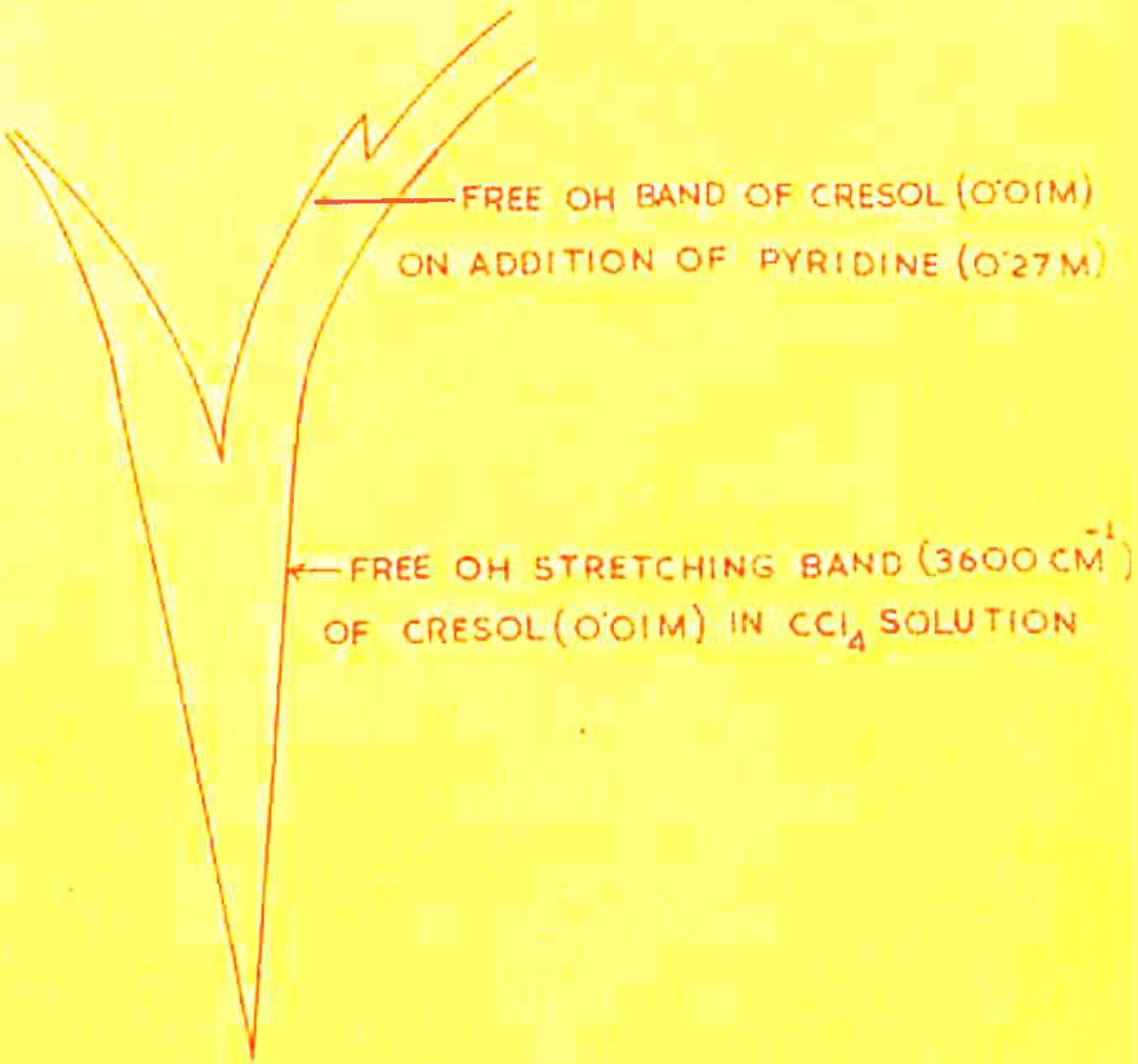
FREE OH BAND OF CRESOL (0·01M)
ON ADDITION OF PYRIDINE (0·27 M)
FREE OH STRETCHING BAND (3600 CM^{-1})
OF CRESOL (0·01M) IN CCl_4 SOLUTION

FIG. 1

interaction of n-amyl alcohol with pyridine is about 420 cm^{-1}. The $\Delta\nu_{OH}$ value in n-propanol-trieltrylamine is found to be 465 cm^{-1}, while the enthalpy of formation is about 4.5 k.cal/mole. Considering the lower value of $\Delta\nu_{OH}$ in the n-amyl alcohol pyridine system, it appears that the enthalpy is also lower than the propanol-amine system. Further, the equilibrium constant, $\Delta\nu_{OH}$ and ΔH^{o} for the hydrogen bonding interaction of pyridine with n-amyl alcohol are appreciably smaller than the corresponding values for the interaction with o-cresol or phenol. This is to be expected since n-amyl alcohol is a much weaker acid than phenol or o-cresol.

The studies reported in this paper clearly established the formation of hydrogen bonded complexes in both o-cresol-pyridine and an-amyl alcohol pyridine systems, while it would have been good to have experimentally determined enthalpy values as well. The $\Delta\nu_{OH}$ values are clearly indicative of the magnitude of the hydrogen bonding interaction of these systems.

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