THESIS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

on

CHELATES OF URANIUM (VI) WITH OXYGEN DONOR LIGANDS AND A STUDY OF THEIR STABILITY AND POLYMERIZATION

by

SUDARSHAN KUMAR VERMA

DEPARTMENT OF CHEMISTRY,

UNIVERSITY OF ROORKEE,
ROORKEE (India)

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Sudarshan Kumar Verma
Sudarshan Kumar Verma

CERTIFICATE

Certified that the thesis entitled 'CHELATES OF URANIUM (VI) WITH OXYGEN DONOR LIGANDS AND A STUDY OF THEIR STABILITY AND POLYMERIZATION' which is being submitted by Sri Sudarshan Kumar Verma in fulfilment for the award of the Degree of Doctor of Philosophy in Chemistry to the University of Roorkee, is a record of his own work carried out by him under my supervision and guidance. The matter embodied in this thesis has not been submitted to any other University for the award of any degree.

This is further to certify that Sri Verma has worked for a period equivalent to 26 months full time research in the department of Chemistry for preparing his thesis for Ph.D. Degree at this University.

R.P. Agarwal

Dated February 25, 1967.

(R.P. Agarwal)
Ph.D.

Department of Chemistry
University of Roorkee,
Roorkee.

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PART I

INTRODUCTION

INTRODUCTION

Oxycations of the types MO^{n+} and MO_2^{n+} are found mainly among the lighter transition elements (in their higher oxidation states) of a given period, for example, in groups IV, V and VI. They are almost non-existent with the later group metals, although exceptions, such as OsO_2^{2+} and RuO_2^{2+}, are known. The most extensively[1-10] studied and the best characterized oxycation is the dioxouranium (VI) or uranyl ion, UO_2^{2+}.

It may be assumed that the uranyl ion is linear. Although such linearity may not be deduced completely unambiguously from any one experiment, there is general accord that a collinear O-U-O structure affords better interpretation of the Raman[10-14] infrared[15], and electronic spectra[16], and of x-ray diffraction intensities[17]. It is also an established fact that the uranyl ion possesses three characteristic frequencies: the symmetric stretching frequency ν_1, lying in the range 780-900 cm^{-1}; the asymmetric stretching frequency ν_3, lying in the range 800-1000 cm^{-1}; and the bending vibration ν_2, appearing in the neighbourhood of 200 cm^{-1}. The rather large frequency intervals quoted by ν_1 and ν_3 are indicative[18] of the fact that appropriate complexation of the uranyl ion by ligand groups presumed to lie in, or nearly in, a plane perpendicular to the axial O-U-O direction, produce extremely large variations in ν_1 and ν_3.

HYDROLYSIS OF UO_2^{2+} :

Aqueous solutions of uranyl salts are distinctly acidic and it has also long been known that large amounts of UO_3 can be dissolved by solutions of uranyl salts. To account for these observations as well as for the steep rise in electrical conductance of dilute solutions in comparison with other salts of similar valence type, MacInnes Longsworth[19] proposed the formation of the polymeric species $UO_2(UO_3)^{2+}$. On the basis of cryscopic measurements, potentiometric titrations and spectrophotometric studies, Sutton[20] proposed structures corresponding to $U_2O_5^{2+}$ and $U_3O_8^{2+}$ as well as a number of ions containing additional hydroxo groups, viz., $U_3O_8(OH)^+$, $U_3O_8(OH)_2$ and $U_3O_8(OH)_4^{2-}$ and calculated equilibrium constants for the formation of various species:

$$2UO_2^{2+} + H_2O \rightleftharpoons U_2O_5^{2+} + 2H^+ \qquad K = 1.1\times10^{-6}$$

$$U_2O_5^{2+} + UO_2^{2+} + H_2O \rightleftharpoons U_3O_8^{2+} + 2H^+ \qquad K = 5\times10^{-9}$$

$$U_3O_8^{2+} + H_2O \rightleftharpoons U_3O_8(OH)^+ + H^+ \qquad K = 2.8\times10^{-4}$$

Sillen and coworkers[21] have been active in advancing the 'core-link' hypothesis for the formation of polynuclear complexes and have described methods for determining formula of polymeric olated metal species of the general formula $M([OH]_t M)_n$. In a number of cases, they found that the curves, obtained by plotting Z (average number of hydroxo groups bound per mole of the metal ion) as ordinate vs. $-\log [H^+]$ as abscissae for different values of total metal ion concentration (T_M), were essentially parallel and that the horizontal spacing between the two curves was proportional to the difference between the two values of $-\log T_M$. Mathematically this may be expressed by the relationship:

$$\left(\frac{\partial \log T_M}{\partial \log [H^+]} \right)_Z = t$$

where 't' is the number of hydroxo groups bound per polynuclear link in a 'core plus links' type of complex. Ahrland, Heitanen and Sillen[22] have interpreted their potentiometric data on hydrolytic reactions of UO_2^{2+} to indicate the formation of sheet-like complexes with double OH bridges:

$$UO_2([OH]_2\ UO_2)_n^{2+}$$

Recently Gustafson, <u>et al.</u>[23] employing the mathematical treatment described by Sillen and co-workers, have determined equilibrium constants for the reactions associated with the formation of various species in the hydrolysis of UO_2^{2+}. A plot of $-\log T_M$ against $-\log [H^+]$ at constant Z , obtained from the potentiometric titrations of uranyl nitrate with KOH, corresponded to slopes of

2.08, 2.16, 2.20, 2.25 and 2.34 at Z values of 0.20, 0.40, 0.60, 0.80 and 1.00 respectively. These values are somewhat higher than the value of 2.00 which would be predicted on the basis of the formula suggested by Sillen and co-workers, i.e., polymers containing two hydroxo bridges per link. Gustafson <u>et al.</u>[23] have explained this behaviour on the basis of the presence of complexes such as $UO_2(OH)^+$ in the system. They concluded that the hydrolysis of UO_2^{2+}, in the initial stages ($Z < 0.3$), proceeds by the reactions

$$UO_2^{2+} + H_2O \rightleftharpoons UO_2(OH)^+ + H^+$$

$$2UO_2^{2+} + 2H_2O \rightleftharpoons UO_2(OH)_2UO_2^{2+} + 2H^+$$

or $$2UO_2(OH)^+ \rightleftharpoons UO_2(OH)_2\ UO_2^{2+}$$

The values of K_1, K_2 and K_d, defined by the equations

$$K_1 = \frac{[UO_2(OH)^+]\ [H^+]}{[\ UO^{2+}\ ]}$$

$$K_2 = \frac{[UO_2(OH)_2\ UO_2^{2+}]\ [H^+]^2}{[UO_2^{2+}\ ]^2}$$

and

$$K_d = \frac{[\ UO_2(OH)_2\ UO_2^{2+}\ ]}{[UO_2^{2+}]^2}$$

were found to be $10^{-6.10}$, $10^{-5.84}$ and $10^{-6.36}$ respectively. It is of interest to note that the value of K_d for the uranyl ion is considerably greater than those calculated for copper[20], aluminium[25], iron[26-29](III), and thorium[30] indicating that the monohydroxy species of uranyl ion has a relatively greater tendency to form polynuclear complexes.

URANYL CHELATES

Among the uranyl chelates of oxygen donor ligands, complexes of α-hydroxy carboxylic acids have received an extensive attention. Uranyl tartrate has been known[31] s[illegible] the earliest investigations of uranium chemistry. Peligot[32,33], Courtois[34] and Itzig[35] have described the preparation of solid compounds. A considerable amount of work has been done on the optical properties of uranyl complexes of aliphatic hydroxy acids. Walden[36] found that the addition of KOH and uranyl nitrate to solutions of tartaric, malic, mandelic, and quinic acids cause a large increase in the optical rotatory powers of the solutions. Bruhat[37] has reported that uranyl tartrate solutions exhibit cotton effect.

Recently, Feldman and co-workers[38-40] have concluded on the basis of potentiometric, spectrophotometric and polarographic studies that tartaric, malic and citric acids react with uranyl ion in the pH range 2-4 by terdentate chelation to form binuclear chelates which are held together by hydroxy bridges between uranium atoms. They have also concluded that binuclear diolated chelates react further with hydroxyl ions at pH > 4 to form ternuclear species. Dimerization and trimerization constants for the uranyl tartrate and malate complexes have been reported[41]. More recently, Rajan and Martell[42], by a mathematical analysis of the potentiometric data, have reported that in the polymerization of uranyl tartrate and malate chelates the bridging between the metal ions occurs through the ligand groups. Formation constants of the uranyl chelates of glycolic, lactic, β-hydroxy propionic, α-hydroxy butyric and β-hydroxy butyric acids[43-45] have been determined.

Ascorbic acid forms in solution a 1:1 uranyl complex[46,47] which has been used for the colorimetric determination[48-50] of uranium. The solid uranyl ascorbate complex, $UO_2(C_6H_7O_6)_2$ and a basic ammonium uranyl ascorbate have been isolated[51,52].

Hok-Bernstrom has studied the extraction of uranyl ion by solution of salicylic acid in 4-methyl-pentanone[53]. The complexes $UO_2(HO\ C_6\ H_4\ COO)_2$ and $H\ [\ UO_2\ (HO\ C_6\ H_4\ COO)_3\ ]$ or complexes stoichiometrically equivalent to them were present in the organic phase, and $[UO_2\ (HO\ C_6\ H_4\ COO)]^+$ and $UO_2\ (O\ C_6\ H_4\ COO)$ in the aqueous phase. o-methoxy benzoic acid behaves similarly, but does not form a 1:3 complex. The extraction of uranium (VI) by salicylic acid in iso-amyl alcohol has also been studied[54]. Numerous hydrated double salts and addition compounds with organic bases have been reported[55-60].

Foly and Anderson, employing spectrophotometric technique, reported[61] the formation of a 1:1 uranyl-sulphosalicylate complex. Banks and Singh, using Bjerrum's method, obtained evidence for the formation of 1:1 and 1:2 complexes[62] of uranyl ion with 5-sulphosalicylic acid at pH values of 4.5 and 7.5 respectively. More recently, Rajan and Martell have re-investigated the interaction of uranyl ion with 5-sulphosalicylic acid by potentiometric titrations and concluded the formation of only 1:1 complex[63] in aqueous solutions.

2,5-cresotic acid[64] gives the complex $Na_2\ UO_2\ .\ (CH_3\ C_6\ H_3O\ COO)_2$ analogous to the double salicylate complex. 2,3-cresotic acid and hydroxy naphthoic acids have been reported to form 1:1 chelates[65-67] in aqueous solution. Addition compounds of these metal chelates with pyridine have been isolated.

Numerous complexes with β-diketones and related dicarboxyl compounds have been prepared. Among these, the acetylacetonate complex has been studied in detail. This complex[68] in the monohydrate form was apparently first prepared by Bilz and Clinch in 1904. The subsequent workers isolated the anhydrous compound[69-71]. The monohydrate has recently been prepared[72] in three different crystallographic forms. Two of them are yellow in colour, typical of uranyl complexes of aliphatic ligands, while the other is red. The anhydrous complex in benzene solution is dimeric, and it has been proposed that the dimers are held together by coordination with ligand groups.

Stability constants of uranyl-acetyl-acetone complexes have been determined by potentiometric[73,74], spectrophotometric[75] and solvent extraction[76] methods. An evidence for the formation of $UO_2(C_5H_7O_2)_2.C_5H_8O_2$ has been obtained.

Solvent extraction by organic solution of HTTA has been widely used for the laboratory-scale separations of the actinides[77]. The uranyl-HTTA system broadly resembles the uranyl-acetylacetone system. Benzene solutions containing an excess of HTTA extract the uranyl ion in the form of $UO_2(TTA)_2.HTTA$[78-80].

The uranyl-dibenzoyl methane complex crystallizes with water[81,82], ethyl alcohol[83], ammonia, and pyridine[84]. The formation of this complex in dilute solutions forms the basis of a sensitive colorimetric method for the determination[85] of uranium.

With polyhydroxy benzenes (pH_2), $[UO_2(P)]$ complexes are formed in the pH range 3-5, whereas at higher pH values complexes containing 1:2 molar ratio of uranyl to ligand result; the ligands include catechol, resorcinol, pyrogallol and gallic acid[86-90].

Martell and co-workers[23] studied the interaction of uranyl ion with tiron by potentiometric and spectrophotometric techniques and reported equilibrium constants for the formation of various chelate species in the system.

Chromotropic acid (DNS) has been used as a reagent for the colorimetric estimation of uranium (VI)[91,92]. By the electrical and continuous variations measurements, Banerji and Dey have reported[93] the formation of a 1:1 complex. Jantti[94], employing potentiometric titrations have claimed the formation of 1:1 and 1:2 complexes in solutions containing one and two moles of DNS per mole of uranyl ion.

In addition to the above, many other uranyl complexes of oxygen donor ligands have been reported. Some of them are listed in the table given below.

URANYL COMPLEXES WITH ACIDIC OXYGEN DONORS

Ligand	UO_2: ligand in complex	References
3-Oxoglutaric acid	1:1	51.
3-Alizarine sulphonic acid (aluminon)	1:1	95
Aurintricarboxylic acid	1:1	96
Chlorotetracycline	1:1	97
Dihydroxy maleic acid	1:1, 2:1	98
Kojic acid	1:1, 1:2	99,100
2-Naphthol-3, 6-disulphonic acid.	1:1	101
1-Nitroso-2-Naphthol-3,6-disulphonic acid.	3:2	101
Tropolone	1:1, 1:2, 1:3	102,103,104
Resorcinol	1:2	105
Benzilic acid	1:2	106

From the above review on the uranyl chelates it is interesting to note that various noteworthy aspects of the problem have not been given due emphasis. These are:

(i) Quantitative study of the equilibria involved in the formation of these chelates;

(ii) Their hydrolytic behaviour and the factors influencing their stability.

(iii) The unusual behaviour of uranyl complexes to undergo polymerization under suitable pH conditions.

Based on the above considerations, it was thought worthwhile to carry out comprehensive and systematic investigations on these chelates.

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PART II

CHELATES OF URANIUM (VI) WITH SOME ALIPHATIC CARBOXYLIC ACIDS

CHAPTER I

RESULTS AND DISCUSSION

Section I: Uranyl chelates of Mandelic acid.

Section II: Uranyl chelates of Lactic acid.

Section III: Uranyl chelates of Malonic acid.

CHAPTER I

SECTION I

URANYL CHELATES OF MANDELIC ACID

Complexes of uranyl ion with α-hydroxy carboxylic acids viz., glycollic[1], lactic[2], tartaric and malic[3-6] acids have been known since the earliest investigation of the uranium chemistry. But a physico-chemical study of the complexes has been undertaken only in recent years. Feldman and Co-workers[7-10] have established the stoichiometry of the chelates of uranyl ion with α-hydroxy carboxylic acids by potentiometric, spectrophotometric and polarographic techniques and have interpreted their data on the basis of polymerization of the chelates. More recently[11] they have reported the equilibrium constants for the formation of polynuclear chelates in uranyl-malte, -citrate and -tartarate systems. Rajan and Martell[12], by a mathematical analysis of their potentiometric data, have put forward a reaction mechanism for the formation of polynuclear uranyl-tartarate and -malate complexes.

Mandelic acid (phenyl-glycollic acid), a bidentate ligand, forms strong chelates with a number of metals viz., beryllium[13], zinc[14], aluminium[15,16], gallium[17], indium[18], titanium[19], protactinium[20,21], thorium[22] and vanadium[23]. This ligand has long been used as a precipitating reagent in the estimation of zirconium[23-29]. Pande and Misra[30] have recently

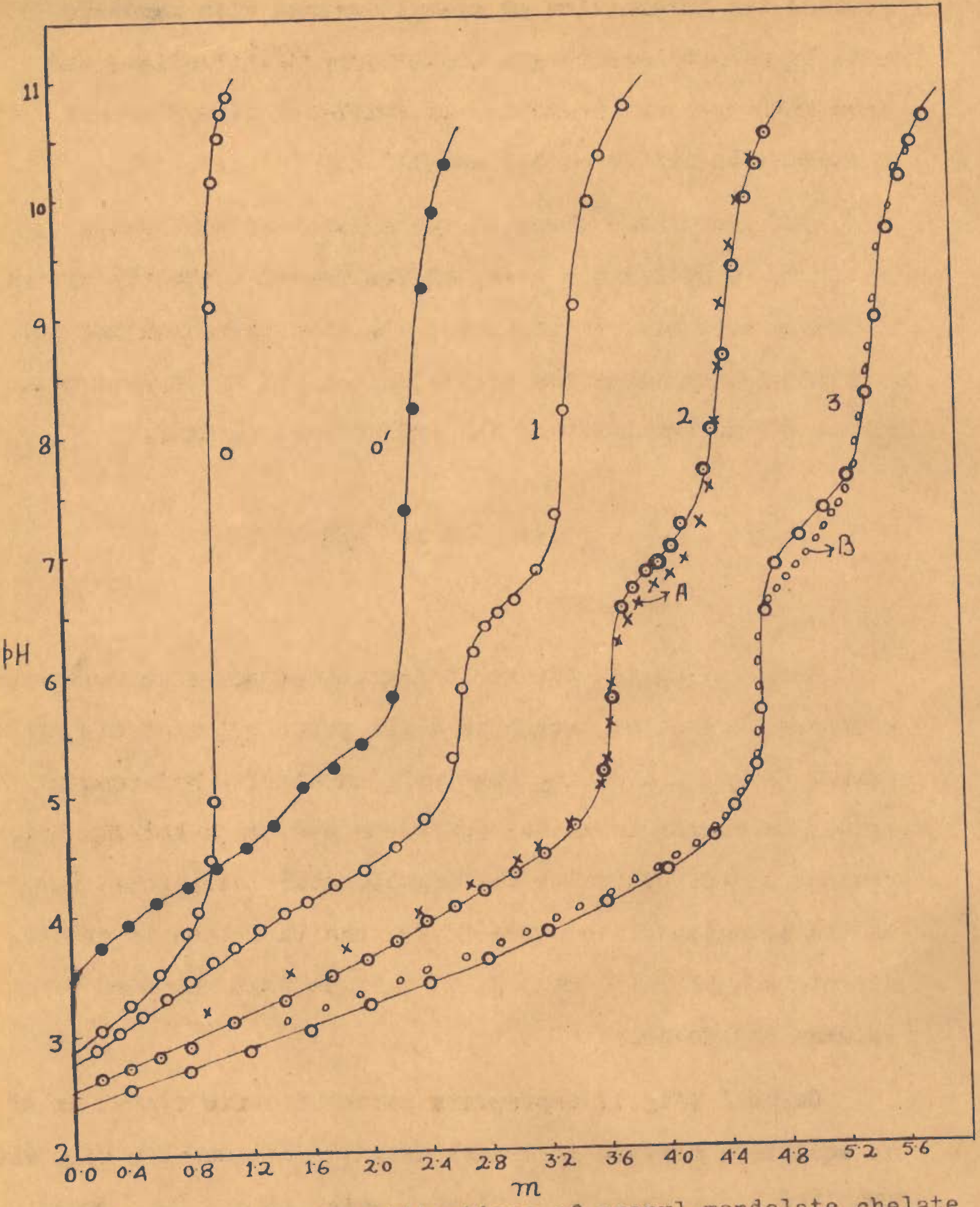


Fig.1. Potentiometric titrations of uranyl-mandelate chelate system with KOH(0.1N): curves 1,2 and 3 represent titrations of 1:1, 1:2 and 1:3 uranyl nitrate-mandelic acid mixtures respectively (T_M=0.005M). Curves O and O' represent titrations of mandelic acid(0.005M) and uranyl nitrate(0.005M) respectively. m=moles of KOH added per mole of the metal ion; Ionic strength = 0.1M(KNO_3). xxx, Composite curve derived from curves O and 1; B, Composite curve derived from curves O and 2.

studied the interaction of uranyl acetate with mandelic acid by potentiometric and conductometric titrations and have indicated the formation of complexes having uranyl to mandelate ratios of 1:1 and 1:2.

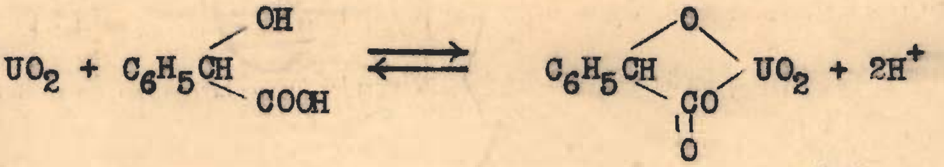
In view of the above it was considered worthwhile to carry out a systematic study of the uranyl-mandelate system. Attempts were made to study the reaction mechanism and the nature of polymerization of the chelate in the system by a mathematical treatment of the potentiometric data.

RESULTS AND DISCUSSION

Potentiometric Study:

Curve O(Fig.1), for the titration of mandelic acid with potassium hydroxide, exhibits a sharp inflexion at one equivalent of KOH indicating that only carboxylic hydrogen of the acid dissociates in acidic solutions and the α-hydroxy hydrogen remains unaffected under the experimental conditions. Nature of the potentiometric curve O' for the titration of uranyl nitrate solution (0.005M) is similar to that obtained by Feldman and Co-workers[10].

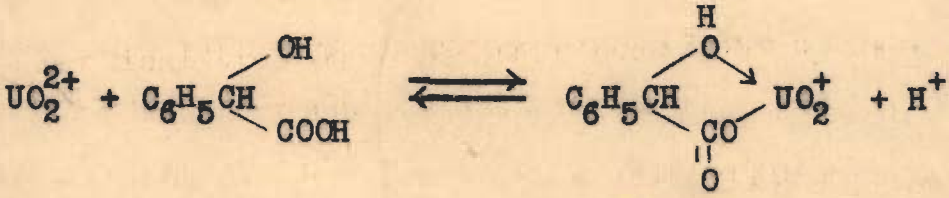
Curve 1 (Fig.1) represents potentiometric titration of an equimolar mixture of uranyl nitrate and mandelic acid with KOH. The curve shows an inflexion point at $m = 2\frac{2}{3}$, where 'm' represents moles of KOH added per mole of the metal ion, above which the precipitation of uranium hydroxide begins to occur. For the formation of the normal 1:1 chelate in accordance with the reaction:



(i)

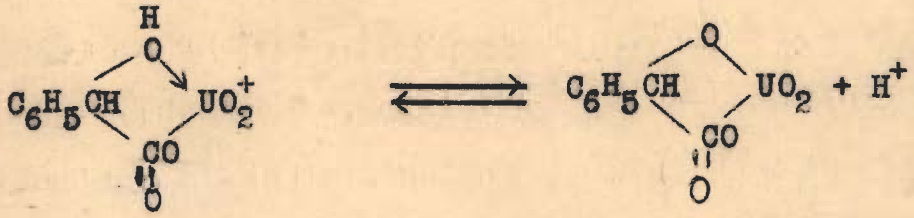
(I) (I)

two moles of KOH per mole of uranyl ion are required. Formation of the chelate (I) may also occur in two overlapping steps:



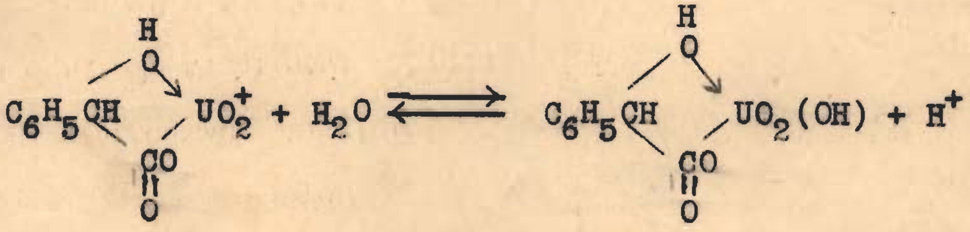
(ii)

(II)



(iii)

The hypothetical reactions (i) and (iii) are based on the assumption of the dissociation of the α-hydroxy hydrogen of mandelic acid as a result of chelation. Liberation of a second hydrogen ion in the system may also take place as:



(iv)

(III)

Formation of the monohydroxo chelate (III) would also give an inflexion point at $m = 2$.

Inflexion point at $m = 2\frac{2}{3}$ exhibited by curve 1 (Fig.1), thus indicates that the 1:1 uranyl mandelate chelate undergoes hydrolysis followed by polymerization reactions. This finds support from the work of Feldman and co-workers[10,11] who have interpreted the factor of $\frac{2}{3}$, in similar titrations of uranyl chelates of some α-hydroxy carboxylic acids, on the basis of polymerization of the chelates. The potentiometric curves, for the titration of uranyl nitrate with NaOH in the presence of an equimolar concentration of malic and tartaric acids respectively have, however, been shown[10-12] to exhibit two inflexion points, one at $m=3$ and the other at $m = 3\frac{2}{3}$. At the first inflexion point the metal chelates have been reported to be mainly present in the binuclear form, above which further polymerization of the complexes has been shown to occur resulting into complete conversion of the binuclear chelate species into the ternuclear form at the second inflexion point. The failure to obtain a titration break at $m = 2$ in the uranyl-mandelate system (curve 1, Fig.1) shows that the successive hydrolytic and polymerization reactions in the system overlap.

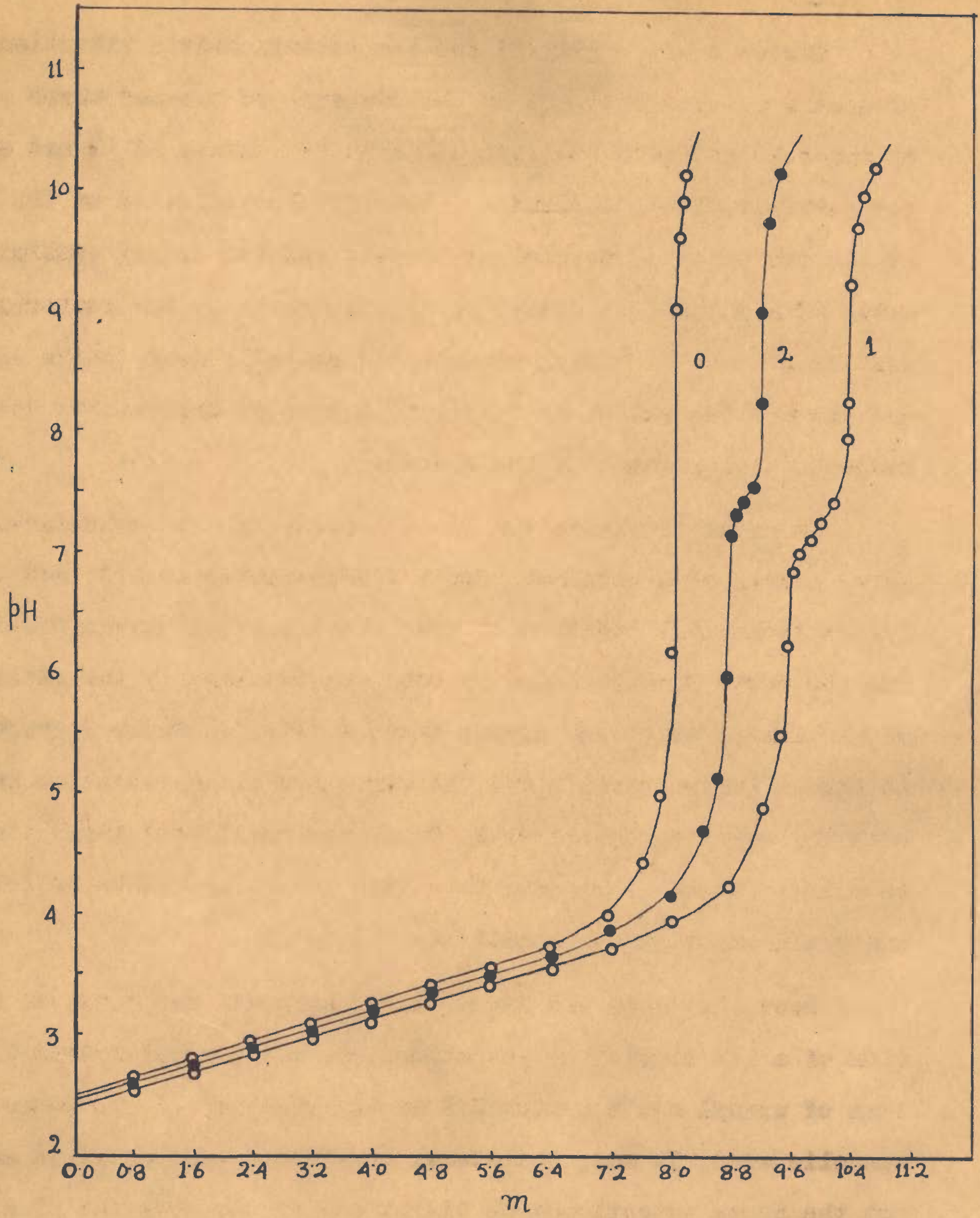


Fig.2.Titrations of 1:8 and 1:16 uranyl nitrate-mandelic acid mixtures: Curve 1, 2.5×10^{-3}M in uranyl nitrate and 2×10^{-2}M in mandelic acid; Curve 2, 1.25×10^{-3}M in uranyl nitrate and 2×10^{-2}M in mandelic acid. Curve 0 represents titration of mandelic acid (2×10^{-2}M) alone with KOH. m=moles of KOH added per mole of metal ion; For curve 2, the actual 'm' values are twice of the 'm' values shown. In curve 0, inflexion point corresponds to one equivalent of alkali. Ionic strength = 0.1M(KNO_3).

Curves 2 and 3 (Fig.1) for the potentiometric titrations of uranyl nitrate with KOH in the presence of two and three moles of mandelic acid exhibit inflexions at 'm' values of $3\frac{2}{3}$ and $4\frac{2}{3}$ respectively. These inflexion points may be explained on the basis of the formation of ternuclear chelate species having combining ratio of mandelate to uranyl of 1:1, as shown in the equimolar raction mixture of uranyl nitrate and mandelic acid (curve 1,Fig.1), and the neutralization of free mandelic acid, one and two moles respectively, present in the systems.

In order to verify the above conclusion, two calculated composite curves were obtained. Curve A(represented by xxx) was obtained by the horizontal addition of the potentiometric curves 0 and 1(Fig. and the curve B(represented by ooo) was obtained by the addition of the abscissae of the curves 0 and 2 (Fig.1). Curve A approximates to the titration curve 2 and the curve B closely resembles in nature with the experimental curve 3. Thus, the metal chelates,having ligan to uranyl ratios of greater than one, do not appear to be formed under the experimental conditions.

Recently Pande and Misra[30] have, however, reported the formation of a 1:2 complex by potentiometric and conductometric titrations of uranyl acetate with KOH in the presence of two moles of mandelic acid. It was, therefore, considered worthwhile to carry out the above potentiometric titrations in the presence of a fairly large excess of the ligand. Nature of curves 1 and 2 (Fig.2), for the titration of uranyl nitrate with KOH in the presence of large excess (8 and 16 moles) of mandelic acid, was found to be similar to that of curve 1 (Fig. 1). In these curves inflexion points at

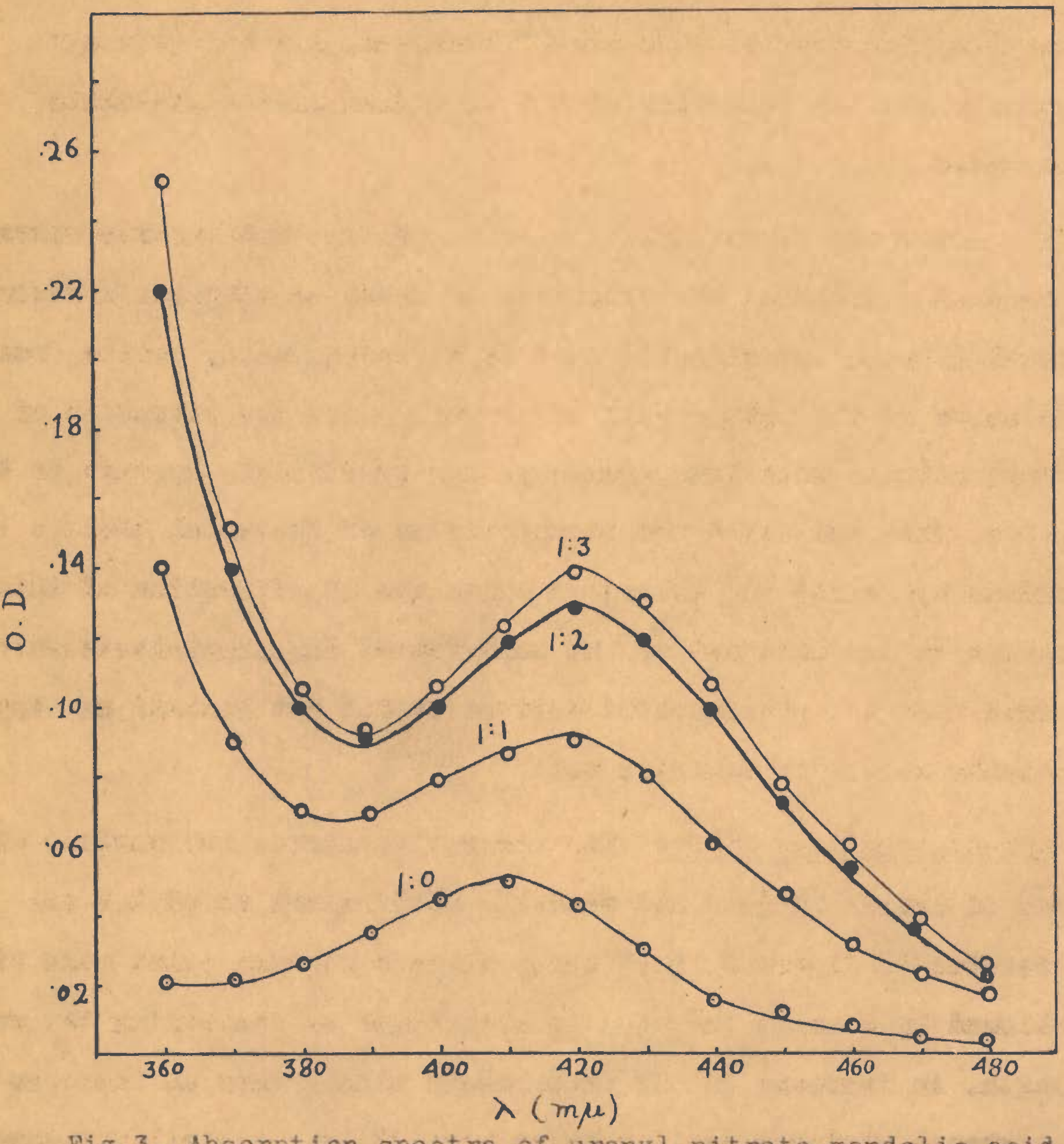


Fig.3. Absorption spectra of uranyl nitrate-mandelic acid mixtures, each solution 0.005M in uranyl nitrate at pH=3.5. The numerical ratios associated with each spectrum represent the initial uranyl/mandelic acid ratio of the solution. Ionic strength = 0.1M(KNO_3).

$m = 9\frac{2}{3}$ and $17\frac{2}{3}$ respectively may be easily accounted for on the basis of the formation of a ternuclear 1:1 chelate and the neutralization of the unbound mandelic acid present in the reaction mixtures. These titrations also, therefore, did not give any evidence for the formation of 1:2 or higher uranyl mandelate complexes.

After the first inflexion point, the potentiometric curves, discussed above, for the titration of reaction mixtures containing uranyl nitrate and mandelic acid in different molar ratios, assume the shape of the latter half of curve O', for the titration of uranyl nitrate with KOH, when a yellow precipitate appears in the system. This indicated the decomposition of the metal chelate into uranium hydroxide and potassium mandelate. Confirmation of this conclusion was obtained by the analysis of the precipitate which showed that the precipitated derivative did not contain any appreciable amount of mandelic acid.

Spectrophotometric Study: The absorption curves for various mixtures of uranyl nitrate and mandelic acid raised to pH 3.5 are presented in figure 3. Each curve shows a minimum point near 390 mμ followed by a rapid increase in absorbance by decreasing the wave length. An increase in the wave length also causes an increase in absorbance giving a maximum point near 420 mμ. A similar nature of these absorption curves indicated the formation of a 1:1 complex in the system.

The above conclusion was confirmed by the Job's method of continuous variations[31,32]. In figure 4 are presented the continuous variations data obtained at pH values of 3.0, 3.5 and 4.0. At all

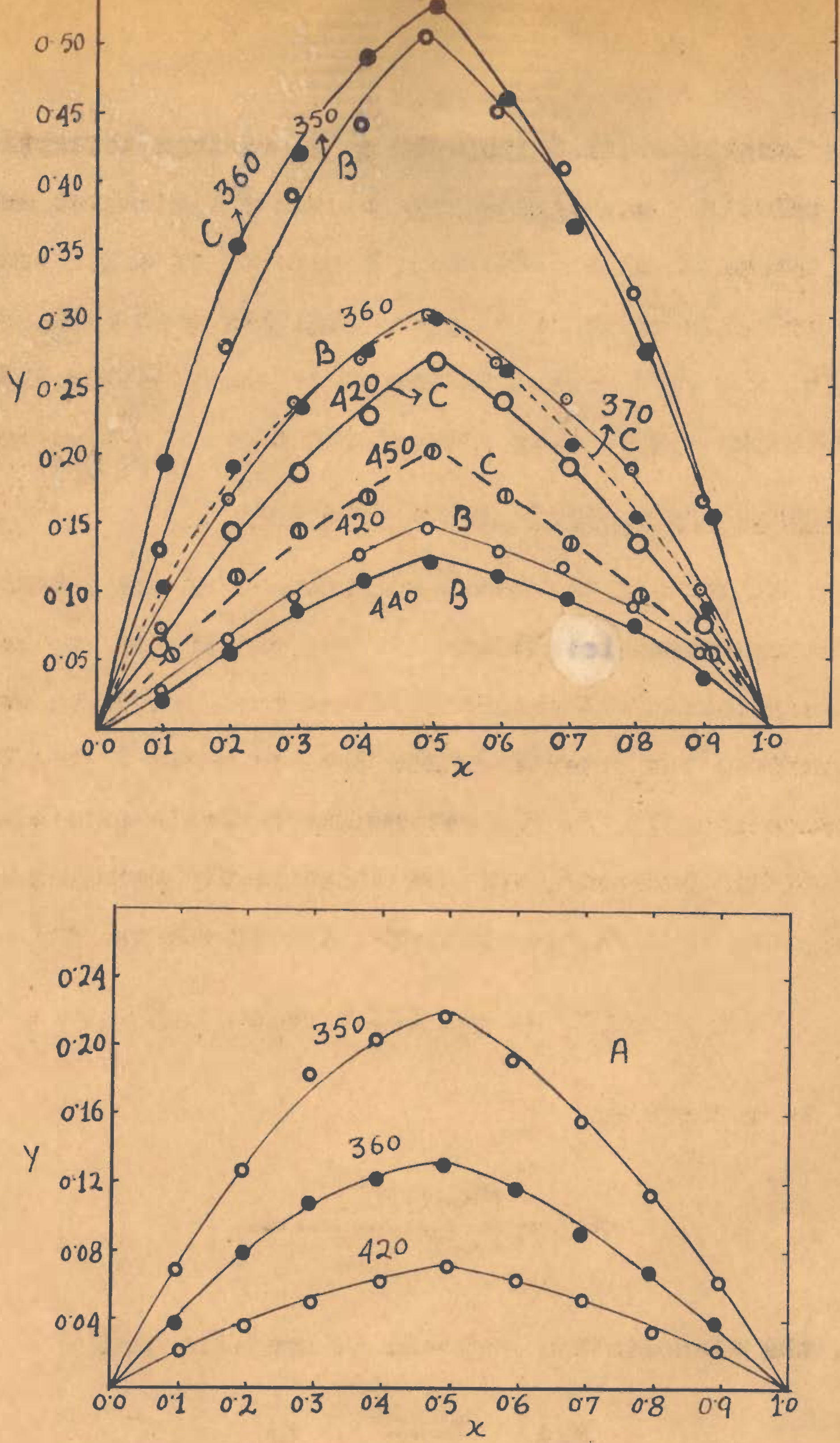


Fig. 4. Method of continuous variations applied to uranyl-mandelate system at different pH: (A) pH 3.0; (B) pH 3.5; (C) pH 4.0. T_A+T_M for each solution = 0.02 M; Ionic strength = 0.1M (KNO_3). Abscissa x represents the added molar ratio $T_M/(T_M+T_A)$. Ordinate Y is the difference between the observed absorbance and that which would be by uranyl-nitrate if no complexation reaction occurred. The number associated with each curve is the wave length in millimicrons at which absorbance was measured.

wave lengths studied (350-450 mμ), maximum absorption was observed for solutions containing approximately equivalent amounts of ligand and the metal ions indicating formation of a 1:1 complex. The non-linearity shown by these plots together with an increase in absorbance with an increase in the pH of the solution indicated that the complex is appreciably dissociated under the experimental conditions.

Determination of Equilibrium Constants

In view of the above conclusions of the potentiometric and spectrophotometric studies, it was considered worthwhile to carry out a mathematical analysis of the data. Attempts were first made to analyse the potentiometric data of curve 1 (Fig.1) on the basis of reaction (i). If H_2A represents mandelic acid having an ionizable carboxylic hydrogen, and the other weakly acidic α-hydroxy hydrogen atom, the equilibrium constant, K', of the reaction:

$$UO_2^{2+} + H_2A \rightleftharpoons UO_2A + 2H^+$$

may be defined as:

$$K' = \frac{[UO_2A]\,[H^+]^2}{[UO_2^{2+}]\;[H_2A]} \qquad (1)$$

K_a, the dissociation constant of mandelic acid

$$H_2A \rightleftharpoons HA^- + H^+$$

may be expressed as:

$$K_a = \frac{[HA^-]\;[H^+]}{[H_2A]} \qquad (2)$$

From a plot of $-\log[H^+]$ against $\log \frac{[HA^-]}{[H_2A]}$, (Fig.5), obtained

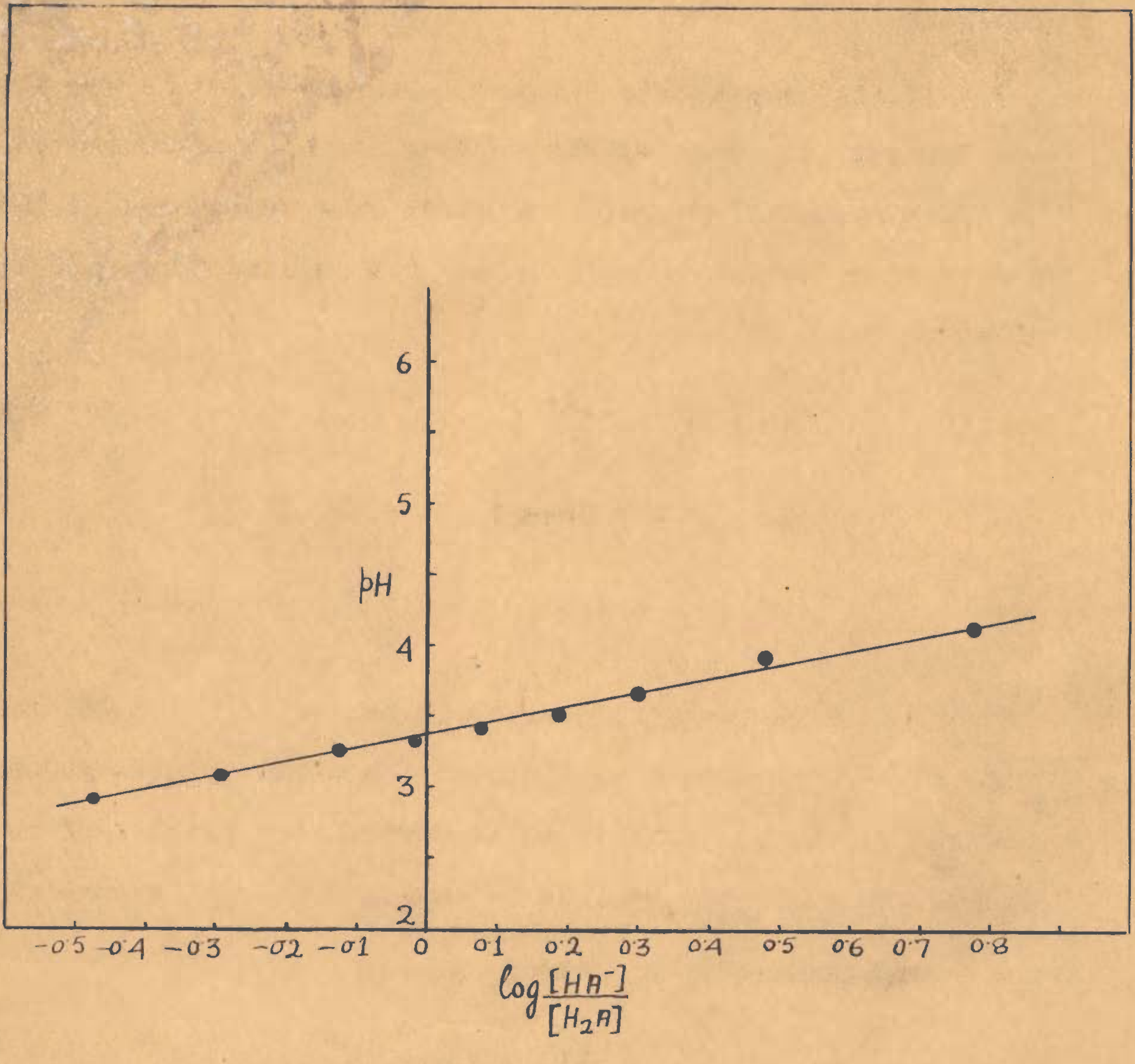


Fig. 5. Graphical evaluation of the dissociation constant of mandelic acid(H_2A). Ionic strength=0.1M(KNO_3).

from the potentiometric data of curve 0 (Fig.1), the value of $-\log K_a$ was found to be 3.37 as an intercept on the $-\log[H^+]$ axis, which is in good agreement with a value of 3.41 reported by Bell and Waind[14].

If T_M represents the total concentration of all the metal species and T_A that of the various ligand species and if T_{OH} be the concentration which the added base would have if there were no reaction, we can readily deduce the following equations for material balance:

$$T_M = [UO_2^{2+}] + [UO_2A] \qquad (3)$$

$$T_{OH} + [H^+] = 2[UO_2A] + [HA^-] \qquad (4)$$

and

$$T_A = [H_2A] + [HA^-] + [UO_2A] \qquad (5)$$

In the pH range studied, concentrations of $[A^{2-}]$ and $[OH^-]$ were negligible as compared to those of the other species present in the system. Concentrations of the hydrolyzed species of uncomplexed uranyl ion were also considered negligible in solutions of pH<3.

Combination of equations 2,4 and 5 gives

$$[H_2A] = \frac{2T_A - T_{OH} - [H^+]}{2 + \frac{K_a}{[H^+]}} \qquad (6)$$

In an equimolar mixture of uranyl nitrate and mandelic acid, since $T_A = T_M$, from equations 2, 3 and 5 we obtain

$$[UO_2^{2+}] = [H_2A]\left(1 + \frac{K_a}{[H^+]}\right) \qquad (7)$$

$$[UO_2A] = T_A - [H_2A]\,(1 + \frac{K_a}{[H^+]}) \qquad (8)$$

After determining the concentrations $[UO_2^{2+}]$, $[H_2A]$ and $[UO_2A]$, the equilibrium constant K' may then be calculated from equation (1). The results of these calculations, obtained from the potentiometric data of curve 1 (Fig.1), for the titration of an equimolar mixture of uranyl nitrate and mandelic acid ($5x10^{-3}$M) with KOH, are presented in Table I.

Table I

Curve 1 (Fig.1), $T_A = T_M = 5x10^{-3}M$

KOH(ml.)	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4
pH	2.75	2.82	2.89	2.96	3.03	3.10	3.17	3.24
-log K'	4.10	4.18	4.27	4.35	4.42	4.48	4.53	4.57

It is evident from Table I that the above mathematical treatment of the data did not give constant values of the equilibrium constant. A gradual increase in the values of -logK', observed in the above table, indicated that the concentration of hydrogen ions in the reaction mixture is less than that would be on the basis of reaction(i).

In view of the failure to fit the potentiometric data in the reaction (i), attempts were made to analyse the data on the basis of reaction (ii) :

$$UO_2^{2+} + H_2A \rightleftharpoons UO_2\,HA^+ + H^+$$

The equilibrium constant, K , for the reaction may be expressed as:

$$K = \frac{[UO_2HA]\,[H^+]}{[UO_2]\,[H_2A]} \tag{9}$$

and the formation constant , k , may be given by:

$$k = \frac{[UO_2HA]}{[UO_2]\,[HA^-]} \tag{10}$$

In calculation of the above constants from the titration data of solutions of pH>3 , it is necessary to account for the equilibria involved in the hydrolysis of the uncomplexed uranyl ions present in the system. From the values of the hydrolysis constants, $K_1 = 10^{-6.10}$, $K_2 = 10^{-5.84}$ and $K_4 = 10^{-17.60}$ reported by Gustafson <u>et al</u>[33]. and the arbitrary assignment of $K_3 = 0$ made by Ahrland <u>et al</u>[34]., where

$$K_{n+1} = \frac{[UO_2((OH)_2UO_2)_n]\,[H^+]^{2n}}{[UO_2]^{n+1}} \tag{11}$$

it may be shown that the concentration of $[UO_2(OH)]$, and also below pH of 4.5, the contribution of $[UO_2((OH)_2UO_2)_3]$ is negligible as compared to the concentrations of the other species present in the system.

In order to make calculations in the range 3<pH<4.5, therefore, use was made of the hydrolysis constant K_2 which is given by the expression:

$$K_2 = \frac{[UO_2(OH)_2UO_2]\,[H^+]^2}{[UO_2]^2} = 10^{-5.84} \tag{12}$$

for applying correction to the uncomplexed uranyl ions present in the system.

From the material balance, thus, we obtain

$$T_M = [UO_2] + 2[(UO_2OH)_2] + [UO_2HA] \qquad (13)$$

$$T_{OH} + [H^+] = [HA^-] + 2[(UO_2OH)_2] + [UO_2HA] \qquad (14)$$

and

$$T_A = [H_2A] + [HA^-] + [UO_2HA] \qquad (15)$$

Charges on the metal species have been eliminated for the sake of clarity.

Elimination of $[UO_2HA]$ between (13) and (14) gives

$$T_M - T_{OH} - [H^+] = [UO_2] - [HA^-] \qquad (16)$$

In an equimolar mixture of uranyl nitrate and mandelic acid, since $T_A = T_M$, from equations 13 and 15 we have

$$[UO_2] + 2[(UO_2OH)_2] = [H_2A] + [HA^-] \qquad (17)$$

Combining equations (2), (12), (16) and (17) and rearranging the terms, gives

$$\frac{2K_2}{[H^+]^2}[UO_2]^2 - \frac{[H^+]}{K_a}[UO_2] - \left(1+\frac{[H^+]}{K_a}\right)\left\{T_{OH}+[H^+] - T_M\right\} = 0 \qquad (18)$$

Concentration of the uncomplexed uranyl ions present in the equilibrium mixture may, therefore, be given by

$$[UO_2] = \frac{b \pm \sqrt{b^2 + 4ac}}{2a} \qquad (19)$$

where,

$$a = \frac{2K_2}{[H^+]^2}, \quad b = \frac{[H^+]}{K_a} \quad \text{and} \quad c = \left(1+\frac{[H^+]}{K_a}\right)\left\{T_{OH} + [H^+] - T_M\right\}$$

After computation of the concentration of free uranyl ions by

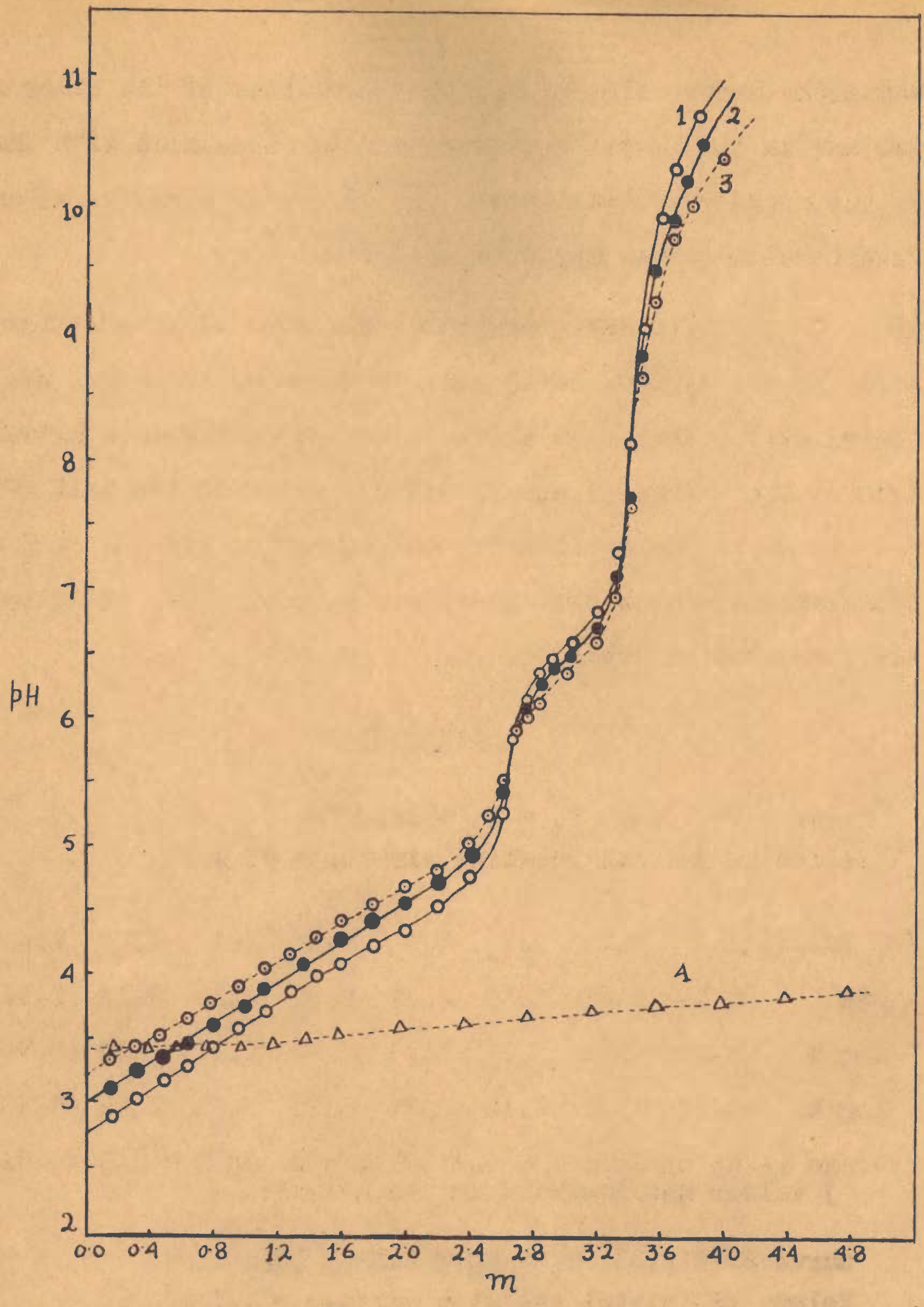


Fig.6. Potentiometric titrations of equimular mixtures of uranyl nitrate and mandelic acid. Concentrations of uranyl nitrate: Curve 1, $5x10^{-3}M$; Curve 2,$2.5x10^{-3}M$; Curve 3, $1.25x10^{-3}M$. m=moles of KOH added per mole of the metal ion; ionic strength=0.1M(KNO_3). Curve 4 represents titration of uranyl nitrate with potassium mandelate. In this case 'm' represents moles of potassium mandelate added per mole of uranyl nitrate.

using the known value of K_2, concentrations of the other specie. present in the reaction mixture may be calculated with the help of the equations given above. The values of equilibrium and formation constants may then be determined.

In order to investigate the presence of polynuclear complexes in the system, total concentration of the metal chelate was varied over a four-fold range in the potentiometric titrations of equimolar mixtures of uranyl nitrate and mandelic acid (Fig.6). The values of the equilibrium and formation constants, K and k, calculated from the potentiometric data of these titration curves, are presented in Table II.

Table II

Curve 1 (Fig.6), $T_A = T_M = 5\text{x}10^{-3}M$;
Volume of initial reaction mixture = 50 ml.

KOH (ml.)	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
pH	2.75	2.82	2.89	2.96	3.03	3.10	3.17	3.24	3.31
-log K	0.90	0.91	0.91	0.90	0.88	0.86	0.83	(0.79	0.59)
log k	2.47	2.46	2.46	2.47	2.49	2.51	2.54	(2.58	2.78)

Average value of -log K = 0.87±0.04 and log k = 2.50±0.04
(   ) values not included in the average.

Curve 2 (Fig.6), $T_A = T_M = 2.5\text{x}10^{-3}M$;
Volume of initial reaction mixture = 100 ml.

KOH (ml.)	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
pH	2.99	3.05	3.11	3.18	3.25	3.30	3.35	3.40	3.47
-log K	0.90	0.90	0.89	0.88	0.89	0.86	(0.68	0.46	0.26)
log k	2.47	2.47	2.48	2.49	2.48	2.51	(2.69	2.91	3.11)

Average value of -log K = 0.88±0.02 and log k = 2.49±0.02
(   ) values not included in the average.

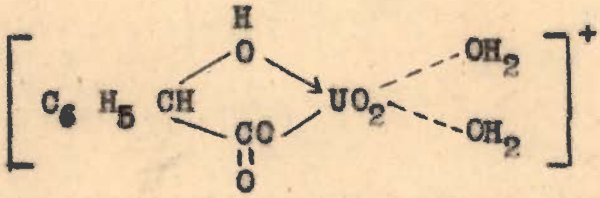
Curve 3(Fig.6), $T_A = T_M = 1.25 \times 10^{-3} M$

Volume of initial reaction mixture = 200 ml.

KOH (ml.)	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
pH	3.22	3.28	3.33	3.38	3.43	3.48	3.53	3.58	3.64
-log K	0.94	0.94	0.94	0.92	0.91	(0.83	0.65	0.33	0.15)
log k	2.43	2.43	2.43	2.45	2.46	(2.54	2.72	3.04	3.22)

Average value of -log K = 0.92±0.02 and log k = 2.44±0.02
(   ) values not included in average.

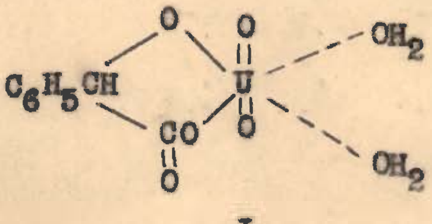
It is evident from Table II that the relatively constant values of -log K, independent of concentration of the metal chelate, could be obtained upto 'm' value of about 0.4 (pH about 3.3) indicating that the mononuclear diaquo 1:1 uranyl mandelate chelate



is the predominant chelate species present in the system upto pH of about 3.3.

<u>Hydrolysis and Polymerization of Uranyl-Mandelate Chelate</u> :

A gradual fall in the values of -log K, observed in Table II, calculated at m>0.4, indicated that either hydrogen of the α-hydroxy group of the ligand begins to dissociate or that one of the water molecules of the normal diaquo chelate undergoes dissociation to give one or a mixture of the following chelate species:



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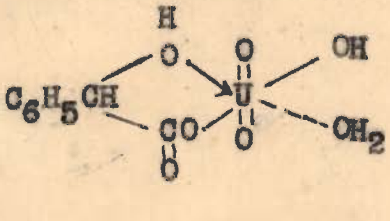


II

From the potentiometric data alone it is difficult to distinguish between the above two possible structures. Structure II, however, appears to be more probable in view of the tendency of uranyl ion and its chelates to undergo hydrolysis and polymerization[34,35] above pH 3. The uranyl glycolate chelate, for example, has been reported[36] to hydrolyse at pH 3.5 with the formation of polynuclear chelate species. Moreover, the potentiometric titration of uranyl nitrate with potassium mandelate (Curve 4, Fig.6) did not show any appreciable fall in the pH of the solution indicating that the α-hydroxy hydrogen of the ligand remains unaffected under the experimental conditions. The above conclusion also obtains support from the polarographic and conductometric studies of a similar uranyl lactate system reported by Lai and Wang[37].

Determination of Hydrolysis Constant

The hydrolysis constant, K_h, of the chelate ($UO_2HA^+ + H_2O \rightleftharpoons UO_2(OH)HA + H^+$) may be defined as

$$K_h = \frac{[UO_2(OH)HA]\,[H^+]}{[UO_2HA^+]} \qquad (20)$$

The equilibrium constant, K_H, of the overall reaction

$$UO_2^{2+} + H_2A + H_2O \rightleftharpoons UO_2(OH)HA + 2H^+$$

may be expressed as:

$$K_H = \frac{[UO_2(OH)HA]\,[H^+]^2}{[UO_2^{2+}]\,[H_2A]} \qquad (21)$$

Other pertinent equations are

$$T_M = [UO_2] + 2[(UO_2OH)_2] + [UO_2HA] + [UO_2(OH)HA] \qquad (22)$$

$$T_{OH} + [H^+] = [HA^-] + 2[(UO_2OH)_2] + [UO_2HA] + 2[UO_2(OH)HA] \qquad (23)$$

and

$$T_A = [H_2A] + [HA^-] + [UO_2HA] + [UO_2(OH)HA] \qquad (24)$$

Elimination of $[UO_2(OH)HA]$ between equations 22 and 23 gives

$$2T_M - T_{OH} - [H^+] = 2[UO_2] + 2[(UO_2OH)_2] + [UO_2HA] - [HA^-] \qquad (25)$$

In an equimolar mixture of uranyl nitrate and mandelic acid, since $T_A = T_M$, from equations 22 and 24 we obtain

$$[UO_2] + 2[(UO_2OH)_2] = [H_2A] + [HA^-] \qquad (26)$$

Combination of (2), (10), (12), (25) and (26) and rearranging the terms into the form of a polynomial yields

$$\frac{2k\,K_2}{[H^+]^2}[UO_2]^3 + \left\{k + \frac{2k_2}{K_a[H^+]}\right\}[UO_2]^2 + \left\{1 + \frac{2[H^+]}{K_a}\right\}[UO_2] - \left\{2T_M - T_{OH} - [H^+]\right\}\left(1 + \frac{[H^+]}{K_a}\right) = 0 \qquad (27)$$

Knowing the values of K_a, K_2 (from expression 12) and k(from table II), equilibrium concentration of the uncomplexed uranyl ions can be determined by solving the above cubic equation, using the Newton's method[38] of successive approximations. After computation of $[UO_2]$, concentrations of the other species present in the reaction mixture may be determined with the help of the equations given above. Values of the constants K_h and K_H, thus calculated from the potentiometric data of curves 1,2 and 3 (Fig.6) are presented in Table III.

Table III

Curve 1 (Fig.6), $T_A = T_M = 5x10^{-3}M$

Volume of reaction mixture before titration = 50 ml.

KOH(ml.)	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6
pH	3.37	3.45	3.52	3.59	3.66	3.74	3.80	3.87	3.94	
$-\log K_h$	3.81	3.82	3.79	3.76	3.74	3.75	(3.69	3.64	3.52)	
$-\log K_H$	4.71	4.72	4.69	4.66	4.64	4.65	(4.59	4.54	4.42)	

Average value of $-\log K_h$ = 3.78±0.04 and $-\log K_H$ = 4.68±0.04
(   ) values not included in average.

Curve 2 (Fig.6), $T_A = T_M = 2.5x10^{-3}M$

Volume of reaction mixture before titration = 100 ml.

KOH(ml.)	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4
pH	3.54	3.62	3.69	3.76	3.83	3.90	3.96	4.02	4.08
$-\log K_h$	3.92	3.95	3.93	3.90	3.88	(3.85	3.79	3.73	3.66)
$-\log K_H$	4.82	4.85	4.83	4.80	4.78	(4.75	4.69	4.63	4.56)

Average value of $-\log K_h$ = 3.92±0.04 and $-\log K_H$ = 4.82±0.04
(   ) values not included in average.

Curve 3 (Fig.6), $T_A = T_M = 1.25x10^{-3}M$
Volume of reaction mixture before titration = 200 ml.

KOH (ml.)	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4
pH	3.71	3.78	3.85	3.92	3.98	4.05	4.11	4.16	4.22
$-\log K_h$	4.03	4.01	4.00	3.99	3.97	(3.91	3.83	3.73	3.59)
$-\log K_H$	4.93	4.91	4.90	4.89	4.87	(4.81	4.73	4.63	4.49)

Average value of $-\log K_h$ = 4.00±0.03 and $-\log K_H$ = 4.90±0.03
(   )Values not included in average.

It is evident from table III that the above mathematical treatment of the data yielded constant values of the equilibrium constant in the range of $m=0.64$ and $m=1.05$. Above this range a gradual fall in the values of $-\log K_h$ and $-\log K_H$ was observed indicating the occurrence of some side reaction which has not been considered in the above treatment. It is also apparent from the average value of the equilibrium constants, given in table III, that the values of $-\log K_h$ and $-\log K_H$ increase with decrease in the total concentration of the metal salt. A difference of 0.14 pK unit, for example, in the equilibrium constants, calculated from the potentiometric data of curves 1 and 2, might possibly be due to an experimental pH error of about 0.04 unit only in the two titrations. But a similar trend observed in the pK_h and pK_H values, calculated from the data of the curve 3, for the titration of an equimolar mixture of uranyl nitrate and mandelic acid of concentration 1.25×10^{-3}M, appears to be real. Such a trend is indicative of the condensation of the monohydro 1:1 metal chelate to form chelate species of higher molecular weight.

Dimerization of the Chelate

Polymerization of the monohydroxo 1:1 uranyl mandelate complex, indicated above, would possibly involve an intermediate formation of a binuclear chelate species. Attempts were, therefore, made to analyse the titration data, in the 'm' range of 0.64-1.05 which yielded constant values of pK_h (table III) on the basis of dimerization reaction :

$$2UO_2HA + 2H_2O \rightleftharpoons (UO_2(OH)HA)_2 + 2H^+$$

The dimerization constant, K_d, may be defined as

$$K_d = \frac{[(UO_2(OH)HA)_2]\ [H^+]^2}{[UO_2\ HA]^2} \tag{28}$$

The equilibrium constant, K_D, for the overall reaction:

$$2UO_2^{2+} + 2H_2A + 2H_2O \rightleftharpoons (UO_2(OH)HA)_2 + 4H^+$$

may then be expressed as

$$K_D = \frac{[(UO_2(OH)HA)_2]\ [H^+]^4}{[UO_2^{2+}]^2\ [H_2A]^2} \tag{29}$$

Other pertinent equations are

$$T_M = [UO_2] + 2[(UO_2OH)_2] + [UO_2HA] + [UO_2(OH)HA] \\ 2[(UO_2(OH)HA)_2] \tag{30}$$

$$T_{OH} + [H^+] = [HA^-] + 2\ [(UO_2OH)_2] + [UO_2HA] + 2[UO_2(OH)HA] + \\ 4[\ (UO_2(OH)HA)_2\ ] \tag{31}$$

and

$$T_A = [H_2A] + [HA^-] + [UO_2HA] + [UO_2(OH)A] + 2\ [(UO_2(OH)HA)_2\ ] \tag{32}$$

Combination of equations 20, 28 and 30 gives

$$\frac{[H^+]\left\{T_M - [UO_2] - 2\ [(UO_2OH)_2\ ] - [UO_2HA]\right\}}{[UO_2HA]} = 2K_d\ \frac{[UO_2HA]}{[H^+]} + K_h \tag{33}$$

Thus if a dimer is formed, a plot of the expression on the left hand side of equation 33 should give a straight line of slope $2K_d$ and the intercept at $\frac{[UO_2HA]}{[\ H^+\ ]} = 0$ would be equal to K_h. This requires a knowledge of concentrations of the various metal species involved in the expression on the left side of equation (33). As shown before here also, it may be demonstrated that the concentration of the

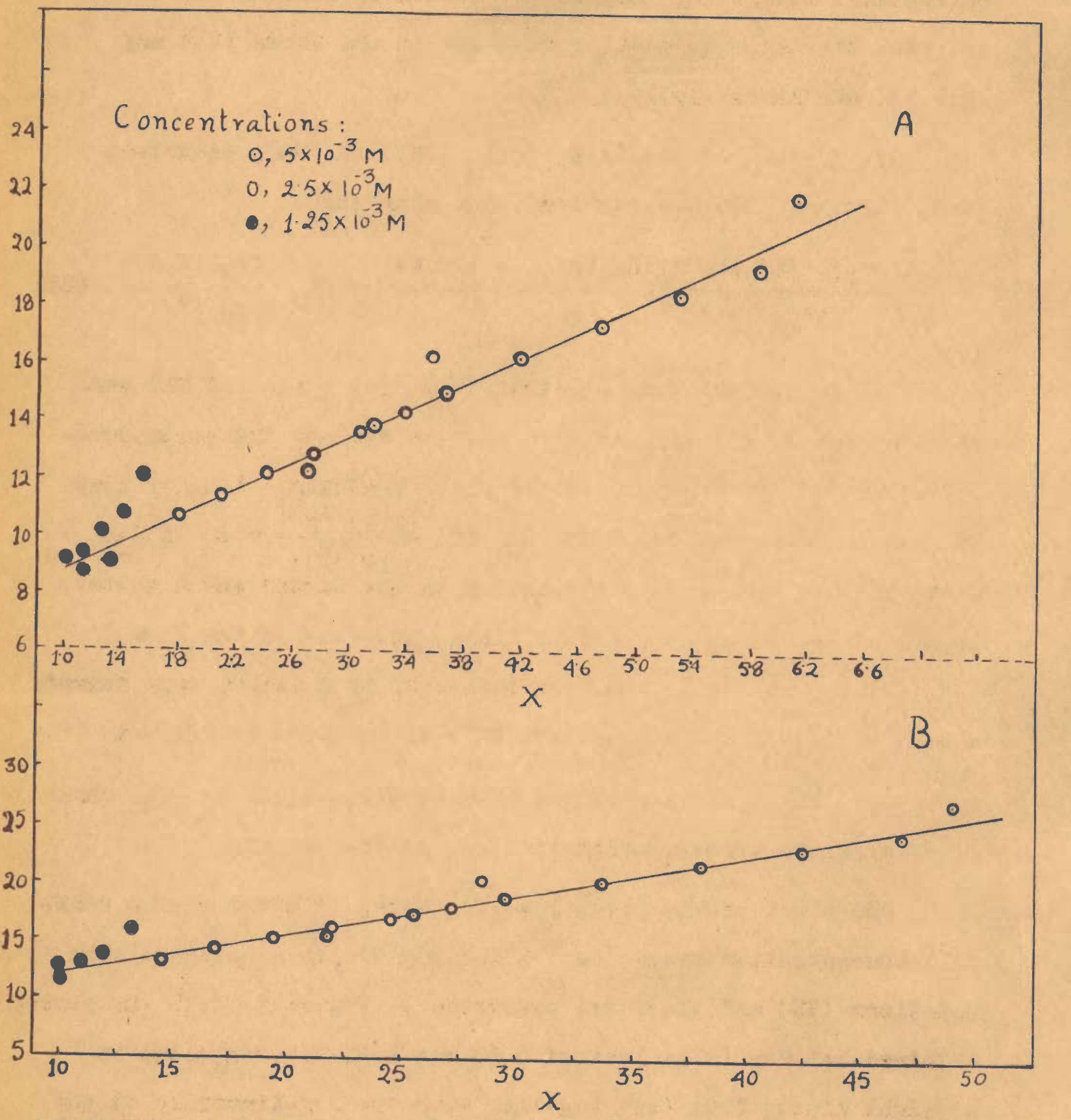


Fig.7. Graphical demonstration of dimerization of mono-hydroxo-uranyl mandelate chelate:

Fig.7A, $X = \frac{[UO_2HA]}{[H^+]}$, $Y = \frac{[H^+]\{T_M - [UO_2] - 2[(UO_2OH)_2] - [UO_2HA]}{[UO_2HA]} \times 10^{-5}$

B, $X = \frac{[UO_2^{2+}][H_2A]}{[H^+]^2}$, $Y = \frac{[H^+]^2\{T_M - [UO_2] - 2[(UO_2OH)_2] - [UO_2HA]\}}{[UO_2][H_2A]} \times 10^{-6}$

uncomplexed uranyl ions may be determined by solving the cubic equation 27. Other quantities required in the above plot may then be calculated easily.

If, instead of combining (20), (28) and (30), equations (21), (29) and (30) are combined, one obtains

$$\frac{[H^+]^2 \left\{T_M - [UO_2] - 2[(UO_2OH)_2] - [UO_2HA]\right\}}{[UO_2]\ [H_2A]} = 2K_D \frac{[UO_2][H_2A]}{[H^+]^2} + K_H \quad (34)$$

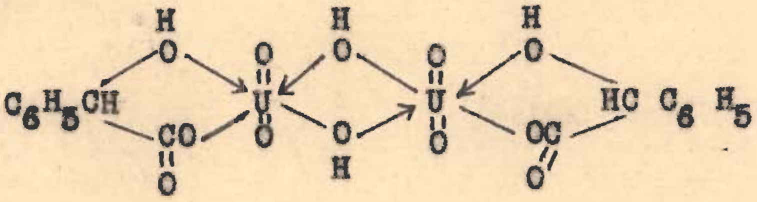
Again, it is evident from equation (34) that a plot of the expression on the left side of the equation against the corresponding values of $\frac{[UO_2][H_2A]}{[H^+]^2}$ should yield a straight line of slope $2K_D$ and an intercept equal to K_H at $\frac{[UO_2][H_2A]}{[H^+]^2} = 0$, if the metal chelate undergoes dimerization in the manner shown above. It is, of course, possible that higher polymers of the form $[UO_2(OH)HA]_n$ may be formed. For instance, if a trimer were formed, a plot of expression on the left side of equation 33 against $\frac{[UO_2HA]^2}{[H^+]^2}$ would give a straight line of slope equal to $3K_t$, where K_t represents trimerization constant of the chelate.

The plots of the potentiometric data, obtained over a fourfold concentration range (Curves 1-3, Fig.6), in accordance with equations (33) and (34), are presented in Figure 7. Both the plots, obtained between 'm' values of 0.64 and 1.05, corresponded to straight lines. This fact together with the non-linearity of the plot of the expression on the left side of equation 33 against $\frac{[UO_2HA]^2}{[H^+]^2}$ (on the basis of trimerization) showed that in the above buffer region (m=0.64-1.05) the monohydroxo chelate is mainly present in the solution in a binuclear form under the experimental conditions. The values of the equilibrium constants obtained from the above plots (Fig.7) are given in Table IV.

Table IV

From Fig. 7A		From Fig. 7B	
$-\log K_h$	4.05	$-\log K_H$	4.92
$-\log K_d$	4.94	$-\log K_D$	6.70

The binuclear chelate species may, thus have the probable structure:



In this connection it may be mentioned that dimerization may also occur through an oxygen bond as suggested by Sutton[35] in the polymerization of uranyl ions.

Hydrolysis of Dimer:

Calculation of hydrolysis constants of 1:1 complex by the algebraic solution of equations 22-27, above 'm' values of about 1.05 (table III), showed a gradual fall in the values of $-\log K_h$ and $-\log K_H$. This fact together with a sharp inflexion exhibited by the potentiometric curves 1-3 (Fig.6) indicated further hydrolysis of the binuclear chelate species followed by polymerization of a higher order. This conclusion is supported by the work of Feldman and Co-workers[10] who have reported the formation of a ternuclear chelate species in the uranyl-lactate system. Mathematical analysis of the potentiometric data, above 'm' values of about 1.05, could not be made due to a greater complexity in the system caused by the overlapping of the successive hydrolytic and polymerization reactions.

SECTION II

URANYL CHELATES OF LACTIC ACID

Although uranyl-lactate system has been studied earlier, a quantitative study of the equilibria involved in the system does not appear to be undertaken by the earlier workers. Feldman and co-workers[9,10] have studied the interaction of uranyl nitrate with lactic acid by spectrophotometric and potentiometric techniques and have indicated the formation of a 1:1 complex. At pH of about 5 the complex has been reported to be in a ternuclear form. More recently Lai and Wang[37] by using polarographic technique, have also shown the formation of a 1:1 complex. Crutchfield et al.[39] have studied the system at pH<3 by pH titrations and have determined the Bjerrum's[40] stepwise formation constants of the complexes by the Fronaeus graphical extrapolation method[41]. Three complexes having molar ratios 1:1, 1:2 and 1:3 of uranyl to lactic acid have been claimed by this study. Pande and Misra[42], by the potentiometric and conductometric titrations of uranyl acetate with KOH in the presence of one and two moles of lactic acid, have reported the formation of 1:1 and 1:2 complexes. In view of the above and the interesting results obtained by a mathematical analysis of the potentiometric data of uranyl-mandelate system, it was considered worthwhile to carry out a quantitative study of the equilibria involved in the interaction of uranyl ion with lactic acid.

RESULTS AND DISCUSSION

Potentiometric titrations of uranyl nitrate with KOH in the presence of lactic acid gave curves similar to those obtained for

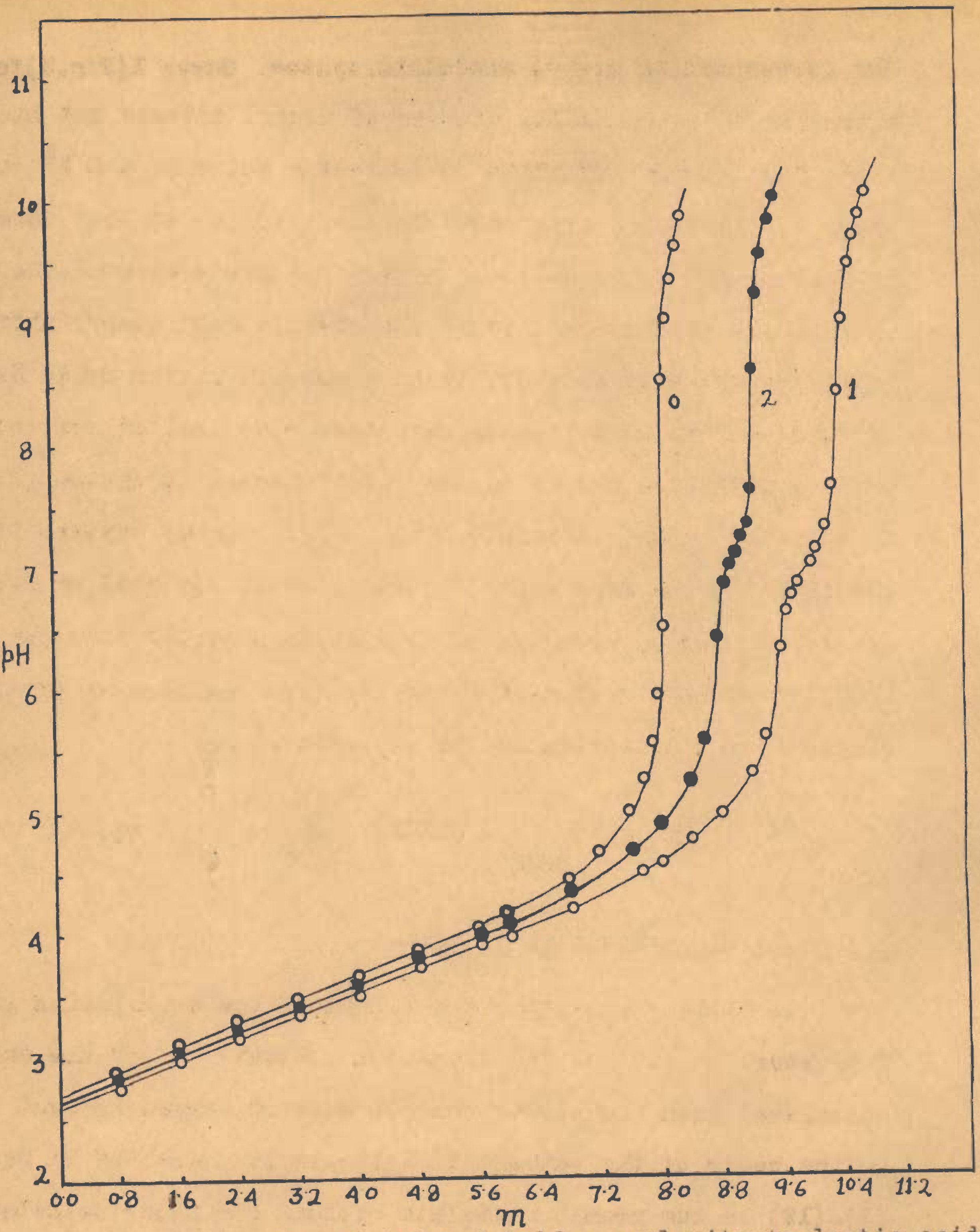


Fig.9. Titrations of 1:8 and 1:16 uranyl nitrate-lactic acid mixtures: Curve 1, 2.5×10^{-3}M in uranyl nitrate and 2×10^{-2}M in lactic acid; curve 2, 1.25×10^{-3}M in uranyl nitrate and 2×10^{-2}M in lactic acid. Curve 0 represents titration of lactic acid (2×10^{-2}M) alone with KOH. m=moles of KOH added per mole of metal ion; For curve 2, the actual 'm' values are twice of the 'm' values shown. In curve 0, inflexion point corresponds to one equivalent of alkali; ionic strength = 0.1M(KNO_3).

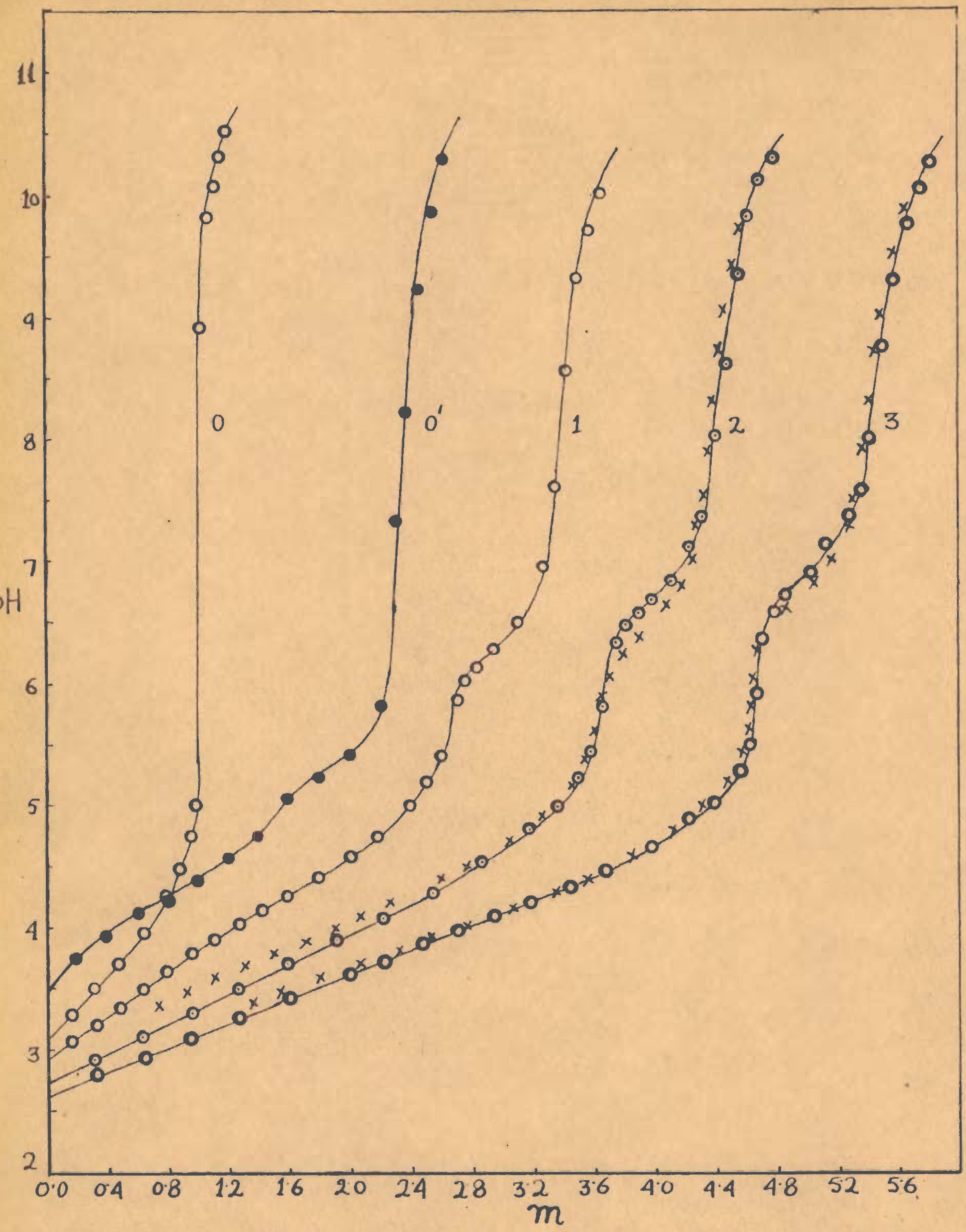
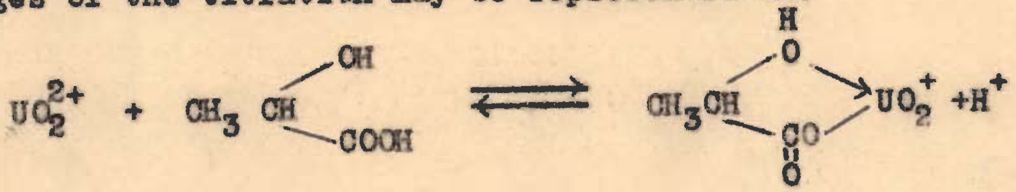


Fig.8. Potentiometric titrations of uranyl-lactate chelate system with KOH(0.1N): Curves 1,2 and 3 represent titrations of 1:1, 1:2 and 1:3 uranyl nitrate-lactic acid mixtures respectively (T_M=0.005M). Curves 0 and 0' represent titrations of lactic acid (0.005M) and uranyl nitrate (0.005M) respectively. m=moles of KOH added per mole of the metal ion; ionic strength = 0.1M(KNO_3). xxx Composite curves derived from curves 0 and 1 and 0 and 2 respectively.

the corresponding uranyl mandelate system. Curve 1(Fig.8)for the titration of an equimolar mixture of uranyl nitrate and lactic acid, for example, exhibits an inflexion point at $m = 2\frac{2}{3}$ (cf. curve 1, figure 1). This curve is also similar to that obtained by Feldman and co-workers[10]. In figure 9 are presented the potentiometric curves obtained by the titration of uranyl nitrate in the presence of a fairly large excess of lactic acid. Nature of these curves also closely resembles with that of the corresponding titration curves of the uranyl-mandelate system (Fig.2). In this case also, therefore, only a 1:1 complex appears to be formed under the experimental conditions as reported by Feldman and co-workers[10]. From the analogy of this system with the uranyl-mandelate system, the complexation reaction at the initial stages of the titration may be represented as:



(i)

Mathematical Analysis of the Data

In table V are given the values of the equilibrium constant K of reaction (i) and the formation constant k of the chelate calculated from the potentiometric data of curves 1,2 and 3 (Fig.10) on the basis of the mathematical treatment presented by equations (9)-(19) in the uranyl-mandelate system. For these calculations dissociation constant of the carboxylic hydrogen of lactic acid was determined from a plot of $-\log[H^+]$ against $\log \frac{[HA^-]}{[H_2A]}$ (Fig.11), obtained from the potentiometric data of curve 0(Fig.8). This plot gave a value of $-\log K_a$ equal to 3.74 which is identical with the value reported by Cannan and Kibrick[43].

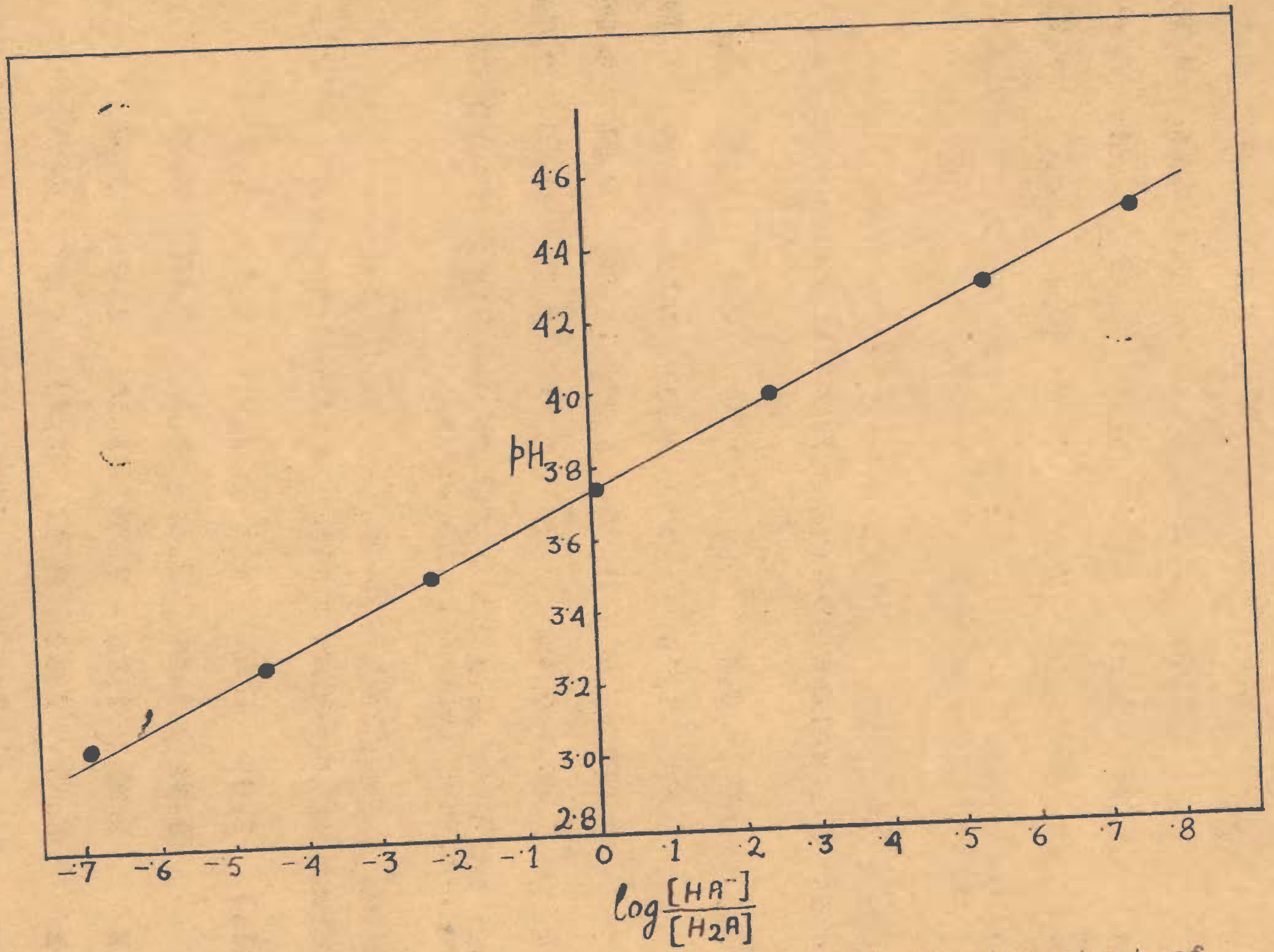


Fig.11. Graphical evaluation of the dissociation constant of lactic acid (H_2A). Ionic strength = 0.1M(KNO_3).

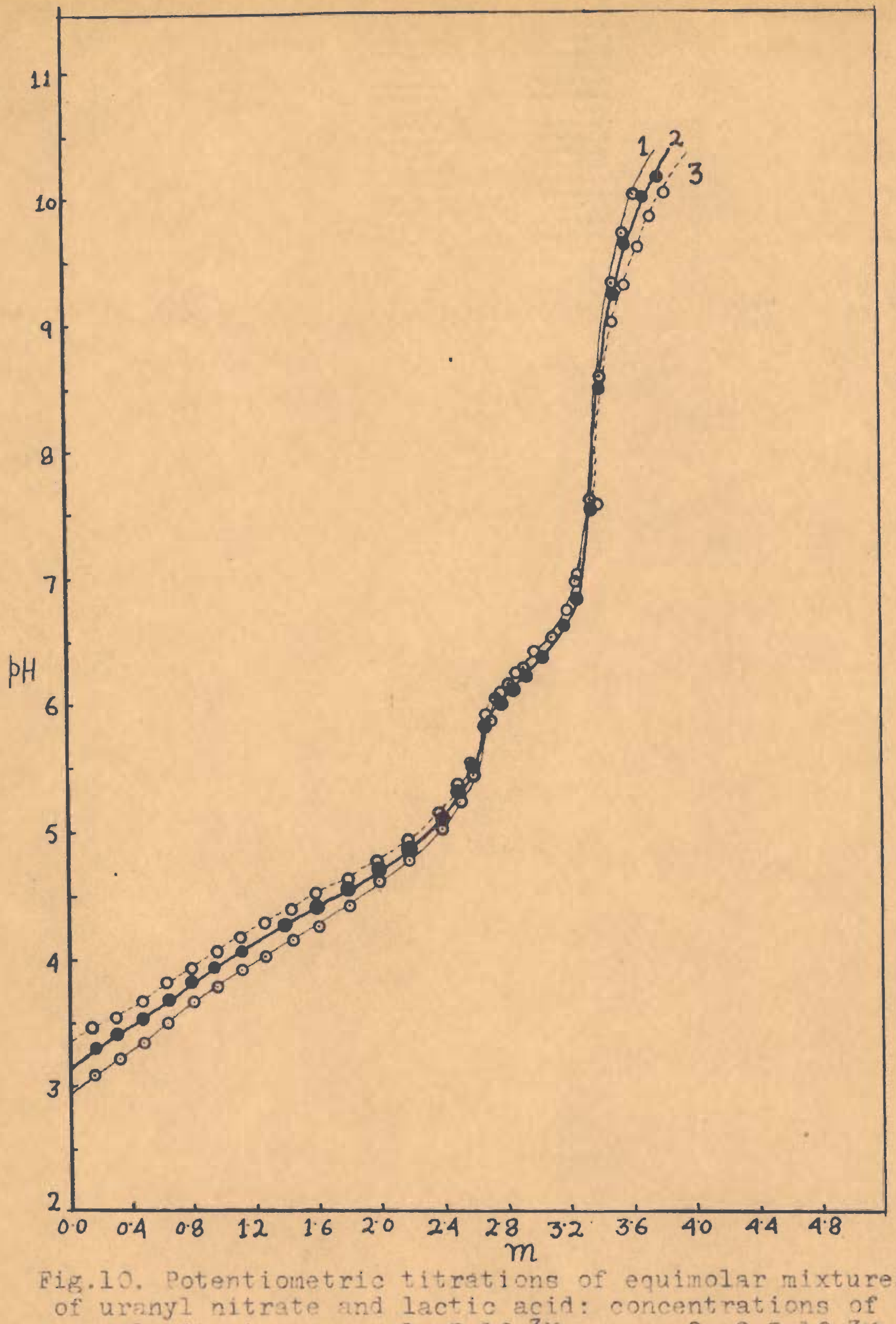


Fig.10. Potentiometric titrations of equimolar mixtures of uranyl nitrate and lactic acid: concentrations of uranyl nitrate: curve 1, 5x10-^{3}M; curve 2, 2.5x10-^{3}M; curve 3, 1.25x10-^{3}M. m=moles of KOH added per mole of the metal ion; ionic strength = 0.1M(KNO_3).

Table V

Curve 1 (Fig.10), $T_A = T_M = 5x10^{-3}M$
Volume of reaction mixture before titration = 50 ml.

KOH(ml.)	0.0	0.2	0.4	0.6	0.8	1.0	1.2
pH	2.90	2.98	3.07	3.15	3.21	3.28	3.35
-log K	1.28	1.26	1.27	1.26	(1.12	1.03	0.93)
log k	2.46	2.48	2.47	2.48	(2.62	2.71	2.81)

Average value of -log K = 1.27±0.01 and log k = 2.47±0.01
(   ) values not included in average.

Curve 2 (Fig.10), $T_A = T_M = 5x10^{-3}M$
Volume of reaction mixture before titration = 100 ml.

KOH(ml.)	0.0	0.2	0.4	0.6	0.8	1.0	1.2
pH	3.13	3.20	3.27	3.33	3.39	3.45	3.52
-log K	1.27	1.25	1.23	1.22	(1.06	0.94	0.80)
log k	2.47	2.49	2.51	2.52	(2.64	2.73	2.85)

Average value of -log K = 1.24±.03 and log k = 2.50±.02
(   )values not included in average.

Curve 3 (Fig.10), $T_A = T_M = 2.5x10^{-3}M$
Volume of reaction mixture before titration = 200ml.

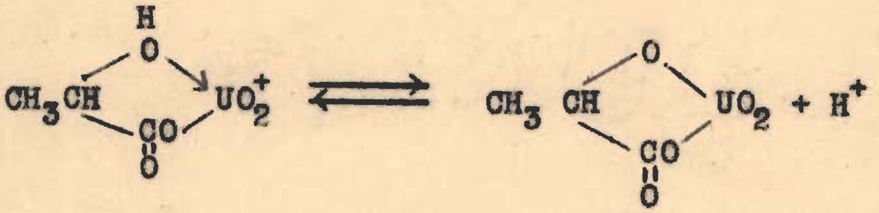
KOH(ml.)	0.0	0.2	0.4	0.6	0.8	1.0
pH	3.34	3.40	3.46	3.52	3.58	3.63
-log K	1.23	1.24	1.23	(1.18	1.12	0.95)
log k	2.51	2.50	2.51	(2.56	2.62	2.78)

Average value of -log K = 1.23±0.01 and log k = 2.50±0.01
(   ) values not included in average.

The relatively constant values of the equilibrium constant, independent of the concentration of the metal salt, obtained upto 'm' value of about 0.2 indicated that (i) is the main reaction which occurs in the system upto this stage of titration.

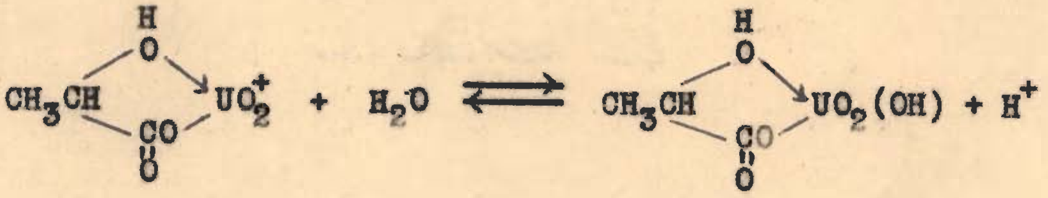
Hydrolysis and Polymerization of Uranyl Lactate Chelate

A gradual fall in the values of -log K observed in Table V (cf. Table II), calculated above 'm' values of about 0.2, indicated the occurrence of either of the reactions :



(ii)

or



(iii

Although it is difficult to distinguish between the above two alternative reactions, from the argument given in the uranyl mandelate system, here also formation of a monohydroxo chelate (reaction iii) appears to be more probable. The results of the determination of hydrolysis constants of the chelate, calculated on the basis of the mathematical treatment given by equations (20-27), are presented in Table VI.

Table VI

Curve 1 (Fig.10), $T_A = T_M = 5\times10^{-3}M$
Volume of initial reaction mixture = 50 ml.

KOH (ml.)	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0
pH	3.42	3.49	3.56	3.64	3.71	3.78	3.84	3.90	3.96
$-\log K_h$	3.93	3.91	3.91	3.93	3.92	3.93	3.89	(3.86	3.82)
$-\log K_H$	5.17	5.15	5.15	5.17	5.18	5.17	5.13	(5.10	5.06)

Average value of $-\log K_h = 3.91\pm0.02$ and $-\log K_H = 5.15\pm0.02$
(   ) Values not included in average.

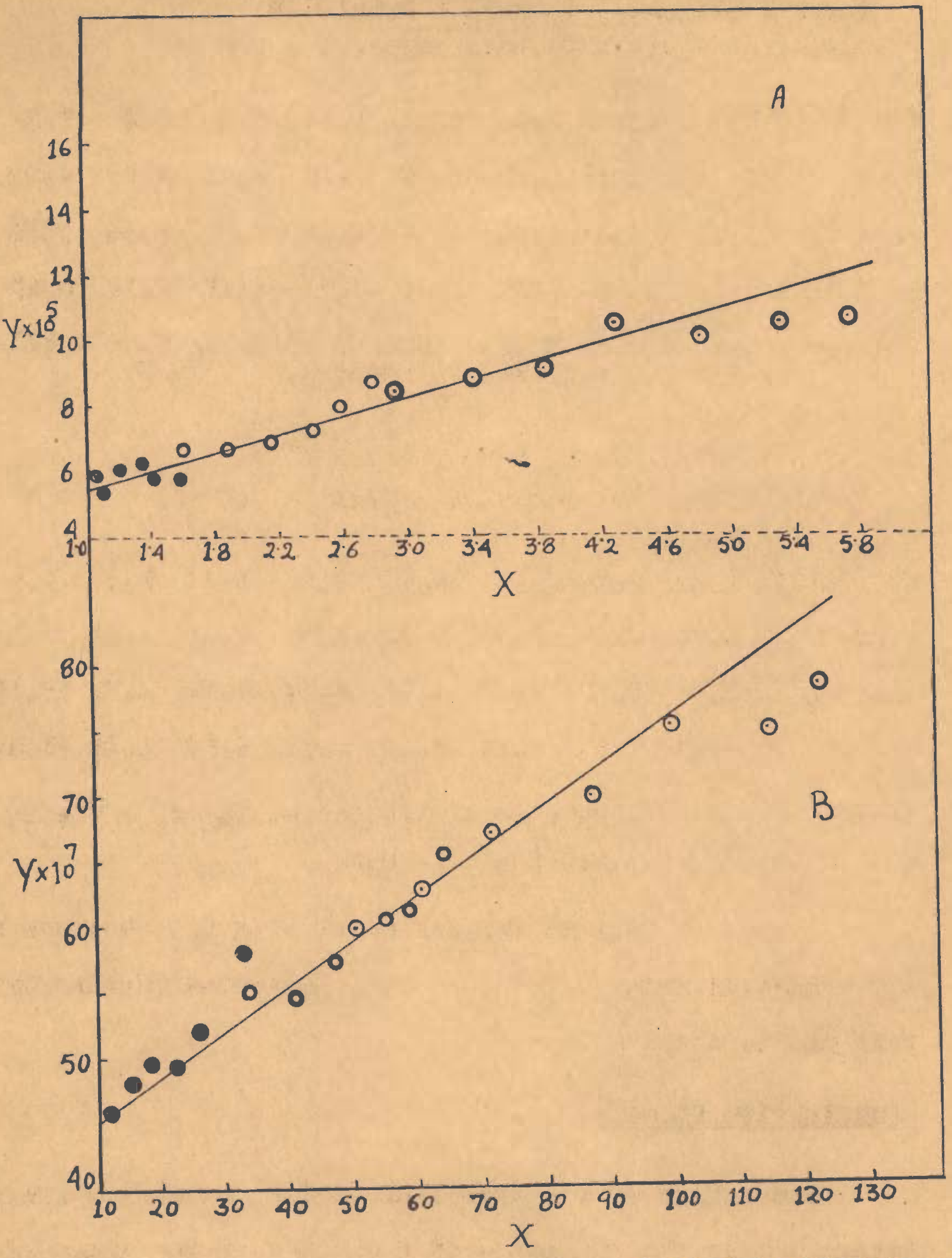


Fig.12. Graphical demonstration of dimerization of mono-hydroxo-uranyl lactate chelate:

Fig. 12 A, $X = \frac{[UO_2HA]}{[H^+]}$, $Y = \frac{[H^+]\{T_M - [UO_2] - 2[(UO_2OH)_2] - [UO_2HA]\}}{[UO_2HA]}$

B, $X = \frac{[UO_2][H_2A]}{[H^+]^2}$, $Y = \frac{[H^+]^2\{T_M - [UO_2] - 2[(UO_2OH)_2] - [UO_2HA]\}}{[UO_2][H_2A]}$

Concentrations : ⊙, 5×10^{-3}M ; ○, $2{\cdot}5\times10^{-3}$M ; ●, $1{\cdot}25\times10^{-3}$M .

Curve 2 (Fig.10), $T_A = T_M = 2.5x10^{-3}M$
Volume of initial reaction mixture = 100 ml.

KOH (ml.)	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0
pH	3.59	3.65	3.72	3.79	3.85	3.91	3.97	4.03	4.09
$-\log K_h$	3.99	4.01	4.02	4.03	4.03	3.98	(3.94	3.92	3.72)
$-\log K_H$	5.23	5.25	5.27	5.28	5.28	5.22	(5.18	5.15	4.90)

Average value of $-\log K_h = 4.01 \pm 0.03$ and $-\log K_H = 5.25 \pm 0.03$
(   ) values not included in average.

Curve 3 (Fig.10), $T_A = T_M = 1.25x10^{-3}M$
Volume of initial reaction mixture = 200 ml.

KOH (ml.)	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0
pH	3.76	3.83	3.89	3.96	4.01	4.06	4.12	4.17	4.23
$-\log K_h$	4.21	4.23	4.22	4.23	4.24	4.25	4.21	(4.10	3.99)
$-\log K_H$	5.43	5.47	5.46	5.47	5.48	5.50	5.43	(5.34	5.23)

Average value of $-\log K_h = 4.23 \pm 0.02$ and $-\log K_H = 5.47 \pm 0.03$
(   ) values not included in average.

A gradual fall in the values of $-\log K_h$, observed above 'm' values of about 1.0 (Table VI), indicated further hydrolysis of the chelate.

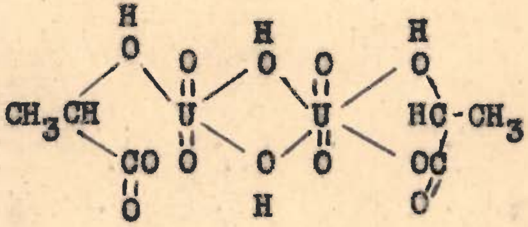
Dimerization Constant

The values of the hydrolysis and dimerization constants, determined in the 'm' range of 0.6-1.0 from the standard slope intercept relationship (equations 33 and 34, Fig.12), are presented in Table VII.

Table VII

From Figure 12A		From Figure 12B	
$-\log K_h$	4.26	$-\log K_H$	5.34
$-\log K_d$	5.13	$-\log K_D$	7.79

A probable structure of the binuclear chelate species may be given as :



Like uranyl mandelate system, here also, no attempt was made to analyse the potentiometric data above 'm' values of about 1.0 due to a greater complexity in the system caused by overlapping of the successive hydrolytic and polymerization reactions.

SECTION III

URANYL CHELATES OF MALONIC ACID

A study of the complexes of uranium (VI) with carboxylic acids has long been a subject of research. Tishkoff[44] and Ahrland[45] have made an extensive study of the uranyl-acetate system and have shown the formation of species of the type $UO_2(OAc)_n^{2-n}$. The values of n have been reported to be 1 to 3 by these workers. Recently, Banerjee and Singh[46] have studied the system by potentiometric measurements and have obtained evidence for the formation of the species upto $UO_2(OAc)_4^{-2}$. Oxalic acid has been reported[47,48] to form a variety of complexes with uranyl ion. After a comprehensive study of a large number of carboxylate complexes of uranium (VI), it has been concluded[49] that the anions of dicarboxylic acids generally have a stronger tendency for complex formation with uranyl ion than does acetate ion. This has been observed even when the acid dissociation constants of the dibasic acid are same as for acetic acid; this is probably due to the effect of chelation in the case of dicarboxylic acids.

Malonic acid, although is a well known ligand and forms complexes with a large number of metals viz., copper [50-53], cadmium[54-56], beryllium[57], aluminium[58], lanthanum[59], iron[60], thorium[61] and vanadium[62-63], has, however, received little attention for complex formation with uranyl ion. Feldman and co-workers[10] have studied absorption spectra of uranyl-malonic

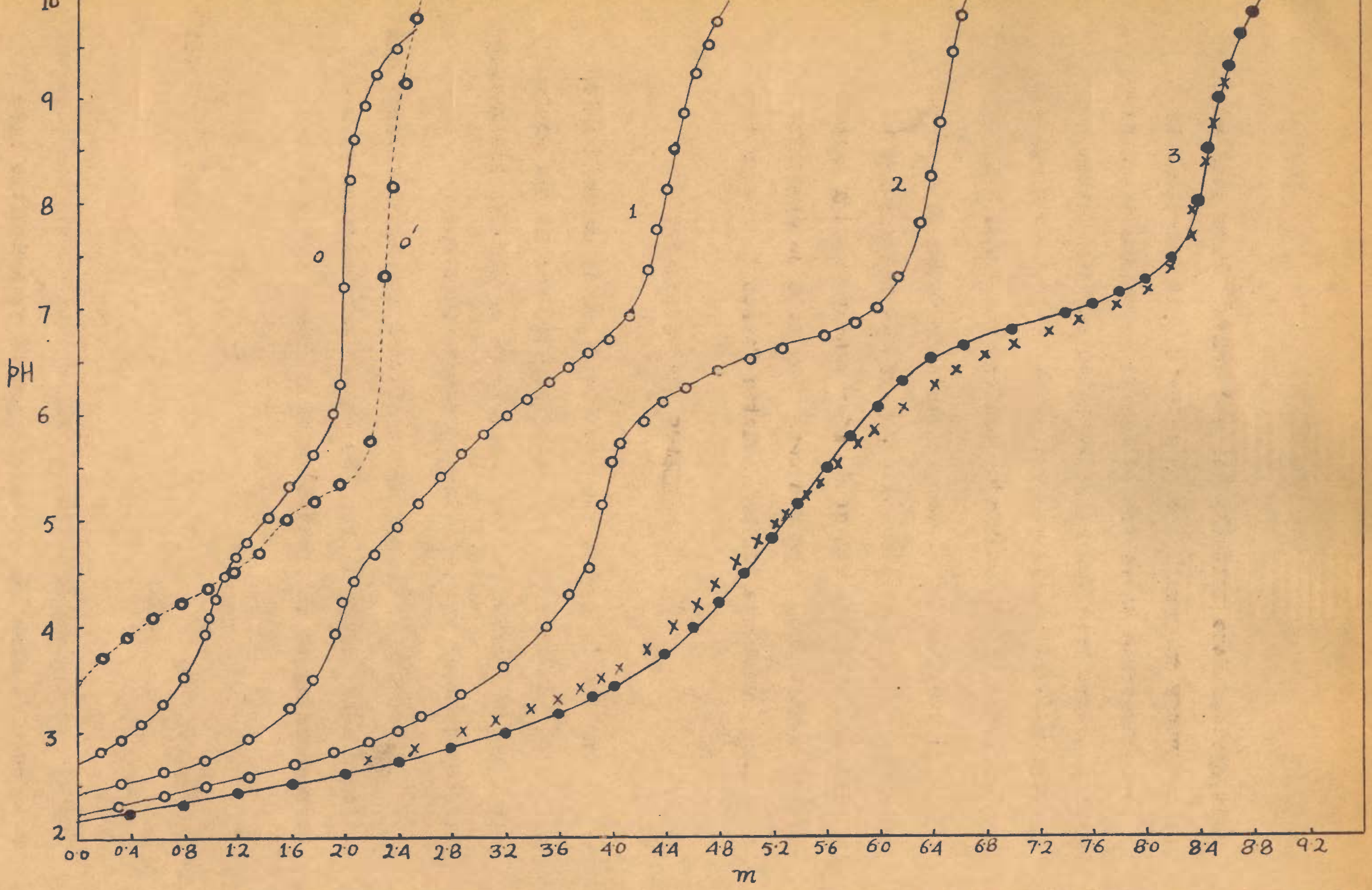


Fig.13. Potentiometric titrations of uranyl-malonate system with KOH(0.1M): curves 1,2 and 3 represent titrations of 1:1, 1:2 and 1:3 uranyl nitrate-malonic acid mixtures respectively (T_M=0.005M). Curves 0 and 0' represent titrations of malonic acid (0.005M) and uranyl nitrate (0.005M) respectively. m=moles of KOH added per mole of the metal ion. Ionic strength = 0.1M(KNO_3).xxx, composite curve derived from curves 0 and 2.

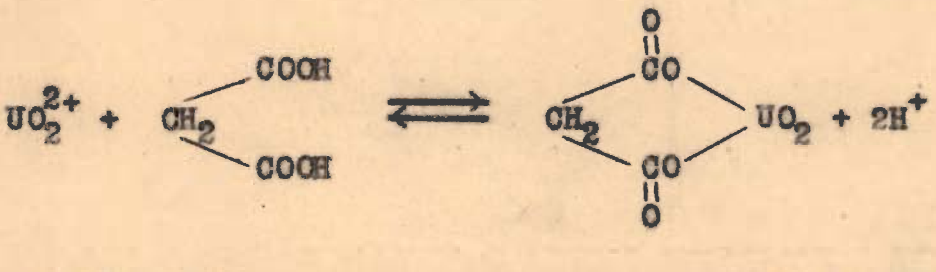
acid system. More recently Lai and Hsieh[64] have studied polarography of uranyl ion in malonic acid solution. By a conductometric titration of uranyl perchlorate solution with a sodium hydrogen malonate solution, the latter workers have indicated the formation of two complexes having metal to ligand combining ratios of 1:1 and 1:2.

In view of the above, it was considered of interest to carry out a quantitative study of the interaction of uranyl ion with malonic acid under widely varying experimental conditions. Attempts were also made to determine stability constants of the chelates formed in the system.

RESULTS AND DISCUSSION

Curve 0 (Fig.13), for the titration of malonic acid with KOH, exhibits two inflexion points, one at one equivalent and the other at two equivalents of alkali, indicating dissociation of the acid in two separated steps.

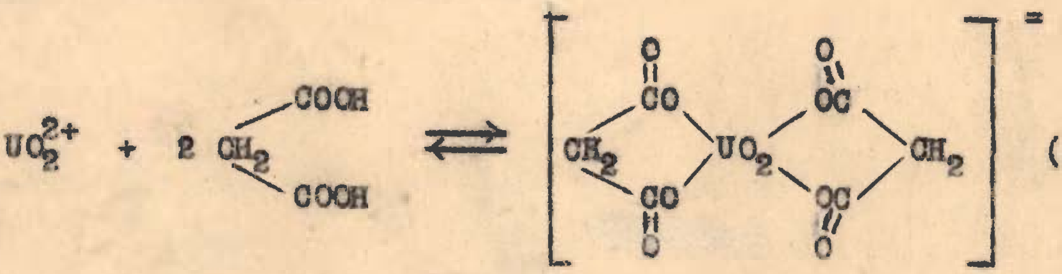
Titration of an equimolar mixture of uranyl nitrate and malonic acid (curve 1, Fig.13) showed an inflexion at m = 2, corresponding to the formation of a normal 1:1 chelate:



(1)

Beyond the inflexion point, a yellow precipitate was observed near pH of 5 when the chelate appeared to hydrolyze into uranium hydroxide and free ligand anions.

The first inflexion point in curve 2 (Fig.13), for the titration of uranyl nitrate with KOH in the presence of two moles of malonic acid, approaches at about $m = 4$. This corresponds to the formation of a 1:2 complex in accordance with the reaction :



(ii)

As in the case of 1:1 chelate, this complex also appears to hydrolyze beyond the inflexion point (near pH 6), when a yellow precipitate of uranium hydroxide begins to separate out from the solution.

Curve 3 (Fig.13), for the titration of a 1:3 mixture of uranyl nitrate and malonic acid, shows a sloping inflexion between $m = 5$ and 6 and does not give any indication for the combination of the 1:2 complex with another mole of the ligand. In order to verify this conclusion, a calculated composite curve (shown in figure 13 by crosses) was obtained by the addition of the abscissae of the separate potentiometric curves for the titration of malonic acid (curve 0) and the 1:2 uranyl nitrate-malonic acid chelate system (curve 2). This calculated curve was found to be similar in nature to the experimental curve 3 and thus indicated that a 1:3 complex is not formed in significant amount under the experimental conditions. The above conclusions are supported by a polarographic and conductometric study of the system reported recently by Lai and Hsieh[64].

Stability Constants of the Chelates.

For the determination of formation constants of the chelates, the dissociation constants of malonic acid, Ka_1 and Ka_2, were determined from the potentiometric data of curve 0 (Fig.13) for the titration of the acid with KOH in aqueous medium, 0.1M in potassium nitrate. The values of pKa_1 and pKa_2 were found to be 3.08 and 5.14 respectively.

If K_1 represents equilibrium constant of the reaction:

$$UO_2^{2+} + H_2A \rightleftharpoons UO_2A + 2H^+$$

(where H_2A represents malonic acid)

we have,

$$K_1 = \frac{[UO_2A]\,[H^+]^2}{[UO_2^{2+}]\,[H_2A]} \qquad (35)$$

Formation constant, k_1, of the 1:1 chelate may be defined as:

$$k_1 = \frac{[UO_2A]}{[UO_2^{2+}]\,[A^{2-}]} \qquad (36)$$

Dissociation constants of malonic acid may be expressed as:

$$Ka_1 = \frac{[HA^-]\,[H^+]}{[H_2A]} \qquad (37)$$

and

$$Ka_2 = \frac{[A^{2-}]\ [H^+]}{[HA^-]} \tag{38}$$

If, in an equimolar mixture of uranyl nitrate and malonic acid and in the initial stages of the titration of a 1:2 mixture of uranyl nitrate and the ligand, concentration of the 1:2 complex in solution be assumed to be negligibly small, from the usual material balance we have:

$$T_M = [UO_2^{2+}] + [UO_2A] \tag{39}$$

$$T_{OH} + [H^+] = [HA^-] + 2[A^{2-}] + 2\ [UO_2A] \tag{40}$$

and $$T_A = [H_2A] + [HA^-] + [UO_2A] + [A^{2-}] \tag{41}$$

In solutions of pH upto about 3, concentrations of the hydrolyzed species of the uranyl ion were negligible as compared to those of the other species present in the equilibrium mixture.

Combination of equations (37), (38), (40) and (41) gives

$$[A^{2-}] = \frac{2T_A - T_{OH} - [H^+]}{\frac{[H^+]}{Ka_2} + \frac{2[H^+]^2}{Ka_1\ Ka_2}} \tag{42}$$

Again, combination of (37)-(39) and (41) yields

$$[UO_2^{2+}] = [A^{2-}] \left\{ 1 + \frac{[H^+]}{Ka_2} + \frac{[H^+]^2}{Ka_1\ Ka_2} \right] - (T_A - T_M) \tag{43}$$

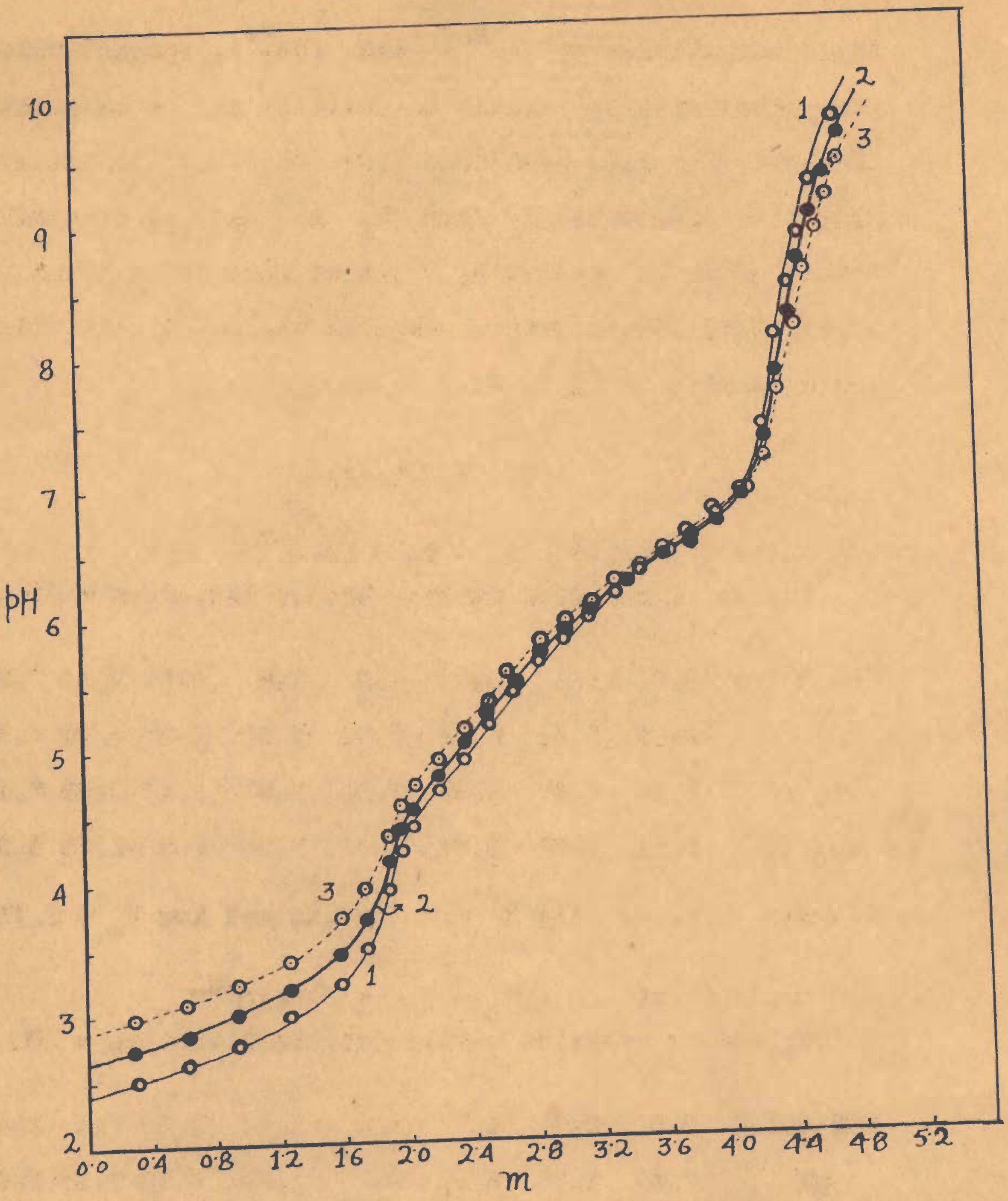


Fig.14. Potentiometric titrations of equimolar mixtures of uranyl nitrate and malonic acid. Concentrations: curve 1, 5×10^{-3}M; curve 2, 2.5×10^{-3}M; curve 3, 1.25×10^{-3}M. m=moles of KOH added per mole of the metal ion.

After computation of $[A^{2-}]$ and $[UO_2^{2+}]$, concentration of the other species present in solution may be calculated algebraically from equations (39)-(41). Equilibrium and formation constants K_1 and k_1 may then be determined. Values of these constants, obtained upto pH of about 3 over a four-fold concentration range of the metal salt (Fig.14) are presented in table VIII.

Table VIII

Curve 1 (Fig.14), $T_A = T_M = 5 \times 10^{-3}$M
Volume of reaction mixture before titration = 50 ml.

KOH (ml.)	0.0	0.4	0.8	1.2	1.6	2.0	2.4	2.8	3.2
pH	2.39	2.44	2.49	2.54	2.60	2.67	2.75	2.83	2.94
$-\log K_1$	2.48	2.47	2.45	2.46	2.41	2.42	2.43	2.41	2.43
$\log k_1$	5.74	5.75	5.77	5.76	5.80	5.80	5.79	5.80	5.79

Average value of $-\log K_1 = 2.44 \pm 0.04$ and $\log k_1 = 5.77 \pm 0.03$

Curve 2 (Fig.14), $T_A = T_M = 2.5 \times 10^{-3}$M
Volume of reaction mixture before titration = 100 ml.

KOH (ml.)	0.0	0.4	0.8	1.2	1.6	2.0	2.4	2.8
pH	2.62	2.66	2.71	2.77	2.83	2.90	2.97	3.05
$-\log K_1$	2.46	2.42	2.43	2.45	2.46	2.47	2.46	2.44
$\log k_1$	5.76	5.79	5.79	5.76	5.76	5.74	5.76	5.78

Average value of $-\log K_1 = 2.45 \pm 0.02$ and $\log k_1 = 5.77 \pm 0.02$

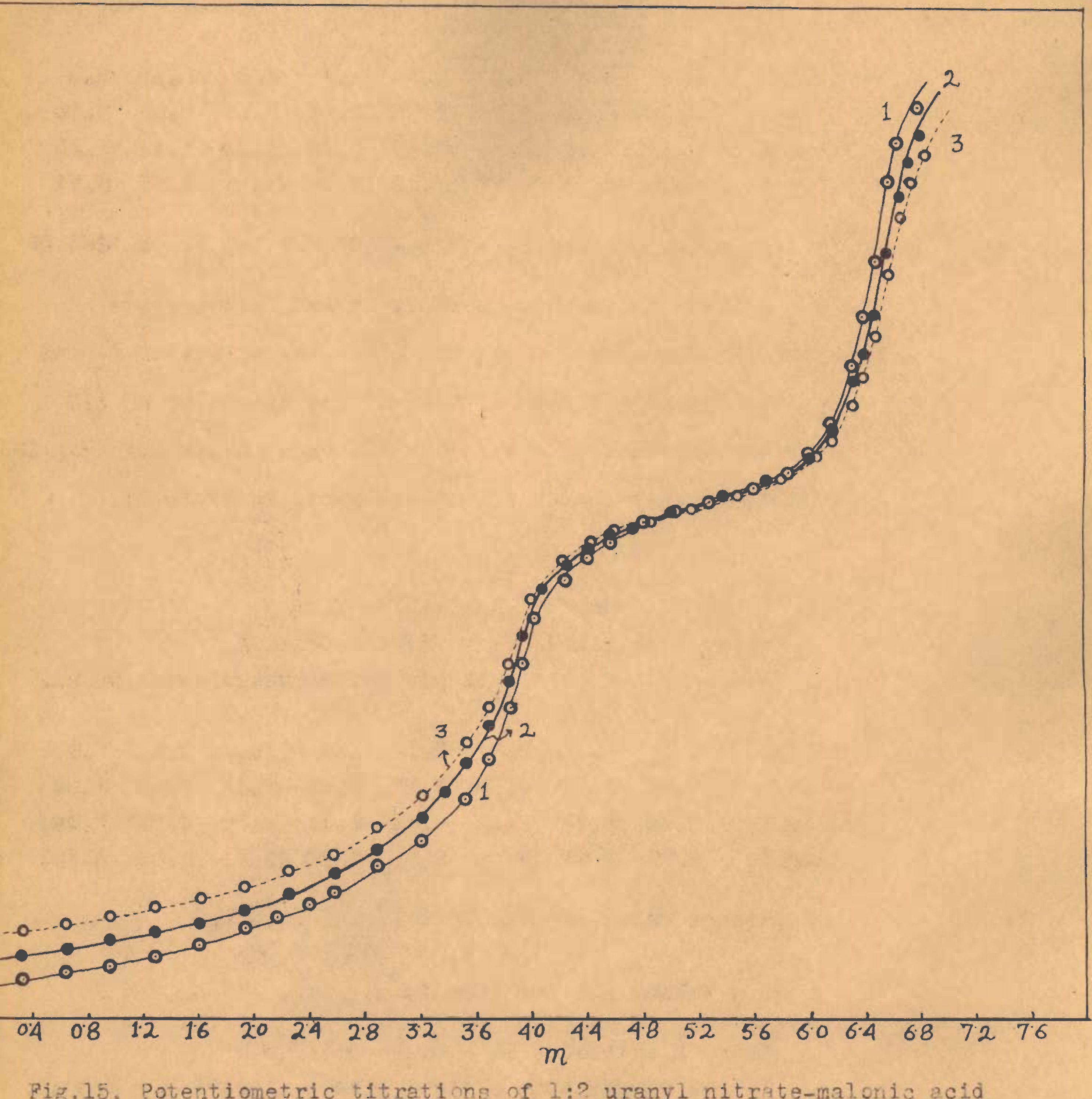


Fig.15. Potentiometric titrations of 1:2 uranyl nitrate-malonic acid mixtures. Concentrations of uranyl nitrate: curve 1, $5x10^{-3}M$; curve 2, $2.5x10^{-3}M$; curve 3, $1.25x10^{-3}M$. m=moles of KOH added per mole of the metal ion.

Curve 3 (Fig.14), $T_A = T_M = 1.25x10^{-3}M$
Volume of reaction mixture before titration = 200 ml.

KOH(ml.)	0.0	0.4	0.8	1.2	1.6	2.0	2.4	2.8
pH	2.86	2.90	2.95	3.00	3.06	3.12	3.20	3.28
$-\log K_1$	2.45	2.42	2.44	2.43	2.45	2.44	2.45	2.43
$\log k_1$	5.77	5.79	5.78	5.79	5.77	5.78	5.77	5.79

Average value of $-\log K_1 = 2.44 \pm 0.02$ and $\log k_1 = 5.78 \pm 0.02$

From the mathematical treatment, given above, attempts were also made to calculate the values of K_1 and k_1 from the potentiometric data of the titration of 1:2 reaction mixtures of uranyl nitrate and malonic acid(Fig.15). Results of these calculations are given in table IX.

Table IX

Curve 1 (Fig.15), $T_A = 2TM = 1.0x10^{-2}M$
Volume of reaction mixture before titration = 50 ml.

KOH(ml.)	0.0	0.4	0.8	1.2	1.6	2.0	2.4	2.8
pH	2.26	2.30	2.34	2.37	2.41	2.45	2.49	2.54
$-\log K_1$	2.44	2.45	2.46	2.41	2.41	(2.38	2.34	2.29)
$\log k_1$	5.78	5.77	5.76	5.80	5.80	(5.83	5.85	5.90)

Average value of $-\log K_1 = 2.43 \pm 0.03$ and
$\log k_1 = 5.78 \pm 0.02$
( ) values not included in average.

Curve 2 (Fig.15), $T_A = 2T_M = 5x10^{-2}M$
Volume of reaction mixture before titration = 100 ml.

KOH(ml.)	0.0	0.4	0.8	1.2	1.6	2.0	2.4	2.8
pH	2.49	2.52	2.56	2.59	2.62	2.65	2.69	2.73
$-\log K_1$	2.49	2.47	2.48	2.45	2.41	(2.35	2.33	2.31)
$\log k_1$	5.73	5.75	5.74	5.77	5.80	(5.87	5.89	5.91)

Average value of $-\log K_1 = 2.45 \pm 0.04$ and $\log k_1 = 5.77 \pm 0.04$
( ) values not included in average.

Curve 3 (Fig.15), $T_A = 2T_M = 2.5\times10^{-3}$M
Volume of reaction mixture before titration = 200 ml.

KOH(ml.)	0.0	0.4	0.8	1.2	1.6	2.0	2.4	2.8
pH	2.72	2.75	2.78	2.81	2.84	2.86	2.90	2.94
$-\log K_1$	2.48	2.48	2.47	2.46	2.43	(2.38	2.36	2.35)
$\log k_1$	5.74	5.74	5.75	5.76	5.79	(5.84	5.86	5.87)

Average value of $-\log K_1 = 2.46\pm0.02$ and $\log k_1 = 5.76\pm0.02$
( ) values not included in average.

The relatively constant values of $\log k_1$, obtained upto 'm' equal to about 0.6 (table IX), which are in close agreement with those presented in table VIII, indicated that upto this stage of titration ($m \sim 0.6$) only the 1:1 complex is formed in the reaction mixture containing two moles of malonic acid per mole of the metal ion.

Stability of 1:2 Chelate

In view of the conclusions arrived at from potentiometric data of the curves (Fig.15) obtained by the titration of uranyl nitrate with KOH in the presence of different concentrations of malonic acid, a gradual increase in the values of $\log k_1$ observed in table IX, calculated above 'm' values of about 0.6, may be taken as an indication for the commencement of the formation of a 1:2 complex in accordance with the reaction:

$$UO_2A + H_2A \rightleftharpoons UO_2A_2^{2-} + 2H^+$$

If K_2 represents equilibrium constant of the above reaction, we have

$$K_2 = \frac{[UO_2A_2^{2-}][H^+]^2}{[UO_2A][H_2A]} \qquad (44)$$

Formation constant, k_2, of the chelate may be defined as:

$$k_2 = \frac{[UO_2A_2^{2-}]}{[UO_2A][A^{2-}]} \qquad (45)$$

The overall stability constant of the 1:2 complex or equilibrium constant of the overall reaction :

$$UO_2^{2+} + 2A^{2-} \rightleftharpoons UO_2A_2^{2-}$$

may be expressed as :

$$K = \frac{[UO_2A_2^{2-}]}{[UO_2^{2+}][A^{2-}]^2} \qquad (46)$$

Other pertinent equations are:

$$T_M = [UO_2^{2+}] + [UO_2A] + [UO_2A_2^{2-}] \qquad (47)$$

$$T_{OH} + [H^+] = [HA^-] + 2[A^{2-}] + 2[UO_2A] + 4[UO_2A_2^{2-}] \qquad (48)$$

and $$T_A = [H_2A] + [HA^-] + [A^{2-}] + [UO_2A] + 2[UO_2A_2^{2-}] \qquad (49)$$

In a system having two moles of malonic acid per mole of uranyl nitrate (Fig.13 and 15), since $T_A = 2T_M$, combination of equations (36-38), 47 and 49 gives,

$$\left[UO_2^{2+}\right] = \frac{\left[A^{2-}\right]\left\{1 + \frac{\left[H^+\right]}{Ka_2} + \frac{\left[H^+\right]^2}{Ka_1\ Ka_2}\right\}}{2 + k_1\left[A^{2-}\right]} \qquad (50)$$

Thus, knowing k_1 (from tables VIII and IX), $\left[A^{2-}\right]$ (from expression 42) and the dissociation constants of malonic acid, $\left[UO_2^{2+}\right]$ may be calculated. Concentrations of the other species, present in solution, may then be determined algebraically from equations (47)-(49). Values of the equilibrium constants, calculated from the potentiometric data of figure 15 are presented in table X.

Table X

Curve 1 (Fig.15), $T_A = 2T_M = 1x10^{-2}M$
Volume of reaction mixture before titration = 50 ml.

KOH (ml.)	2.0	2.4	2.8	3.2	3.6	4.0	4.4	4.8	5.6
pH	2.45	2.49	2.54	2.58	2.63	2.69	2.75	2.80	2.94
$-\log K_2$	3.99	3.90	4.00	4.00	4.00	3.96	3.99	3.91	3.98
$\log k_2$	4.21	4.30	4.20	4.20	4.20	4.26	4.21	4.29	4.24

Average value of $-\log K_2 = 3.95 \pm 0.05$ and $\log k_2 = 4.25 \pm 0.05$

Curve 2 (Fig.15), $T_A = 2T_M = 5x10^{-3}M$
Volume of reaction mixture before titration = 100 ml.

KOH (ml.)	2.0	2.4	2.8	3.2	3.6	4.0	4.4	4.8	5.2
pH	2.65	2.69	2.73	2.77	2.82	2.86	2.91	2.97	3.03
$-\log K_2$	3.94	3.96	3.93	3.88	3.94	3.86	3.89	3.88	3.93
$\log k_2$	4.28	4.26	4.28	4.34	4.28	4.35	4.32	4.33	4.28

Average value of $-\log K_2 = 3.91 \pm 0.05$ and $\log k_2 = 4.30 \pm 0.05$

Curve 3 (Fig.15), $T_A = 2T_M = 2.5 \times 10^{-2} M$

Volume of reaction mixture before titration = 200 ml.

KOH(ml.)	2.0	2.4	2.8	3.2	3.6	4.0	4.4	4.8
pH	2.86	2.90	2.94	2.98	3.02	3.06	3.11	3.16
$-\log K_2$	3.98	3.98	4.00	4.00	3.95	3.88	3.99	3.98
$\log k_2$	4.24	4.24	4.20	4.20	4.27	4.34	4.21	4.24

Average value of $-\log K_2 = 3.95 \pm 0.05$ and
$\log k_2 = 4.25 \pm 0.05$

It is evident from the above table that stability constant of the 1:2 complex is almost independent of concentration indicating that the metal chelate does not polymerize under the experimental conditions.

In order to confirm the above conclusions, attempts were also made to determine the formation constants of the chelates by Bjerrum's method[40]. $\bar{n}$, the average number of donor groups bound per metal ion, may be given by the expression:

$$\bar{n} = \frac{T_A - [A^{2-}]\left\{1 + \frac{[H^+]}{Ka_2} + \frac{[H^+]^2}{Ka_1\ Ka_2}\right\}}{T_M} \tag{51}$$

After calculating $[A^{2-}]$ from (42), the evaluation of $\bar{n}$ may, therefore, be made from equation (51). Thus, a set of values of $\bar{n}$ and $[A^{2-}]$ was obtained (table XI) from the potentiometric data of each of the curves presented in figure 15.

Table XI

Curve 1 (Fig.15), $T_A = 2T_M = 1x10^{-2}M$

KOH(ml)	pH	$-\log[A^{2-}]$	$\bar{n}$	KOH(ml.)	pH	$-\log[A^{2-}]$	$\bar{n}$
0.0	2.26	5.87	0.45	4.0	2.69	5.26	0.85
0.4	2.30	5.80	0.48	4.8	2.80	5.12	0.95
0.8	2.34	5.74	0.51	5.4	2.90	5.00	1.02
1.2	2.37	5.70	0.56	6.0	3.02	4.84	1.09
1.6	2.41	5.65	0.60	7.2	3.34	4.47	1.25
2.0	2.45	5.59	0.64	8.0	3.58	4.27	1.39
2.4	2.49	5.54	0.68	8.4	3.77	4.11	1.47
2.8	2.54	5.47	0.73	8.8	3.98	3.97	1.56
3.2	2.58	5.41	0.77	9.2	4.30	3.78	1.67
3.6	2.63	5.35	0.82	9.8	5.16	3.50	1.85

Curve 2 (Fig.15), $T_A = 2T_M = 5x10^{-3}M$

0.0	2.49	5.74	0.47	4.0	2.86	5.27	0.87
0.4	2.52	5.70	0.51	4.8	2.97	5.13	0.95
0.8	2.56	5.66	0.55	5.6	3.10	4.97	1.04
1.2	2.59	5.62	0.59	6.4	3.28	4.76	1.11
1.6	2.62	5.58	0.63	7.2	3.50	4.50	1.22
2.0	2.65	5.54	0.68	8.0	3.78	4.27	1.36
2.4	2.69	5.49	0.71	8.4	4.02	4.11	1.45
2.8	2.73	5.44	0.75	8.8	4.27	3.94	1.56
3.2	2.77	5.38	0.79	9.2	4.60	3.74	1.66
3.6	2.82	5.31	0.82	9.8	5.40	3.53	1.80

Curve 3 (Fig.15), $T_A = 2T_M = 2.5x10^{-3}M$

0.0	2.72	5.68	0.54	4.0	3.06	5.25	0.88
0.4	2.75	5.63	0.56	4.8	3.16	5.14	0.95
0.8	2.78	5.59	0.59	5.6	3.30	4.97	0.99
1.2	2.81	5.56	0.62	6.0	3.38	4.88	1.05
1.6	2.84	5.52	0.66	7.2	3.69	4.57	1.19
2.0	2.86	5.50	0.71	8.0	4.00	4.31	1.33
2.4	2.90	5.45	0.74	8.8	4.45	4.04	1.49
2.8	2.94	5.39	0.76	9.2	4.76	3.82	1.50
3.2	2.98	5.34	0.79	9.6	5.14	3.73	1.61
3.6	3.02	5.30	0.84	9.8	5.39	3.68	1.80

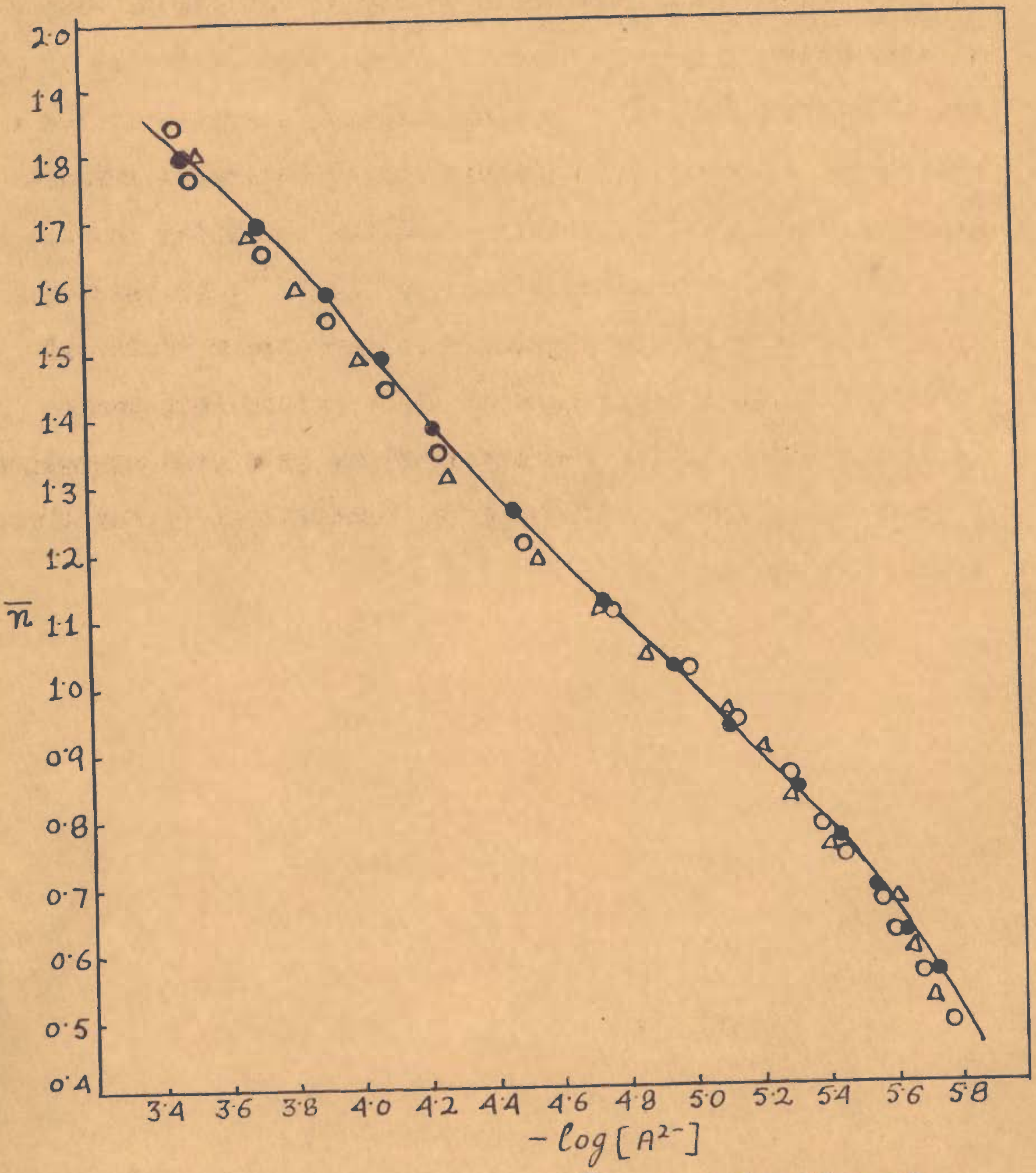


Fig.17. Degree of formation, $\bar{n}$, as a function of $-\log$[ligand]: ooo and ΔΔΔ experimental curves obtained from potentiometric data of curves 2 and 3 (Fig.15); ●●●, calculated curve.

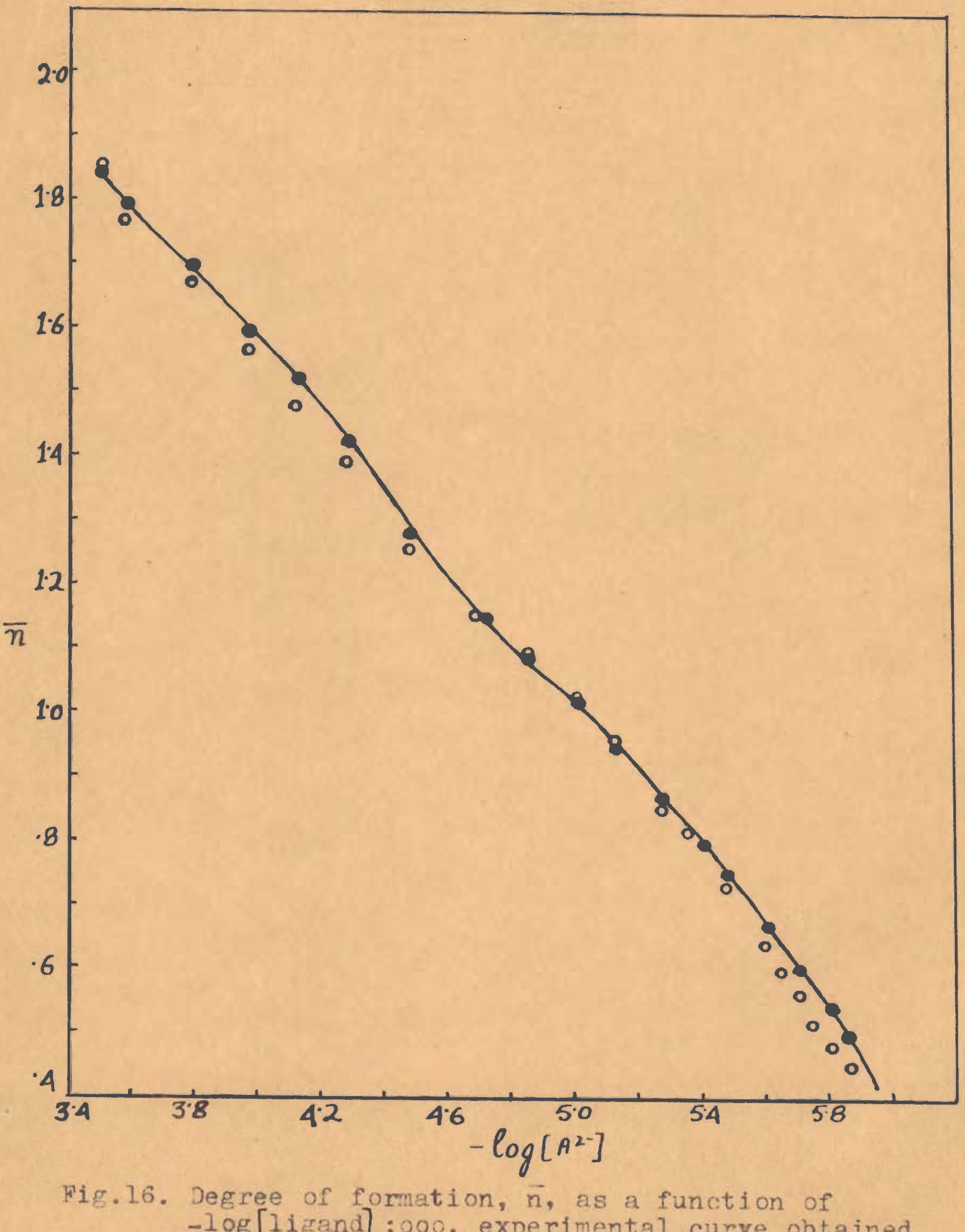


Fig.16. Degree of formation, $\bar{n}$, as a function of -log[ligand] :ooo, experimental curve obtained from potentiometric data of curve 1(Fig.15); ●●●, calculated curve.

The values of $\bar{n}$ were plotted against $-\log[A^{2-}]$ (Fig.16 and 17). As a first approximation, the values of $-\log[A^{2-}]$ at $\bar{n} = 0.5$ and 1.5 are equal to $\log k_1$ and $\log k_2$ respectively. These temporary constants were then corrected by the method of successive approximations[65]. A plot of the calculated values of $\bar{n}$ (determined by using the average value of the stability constant and the spreading factor) against the corresponding values of $-\log[A^{2-}]$ is presented by a solid line in the figure. This gave $\log k_1 = 5.84$ and $\log k_2 = 4.15$. A comparison of these values from those given in tables VIII-X shows that there is a good agreement between them, thus, confirming the conclusions of the algebraic method.

CHAPTER II

EXPERIMENTAL

General Description.

(i) Uranyl chelates of Mandelic acid.
(ii) Uranyl chelates of Lactic acid.
(iii) Uranyl chelates of Malonic acid.

PART - II

CHAPTER - II

EXPERIMENTAL

GENERAL DESCRIPTION:

MATERIALS :

Uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, was of B.D.H. analytical reagent quality.

Mandelic and malonic acids were B.D.H.(L.R.) products and were purified by recrystallization (Melting points 118.6 and 136°C respectively). Lactic acid (A.R.) was a B.D.H. product.

Catechol was a G.R. sample of E. Merck. 1-hydroxy-2-naphthoic and 2-hydroxy-3-naphthoic acids and 1-hydroxy-2-naphthaldehyde (B.D.H) were purified by repeated crystallization from alcohol until their melting points rose to 186, 222 and 60 °C respectively. Salicylic and 5-sulphosalicylic acids were of B.D.H. reagent grade quality.

Stock solutions of uranyl nitrate were standardized gravimetrically by precipitation with 8-hydroxy quinoline[66] and subsequent ignition to U_3O_8. Because of the possibility of photochemical reduction of the uranyl ion[67], uranyl nitrate solutions were stored in a dark place and were frequently tested for the presence of uranous ion by titration with dichromate solutions.

Standardization of the aqueous solutions of the ligands was effected by means of potentiometric titrations with standard potassium hydroxide solution. The solution of KOH was standardized against primary standard potassium hydrogen phthalate.

ANALYTICAL METHODS

The precipitated compounds, after being washed and dried, were analyzed as given below:

METAL:

The metal content of the compounds was, in general, determined by direct ignition to U_3O_8. It was also determined by the precipitation method, i.e., the compound was decomposed with aqua-regia, the metal precipitated as its oxinate with oxine, washed with distilled water and then weighed either as such or after ignition to U_3O_8.

MANDELIC ACID

The mandelic acid was estimated by oxidation with ceric sulphate[68]. A known weight of the compound was dissolved in dilute sulphuric acid and made up to 100 ml. in water. An aliquot of this solution was boiled for twenty minutes with an excess of $\frac{N}{10}$ ceric sulphate solution. In a separate conical flask, the same volume of ceric sulphate was boiled under identical conditions to serve as a blank. The solutions were cooled and the excess of ceric sulphate titrated against a standard ferrous ammonium sulphate solution (0.1N) using N-phenyl anthralinic acid as indicator. Mandelic acid was calculated on the basis of the reaction:

$$C_6H_5CH(OHCOOH) \xrightarrow{O} C_6H_5CHO + CO_2 + H_2O$$

LACTIC ACID

Lactic acid content of the compounds was determined by oxidation with an excess of acid permanganate solution, a method reported by Ernst and Horvath[69].

CATECHOL

The catechol was estimated by oxidation with alkaline potassium permanganate[69a]. It was observed that catechol was oxidized quantitatively to carbon dioxide and water after being treated with an excess (100 percent) of alkaline potassium permanganate solution for about 15 to 20 minutes at the room temperature:

$$C_6H_6O_2 + 13O \longrightarrow 6CO_2 + 3H_2O$$

TECHNIQUE FOR PHYSICO-CHEMICAL MEASUREMENTS

POTENTIOMETRIC STUDIES!

Potentiometric study of the metal-chelate system was carried out by the direct and the pointwise titration procedures. In the direct titrations, known amounts of uranyl nitrate, potassium nitrate and the ligand solutions were pipetted into the titration cell. Conductivity water was added to provide the desired volume and ionic strength (0.1M). The reaction mixture was then titrated with a standard KOH solution and the pH recorded after the system had reached equilibrium by using a Cambridge pH meter (No.317044). A slow stream of purified nitrogen was bubbled through the solution during the course of titration to make a carbon dioxide free and inert atmosphere.

In certain cases the equilibrium was reached slowly and some times several days were required for the completion of a titration. In these cases, therefore, a pointwise titration method was adopted. In this procedure KOH solution was added slowly to reaction mixtures containing known amounts of uranyl nitrate and the ligand in volumetric flasks. After adding the necessary amounts of potassium nitrate to keep the ionic strength constant (0.1M), the solutions were diluted to the desired volume, shaken and allowed to age for several hours in the dark at room temperature, after which pH readings were taken. In order to ensure equilibrium, these solutions were again kept for several hours and the pH of the solutions was again measured.

SPECTROPHOTOMETRIC STUDIES

The solutions under study containing the necessary amounts of KNO_3 to furnish the desired ionic strength (0.1M) were adjusted to proper pH by small additions of a KOH solution. After standing for several hours in the dark at room temperature, the absorbance of each solution was measured using either a Bausch and Lomb Spectronic 20 or a Unicam SP 500 with a silica cell of 10 mm. thickness.

PART II

(i) URANYL CHELATES OF MANDELIC ACID POTENTIOMETRIC STUDIES

TABLE 1

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 50 ML. OF 5×10^{-3}M MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 0, FIG. 1)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.88	2.5	4.95
0.5	3.10	2.6	9.10
1.0	3.30	2.7	10.15
1.5	3.60	2.8	10.50
2.0	3.90	2.9	10.70
2.2	4.10	3.0	10.85
2.4	4.45	3.2	11.01

TABLE 2

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 50 ML. OF 5×10^{-3}M IN URANYL NITRATE WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE O', FIG.1)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	3.44	4.5	5.20
0.5	3.74	5.0	5.40
1.0	3.92	5.5	5.82
1.5	4.10	5.8	7.35
2.0	4.23	6.0	8.20
2.5	4.38	6.2	9.20
3.0	4.54	6.4	9.85
3.5	4.72	6.6	10.25
4.0	5.05	7.0	10.52

TABLE 3

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M URANYL NITRATE AND 5×10^{-3}M IN MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH=0.1M (KNO_3)

(CURVE 1, FIGS 1 AND 6)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.75	4.0	4.08
0.2	2.82	4.5	4.22
0.4	2.89	5.0	4.36
0.6	2.96	5.5	4.55
0.8	3.03	6.0	4.78
1.0	3.10	6.5	5.28
1.2	3.17	6.7	5.85
1.4	3.24	6.9	6.15
1.6	3.31	7.1	6.38
1.8	3.37	7.3	6.48
2.0	3.45	7.6	6.60
2.2	3.52	8.0	6.85
2.4	3.59	8.3	7.30
2.6	3.66	8.5	8.15
2.8	3.74	8.7	9.05
3.0	3.80	9.0	9.90
3.2	3.87	9.2	10.30
3.4	3.94	9.6	10.69
3.6	4.01		

TABLE 4

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN URANYL NITRATE AND 1.0×10^{-2}M IN MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 2, FIG.1)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.54	9.0	5.15
0.5	2.63	9.2	5.76
1.0	2.73	9.4	6.50
1.5	2.83	9.6	6.65
2.0	2.88	9.8	6.80
2.8	3.07	10.0	6.86
3.6	3.28	10.2	7.02
4.4	3.48	10.4	7.20
5.0	3.60	10.8	7.65
5.5	3.75	11.0	7.99
6.0	3.90	11.2	8.60
6.5	4.02	11.4	9.35
7.0	4.15	11.6	9.90
7.5	4.30	11.8	10.20
8.0	4.47	12.0	10.48
8.5	4.70		

TABLE -5

TEMPERATURE = 25 ± 1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN URANYL NITRATE AND 1.5×10^{-2}M IN MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 3, FIG.1)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.40	11.6	5.18
1.0	2.55	11.8	6.45
2.0	2.70	12.0	6.85
3.0	2.87	12.4	7.10
4.0	3.04	12.8	7.33
5.0	3.23	13.2	7.53
6.0	3.42	13.6	8.28
7.0	3.62	13.8	8.90
8.0	3.83	14.0	9.65
9.0	4.06	14.2	10.10
10.0	4.31	14.4	10.36
10.8	4.60	14.6	10.53
11.2	4.83	14.8	10.67

TABLE 6

TEMPERATURE = 25 ± 1°C

POTENTIOMETRIC TITRATION OF 100 ML. OF 2×10^{-2}M MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE

IONIC STRENGTH = 0.1M(KNO_3)

(CURVE O, FIG.2)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.52	18.0	4.02
2.0	2.65	19.0	4.41
4.0	2.80	19.5	5.00
6.0	2.96	19.8	5.90
8.0	3.10	20.0	8.50
10.0	3.25	20.2	9.05
12.0	3.40	20.4	9.75
14.0	3.56	20.5	10.05
15.0	3.68	20.6	10.30
16.0	3.75	20.8	10.54
17.0	3.88		

TABLE 7

TEMPERATURE=25±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF $2x10^{-2}$M IN MANDELIC ACID AND $2.5x10^{-3}$M IN URANYL NITRATE WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 1, FIG.2)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.40	22.0	4.25
2.0	2.54	23.0	4.90
4.0	2.66	23.5	5.50
6.0	2.81	23.8	6.20
8.0	2.95	24.0	6.85
10.0	3.10	24.2	7.00
12.0	3.25	24.6	7.10
14.0	3.41	25.0	7.25
15.0	3.50	25.4	7.40
16.0	3.58	25.8	7.95
17.0	3.69	26.0	9.25
18.0	3.75	26.2	9.70
19.0	3.83	26.4	10.00
20.0	3.95	26.6	10.20

TABLE 8

TEMPERATURE 25±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF $2x10^{-2}$M IN MANDELIC ACID AND $1.25x10^{-3}$M IN URANYL NITRATE WITH 0.1M POTASSIUM HYDROXIDE, IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 2, FIG.2)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.45	21.0	4.70
2.0	2.57	21.6	5.15
4.0	2.73	21.8	5.96
6.0	2.87	22.0	7.15
8.0	3.02	22.0	7.30
10.0	3.14	22.4	7.40
12.0	3.30	22.6	7.58
14.0	3.45	23.0	8.25
15.0	3.53	23.2	9.00
16.0	3.65	23.3	9.50
18.0	3.88	23.4	9.90
19.0	4.00	23.6	10.25
20.0	4.15	23.8	10.40

TABLE 9

TEMPERATURE=25±1°C

SPECTROPHOTOMETRIC DETERMINATION OF MAXIMUM ABSORBANCE OF URANYL-MANDELETE SYSTEM AT DIFFERENT MOLAR RATIOS AT pH 3.5 CONCENTRATION OF UO_2^{2+}= $5x10^{-3}$M

(FIG.3)

Wave length m/μ	Ratio 1:0	Ratio 1:1	Ratio 1:2	Ratio 1:3
340	.052	.35	.547	
350	.030	.225	.355	.415
360	.022	.140	.220	.252
370	.022	.090	.140	.152
380	.026	.070	.100	.105
390	.035	.070	.090	.090
400	.045	.080	.100	.107
410	.050	.087	.118	.123
420	.043	.096	.128	.138
430	.030	.080	.120	.130
440	.015	.060	.095	.107
450	.012	.046	.070	.077
460	.008	.030	.060	.053
470	.006	.025	.050	.050
480	.004	.023	.030	.025

TABLE -10

TEMPERATURE = 25±1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-MANDELATE SYSTEM AT PH 3.0 KEEPING THE TOTAL VOLUME CONSTANT (50 ML) OF EACH SOLUTION. IONIC STRENGTH = 0.1M(KNO_3). INITIAL (UO_2^{2+} + MANDELIC ACID) CONCENTRATION = 0.02 M.

(FIG. 4A)

x	O.D.complex.	O.D. UO_2^{2+}	Diff.in O.D.	O.D. complex	O.D. UO_2^{2+}	Diff.in O.D.
Wave length = 350 mμ				**Wave length = 360 mμ**		
0.1	.075	.005	.070	.04	.002	.038
0.2	.138	.010	.128	.085	.005	.080
0.3	.200	.015	.185	.120	.010	.110
0.4	.225	.02	.205	.140	.018	.122
0.5	.240	.025	.215	.152	.022	.130
0.6	.225	.032	.193	.145	.030	.115
0.7	.200	.045	.155	.130	.040	.090
0.8	.166	.055	.111	.112	.046	.066
0.9	.120	.060	.060	.088	.050	.038
Wave length =420 mμ				**Wave length = 430 mμ**		
0.1	.033	.01	.023	.026	.006	.020
0.2	.058	.02	.038	.050	.010	.040
0.3	.085	.035	.050	.075	.02	.055
0.4	.108	.045	.063	.088	.028	.060
0.5	.130	.060	.070	.106	.040	.066
0.6	.136	.072	.064	.108	.048	.060
0.7	.140	.088	.052	.109	.059	.050
0.8	.140	.105	.035	.105	.065	.040
0.9	.143	.120	.023	.102	.072	.030

TABLE -11

TEMPERATURE = 25±1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-MANDELATE SYSTEM AT PH 3.5 KEEPING THE TOTAL VOLUME CONSTANT (50 ML) OF EACH SOLUTION. IONIC STRENGTH = 0.1M(KNO_3). INITIAL (UO_2^{2+}+ MANDELIC ACID)CONCENTRATION = 0.02 M.

(FIG. 4B)

x	O.D. complex	O.D. UO_2^{2+}	Difference in O.D.	O.D. complex	O.D. UO_2^{2+}	Difference in O.D.
Wave length = 350 m u				Wave length = 350 m u		
0.1	.150	.018	.132	.090	.016	.074
0.2	.305	.023	.282	.190	.020	.170
0.3	.420	.030	.390	.265	.025	.240
0.4	.480	.040	.440	.305	.035	.270
0.5	.560	.055	.505	.350	.045	.305
0.6	.518	.065	.453	.320	.053	.267
0.7	.485	.075	.410	.300	.060	.240
0.8	.410	.090	.320	.260	.070	.190
0.9	.270	.105	.165	.180	.080	.100
Wave length = 420 m u				Wave length = 440 m u		
0.1	.045	.020	.025	.035	.015	.020
0.2	.098	.035	.063	.075	.020	.055
0.3	.145	.050	.095	.110	.025	.085
0.4	.192	.067	.125	.136	.030	.106
0.5	.235	.090	.145	.160	.040	.120
0.6	.240	.110	.129	.160	.050	.110
0.7	.250	.132	.118	.155	.060	.095
0.8	.245	.155	.090	.145	.070	.075
0.9	.230	.175	.055	.120	.085	.035

TABLE -12

TEMPERATURE = 25±1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-MANDELATE SYSTEM AT pH 4.0 KEEPING THE TOTAL VOLUME CONSTANT (50 ML) OF EACH SOLUTION. IONIC STRENGTH= 0.1M(KNO_3). INITIAL (UO_2^{2+}+ MANDELIC ACID) CONCENTRATION =0.02 M

(FIG. 4C)

x	O.D. complex	O.D. UO_2^{2+}	Diff.in O.D.	O.D. Complex	O.D. UO_2^{2+}	Diff.in O.D.
Wave length = 360 m µ				Wave length = 370 m µ		
0.1	.210	.020	.190	.12	.020	.100
0.2	.390	.036	.354	.225	.032	.193
0.3	.460	.048	.412	.280	.046	.234
0.4	.548	.063	.485	.325	.057	.268
0.5	.600	.080	.520	.370	.070	.300
0.6	.560	.105	.455	.340	.086	.254
0.7	.485	.125	.360	.305	.105	.200
0.8	.420	.150	.270	.270	.120	.150
0.9	.325	.170	.150	.223	.140	.083
Wave length = 420 m µ				Wave length = 450 m µ		
0.1	.088	.028	.060	.070	.015	.055
0.2	.200	.055	.145	.134	.020	.114
0.3	.270	.090	.180	.170	.030	.140
0.4	.350	.125	.225	.206	.040	.166
0.5	.440	.168	.272	.250	.050	.200
0.6	.460	.220	.240	.235	.070	.165
0.7	.470	.275	.195	.215	.086	.130
0.8	.460	.326	.134	.190	.098	.092
0.9	.440	.366	.074	.160	.110	.050

TABLE 13

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN URANYL NITRATE AND 2.5×10^{-3}M IN MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH=0.1M(KNO_3)

(CURVE 2, FIG. 6)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.99	4.5	4.44
0.2	3.05	5.0	4.57
0.4	3.11	5.5	4.74
0.6	3.18	6.0	4.97
0.8	3.25	6.5	5.43
1.0	3.30	6.7	5.85
1.2	3.35	6.9	6.08
1.4	3.40	7.1	6.28
1.6	3.47	7.3	6.39
1.8	3.54	7.6	6.50
2.0	3.62	8.0	6.70
2.2	3.69	8.3	7.10
2.4	3.76	8.5	7.75
2.6	3.83	8.7	8.80
2.8	3.90	8.9	9.50
3.0	3.96	9.2	9.90
3.2	4.02	9.4	10.20
3.4	4.08	9.6	10.50
3.6	4.17	9.8	10.62
4.0	4.30	10.0	10.80

TABLE 14

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 200 ML. SOLUTION OF 1.25×10^{-3}M IN URANYL NITRATE AND 1.25×10^{-3}M IN MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 3, FIG.6)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	3.22	4.5	4.53
0.2	3.28	5.0	4.68
0.4	3.33	5.5	4.80
0.6	3.38	6.0	5.01
0.8	3.43	6.3	5.22
1.0	3.48	6.5	5.50
1.2	3.53	6.7	5.85
1.4	3.58	6.9	6.01
1.6	3.64	7.1	6.10
1.8	3.71	7.5	6.35
2.0	3.78	8.0	6.60
2.2	3.85	8.3	6.95
2.4	3.92	8.5	7.65
2.6	3.98	8.7	8.65
2.8	4.05	8.9	9.25
3.0	4.11	9.2	9.75
3.2	4.16	9.5	10.00
3.4	4.22	9.8	10.24
3.6	4.28	10.0	10.36
4.0	4.42		

TABLE 15

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 50 ML. OF 5x10^{-3}M URANYL NITRATE WITH (0.1M) POTASSIUM MANDELATE. IONIC STRENGTH=0.1M(KNO$_3$)

(CURVE 4, FIG.6)

Ml.of 0.1M Potassium Mandelate	pH	Ml.of 0.1M Potassium Mandelate	pH
0.0	3.44	6.0	3.64
0.5	3.44	7.0	3.69
1.0	3.44	8.0	3.74
1.5	3.44	9.0	3.78
2.0	3.44	10.0	3.81
2.5	3.46	11.0	3.84
3.0	3.50	12.0	3.87
3.5	3.53	13.0	3.89
4.0	3.56	14.0	3.91
5.0	3.60	15.0	3.92

(ii) URANYL CHELATES OF LACTIC ACID

POTENTIOMETRIC STUDIES

TABLE 16

TEMPERATURE = 25 ± 1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE

IONIC STRENGTH = 0.1M (KNO_3)

(CURVE O, FIG. 8)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	3.08	2.4	4.75
0.4	3.28	2.5	5.00
0.8	3.52	2.6	8.90
1.2	3.74	2.7	9.80
1.6	3.99	2.8	10.05
2.0	4.28	2.9	10.35
2.2	4.48	3.0	10.50

TABLE 17

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 50 ML.SOLUTION OF $5x10^{-3}M$ IN IN URANYL NITRATE AND $5x10^{-3}M$ IN LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 1, FIG.8 AND 10)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.90	4.0	4.26
0.2	2.98	4.5	4.40
0.4	3.07	5.0	4.57
0.6	3.15	5.5	4.75
0.8	3.21	6.0	5.00
1.0	3.28	6.3	5.20
1.2	3.35	6.5	5.42
1.4	3.42	6.8	5.80
1.6	3.49	6.9	5.98
1.8	3.56	7.1	6.10
2.0	3.64	7.4	6.28
2.2	3.71	7.8	6.52
2.4	3.78	8.0	6.70
2.6	3.84	8.2	6.92
2.8	3.90	8.4	7.60
3.0	3.96	8.6	8.55
3.2	4.02	8.8	9.30
3.4	4.08	9.0	9.70
3.6	4.15	9.2	10.00

TABLE 18

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN URANYL NITRATE AND 1.0×10^{-2}M IN LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 2, FIG.8)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.71	8.8	5.22
0.4	2.80	9.0	5.42
0.8	2.90	9.2	5.79
1.2	2.99	9.4	6.32
1.6	3.09	9.6	6.45
2.0	3.19	9.8	6.55
2.4	3.30	10.0	6.67
2.8	3.40	10.3	6.80
3.2	3.50	10.6	7.10
4.0	3.70	10.8	7.35
4.8	3.88	11.0	8.01
5.6	4.07	11.2	8.60
6.4	4.28	11.4	9.35
7.2	4.51	11.6	9.80
8.2	4.80	11.8	10.15
8.4	4.98	12.0	10.25

TABLE 19

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 50 ML.SOLUTION OF $5x10^{-3}$M IN URANYL NITRATE AND $1.5x10^{-2}$M IN LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 3, FIG.8)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.63	10.6	4.88
0.8	2.79	11.0	5.02
1.6	2.94	11.4	5.25
2.4	3.09	11.6	5.50
3.2	3.26	11.8	6.35
4.0	3.42	12.0	6.55
4.4	3.50	12.2	6.70
5.0	3.62	12.6	6.92
5.6	3.73	12.8	7.13
6.2	3.84	13.2	7.35
6.8	3.98	13.6	8.00
7.4	4.07	13.8	8.75
8.0	4.18	14.0	9.30
8.6	4.32	14.2	9.75
9.2	4.47	14.4	10.05
9.6	4.56	14.6	10.25
10.0	4.65	14.8	10.37

TABLE 20

TEMPERATURE=25±1°C
POTENTIOMETRIC TITRATION OF 100 ML. OF 2x10^{-2}M LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE.
IONIC STRENGTH = 0.1M(KNO_3)
(CURVE O, FIG. 9)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.70	19.5	5.25
2.0	2.90	19.8	5.55
4.0	3.10	20.0	5.95
5.0	3.20	20.1	6.30
6.0	3.30	20.2	8.50
8.0	3.50	20.4	8.98
10.0	3.68	20.5	9.15
12.0	3.87	20.6	9.30
14.0	4.07	20.7	9.45
15.0	4.18	20.8	9.56
17.0	4.45	21.0	9.87
18.0	4.65	21.2	10.08
19.0	4.98		

TABLE 21

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2×10^{-2}M IN LACTIC ACID AND 2.5×10^{-3}M IN URANYL NITRATE WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 1, FIG.9)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.54	23.4	5.60
2.0	2.75	23.8	6.00
4.0	2.95	24.0	6.35
6.0	3.15	24.2	6.56
8.0	3.34	24.4	6.70
10.0	3.51	24.6	6.80
12.0	3.70	25.0	7.00
14.0	3.87	25.4	7.25
16.0	4.10	25.8	7.65
17.0	4.20	26.0	8.45
18.0	4.31	26.2	9.00
19.0	4.42	26.4	9.45
20.0	4.58	26.6	9.70
21.0	4.75	26.8	9.82
22.0	5.00	27.0	10.05
23.0	5.25	27.2	10.13

TABLE 22

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF $2x10^{-2}M$ IN LACTIC ACID AND $1.25x10^{-3}M$ IN URANYL NITRATE WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH=0.1M(KNO_3)

(CURVE 2, FIG. 9)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.63	21.8	5.95
2.0	2.83	22.0	6.40
4.0	3.03	22.2	6.80
6.0	3.22	22.4	6.98
8.0	3.42	22.6	7.08
10.0	3.60	22.8	7.25
12.0	3.80	23.0	7.55
14.0	3.98	23.2	8.60
16.0	4.20	23.4	9.20
17.0	4.35	23.6	9.52
19.0	4.65	23.8	9.80
20.0	4.88	24.0	9.96
21.0	5.25	24.2	10.12
21.4	5.54	24.4	10.25

TABLE 23

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN URANYL NITRATE AND 2.5×10^{-3}M IN LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 2, FIG. 10)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	3.13	5.0	4.65
0.2	3.20	5.5	4.82
0.4	3.27	6.0	5.05
0.6	3.33	6.3	5.25
0.8	3.39	6.5	5.46
1.0	3.45	6.7	5.80
1.2	3.52	7.0	5.98
1.4	3.59	7.2	6.12
1.6	3.65	7.4	6.28
1.8	3.72	7.6	6.40
2.0	3.79	8.0	6.60
2.2	3.85	8.2	6.80
2.4	3.91	8.4	7.60
2.6	3.97	8.6	8.50
2.8	4.03	8.8	9.30
3.0	4.09	9.0	9.65
3.5	4.23	9.3	10.00
4.0	4.35	9.6	10.15
4.5	4.50	10.0	10.32

TABLE 24

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 200 ML.SOLUTION OF $1.25\text{x}10^{-3}$M IN URANYL NITRATE AND $1.25\text{x}10^{-3}$M IN LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE.IONIC STRENGTH=0.1M(KNO_3)

(CURVE 3, FIG.10)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	3.34	4.0	4.49
0.2	3.40	4.5	4.60
0.4	3.46	5.0	4.74
0.6	3.52	5.5	4.92
0.8	3.58	6.0	5.12
1.0	3.63	6.3	5.35
1.2	3.68	6.5	5.50
1.6	3.83	6.7	5.90
1.8	3.89	6.9	5.99
2.0	3.96	7.2	6.25
2.2	4.01	7.5	6.40
2.4	4.06	8.0	6.75
2.6	4.12	8.2	7.00
2.8	4.17	8.5	7.55
3.0	4.23	8.8	9.00
3.2	4.28	9.0	9.30
3.4	4.33	9.2	9.60
3.6	4.38	9.4	9.85
3.8	4.44	9.6	10.05

(iii) URANYL CHELATES OF MALONIC ACID

POTENTIOMETRIC STUDIES

TABLE 25

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML.SOLUTION OF 5×10^{-3}M IN MALONIC ACID WITH 0.1M POTASSIUM HYDROXIDE.

IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 0, FIG.13)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.68	4.0	5.32
0.4	2.79	4.4	5.62
0.8	2.90	4.8	6.00
1.2	3.04	4.9	6.27
1.6	3.24	5.0	7.20
2.0	3.50	5.1	8.20
2.4	3.90	5.2	8.60
2.6	4.22	5.4	8.90
2.8	4.44	5.6	9.20
3.0	4.65	6.0	9.46
3.2	4.76	6.4	9.61

TABLE 26

TEMPERATURE = $30 \pm 1^\circ C$

POTENTIOMETRIC TITRATION OF 50 ML.SOLUTION OF $5 \times 10^{-3}M$ IN URANYL NITRATE AND $5 \times 10^{-3}M$ IN MALONIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 1,FIG.13 AND
CURVE 1, FIG.14)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.39	6.4	5.16
0.4	2.44	6.8	5.40
0.8	2.49	7.2	5.63
1.2	2.54	7.6	5.80
1.6	2.60	8.0	5.95
2.0	2.67	8.4	6.15
2.4	2.75	8.8	6.30
2.8	2.83	9.2	6.43
3.2	2.94	9.6	6.57
3.6	3.02	10.0	6.70
4.0	3.22	10.4	6.92
4.4	3.47	10.8	7.40
4.8	3.92	11.0	8.10
5.0	4.20	11.2	8.46
5.2	4.38	11.4	8.86
5.6	4.66	11.6	9.26
6.0	4.90	12.0	9.76

TABLE 27

TEMPERATURE = 30±1°C
POTENTIOMETRIC TITRATION OF 50 ML.SOLUTION OF 5×10^{-3}M IN URANYL NITRATE AND 1.0×10^{-2}M IN MALONIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M(KNO_3)
(CURVE 2, FIG.13 AND CURVE 1, FIG.15)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.26	9.2	4.30
0.4	2.30	9.6	4.77
0.8	2.34	9.8	5.16
1.2	2.37	10.0	5.55
1.6	2.41	10.2	5.68
2.0	2.45	10.6	5.90
2.4	2.49	11.0	6.10
2.8	2.54	11.4	6.24
3.2	2.58	12.0	6.40
3.6	2.63	12.6	6.50
4.0	2.69	13.2	6.60
4.4	2.75	14.0	6.68
4.8	2.80	14.6	6.84
5.4	2.90	15.0	7.00
6.0	3.02	15.4	7.32
6.4	3.11	15.8	7.80
7.2	3.34	16.0	8.25
8.0	3.58	16.2	8.75
8.8	3.98	16.4	9.45

TABLE 28

TEMPERATURE = 30±1°C
POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN URANYL NITRATE AND 1.5×10^{-2}M IN MALONIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M(KNO_3)
(CURVE 3, FIG.13)

ML. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.18	14.0	5.48
1.0	2.26	14.5	5.78
2.0	2.33	15.0	6.06
3.0	2.41	15.5	6.30
4.0	2.50	16.0	6.50
5.0	2.60	16.5	6.60
6.0	2.72	17.0	6.65
7.0	2.84	17.5	6.70
8.0	2.99	18.0	6.78
9.0	3.17	18.5	6.92
10.0	3.42	19.0	7.02
11.0	3.74	19.5	7.12
11.5	4.00	20.0	7.25
12.0	4.25	20.5	7.45
12.5	4.51	21.0	8.02
13.0	4.84	21.2	8.50
13.5	5.15	21.4	9.00

TABLE 29

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML.SOLUTION OF 2.5×10^{-3}M IN URANYL NITRATE AND 2.5×10^{-3}M IN MALONIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 2, FIG.14)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.62	6.8	5.48
0.4	2.66	7.2	5.70
0.8	2.71	7.6	5.84
1.2	2.77	8.0	6.00
1.6	2.83	8.6	6.20
2.0	2.90	9.2	6.43
2.4	2.97	9.6	6.52
2.8	3.05	10.0	6.68
3.2	3.15	10.4	6.90
3.6	3.28	10.8	7.30
4.0	3.43	11.0	7.80
4.4	3.68	11.2	8.25
4.8	4.12	11.4	8.65
5.0	4.35	11.6	9.00
5.2	4.50	11.8	9.30
5.6	4.78	12.0	9.60
6.0	5.02	12.2	9.88
6.4	5.25		

TABLE 30

TEMPERATURE = 30±1°C
POTENTIOMETRIC TITRATION OF 200 ML. SOLUTION OF 1.25×10^{-3}M IN URANYL NITRATE AND 1.25×10^{-3}M IN MALONIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M (KNO_3)
(CURVE 3, FIG.14)

ML. of 0.1M KOH	pH	ML. of 0.1M KOH	pH
0.0	2.86	6.4	5.35
0.4	2.90	6.8	5.60
0.8	2.95	7.2	5.80
1.2	3.00	7.6	5.95
1.6	3.06	8.0	6.10
2.0	3.12	8.4	6.22
2.4	3.20	8.8	6.35
2.8	3.28	9.2	6.45
3.2	3.38	9.6	6.60
3.6	3.51	10.0	6.75
4.0	3.71	10.4	6.88
4.4	3.96	10.8	7.15
4.8	4.34	11.0	7.65
5.0	4.55	11.2	8.15
5.2	4.70	11.4	8.55
5.6	4.92	11.6	8.90
6.0	5.13	11.8	9.20

TABLE 31

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML.SOLUTION OF 2.5×10^{-3}M IN URANYL NITRATE AND 5.0×10^{-3}M IN MALONIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 2, FIG.15)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.49	10.2	5.80
0.4	2.52	10.6	6.00
0.8	2.56	11.0	6.20
1.2	2.59	11.4	6.28
1.6	2.62	11.8	6.38
2.0	2.65	12.6	6.50
2.4	2.69	13.4	6.65
2.8	2.73	14.2	6.78
3.2	2.77	15.0	7.02
3.6	2.82	15.4	7.24
4.0	2.86	15.8	7.65
4.8	2.97	16.0	7.88
5.6	3.10	16.2	8.24
6.4	3.28	16.4	8.82
7.2	3.50	16.6	9.30
8.0	3.78	16.8	9.60
8.4	4.02	17.0	9.80
8.8	4.27	17.2	9.98
9.2	4.60	17.4	10.15
9.8	5.40		

TABLE 32

TEMPERATURE = 30±1°C
POTENTIOMETRIC TITRATION OF 200 ML. SOLUTION OF 1.25×10^{-3}M IN URANYL NITRATE AND 2.50×10^{-3}M IN MALONIC ACID WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 3, FIG.15)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.72	10.0	5.71
0.4	2.75	10.2	5.84
0.8	2.78	10.6	6.03
1.2	2.81	11.0	6.21
1.6	2.84	11.4	6.28
2.0	2.86	12.0	6.38
2.4	2.90	12.8	6.50
2.8	2.94	13.6	6.63
3.2	2.98	14.4	6.77
3.6	3.02	15.0	6.95
4.0	3.06	15.4	7.15
4.4	3.11	15.8	7.45
4.8	3.16	16.0	7.70
5.6	3.30	16.2	8.05
6.4	3.46	16.4	8.62
7.2	3.69	16.6	9.15
8.0	4.00	16.8	9.45
8.8	4.45	17.0	9.70
9.2	4.76	17.2	9.86
9.6	5.14		

PART III

CHELATES OF URANIUM (VI) WITH SOME α-HYDROXY CARBOXYLIC ACIDS

Chapter I: Results and Discussion.

Chapter II: Experimental.

CHAPTER I

RESULTS AND DISCUSSION

Section 1: Uranyl chelates of 1-Hydroxy-2-Naphthoic and 2-Hydroxy-3-Naphthoic acids.

Section II: Uranyl chelates of Salicylic and 5-Sulphosalicylic acids.

Section III: Uranyl chelates of 1-Hydroxy-2-Naphthaldehyde.

CHAPTER I

SECTION I

URANYL CHELATES OF 1-HYDROXY-2-NAPHTHOIC AND 2-HYDROXY-3-NAPHTHOIC ACIDS

Complexes of uranium (VI) with salicylic and 5-sulphosalicylic acids have long been known. Chelates of hydroxy naphthoic acids have, however, received little attention. Fernandes[70] has isolated a number of derivatives of uranium (VI) with o-hydroxy naphthoic acids having uranyl to ligand ratio of 1:2. Tripathi and Satya Prakash[71] have shown the formation of a 1:1 complex with 1-hydroxy-2-naphthoic acid. More recently, Soni and Gupta[72] have studied the interaction of uranyl ion with 2-hydroxy-3-naphthoic acid by spectrophotometry and conductometry and have indicated the formation of a 1:1 complex.

In view of the above and the interesting results obtained on α-hydroxy carboxylic acid derivatives of uranium (VI), it was considered worthwhile to carry out a systematic physico-chemical study of the interaction of uranyl ion with 1-hydroxy-2-naphthoic and 2-hydroxy-3-naphthoic acids.

Due to the insoluble nature of the hydroxy naphthoic acids in water, 50 per cent ethanol solution (equal volume ethanol-water) was used as a solvent. Attempts were also

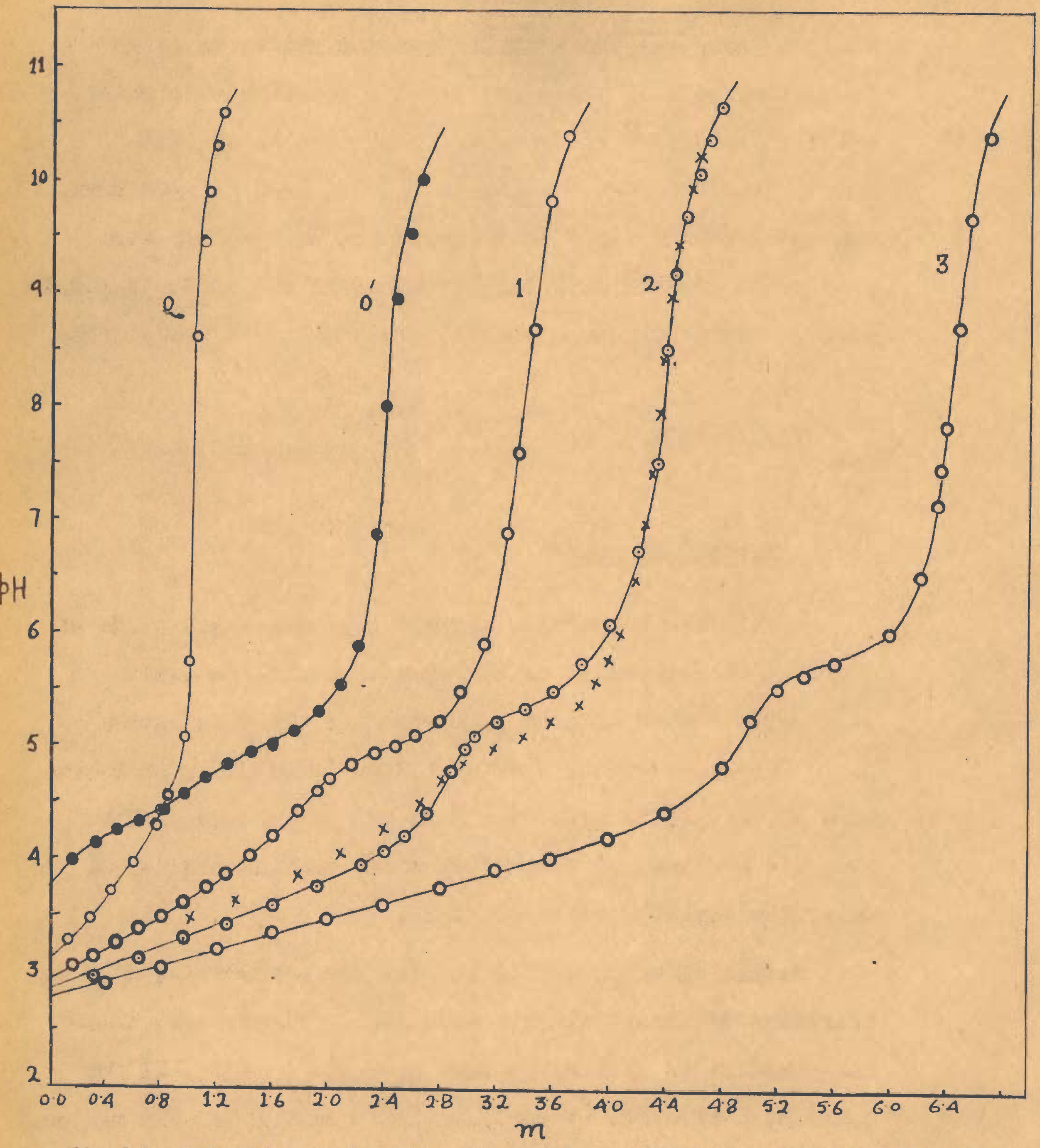


Fig.19. Potentiometric titrations of uranyl-2-Hydroxy-3-Naphthoate system with KOH(0.1N): Curves 1,2 and 3 represent titrations of 1:1, 1:2 and 1:4 uranylnitrate-2-Hydroxy-3-Naphthoic acid mixtures respectively (T_M=0.005M) in 50 % alcoholic medium. Curves O and O' represent titrations of 2-Hydroxy-3-Naphthoic acid (0.005M) and uranyl nitrate (0.005M) respectively in 50 % alcoholic medium. m = moles of KOH added per mole of the metal ion; ionic strength = 0.1M(KNO_3). xxx, composite curve of curves O and 1.

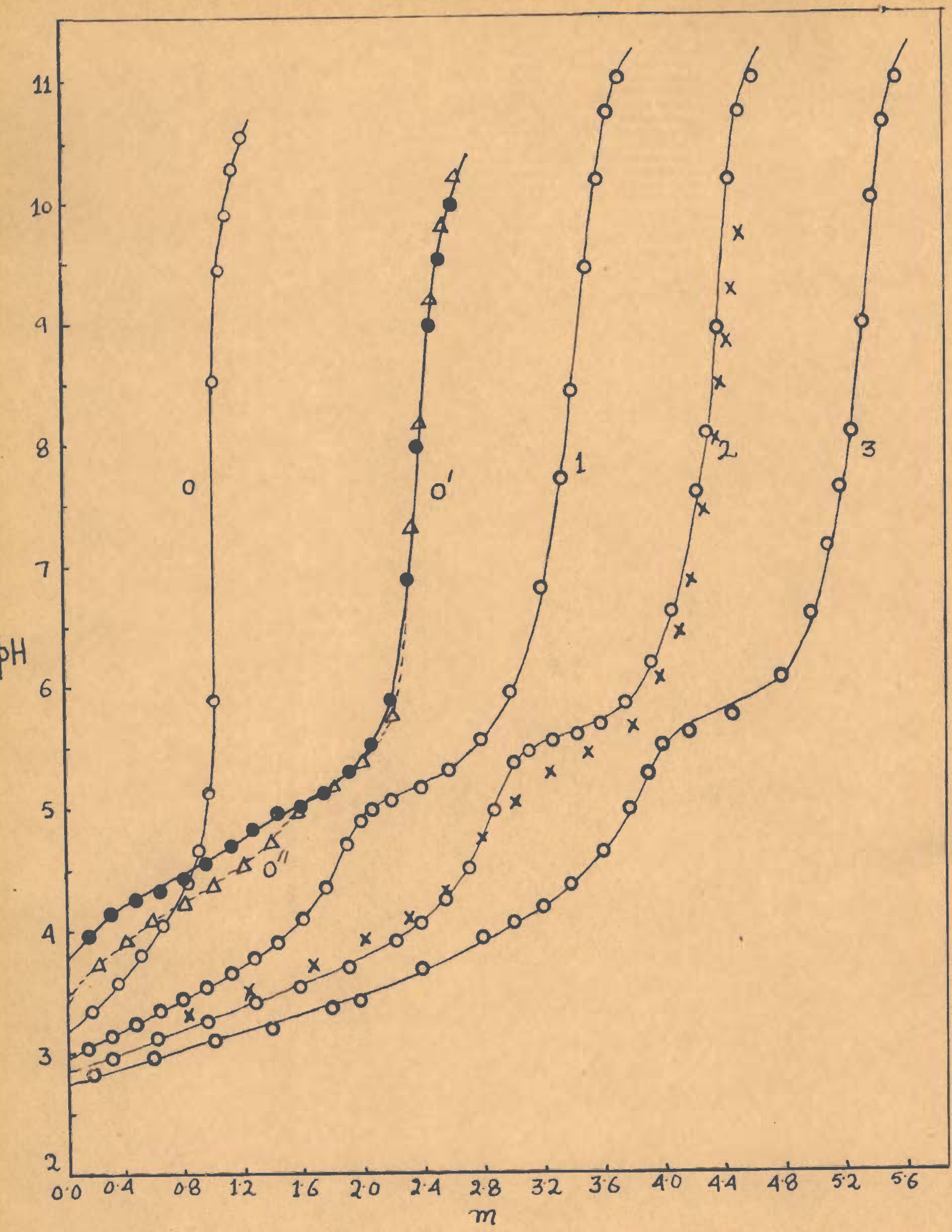


Fig.18. Potentiometric titrations of uranyl-1-Hydroxy-2-Naphthoate, system with KOH(0.1N in 50 % alcohol): curves 1,2 and 3 represent titrations of 1:1, 1:2 and 1:3 uranyl nitrate-1-Hydroxy-2-Naphthoic acid mixtures respectively (T_M=0.005M) in 50 % alcoholic medium. Curves 0 and 0' represent titrations of 1-Hydroxy-2-Naphthoic acid (0.005M) and uranyl nitrate (0.005M) respectively in 50 % alcoholic medium, curve 0" represents titration of uranyl nitrate (0.005M) in aqueous medium. m=moles of KOH added per mole of the metal ion: Ionic strength=0.1M(KNO_3).xxx, represents composite curve derived from curves 0 and 1.

made to carry out the study in aqueous medium by using potassium salts of the acids which were soluble in water. But a quantitative study of the reactions in aqueous medium could not be made, since the ligands, in acid form, separated out slowly from the solution on standing even when small amounts of potassium salts of the acids (0.4-0.5 mole per mole of uranyl nitrate) were added to uranyl nitrate solution.

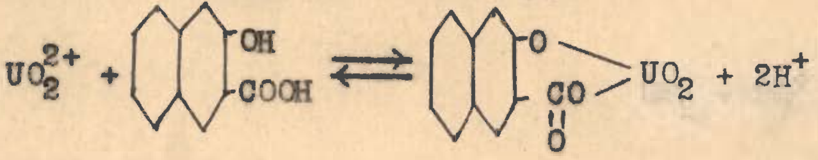
RESULTS AND DISCUSSION

Potentiometric Study:

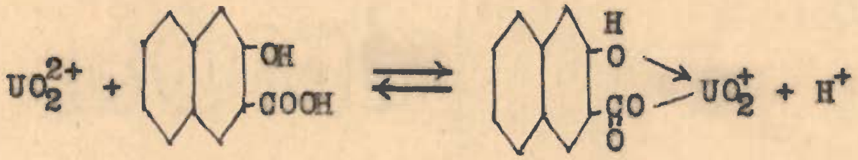
In figures 18 and 19, curve 0 represents titration of 1-hydroxy-2-naphthoic and 2-hydroxy-3-naphthoic acids respectively with KOH. In both cases, a sharp inflexion occurs at one equivalent of alkali indicating the dissociation of carboxylic proton only in acidic solutions. The phenolic hydrogen of the acids, thus, remains unaffected under the experimental conditions.

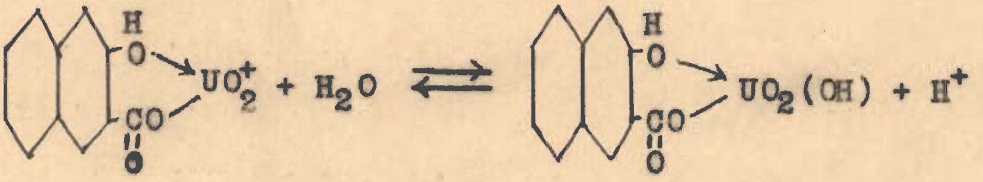
Nature of curve 0'(Fig.18) for the potentiometric titration of uranyl nitrate with KOH in 50 per cent alcoholic medium is similar to that of curve 0" (Fig.18) for a similar titration of uranyl nitrate in the aqueous medium. Curve 0" is, however, throughout lower than the curve 0'. In view of the fact that uranyl ions in aqueous medium do not hydrolyze below pH of 3, by a comparison of the potentiometric data of curves 0' and 0" , it is reasonable to assume that the hydrolysis of uranyl ion in 50 per cent alcoholic medium (including reaction of the type: $(UO_2^{2+} + C_2H_5OH \rightleftharpoons UO_2OC_2H_5^+ + H^+)$ to be negligible up to pH of about 3.5.

Curve 1, presented in figures 18 and 19, represents titration of uranyl nitrate in the presence of an equimolar concentration of 1-hydroxy-2-naphthoic and 2-hydroxy-3- naphthoic acids in 50 per cent alcoholic medium. In both cases, the titration curve is throughout lower than the potentiometric curves for uranyl nitrate and the ligands alone indicating chelation. Both the curves (curve 1, figs.18 and 19) approach an inflexion point at m = 2. This is in accord with a reaction of the type :


(i)

A titration break at m = 2 in the curves may also occur in accordance with the reactions:


(ii)


(iii)

Beyond m = 2, curve 1 (Figs.18 and 19) assumes the shape of the latter half portion of curve O' (Fig.18) for the titration of uranyl nitrate with KOH. This fact together with the formation of a yellow precipitate, similar to uranium hydroxide in appearance, indicated decomposition of the 1:1 metal chelate into uranium hydroxide and the free ligand anions. This conclusion was confirmed by the actual isolation and analysis of the precipitate. The precipitate, after being washed with 50 per cent alcohol, was treated with dilute hydrochloric acid when a clear yellow solution was obtained. Had there been any ligand, it would be precipitated in aqueous solution. Further, the solution in hydrochloric acid did not give a blue colour with ferric chloride which has been reported[73] to be a characteristic test for o-hydroxy naphthoic acids.

In figures 18 and 19, curve 2 represents titration of uranyl nitrate in the presence of two moles of 1-hydroxy-2-naphthoic and 2-hydroxy-3-naphthoic acids. In both cases, the curve approaches an inflexion point at about $m = 3$. This observation may be explained on the basis of the assumption that there is no interaction between 1:1 chelate and a second mole of the ligand, two moles of alkali being consumed by the 1:1 complex and the third mole being used up by the free acid ligand (one mole) present in the system. This assumption was verified by the addition of the abscissae of curves 0 and 1 (Figs.18 and 19). The calculated curve so obtained (shown by crosses in Figs. 18 and 19), closely approximates to the experimental curve thus confirming the above conclusion.

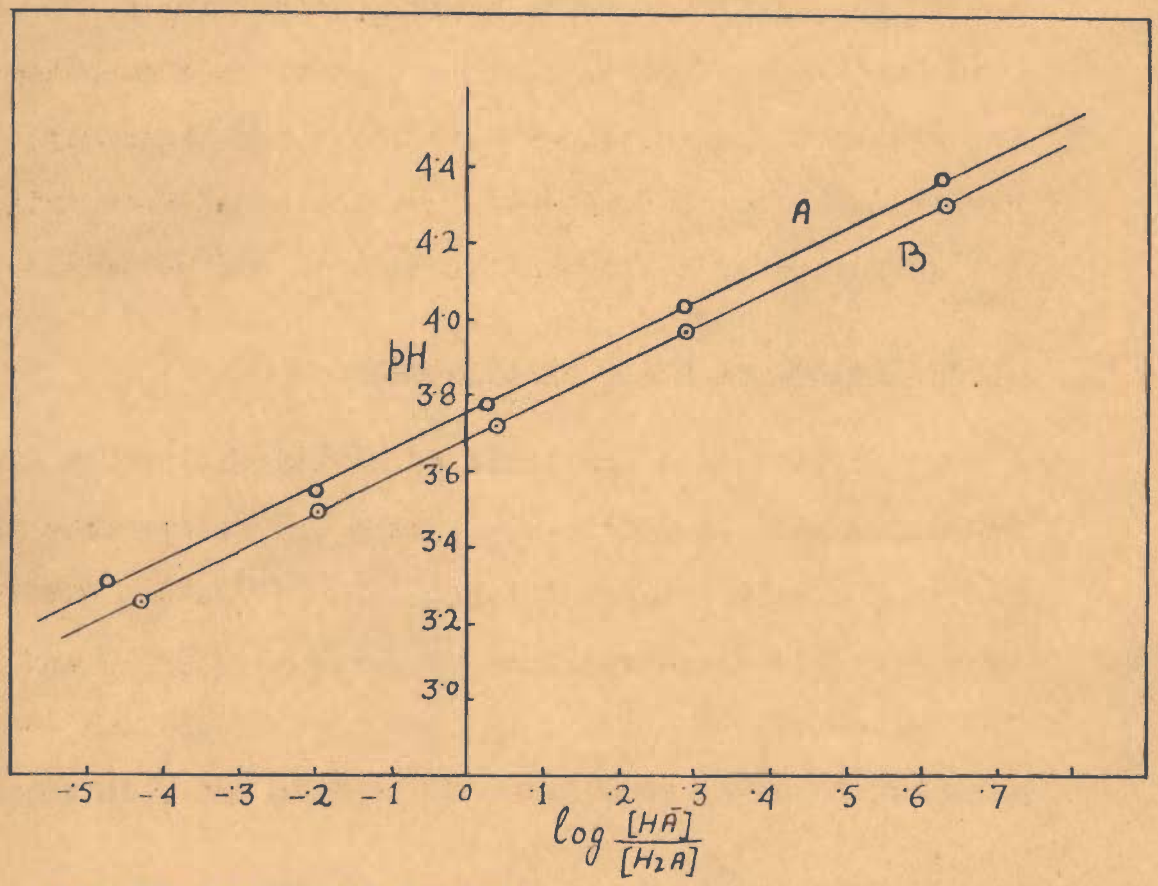


Fig.22. Graphical evaluation of the dissociation constants of 1-Hydroxy-2-Naphthoic acid (Curve A) and 2-Hydroxy-3-Naphthoic acid (Curve B) in 50 per cent alcoholic medium. Ionic strength = 0.1M(KNO_3).

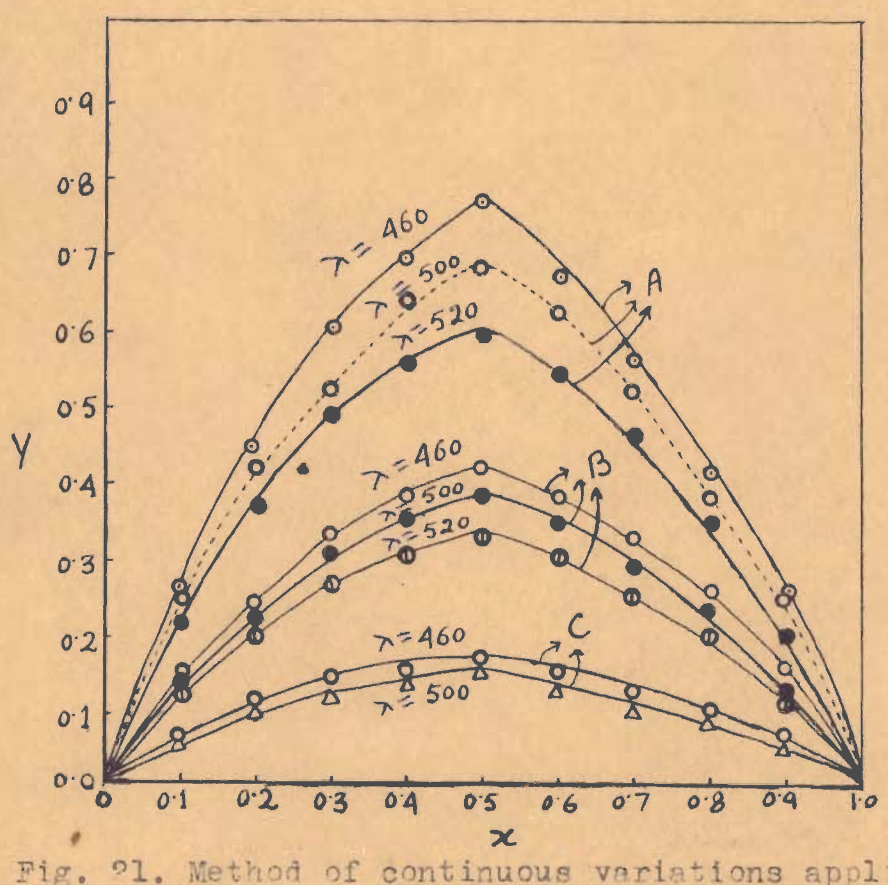


Fig. 21. Method of continuous variations applied to uranyl-2-Hydroxy-3-Naphthoate system at different pH: (A) pH 4.3; (B) pH 3.8; (C) pH 3.3. ($T_A = T_M$) for each solution = 0.004 M; Ionic Strength = 0.1m(KNO_3).

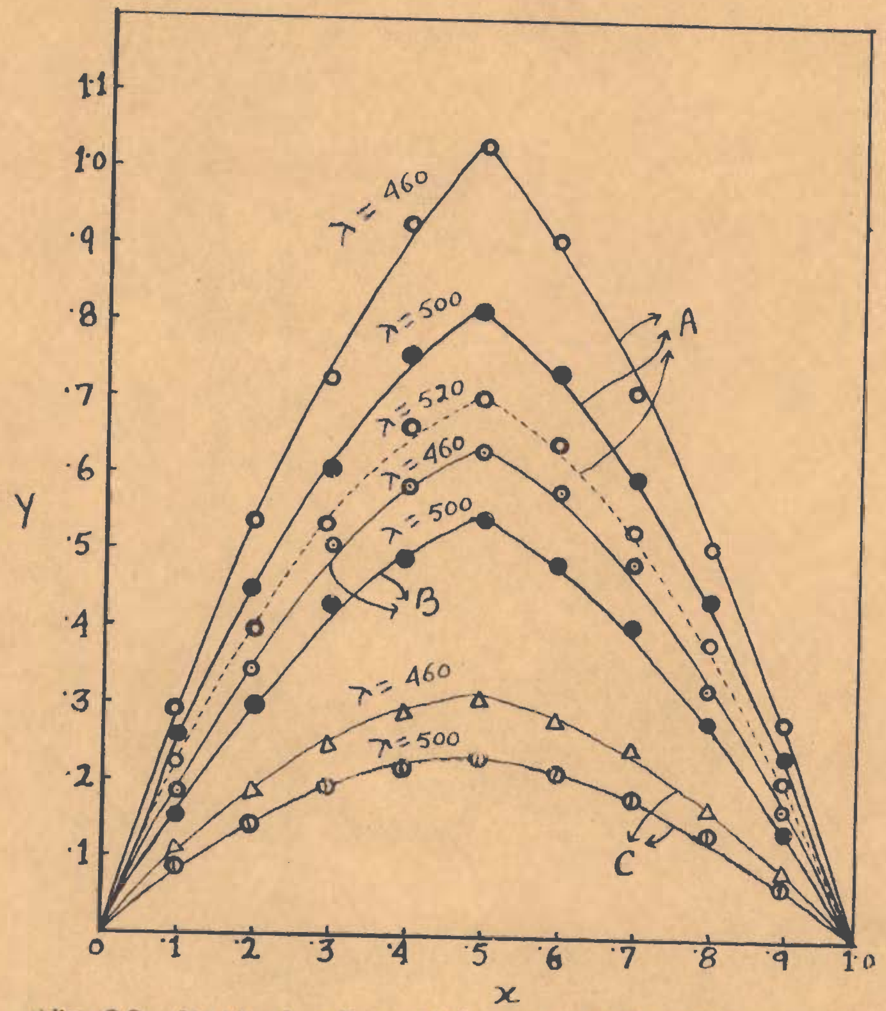


Fig.20. Method of continuous variations applied to uranyl-1-Hydroxy-2-Naphthoate system at different pH: (A) pH 4.3; (B)pH 3.8; (C) pH 3.3. $(T_A + T_M)$ for each solution = 0.004M; Ionic Strength = 0.1M (KNO_3).

Spectrophotometric Study

In Figs.20 and 21 are shown the continuous variations data obtained for uranyl-1-Hydroxy-2-Naphthoate and-2-Hydroxy-3-Naphthoate systems respectively. At all wave lengths studied (460-520 mμ) maximum absorption was observed for solutions containing approximately equivalent amounts of ligands and the metal ions indicating formation of a 1:1 complex in both the systems.

Determination of Equilibrium Constants

Dissociation constants of carboxylic proton of the hydroxy naphthoic acids (H_2A), were determined from the plots of $-\log[H^+]$ against $\log \frac{[HA^-]}{[H_2A]}$ (Fig.22), obtained from the potentiometric data of curve 0 (Figs.18 and 19). The values of pK_a for 1-hydroxy-2-naphthoic and 2-hydroxy-3-naphthoic acids were found to be 3.75 and 3.68 respectively.

If K be the equilibrium constant of the reaction

$$UO_2^{2+} + H_2A \rightleftharpoons UO_2A + 2H^+ \qquad (1)$$

we have

$$K = \frac{[UO_2A]\,[H^+]^2}{[UO_2^{2+}]\,[H_2A]}$$

The equilibrium constant K' of reaction

$$UO_2^{2+} + HA^- \rightleftharpoons UO_2A + H^+$$

may be defined as

$$K' = \frac{[UO_2A]\,[H^+]}{[UO_2^{2+}]\,[HA^-]} \qquad (52)$$

With the help of expressions for K and K_a, it may be shown that

$$K' = \frac{K}{K_a}$$

From the mathematical treatment presented by equations (3-8) in the uranyl-mandelate system, values of the equilibrium constants K and K', calculated over a four-fold concentration range of the metal chelate up to pH of about 3.5, are given in tables XII and XIII.

Table XII

Ligand: 1-hydroxy-2-naphthoic acid

Curve 1 (Fig.23), $T_A = T_M = 5\text{x}10^{-3}M$

Volume of reaction mixture before titration = 50 ml.

KOH(ml)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
pH	2.96	3.03	3.09	3.15	3.20	3.24	3.30	3.35	3.40	3.45
-log K	4.54	4.58	4.58	4.59	4.58	4.58	4.56	4.56	4.55	4.54
-log K'	0.79	0.83	0.83	0.84	0.83	0.83	0.81	0.81	0.80	0.79

Average value of -log K = 4.57 ± 0.02 and
-log K' = 0.81 ± 0.02

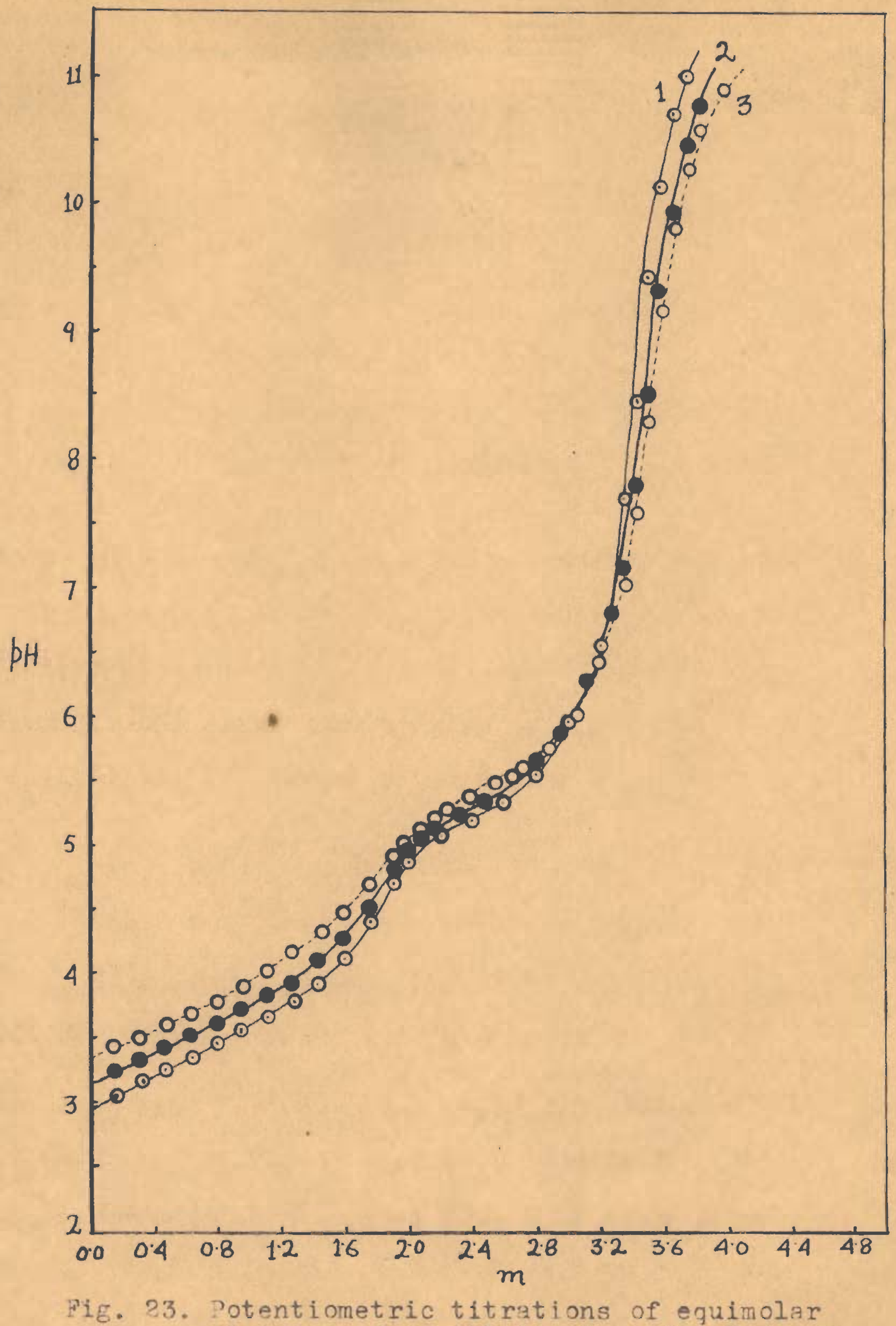


Fig. 23. Potentiometric titrations of equimolar mixtures of uranylnitrate and 1-Hydroxy-2-Naphthoic acid with KOH(0.1N) in 50 % alcoholic medium: curve 1, $5x10^{-3}M$; curve 2, $2.5x10^{-3}M$; curve 3, $1.25x10^{-3}M$. m = moles of base added per mole of the metal ion; ionic strength = $0.1M(KNO_3)$.

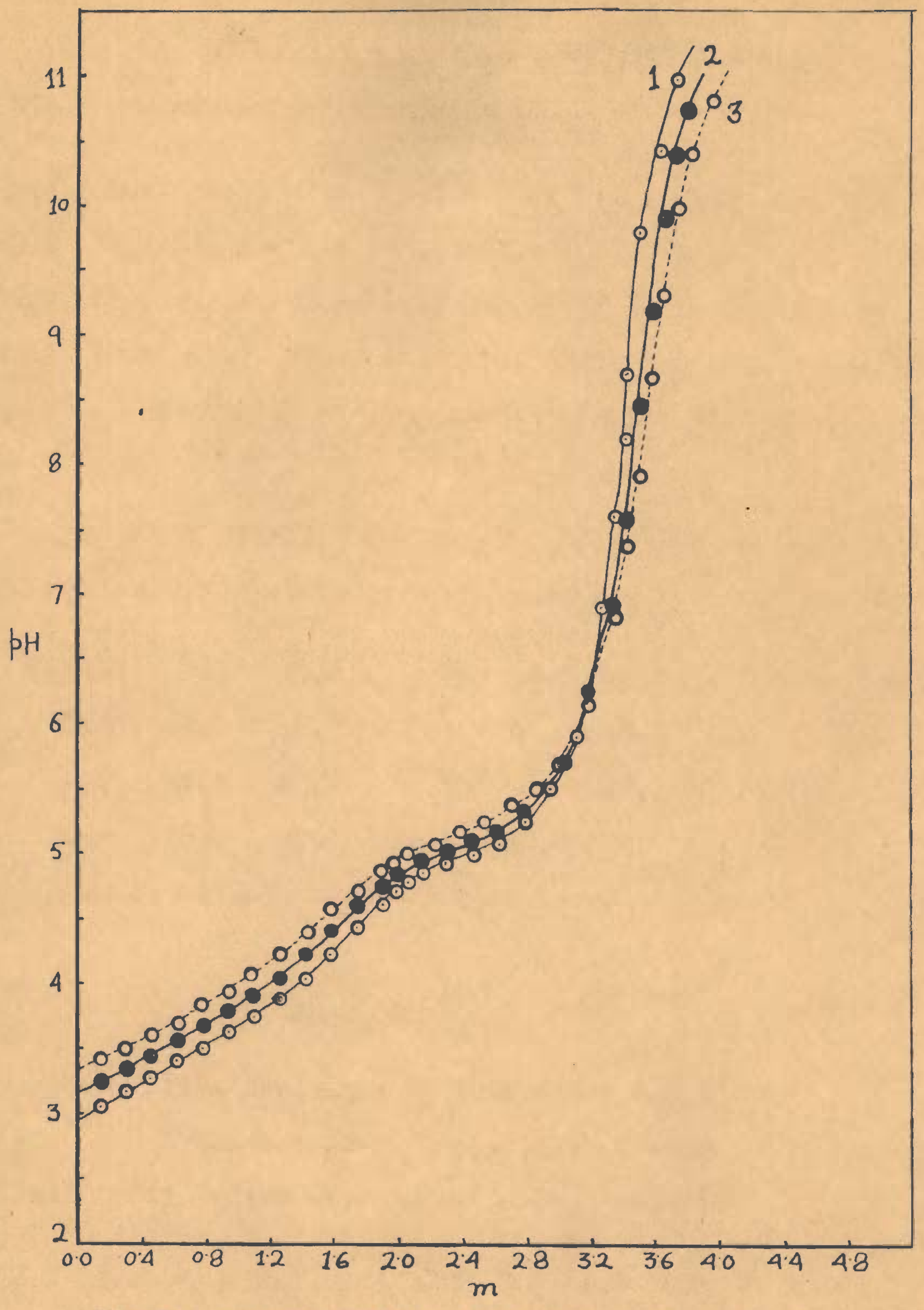


Fig.24. Potentiometric titrations of equimolar mixtures of uranyl nitrate and 2-Hydroxy-3-Naphthoic acid with KOH(0.1N) in 50% alcoholic medium: curve 1, 5x10-3M; curve 2, 2.5x10-3M; curve 3, 1.25x10-3M. m=moles of base added per mole of the metal ion; ionic strength = 0.1M(KNO_3).

Curve 2 (Fig.23), $T_A = T_M = 2.5x10^{-3}M$

Volume of reaction mixture before titration = 100 ml.

KOH(ml)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
pH	3.15	3.20	3.25	3.31	3.36	3.41	3.46	3.51	3.56
-log K	4.55	4.58	4.55	4.58	4.58	4.59	4.56	4.57	4.56
-log K'	0.80	0.83	0.80	0.83	0.83	0.84	0.81	0.82	0.81

Average value of $-\log K = 4.57 \pm 0.02$ and
$-\log K' = 0.82 \pm 0.02$

Curve 3 (Fig.23), $T_A = T_M = 1.25x10^{-3}M$

Volume of reaction mixture before titration = 200 ml.

KOH (ml)	0.2	0.4	0.6	0.8	1.0	1.2
pH	3.34	3.38	3.43	3.48	3.52	3.57
-log K	4.56	4.59	4.56	4.59	4.55	4.57
-log K'	0.81	0.84	0.81	0.84	0.81	0.82

Average value of $-\log K = 4.57 \pm 0.02$ and $-\log K' = 0.82 \pm 0.02$

Table XIII

Ligand : 2-hydroxy-3-naphthoic acid

Curve 1 (Fig.24), $T_A = T_M = 5x10^{-3}M$

Volume of reaction mixture before titration = 50 ml.

KOH(ml.)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
pH	3.00	3.06	3.11	3.17	3.23	3.28	3.34	3.40	3.45	3.51
-log K	4.73	4.75	4.72	4.70	4.71	4.70	4.71	4.72	4.71	4.72
-log K'	1.05	1.07	1.04	1.02	1.03	1.02	1.03	1.04	1.03	1.04

Average value of $-\log K = 4.73 \pm 0.03$ and
$-\log K' = 1.04 \pm 0.03$

Curve 2 (Fig.24), $T_A = T_M = 2.5\text{x}10^{-3}M$

Volume of reaction mixture before titration = 100 ml.

KOH (ml.)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
pH	3.19	3.23	3.28	3.34	3.39	3.45	3.51	3.56
-log K	4.76	4.76	4.73	4.75	4.73	4.75	4.74	4.76
-log K'	1.08	1.08	1.05	1.07	1.05	1.07	1.06	1.08

Average value of -log K = 4.74 ± 0.02 and
-log K' = 1.06 ± 0.02

Curve 3 (Fig.24), $T_A = T_M = 1.25\text{x}10^{-3}M$

Volume of reaction mixture before titration = 200 ml.

KOH (ml.)	0.2	0.4	0.6	0.8	1.0
pH	3.36	3.40	3.45	3.50	3.56
-log K	4.74	4.73	4.73	4.73	4.76
-log K'	1.06	1.05	1.05	1.05	1.08

Average value of -log K = 4.74 ± 0.02 and -log K' = 1.06 ± 0.02

The relatively constant values of -log K obtained in tables XII and XIII indicated that in both cases, reaction (1) is the only one occurring in the system. It is also evident from the above tables that the values of -log K are almost independent of concentration of the metal chelate showing that the uranyl chelates of 1-hydroxy-2-naphthoic and 2-hydroxy-3-naphthoic acids do not polymerize under the experimental conditions employed.

The stoichiometry of 1:1 of the chelates was further confirmed by the calculation of pK from the potentiometric data of curve 2 (Figs. 18 and 19). Results of these calculations are presented in tables XIV and XV.

Table XIV

Ligand: 1-hydroxy-2-naphthoic acid
Curve 2 (Fig.18), $T_A = 2T_M = 1.0 \times 10^{-2}$M.
Volume of reaction mixture before titration=50ml

KOH(ml.)	0.0	0.4	0.8	1.2	1.6	2.0	2.4	2.8	3.2	3.6
pH	2.76	2.86	2.95	3.03	3.10	3.18	3.25	3.32	3.39	3.47
-log K	4.60	4.57	4.56	4.56	4.53	4.55	4.56	4.56	4.56	4.57
-log K'	0.85	0.82	0.81	0.81	0.78	0.80	0.81	0.81	0.81	0.82

Average value of -log K = 4.56 ± 0.03 and -logK' = 0.81 ± 0.03

Table XV

Ligand : 2-hydroxy-3-naphthoic acid
Curve 2 (Fig.19), $T_A = 2T_M = 1.0 \times 10^{-2}$M

Volume of reaction mixture before titration = 50 ml.

KOH(ml.)	0.0	0.4	0.8	1.2	1.6	2.0	2.4	2.8	3.2	3.6
pH	2.77	2.87	2.97	3.06	3.13	3.21	3.30	3.37	3.43	3.50
-log K	4.76	4.72	4.74	4.73	4.71	4.72	4.74	4.72	4.72	4.71
-log K'	1.08	1.04	1.06	1.05	1.03	1.04	1.06	1.04	1.04	1.03

Average value of -log K = 4.73 ± 0.02 and -log K' =1.05±0.03

The constant values of -log K, obtained in tables XIV and XV are in good agreement with those given in tables XII and XIII indicating that, in both cases, only a 1:1 complex is formed even when an excess of ligand is present in the system.

SECTION II

URANYL CHELATES OF SALICYLIC AND 5-SULPHO-SALICYLIC ACIDS

Although much work has been done on the salicylic acid derivatives of uranium (VI), a survey of literature revealed that a quantitative study of the equilibria involved in the interaction of uranyl ion with salicylic acid has not been undertaken by the earlier workers. Canneri and Fernandes[74] in 1924, showed that uranyl salicylate forms addition compounds with a number of metals (Na, K and Ba) and organic bases. Uranyl salicylate, $UO_2(HOC_6H_4COO)_2$, has been crystallized in the anhydrons state[75,76] and also as hydrates[77-80]. Formation of a 1:2 uranyl salicylate has been reported by Dutt and Goswami[81] in aqueous medium.

Hok-Bernstrom[82] has studied the extraction of uranyl ions by a salicylic solution in 4-methyl-2-pentanone. The complexes $UO_2(HOC_6H_5COO)_2$ and $H[UO_2(HO\ C_6H_4COO)_3]$ were shown to be present in the organic phase whereas the complexes $[UO_2(HO\ C_6H_5COO)]^+$ and $UO_2(O\ C_6H_5COO)$ or $UO_2(HO\ C_6H_4COO)(OH)$ were present in the aqueous phase. The extraction of uranium(VI) with salicylic acid in isoamyl alcohol has also been studied[83].

In view of the above and the study carried out on the uranyl chelates of hydroxy naphthoic acids, it was considered of interest to extend this work to the uranyl-salicylate system.

An equilibrium study of the interaction of uranyl ion with 5-sulphosalicylic acid in the aqueous medium has recently been

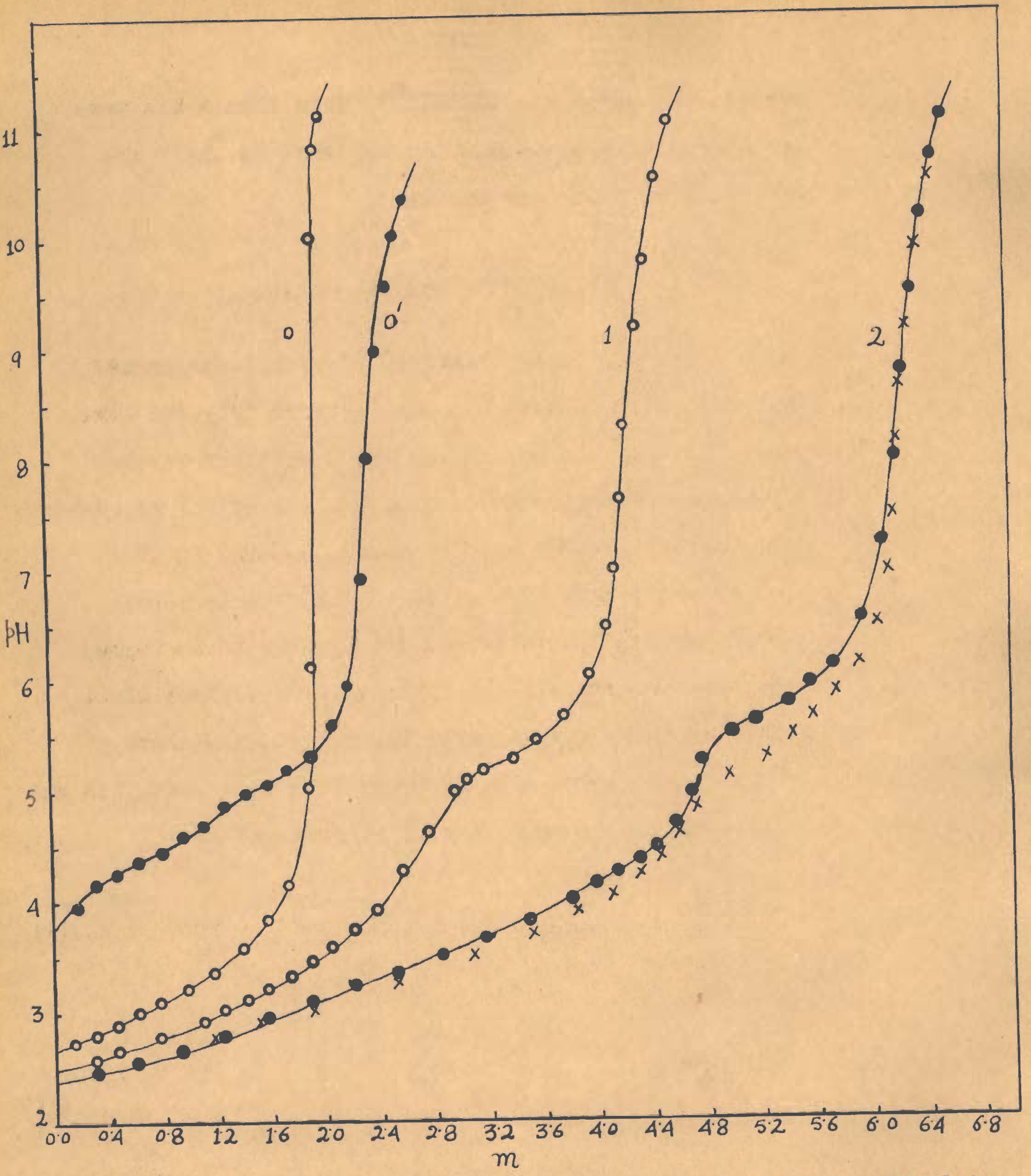


Fig. 26. Potentiometric titrations of uranyl-5-Sulphosalicylate system with KOH(0.1N): curves 1 and 2 represent titrations of 1:1 and 1:2 uranylnitrate-5-Sulphosalicylic acid mixtures respectively in 50 % alcoholic medium. (T_M=0.005M). Curves 0 and 0' represent titrations of 5-Sulphosalicylic acid (0.005M) and uranyl nitrate (0.005M) respectively in 50 % alcoholic medium. m=moles of base added per mole of the metal ion; ionic strength=0.1M(KNO_3).xxx, composite curve of curves 0 and 1.

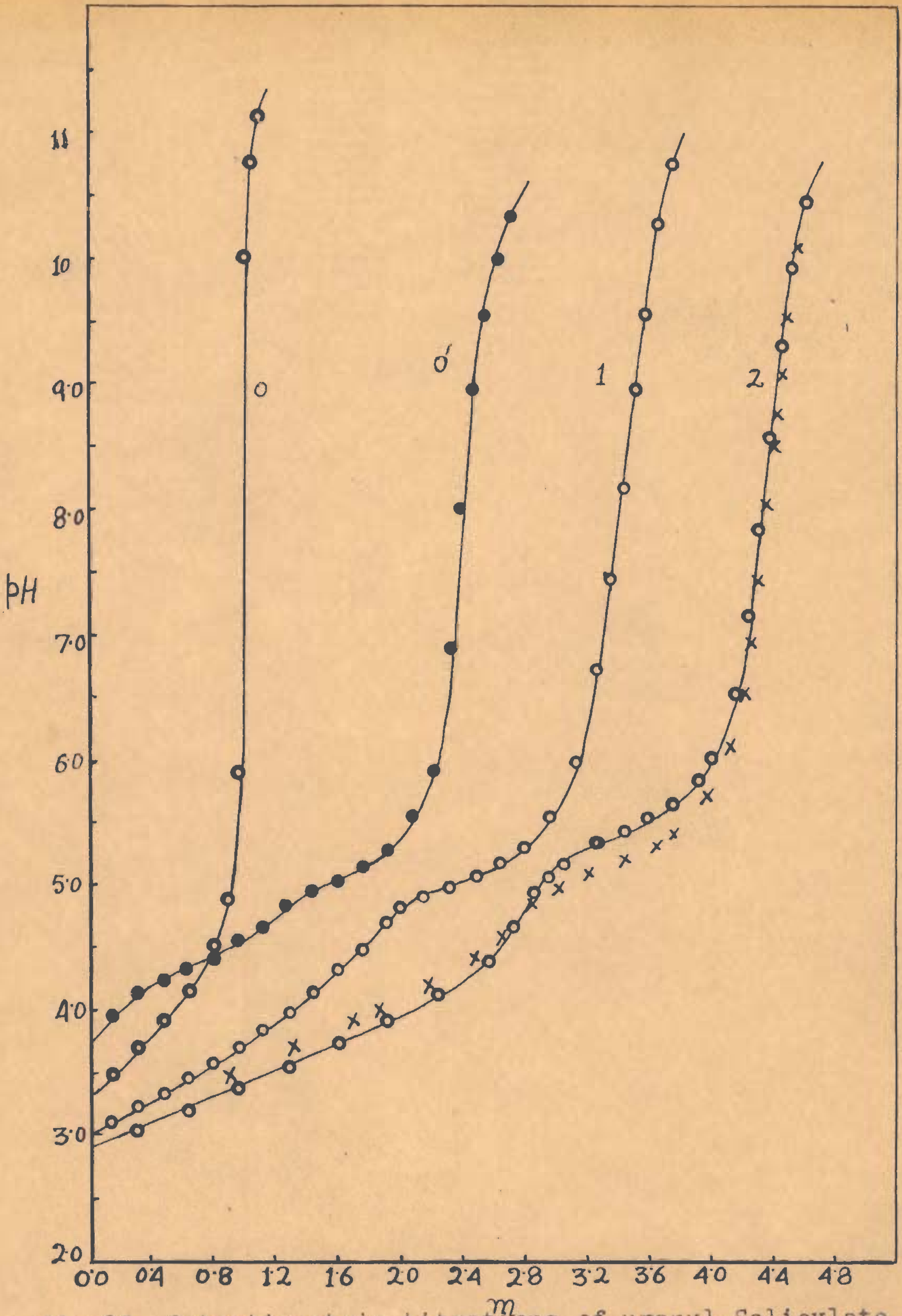
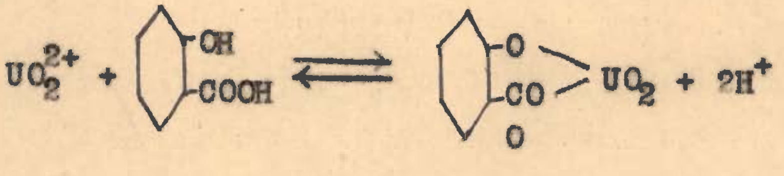


Fig.25. Potentiometric titrations of uranyl-Salicylate system with KOH(0.1N):Curves 1 and 2 represent titrations of 1:1 and 1:2 uranyl nitrate-Salicylic acid mixtures respectively in 50% alcoholic medium (T_M=0.005M).Curves 0and 0' represent titrations of Salicylic acid(0.005M) and uranyl nitrate(0.005M) respectively in 50 % alcoholic medium. m=moles of base added per mole of the metal ion; ionic strength = 0.1M(KNO_3). xxx, composite curve of curves 0 and 1.

reported by Rajan and Martell[84]. This ligand has been included in the present study in order to check the experimental technique employed.

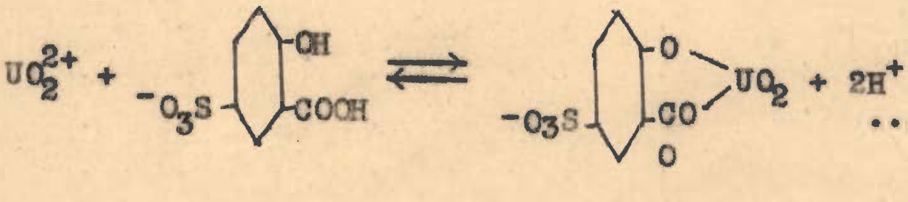
RESULTS AND DISCUSSION

Potentiometric titrations of uranyl-salicylate (Fig.25) and-5-sulphosalicylate systems (Fig.26) gave curves essentially similar to those obtained in the uranyl-naphthoate systems. On the basis of the arguments given before (see uranyl-naphthoate system) in these systems also, from the nature of the potentiometric curves, only a 1:1 metal chelate appears to be formed under the experimental conditions. From a close similarity of these systems with the uranyl-naphthoate systems, the interaction of uranyl ion with salicylic and 5-sulphosalicylic acids may be represented as :



...(i)

and



...(ii)

In both the systems, beyond the inflexion point, a precipitate of uranium hydroxide was formed.

The stoichiometry of 1:1 of the chelates was further confirmed by the Job's method of continuous variations.

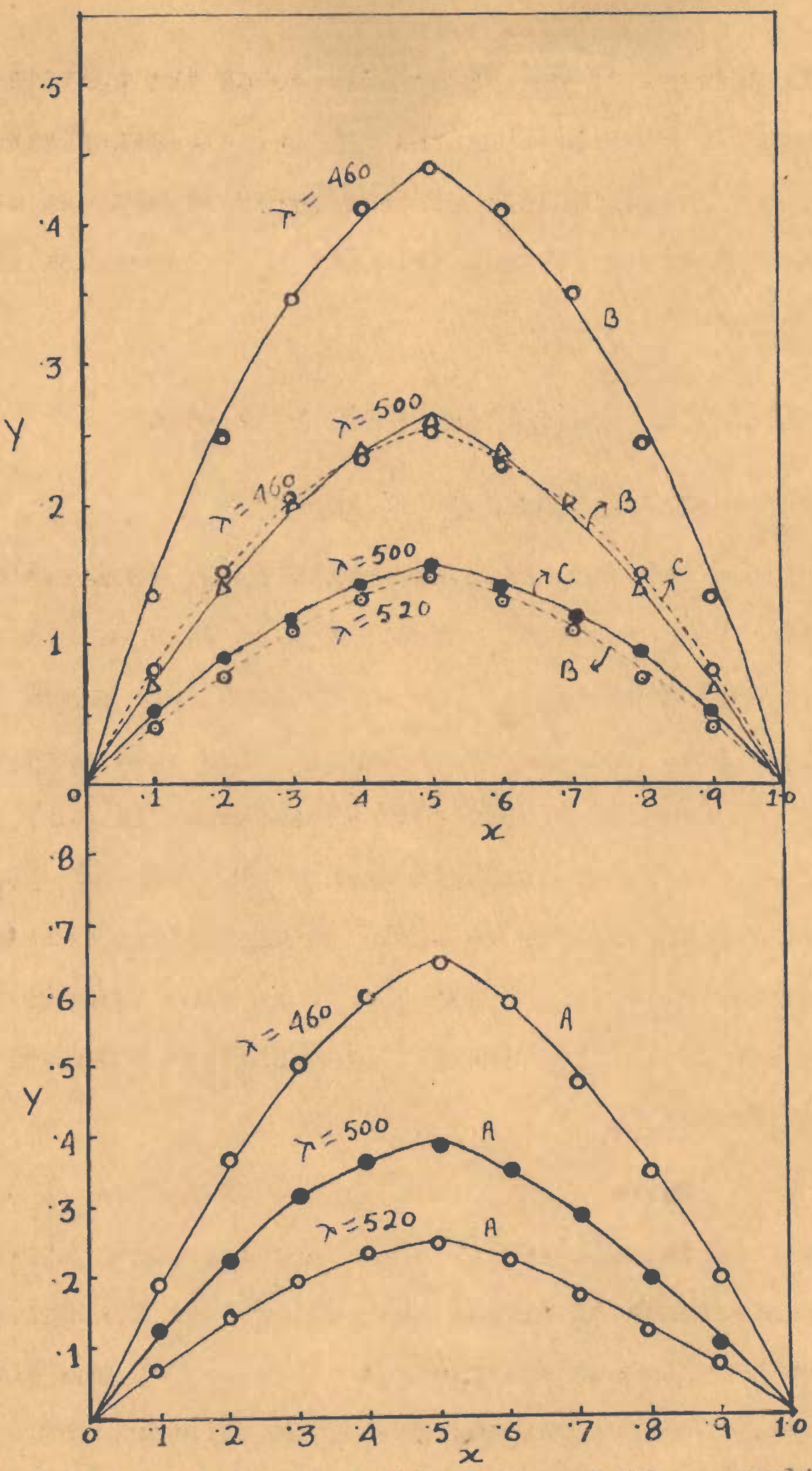


Fig.28. Method of continuous variations applied to uranyl-5-sulphosalicylate system at different pH: (A) pH 4.3; (B) pH 3.8; (C) 3.3. $(T_A + T_M)$ for each solution = 0.004M; Ionic Strength = 0.1M (KNO_3).

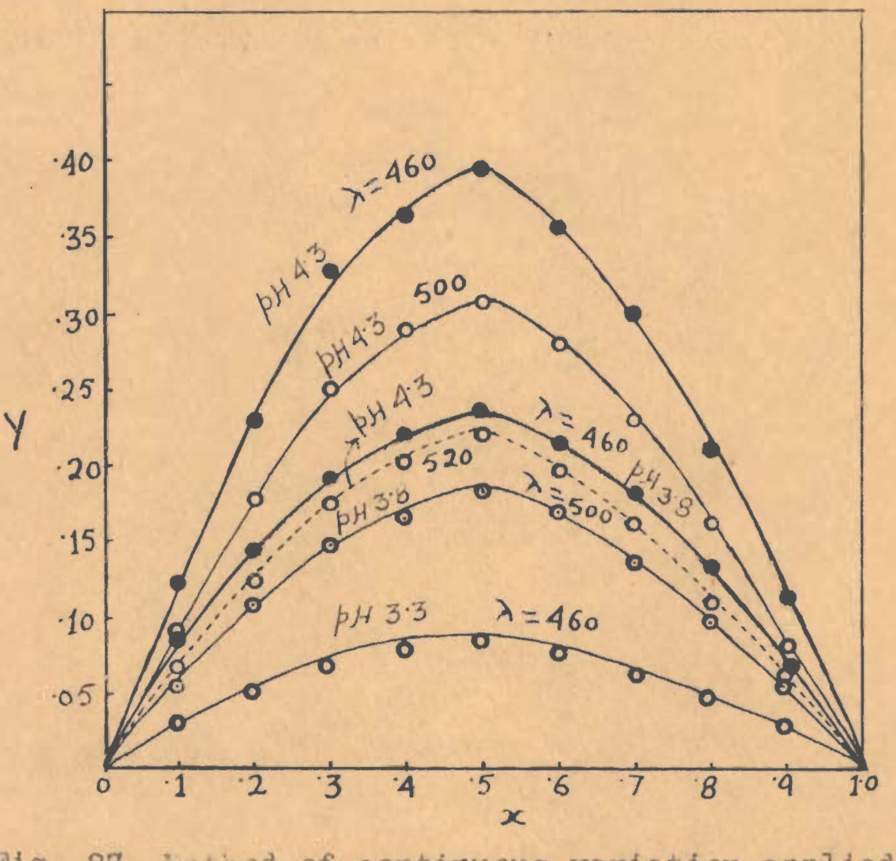


Fig. 27. Method of continuous variation applied to uranyl-salicylate system. $(T_A + T_M)$ for each solution = 0.004M; μ = 0.1M (KNO_3).

In figures 27 and 28 are presented the continuous variations data obtained for uranyl-salicylate and -5-sulphosalicylate systems respectively. At all wave lengths studied (460-520 m) formation of a 1:1 complex is indicated.

Determination of Equilibrium Constants

Dissociation Constants of Acids:

Determination of equilibrium constants of the reactions required a knowledge of dissociation constants of the acid ligands. It is evident from curve O (Fig.25) for the titration of salicylic acid that only the carboxylic proton of the acid dissociates in acid solution. From the potentiometric data of the curve, pK_a of the acid was found to be 3.94. Weakly acidic nature of the phenolic proton of the ligand is also evident from a value of $10^{-13.6}$ for its dissociation constant reported by Perrin[85].

Curve O (Fig.26) for the titration of 5-sulphosalicylic acid exhibits a sharp inflexion point at two equivalents of alkali indicating that dissociation of the carboxylic and sulphonic acid groups of the ligand takes place in overlapping steps. The dissociation constants, K_{a_1} and K_{a_2}, of the acid (H_3A) having a weakly acidic phenolic proton, may be expressed as :

$$K_{a_1} = \frac{[H_2A^-]\ [H^+]}{[H_3A]} \qquad (53)$$

$$K_{a_2} = \frac{[HA^{2-}]\,[H^+]}{[H_2A^-]} \qquad (54)$$

If T_A represents total concentration of 5-sulphosalicylic acid and T_{OH} be the concentration which the added base would have if there were no reaction, from the material balance we obtain

$$T_A = [H_3A] + [H_2A^-] + [HA^{2-}] \qquad (55)$$

$$T_{OH} + [H^+] = [H_2A^-] + 2\,[HA^{2-}] \qquad (56)$$

In the lower buffer region of the titration curve (curve O, Fig.26), concentrations of A^{3-} and OH^- were negligible as compared to those of other species present in the solution.

Combination of equations(53-56)gives

$$[HA^{2-}] = \frac{T_A - T_{OH} - [H^+]}{\dfrac{[H^+]^2}{K_{a_1}\,K_{a_2}} - 1} \qquad (57)$$

Elimination of $[H_2A^-]$ and $[HA^{2-}]$ between (54),(56) and (57) and rearranging the terms yield

$$\frac{[H^+]^2\left\{T_{OH} + [H^+]\right.}{2T_A - T_{OH} - [H^+]} = \frac{[H^+]\left\{T_A - T_{OH} - [H^+]\right\}}{2T_A - T_{OH} - [H^+]}\,K_{a_1} + K_{a_1}\,K_{a_2} \quad \ldots (58)$$

Thus a plot of the values of the expression on the left hand side of equation 58, obtained from the potentiometri

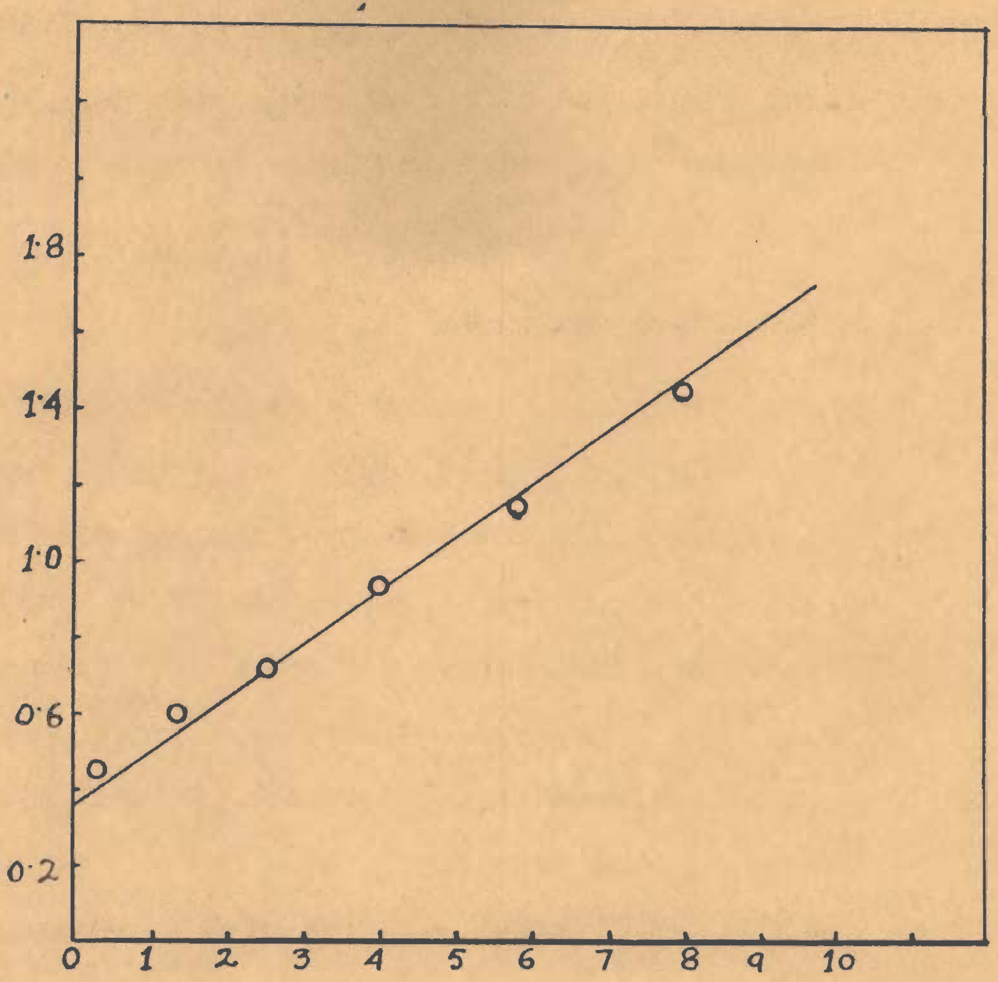


Fig. 29 Graphical evaluation of the dissociation constants of 5-sulphosalicylic acid (H_3A) in 50 per cent alcoholic medium. Ionic strength = 0.1M (KNO_3).

$$X = \frac{[H^+]\left\{T_A - T_{OH} - [H^+]\right\}}{2T_A - T_{OH} - [H^+]} \times 10^{-4}, \quad Y = \frac{[H^+]^2\left\{T_{OH} + [H^+]\right\}}{2T_A - T_{OH} - [H^+]} \times 10^{-6}$$

data of curve 0, against the corresponding values of $[H^+]\left\{T_A - T_{OH} - [H^+]\right\}/(2T_A - T_{OH} - [H^+])$ should yield a straight line of slope K_{a_1} and intercept on the $[H^+]^2\left\{T_{OH} + [H^+]\right\}/(2T_A - T_{OH} - [H^+])$ axis equal to $K_{a_1} K_{a_2}$. The values of pK_{a_1} and pK_{a_2} from the above plot presented in figure 29 were found to be 2.84 and 3.60 respectively.

Equilibrium Constants:

Since sulphonic acid group of 5-sulphosalicylic acid is strongly acidic and it is a well known fact that this group does not take part in chelation reactions with metals, as a first approximation, H_2A^- may be considered to be the ligand after the addition of one equivalent of alkali to a reaction mixture containing an equimolar concentration of uranyl nitrate and 5-sulphosalicylic acid. Values of the equilibrium constant K of reaction (i) and K', equilibrium constant of the reaction:

$$UO_2^{2+} + HA^- \rightleftharpoons UO_2A + H^+$$

obtained from the titration data of uranyl salicylate and -5-sulphosalicylate systems are listed in tables XVI and XVII respectively.

Table XVI

Curve 1 (Fig.30), Ligand: Salicylic acid: $T_A = T_M = 5\times10^{-3}M$

Volume of initial reaction mixture = 50 ml.

KOH(ml.)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
pH	3.06	3.13	3.19	3.25	3.31	3.36	3.42	3.48
-log K	4.83	4.84	4.82	4.82	4.82	4.82	4.83	4.84
-log K'	0.89	0.90	0.88	0.88	0.88	0.88	0.89	0.90

Average value of -log K = 4.83 ± 0.01 and -logK'=0.89±0.01

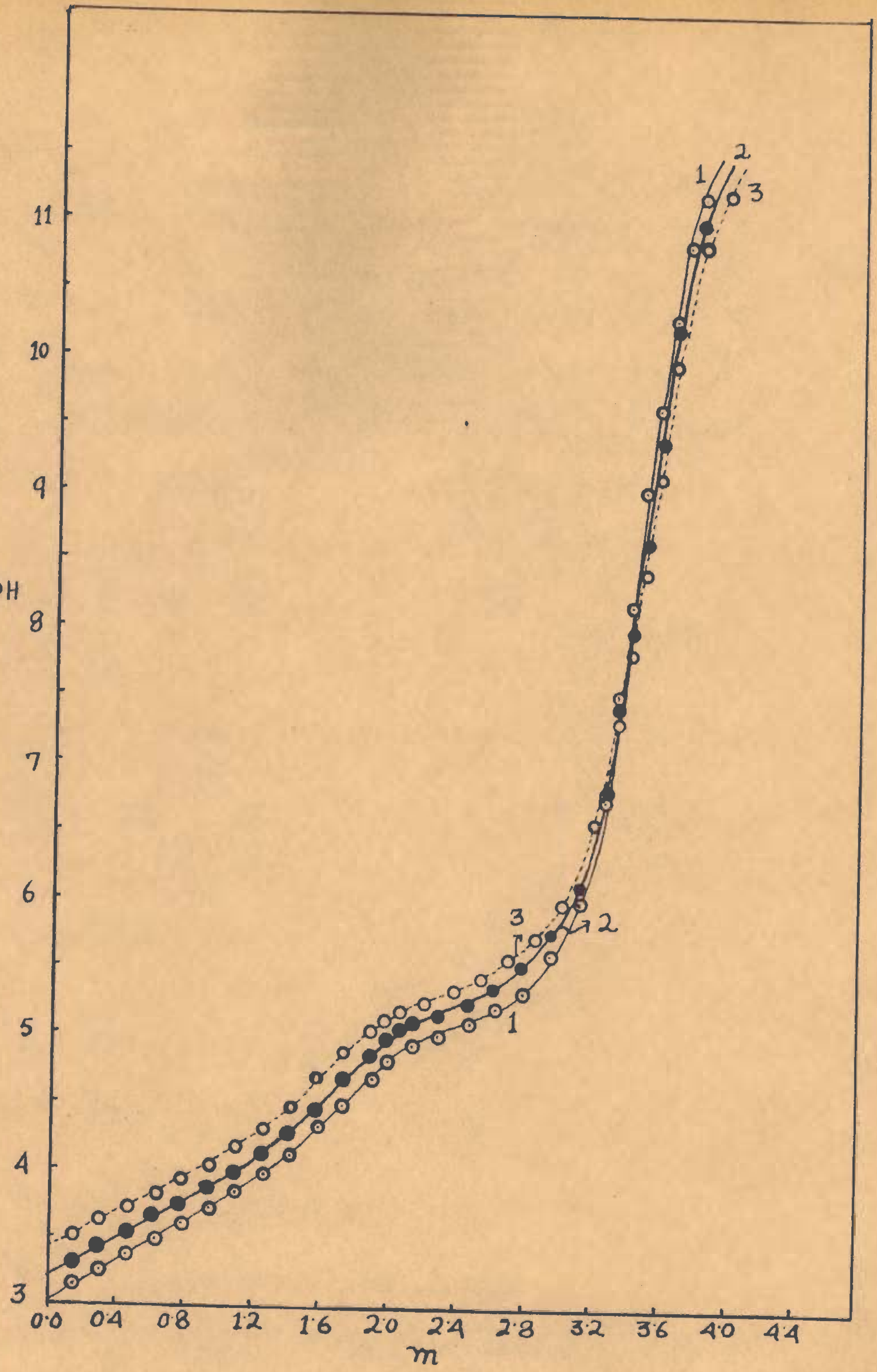


Fig.30. Potentiometric titrations of equimolar mixtures of uranyl nitrate and Salicylic acid in 50 % alcoholic medium: curve 1, 5×10^{-3}M; curve 2, 2.5×10^{-3}M; curve 3, 1.25×10^{-3}M. m = moles of base added per mole of the metal ion; ionic strength = 0.1M (KNO_3).

Curve 2 (Fig.30), $T_A = T_M = 2.5x10^{-3}M$

Volume of initial reaction mixture = 100 ml.

KOH(ml.)	0.2	0.4	0.6	0.8	1.0	1.2
pH	3.25	3.31	3.36	3.42	3.47	3.53
-log K	4.88	4.88	4.84	4.86	4.84	4.86
-log K'	0.94	0.94	0.90	0.92	0.90	0.92

Average value of -log K = 4.86 ± 0.02 and

-log K'= 0.92 ± 0.02

Curve 3 (Fig.30), $T_A = T_M = 1.25x10^{-3}M$

Volume of initial reaction mixture = 200 ml.

KOH(ml.)	0.0	0.2	0.4	0.6	0.8
pH	3.37	3.43	3.48	3.53	3.59
-log K	4.82	4.87	4.89	4.85	4.88
-log K'	0.88	0.93	0.95	0.91	0.94

Average value of -log K = 4.86 ± 0.03 and

-log K' = 0.92 ± 0.03

Table XVII

Ligand: 5-sulphosalicylic Acid

Curve 1(Fig.31), $T_A = T_M = 5x10^{-3}M$

Volume of initial reaction mixture = 50 ml.

KOH(ml.)	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8
pH	2.98	8.03	3.08	3.13	3.18	3.23	3.28	3.33	3.38	3.44
-log K	4.32	4.31	4.31	4.31	4.31	4.32	4.32	4.32	4.33	4.33
-log K'	0.72	0.71	0.71	0.71	0.71	0.72	0.72	0.72	0.73	0.73

Average value of -logK = 4.32 ± 0.02 and -logK'=0.72 ± 0.01

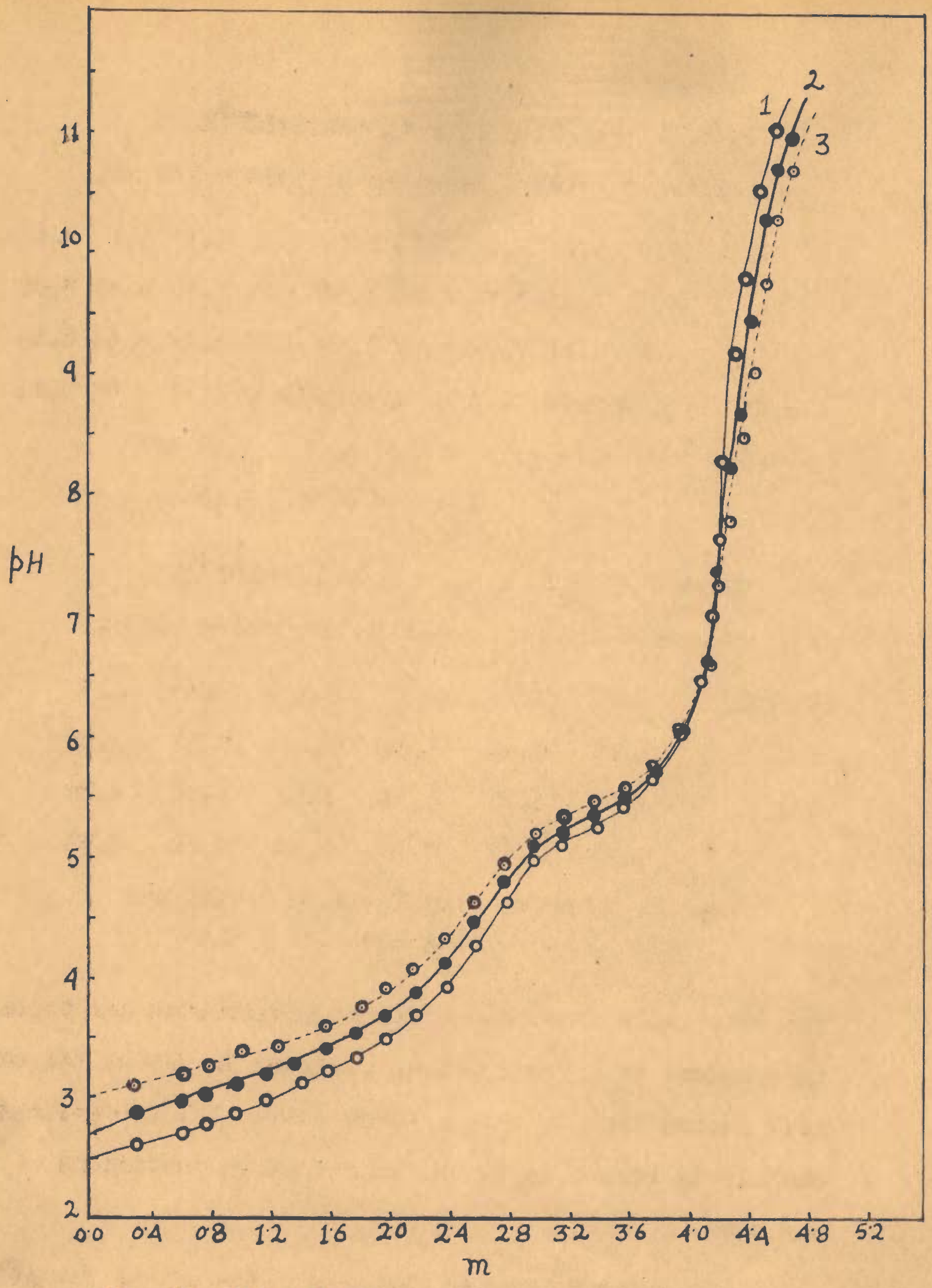


Fig. 31. Potentiometric titrations of equimolar mixtures of uranyl nitrate and 5-Sulphosalicylic acid in 50 % alcoholic medium: curve 1, 5×10^{-3}M; curve 2, 2.5×10^{-3}M; curve 3, 1.25×10^{-3}M. m=moles of base added per mole of the metal ion; ionic strength= 0.1M(KNO_3).

Curve 2 (Fig.31), $T_A = T_M = 2.5x10^{-3}M$

Volume of initial reaction mixture = 100 ml.

KOH(ml.)	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6
pH	3.16	3.20	3.24	3.30	3.35	3.39	3.44	3.49	3.53
-log K	4.34	4.32	4.30	4.34	4.35	4.33	4.32	4.34	4.34
-log K'	0.74	0.72	0.70	0.74	0.75	0.73	0.72	0.74	0.74

Average value of -log K = 4.33 ± 0.01 and
-log K'= 0.73 ± 0.02

Curve 3 (Fig.31), $T_A = T_M = 1.25x10^{-3}M$

Volume of initial reaction mixture = 200 ml.

KOH(ml.)	3.0	3.2	3.4	3.6	3.8	4.0
pH	3.36	3.40	3.44	3.48	3.53	3.57
-log K	4.39	4.38	4.36	4.39	4.40	4.38
-log K'	0.79	0.78	0.76	0.79	0.80	0.78

Average value of -log K = 4.38 ± 0.02 and
-log K'= 0.78 ± 0.02

The relatively constant values of equilibrium constants, independent of concentration, observed in tables XVI and XVII showed that in both systems only a 1:1 mononuclear chelate is formed under the experimental conditions employed.

In order to verify the conclusion of the formation of 1:1 uranyl-salicylate and -5-sulphosalicylate chelates attempts were made to calculate the equilibrium constants, given above, from the potentiometric data of solutions containing two moles of ligand per mole of the metal salt. The results of these calculations are presented in tables XVIII and XIX for the salicylate and sulphosalicylate chelate systems respectively.

Table XVIII

Ligand-Salicylic Acid

Curve 2 (Fig.25), $T_A = 2T_M = 1.0\times10^{-2}M$

Volume of initial reaction mixture = 50 ml.

KOH (ml.)	0.0	0.4	0.8	1.2	1.6	2.0	2.4	2.8	3.2
pH	2.86	2.97	3.06	3.15	3.23	3.30	3.38	3.47	3.54
-log K	4.88	4.84	4.82	4.85	4.85	4.83	4.83	4.86	4.86
-log K'	0.94	0.90	0.88	0.90	0.91	0.89	0.89	0.92	0.92

Average value of -log K = 4.85 ± 0.03 and
-log K' = 0.91 ± 0.03

Table XIX

Curve 2 (Fig.26), $T_A = 2T_M = 1.0\times10^{-2}M$

Volume of initial reaction mixture = 50 ml.

KOH (ml.)	3.0	3.4	3.8	4.2	4.6	5.0	5.4	5.8	6.2
pH	2.81	2.90	2.97	3.04	3.10	3.15	3.22	3.30	3.42
-log K	4.34	4.31	4.34	4.36	4.32	4.32	4.32	4.32	4.33
-log K'	0.74	0.71	0.74	0.76	0.72	0.72	0.72	0.72	0.73

Average value of -log K = 4.33 ± 0.03 and
-log K' = 0.73 ± 0.03

The success thus achieved in obtaining constant values of the equilibrium constants which are in close agreement with the values calculated from the potentiometric data of systems containing equimolar concentration of uranyl nitrate and ligand, shows that even in the presence of an excess of the ligands only a 1:1 complex is formed. This conclusion obtains a further support from the work of Rajan and Martell[84]. Recently, however, Banks and Singh[86] have reported the formation of a 1:2 complex in system containing two moles of 5-sulphosalicylic acid per mole of uranyl nitrate.

SECTION III

URANYL CHELATES OF 1-HYDROXY-2-NAPHTHALDEHYDE

Although salicyldehyde derivatives of uranium(VI) have been investigated earlier[87], a survey of literature revealed that the complexes of 1-hydroxy-2-naphthaldehyde have not been studied. In view of the above and the chelation studies of hydroxy-naphthoic acids, it was considered of interest to carry out a study of the interaction of uranyl ion with 1-hydroxy-2-naphthaldehyde which has been reported[88] to be a strong chelating agent. In this case also due to an insoluble nature of the ligand in aqueous medium, physico-chemical investigations were carried out in 50 per cent alcohol.

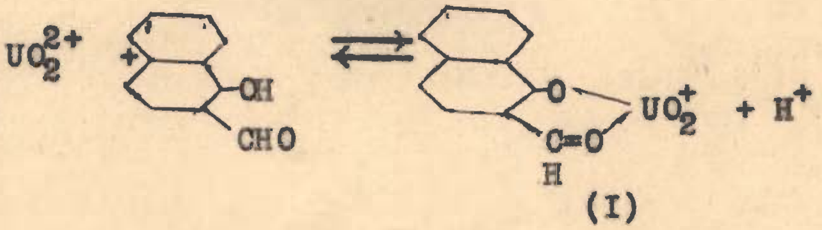
Compared to the formation of only 1:1 uranyl chelates of hydroxy-naphthoic and salicylic acids, the aldehyde also formed a 1:2 complex in solutions of pH > 4.4.

RESULTS AND DISCUSSION

Curve 0 (Fig.32) for the titration of 1-hydroxy-2-naphthaldehyde exhibited a sharp inflexion at one equivalent of alkali showing neutralization of the weakly acidic phenolic proton of the ligand.

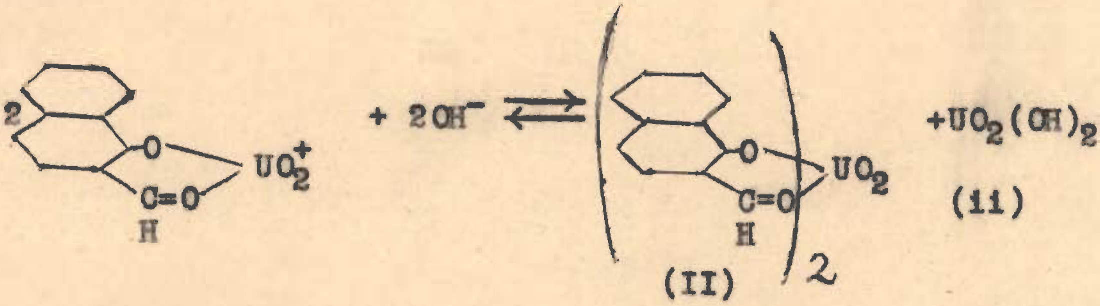
Curve 1 (Fig.32) for the titration of uranyl nitrate in the presence of an equimolar concentration of

1-hydroxy-2-naphthaldehyde showed a bend near m = 1, followed by a sharp inflexion point at about m = 2.2. In the range m = 0-1, we may have a reaction of the type



(1)

Beyond m = 1, the curve assumes a shape composite of the latter half portions of curves 0' and 2 indicating the disproportionation reaction



(ii)

The inflexion point corresponding to the above disproportionation reaction is followed by another inflexion point at about m = 3.3 when the orange coloured complex (II) appears to be converted into uranium hydroxide.

In the range m = 0-1, nature of curves 2 and 3

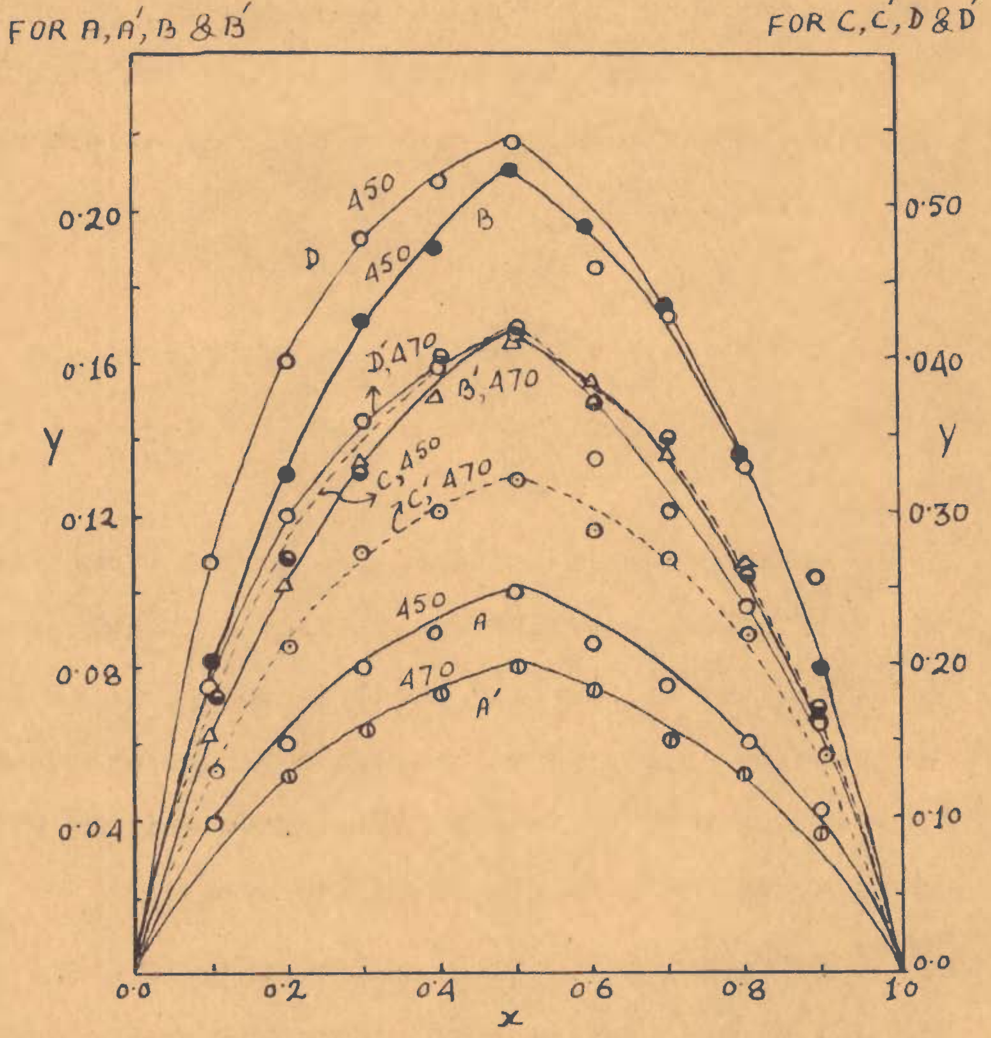


Fig.33. Method of continuous variations applied to uranyl-1-Hydroxy-2-Naphthaldehyde system at different pH: (A,A') pH 3.3; (B,B') pH 3.8; (C,C') pH 4.3; (D,D') pH 4.8. ($T_A + T_M$) for each solution = 0.002M ; μ = 0.1M (KNO_3).

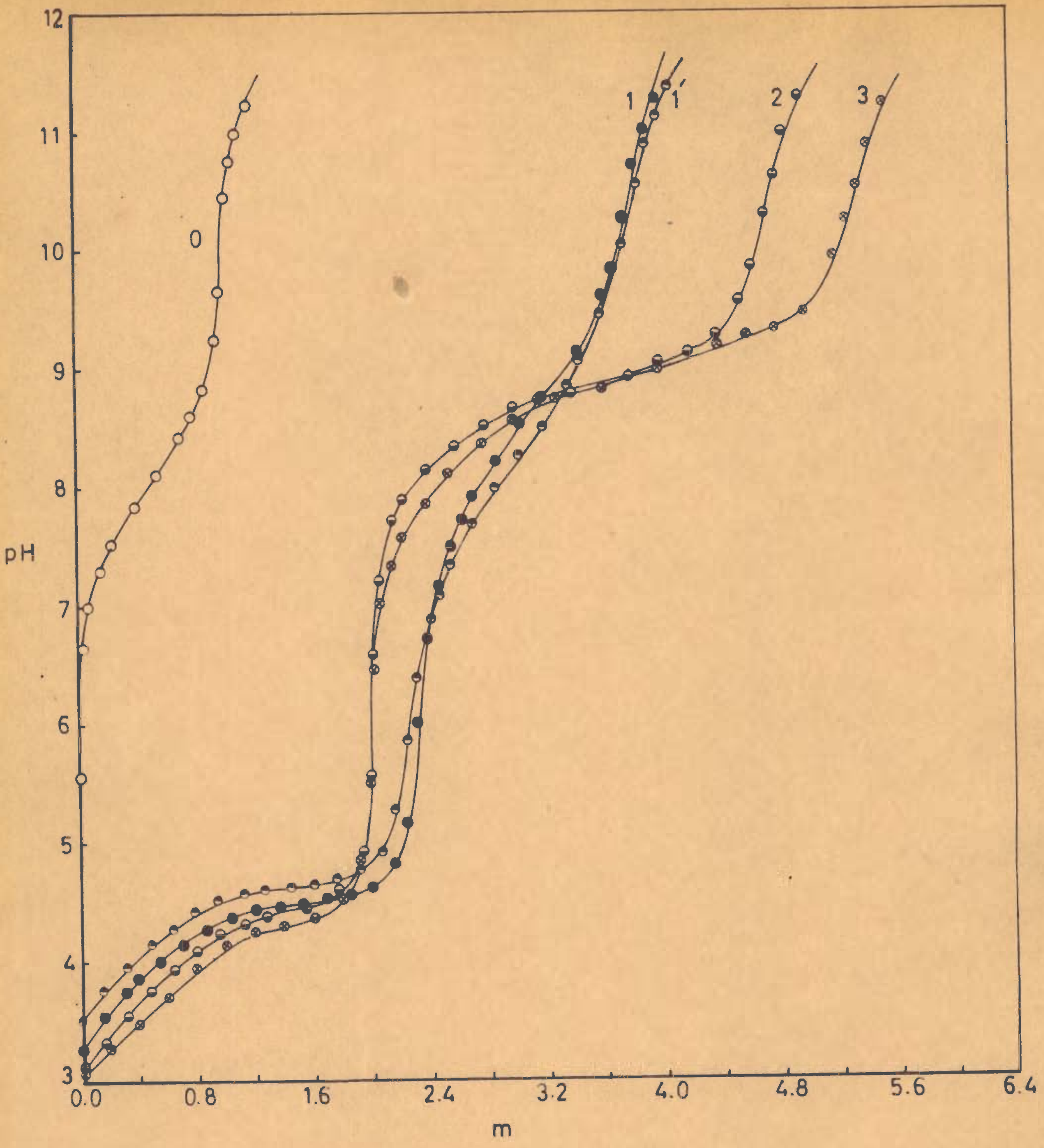
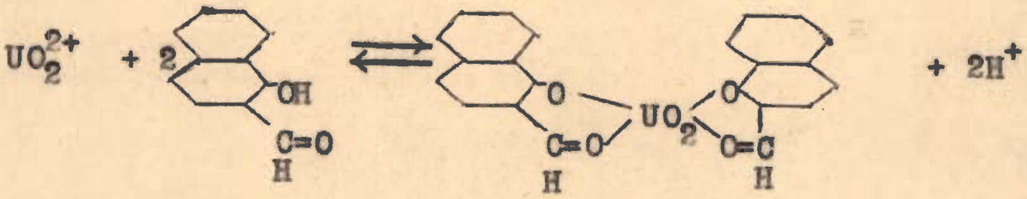


Fig.32. Potentiometric titrations of uranyl-1-Hydroxy-2-Naphthaldehyde chelate system with KOH in 50 per cent alcoholic medium. Curves 1,2 and 3 represent titrations of 1:1,1:2 and 1:3 uranyl nitrate-1-Hydroxy-2-Naphthaldehyde mixtures respectively (T_M = 0.005M). Curves 0 and 1' represent titrations of 1-Hydroxy-2-Naphthaldehyde (0.005M) and equimolar mixture of uranyl nitrate and 1-Hydroxy-2-Naphthaldehyde. (T_M = 0.0025M). m = moles of base added per mole of the metal ion. Ionic strength = 0.1M (KNO_3).

(fig.32) for the titration of uranyl nitrate in the presence of 2 and 3 moles of the ligand is similar to that of curve 1. Lowering in these curves, as compared with curve 1, increases beyond m = 1. A sharp inflexion, shown by both the curves at m = 2, is in accord with the reaction.



(iii)

The reaction product is, however, unstable and disproportionates giving a yellow precipitate in alkaline solutions. Buffer region in curves 2 and 3 in the pH range 7.5-9.5 may thus be explained on the basis of conversion of the 1:2 complex into hydrous uranium oxide and the utilization of KOH by the free ligand in the system.

Formation of a 1:1 chelate in acid solutions (pH $<$ 4.4) was confirmed by spectrophotometry employing Job's method of continuous variations (Fig.33). At all wave lengths studied (450-470 mu) formation of a 1:1 complex was indicated. At higher pH, due to the formation of an orange coloured solid phase, it was not possible to investigate the system by this technique.

Values of the equilibrium constant for reaction(i) calculated up to pH of about 3.5, are given in the table XX.

TABLE XX

Curve 1 (Fig.32), $T_A = T_M = 5x10^{-3}M$

Volume of initial reaction mixture = 50 ml.

KOH (ml.)	0.0	0.2	0.4	0.6
pH	3.26	3.41	3.53	3.65
-log K	1.79	1.76	1.68	(1.62)

Mean value of -log K = 1.74 ± 0.05

( ) Value not included in average.

Curve 2 (Fig.32), $T_M = 5.0x10^{-3}$ M; $T_A = 1.0x10^{-2}M$

KOH (ml.)	0.0	0.2	0.4	0.6	0.8	1.0
pH	3.10	3.20	3.32	3.42	3.53	3.62
-log K	1.79	1.74	1.71	1.67	1.66	(1.59)

Mean value of -log K = 1.72 ± 0.06

( ) Value not included in average.

Constant values of -log K, independent of concentration of the metal chelate, show that up to pH of about 3.5 only a 1:1 complex is formed in the system. Due to the appearance of solid phase beyond m = 0.4, mathematical analysis of the data could not be made.

PART III

EXPERIMENTAL

(i) Uranyl chelates of 1-Hydroxy-2-Naphthoic and 2-Hydroxy-3-Naphthoic acids.

(ii) Uranyl chelates of salicylic and 5-sulphosalicylic acids.

(iii) Uranyl chelates of 1-Hydroxy- 2-Naphthaldehyde.

PART III

CHAPTER - II

EXPERIMENTAL

(i) URANYL CHELATES OF 1-HYDROXY-2-NAPHTHOIC AND 2-HYDROXY-3-NAPHTHOIC ACIDS

POTENTIOMETRIC STUDIES

TABLE 1

TEMPERATURE = 30 ± 1°C
POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN 1-HYDROXY-2-NAPHTHOIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 PER CENT ALCOHOLIC MEDIUM.
IONIC STRENGTH = 0.1M (KNO_3).
(CURVE 0, FIG. 18)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	3.17	2.4	5.10
0.4	3.30	2.5	5.90
0.8	3.53	2.6	8.50
1.2	3.77	2.7	9.40
1.6	4.03	2.8	9.85
2.0	4.37	2.9	10.25
2.2	4.62	3.0	10.53

TABLE 2

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN URANYL NITRATE WITH 0.1 M KOH IN 50 % ALCOHOLIC MEDIUM.

IONIC STRENGTH = 0.1 M(KNO_3)

(CURVE O', FIG.18)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	3.72	4.4	5.14
0.4	3.97	4.8	5.30
0.8	4.15	5.2	5.55
1.2	4.24	5.5	5.90
1.6	4.33	5.8	6.90
2.0	4.42	6.0	8.00
2.4	4.57	6.2	8.98
2.8	4.68	6.4	9.55
3.2	4.85	6.6	10.00
3.6	4.97	6.8	10.38
4.0	5.03		

TABLE 3

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}$M IN URANYL NITRATE AND $5x10^{-3}$M IN 1-HYDROXY-2-NAPHTHOIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 % ALCOHOLIC MEDIUM

IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 1, FIG.18)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.90	5.2	5.00
0.4	3.03	5.5	5.08
0.8	3.15	6.0	5.17
1.2	3.24	6.5	5.33
1.6	3.35	7.0	5.57
2.0	3.45	7.5	5.95
2.4	3.54	8.0	6.58
2.8	3.65	8.4	7.70
3.2	3.78	8.6	8.45
3.6	3.92	8.8	9.45
4.0	4.10	9.0	10.15
4.4	4.40	9.2	10.70
4.8	4.70	9.4	11.00
5.0	4.87	9.6	11.20

TABLE 4

TEMPERATURE = 30±1°C
POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}$M IN URANYL NITRATE AND $1.0x10^{-2}$M IN 1-HYDRONY-2-NAPHTHOIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50% ALCOHOLIC MEDIUM. IONIC STRENGTH = 0.1 M(KNO_3)
(CURVE 2, FIG.18)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.76	6.8	4.52
0.4	2.86	7.2	5.00
0.8	2.95	7.4	5.25
1.2	3.03	7.6	5.40
1.6	3.10	7.8	5.46
2.0	3.18	8.2	5.54
2.4	3.25	8.6	5.62
2.8	3.32	9.0	5.70
3.2	3.39	9.4	5.85
3.6	3.45	9.8	6.20
4.0	3.52	10.2	6.60
4.4	3.60	10.4	7.10
4.8	3.72	10.6	7.60
5.2	3.82	10.8	8.05
5.6	3.91	11.0	9.00
6.0	4.07	11.2	10.20
6.4	4.25	11.4	10.75

TABLE -5

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN URANYL NITRATE AND 1.5×10^{-2}M IN 1-HYDROXY-2-NAPHTHOIC ACID WITH 0.1M KOH IN 50 % ALCOHOLIC MEDIUM

IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 3, FIG.18)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.76	10.0	5.55
0.5	2.86	10.5	5.60
1.5	2.98	11.2	5.78
2.5	3.10	12.0	6.05
3.5	3.24	12.5	6.60
4.5	3.34	12.8	7.13
5.0	3.41	13.0	7.65
6.0	3.73	13.2	8.10
7.0	3.95	13.4	9.00
8.0	4.24	13.6	10.01
9.0	4.64	14.0	11.00
9.5	5.00	14.2	11.20
9.8	5.35		

TABLE -6

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN 2-HYDROXY-3-NAPHTHOIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 % ALCOHOLIC MEDIUM. IONIC STRENGTH=0.1M(KNO_3)

(CURVE O, FIG. 19)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	3.12	2.4	5.05
0.4	3.26	2.5	5.76
0.8	3.48	2.6	8.60
1.2	3.71	2.7	9.45
1.6	3.96	2.8	9.90
2.0	4.30	2.9	10.30
2.2	4.55	3.0	10.60

TABLE 7

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}$M IN URANYL NITRATE AND $5x10^{-3}$M IN 2-HYDRONY-3-NAPHTHOIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 % ALCOHOLIC MEDIUM

IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 1, FIG.19)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.93	5.2	4.79
0.4	3.06	5.4	4.85
0.8	3.17	5.8	4.93
1.2	3.28	6.2	5.00
1.6	3.40	6.6	5.10
2.0	3.51	7.0	5.25
2.4	3.63	7.4	5.50
2.8	3.75	7.8	5.90
3.2	3.88	8.2	6.90
3.6	4.04	8.4	7.60
4.0	4.23	8.6	8.70
4.4	4.43	8.8	9.80
4.8	4.61	9.2	10.40
5.0	4.71	9.4	11.00

TABLE 8

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}$M IN URANYL NITRATE AND $1.0x10^{-2}$M IN 2-HYDROXY-3 NAPHTHOIC ACID WITH 0.1M KOH IN 50 % ALCOHOLIC MEDIUM. IONIC STRENGTH = 0.1 M(KNO_3)

(CURVE 2, FIG.19)

Ml. of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.77	6.4	4.22
0.4	2.87	6.8	4.42
0.8	2.97	7.2	4.80
1.2	3.06	7.4	5.00
1.6	3.13	7.6	5.10
2.0	3.21	8.0	5.25
2.4	3.30	8.5	5.35
2.8	3.37	9.0	5.50
3.2	3.43	9.5	5.75
3.6	3.50	10.0	6.10
4.0	3.60	10.5	6.75
4.4	3.70	10.8	7.50
4.8	3.78	11.0	8.50
5.2	3.88	11.2	9.20
5.6	3.98	11.4	9.70
6.0	4.10	11.6	10.10
6.2	4.16	12.0	10.60

TABLE -9

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN URANYL NITRATE AND 2.0×10^{-2}M IN 2-HYDROXY-3 NAPHTHOIC ACID WITH 0.1M KOH IN 50 % ALCOHOLIC MEDIUM

IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 3, FIG.19)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.80	12.5	5.25
1.0	2.90	13.0	5.55
2.0	3.03	13.5	5.65
3.0	3.18	14.0	5.75
4.0	3.35	14.5	5.90
5.0	3.50	15.0	6.00
6.0	3.63	15.5	6.55
7.0	3.75	15.8	7.20
8.0	3.90	16.0	7.90
9.0	4.05	16.2	8.75
10.0	4.22	16.4	9.75
11.0	4.45	16.6	10.30
12.0	4.86		

TABLE 10

TEMPERATURE = 30 ± 1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-1-HYDROXY-2-NAPHTHOATE COMPLEX AT pH 3.3 KEEPING THE TOTAL VOLUME CONSTANT (50 ML) OF EACH SOLUTION BY THE ADDITION OF 50 PERCENT ALCOHOL. IONIC STRENGTH = 0.1M (KNO_3)

INITIAL (UO_2^{2+} + ORGANIC LIGAND)CONCENTRATION = $4x10^{-3}$M

(FIGURE 20)

	Wave length = 460 mμ			Wave length = 500 m			Wave length = 520 mμ		
x	O.D. Complex.	O.D. UO_2^{2+}	Diff. in O.D.	O.D. complex	O.D. UO_2^{2+}	Diff. in O.D.	O.D. Complex.	O.D. UO_2^{2+}	Diff. in O.D.
0.1	.120	.004	.116	.110	.002	.108	.095	.002	.093
0.2	.193	.004	.189	.163	.003	.160	.140	.002	.138
0.3	.256	.005	.251	.232	.004	.228	.200	.002	.198
0.4	.296	.006	.290	.255	.005	.250	.225	.003	.222
0.5	.320	.008	.312	.266	.006	.260	.235	.004	.231
0.6	.290	.010	.280	.245	.008	.237	.220	.005	.215
0.7	.270	.013	.257	.232	.010	.222	.190	.006	.184
0.8	.190	.018	.172	.165	.012	.153	.150	.006	.144
0.9	.108	.018	.090	.092	.014	.078	.080	.008	.072

TABLE -11

TEMPERATURE = 30±1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-1-HYDROXY-2-NAPHTHOATE COMPLEX AT pH 3.8 KEEPING THE TOTAL VOLUME CONSTANT (50 ML) OF EACH SOLUTION BY THE ADDITION OF 50 % ALCOHOL.

IONIC STRENGTH = 0.1M(KNO_3). INITIAL (UO_2^{2+} + ORGANIC LIGAND) CONCENTRATION = $4x10^{-3}$M.

(FIG. 20)

	Wave length=460 mμ			Wave length=500 mμ			Wave length=520 mμ		
x	O.D. Complex	O.D. UO_2^{2+}	Diff. in O.D	O.D. Complex.	O.D. UO_2^{2+}	Diff. in O.D	O.D. Complex	O.D. UO_2^{2+}	Diff. O.D.
0.1	.190	.005	.185	.155	.004	.151	.140	.004	.136
0.2	.350	.006	.344	.306	.006	.300	.265	.004	.261
0.3	.518	.008	.510	.441	.007	.434	.380	.005	.375
0.4	.596	.009	.587	.500	.008	.492	.435	.005	.430
0.5	.645	.010	.635	.550	.010	.540	.456	.005	.451
0.6	.598	.015	.583	.502	.012	.490	.425	.006	.419
0.7	.510	.018	.492	.425	.013	.412	.372	.007	.365
0.8	.345	.020	.325	.298	.015	.283	.260	.008	.252
0.9	.190	.022	.168	.155	.016	.139	.140	.009	.131

TABLE - 12

TEMPERATURE = 30±1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-1-HYDROXY-2-NAPHTHOATE COMPLEX AT pH 4.3 KEEPING THE TOTAL VOLUME CONSTANT(50ML) OF EACH SOLUTION BY THE ADDITION OF 50 % ALCOHOL. IONIC STRENGTH=0.1M(KNO_3). INITIAL (UO_2^{2+} + ORGANIC LIGAND)CONCENTRATION=$4x10^{-3}$M

(FIG.20)

	Wave length=460 mμ			Wave length=500 m			Wave length = 520 mμ		
x	O.D. Complex	O.D. UO_2^{2+}	Diff. in O.D.	O.D. Complex	O.D. UO_2^{2+}	Diff. in O.D.	O.D. Complex	O.D. UO_2^{2+}	Diff.in O.D.
0.1	.300	.008	.292	.265	.006	.259	.230	.004	.226
0.2	.546	.010	.536	.460	.008	.452	.400	.004	.396
0.3	.742	.012	.730	.620	.008	.612	.540	.005	.535
0.4	.950	.015	.935	.770	.009	.761	.670	.005	.665
0.5	1.050	.018	1.032	.825	.010	.815	.706	.006	.700
0.6	.928	.020	.908	.755	.012	.743	.655	.007	.648
0.7	.736	.022	.714	.610	.014	.596	.536	.008	.528
0.8	.536	.024	.512	.445	.015	.430	.396	.008	.388
0.9	.310	.025	.285	.258	.018	.240	.225	.010	.215

TABLE - 13

TEMPERATURE = 30±1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-2-HYDROXY-3-NAPHTHOATE SYSTEM AT pH 3.3 KEEPING THE TOTAL VOLUME CONSTANT (50 ML) OF EACH SOLUTION BY THE ADDITION OF 50 % ALCOHOL. IONIC STRENGTH = 0.1M(KNO_3). INITIAL(UO_2^{2+} + ORGANIC LIGAND) CONCENTRATION = 4×10^{-3}M

(FIG. 21)

	Wave length = 460 mμ			Wave length = 500 mμ		
x	O.D. Complex	O.D. UO_2^{2+}	Diff. in O.D.	O.D. complex	O.D. UO_2^{2+}	Diff. in O.D.
0.1	.064	.004	.060	.055	.002	.053
0.2	.112	.004	.108	.093	.003	.090
0.3	.140	.005	.135	.115	.004	.111
0.4	.150	.006	.144	.128	.005	.123
0.5	.165	.008	.157	.145	.006	.139
0.6	.145	.010	.135	.126	.008	.118
0.7	.125	.013	.112	.099	.010	.089
0.8	.115	.018	.097	.092	.012	.080
0.9	.076	.018	.058	.059	.014	.045

TABLE - 14

TEMPERATURE = 30±1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-2-HYDROXY-3-NAPHTHOATE SYSTEM AT pH 3.8 KEEPING THE TOTAL VOLUME CONSTANT(50ML)OF EACH SOLUTION BY THE ADDITION OF 50 % ALCOHOL. IONIC STRENGTH = 0.1M(KNO_3). INITIAL (UO_2^{2+}+ORGANIC LIGAND)CONCENTRATION=$4x10^{-3}$M

(FIG.21)

	Wave length=460 mμ			Wave length=500 mμ			Wave length=520 mμ		
x	O.D. Complex.	O.D. UO_2^{2+}	Diff.in O.D.	O.D. Complex.	O.D. UO_2^{2+}	Diff. in O.D.	O.D. complex.	O.D. UO_2^{2+}	Diff. in O.D.
0.1	.156	.005	.151	.140	.004	.136	.122	.004	.118
0.2	.245	.006	.239	.220	.006	.214	.192	.004	.188
0.3	.340	.008	.332	.310	.007	.303	.265	.005	.260
0.4	.385	.009	.376	.350	.008	.342	.300	.005	.295
0.5	.420	.010	.410	.385	.010	.375	.325	.005	.320
0.6	.385	.015	.370	.350	.012	.338	.300	.006	.294
0.7	.335	.018	.317	.295	.013	.282	.250	.007	.243
0.8	.270	.020	.250	.234	.015	.229	.200	.008	.192
0.9	.158	.022	.126	.130	.016	.114	.115	.009	.106

TABLE -15

TEMPERATURE = 30±1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-2-HYDROXY-3-NAPHTHOATE SYSTEM AT pH 4.3 KEEPING THE TOTAL VOLUME CONSTANT (50 ML) OF EACH SOLUTION BY THE ADDITION OF 50 % ALCOHOL. IONIC STRENGTH =0.1M(KNO_3). INITIAL (UO_2^{2+}+ORGANIC LIGAND)CONCENTRATION=$4x10^{-3}$M

(FIG.21)

	Wave length=460 mμ			Wave length=500 mμ			Wave length=520 mμ		
x	O.D. complex.	O.D. UO_2^{2+}	Diff. in.O.D	O.D. complex.	O.D. UO_2^{2+}	Diff. in. O.D.	O.D. complex	O.D. UO_2^{2+}	Diff. in O.D.
0.1	.0270	.008	.262	.246	.006	.240	.210	.004	.206
0.2	.450	.010	.440	.425	.008	.417	.366	.004	.362
0.3	.618	.012	.606	.565	.008	.557	.490	.005	.486
0.4	.700	.015	.685	.645	.009	.636	.560	.005	.555
0.5	.780	.018	.762	.685	.010	.675	.586	.006	.580
0.6	.695	.020	.675	.630	.012	.618	.541	.007	.534
0.7	.588	.022	.566	.530	.014	.516	.462	.008	.454
0.8	.440	.024	.416	.390	.015	.375	.345	.008	.337
0.9	.279	.025	.254	.260	.018	.242	.200	.010	.190

TABLE - 16

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN URANYL NITRATE AND 2.5×10^{-3}M IN 1-HYDROXY-2-NAPHTHOIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 % ALCOHOLIC MEDIUM

IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 2, FIG.23)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	3.12	5.8	5.23
0.4	3.20	6.2	5.34
0.8	3.31	6.6	5.44
1.2	3.41	7.0	5.60
1.6	3.51	7.4	5.85
2.0	3.61	7.8	6.30
2.4	3.71	8.0	6.50
2.8	3.82	8.2	6.80
3.2	3.95	8.4	7.15
3.6	4.08	8.6	7.80
4.0	4.26	8.8	8.50
4.4	4.50	9.0	9.30
4.8	4.80	9.2	9.90
5.0	4.92	9.4	10.45
5.4	5.12	9.6	10.75

TABLE -17

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 200 ML. SOLUTION OF 1.25x10^{-3}M IN URANYL NITRATE AND 1.25x10^{-3}M IN 1-HYDROXY-2-NAPHTHOIC ACID WITH 0.1M KOH IN 50 % ALCOHOLIC MEDIUM

IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 3, FIG.23)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	3.28	5.6	5.26
0.4	3.38	6.0	5.36
0.8	3.48	6.4	5.45
1.2	3.57	6.8	5.60
1.6	3.67	7.2	5.75
2.0	3.78	7.6	6.03
2.4	3.88	8.0	6.47
2.8	4.01	8.4	7.04
3.2	4.14	8.6	7.58
3.6	4.30	8.8	8.30
4.0	4.45	9.0	9.18
4.8	4.90	9.2	9.80
5.0	5.02	9.4	10.28
5.2	5.10	9.6	10.55
5.4	5.20	9.8	10.75

TABLE -18

TEMPERATURE = $30\pm1^{\circ}$C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN URANYL NITRATE AND 2.5×10^{-3}M IN 2-HYDROXY-3-NAPHTHOIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 % ALCOHOLIC MEDIUM

IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 2. FIG.24)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	3.17	5.8	5.00
0.4	3.23	6.2	5.07
0.8	3.34	6.6	5.16
1.2	3.45	7.0	5.33
1.6	3.56	7.2	5.40
2.0	3.67	7.6	5.70
2.4	3.78	8.0	6.25
2.8	3.92	8.4	6.90
3.2	4.05	8.6	7.07
3.6	4.24	8.8	8.45
4.0	4.43	9.0	9.20
4.4	4.60	9.2	9.85
4.8	4.75	9.4	10.40
5.0	4.85	9.6	10.75
5.4	4.95	10.0	11.20

TABLE - 19

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 200 ML. SOLUTION OF 1.25×10^{-3}M IN URANYL NITRATE AND 1.25×10^{-3} M IN 2-HYDROXY-3 NAPHTHOIC ACID WITH 0.1M KOH IN 50 % ALCOHOLIC MEDIUM. IONIC STRENGTH = 0.1M (KNO_3).(CURVE 3,FIG.24)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	3.35	5.6	5.08
0.4	3.40	6.0	5.18
0.8	3.50	6.4	5.26
1.2	3.60	6.8	5.37
1.6	3.71	7.2	5.51
2.0	3.82	7.6	5.70
2.4	3.94	8.0	6.15
2.8	4.08	8.4	6.86
3.2	4.23	8.6	7.35
3.6	4.40	8.8	7.85
4.0	4.56	9.0	8.56
4.4	4.72	9.2	9.30
4.8	4.87	9.4	10.00
5.0	4.93	9.6	10.40
5.2	4.98	10.0	10.80

(ii) URANYL CHELATES OF SALICYLIC AND 5-SULPHO SALICYLIC ACIDS

POTENTIOMETRIC STUDIES

TABLE -20

TEMPERATURE = 30 ± 1° C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN SALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 % ALCOHOLIC MEDIUM.
IONIC STRENGTH = 0.1M (KNO_3)
(CURVE O, FIG.25)

Ml. of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	3.22	2.2	4.88
0.4	3.43	2.3	5.25
0.8	3.69	2.4	5.94
1.2	3.94	2.5	10.10
1.6	4.21	2.6	10.80
2.0	4.56	2.7	11.15

TABLE -21

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN URANYL NITRATE AND 5×10^{-3}M IN SALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 % ALCOHOLIC MEDIUM. IONIC STRENGTH=0.1M(KNO_3)

(CURVE 1, FIG.25)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.99	5.8	4.98
0.4	3.13	6.2	5.06
0.8	3.25	6.6	5.18
1.2	3.36	7.0	5.31
1.6	3.48	7.4	5.57
2.0	3.59	7.8	5.98
2.4	3.69	8.2	6.70
2.8	3.82	8.4	7.50
3.2	3.96	8.6	8.16
3.6	4.12	8.8	9.00
4.0	4.30	9.0	9.60
4.4	4.48	9.2	10.25
4.8	4.68	9.4	10.85
5.0	4.80	9.6	11.10
5.4	4.90		

TABLE -22

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}M$ IN URANYL NITRATE AND $1.0x10^{-2}M$ IN SALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 % ALCOHOLIC MEDIUM. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 2, FIG.25)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.86	6.8	4.67
0.4	2.97	7.2	4.93
0.8	3.06	7.4	5.07
1.2	3.14	7.6	5.18
1.6	3.23	7.8	5.24
2.0	3.30	8.2	5.35
2.4	3.38	8.6	5.45
2.8	3.47	9.0	5.56
3.2	3.54	9.4	5.67
3.6	3.62	9.8	5.80
4.0	3.71	10.0	6.05
4.4	3.82	10.4	6.55
4.8	3.92	10.6	7.15
5.2	4.03	10.8	7.80
5.6	4.15	11.0	8.60
6.0	4.26	11.2	9.30
6.4	4.40	11.4	9.90

TABLE -23

TEMPERATURE = 30 ± 1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}M$ 5-SULPHO-SALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 PER CENT ALCOHOLIC MEDIUM. IONIC STRENGTH = 0.1M (KNO_3). (Curve 0, Fig.26)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	2.65	4.0	3.80
0.4	2.74	4.4	4.12
0.8	2.84	4.6	4.50
1.2	2.95	4.8	5.02
1.6	3.04	4.9	6.09
2.0	3.13	5.0	10.00
2.4	3.22	5.1	10.80
2.8	3.35	5.2	11.10
3.2	3.46	5.3	11.30
3.6	3.63	5.4	11.45

TABLE -24

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}$M IN URANYL NITRATE AND $5x10^{-3}$M IN 5-SULPHO-SALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 % ALCOHOLIC MEDIUM. IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 1, FIG. 26)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.48	7.0	4.61
0.4	2.53	7.3	4.80
0.8	2.58	7.5	4.94
1.2	2.64	7.7	5.00
1.6	2.69	8.0	5.06
2.0	2.76	8.5	5.20
2.4	2.82	9.0	5.41
2.8	2.92	9.5	5.63
3.2	3.03	10.0	6.00
3.6	3.13	10.3	6.45
4.0	3.23	10.5	6.98
4.4	3.33	10.7	8.25
4.8	3.44	10.9	9.15
5.2	3.56	11.1	9.75
5.6	3.70	11.4	10.50
6.0	3.90	11.6	11.00
6.5	4.21		

TABLE -25

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}$M IN URANYL NITRATE AND $1.0x10^{-2}$M IN 5-SULPHO-SALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 % ALCOHOLIC MEDIUM.

IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 2, FIG. 26)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	2.37	11.6	4.58
0.8	2.47	12.0	5.05
1.6	2.56	12.2	5.20
2.4	2.68	12.6	5.37
3.2	2.86	13.0	5.45
4.0	3.01	13.6	5.65
4.8	3.13	14.0	5.80
5.6	3.26	14.4	6.02
6.4	3.36	15.0	6.48
7.2	3.47	15.4	7.18
8.0	3.65	15.6	7.93
8.8	3.80	15.8	8.73
9.6	3.97	16.0	9.45
10.0	4.10	16.2	10.14
10.4	4.20	16.4	10.64
10.8	4.32	16.6	11.05
11.2	4.43	16.8	11.28

TABLE - 26

TEMPERATURE = $30 \pm 1^{\circ}$C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-SALICYLATE SYSTEM AT pH 3.3 KEEPING THE TOTAL VOLUME CONSTANT BY THE ADDITION OF 50 PERCENT ALCOHOL.

IONIC STRENGTH=0.1M(KNO_3)

INITIAL(UO_2^{2+}+SALICYLIC ACID)CONCENTRATION=$4x10^{-3}$M

(FIGURE 27)

	Wave length=460 mμ			Wave length=500 mμ		
x	O.D. Complex	O.D. UO_2^{2+}	Diff.in O.D.	O.D. Complex	O.D. UO_2^{2+}	Diff.in O.D.
0.1	.034	.004	.030	.022	.002	.020
0.2	.054	.004	.050	.034	.003	.040
0.3	.070	.005	.065	.052	.004	.048
0.4	.082	.006	.076	.062	.005	.057
0.5	.092	.008	.084	.070	.006	.064
0.6	.090	.010	.080	.066	.008	.058
0.7	.079	.013	.066	.060	.010	.050
0.8	.066	.018	.048	.050	.012	.038
0.9	.048	.018	.030	.036	.014	.022

TABLE -27

TEMPERATURE = 30±1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-SALICYLATE COMPLEX AT pH 3.8 KEEPING THE TOTAL VOLUME (50 ML) BY THE ADDITION OF 50 PERCENT ALCOHOL.

IONIC STRENGTH = 0.1M(KNO_3)

INITIAL (UO_2^{2+}+ SALICYLIC ACID)CONCENTRATION=$4x10^{-3}$M

(FIGURE 27)

Wave length =460 mμ				Wave length = 500 mμ		
x	O.D. Complex.	O.D. UO_2^{2+}	Diff.in O.D.	O.D. Complex	O.D. UO_2^{2+}	Diff.in O.D.
0.1	.090	.005	.085	.064	.004	.060
0.2	.148	.006	.142	.113	.006	.107
0.3	.195	.008	.187	.153	.007	.146
0.4	.226	.009	.217	.170	.008	.162
0.5	.246	.010	.236	.190	.010	.180
0.6	.226	.015	.211	.170	.012	.168
0.7	.196	.018	.178	.150	.013	.137
0.8	.148	.020	.128	.110	.015	.095
0.9	.085	.022	.063	.07	.016	.054

TABLE -28

TEMPERATURE = 30±1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-SALICYLATE COMPLEX AT pH 4.3 KEEPING THE TOTAL VOLUME CONSTANT (50 ML) BY THE ADDITION OF 50 % ALCOHOL. IONIC STRENGTH=0.1M(KNO_3) INITIAL (UO_2^{2+} + SALICYLIC ACID) CONCENTRATION=$4x10^{-3}$M

(FIG.27)

	Wavel length=460mµ			Wave length=500 mµ			Wave length=520 mµ		
x	O.D. Complex	O.D. UO_2^{2+}	Diff.in O.D.	O.D. Complex	O.D. UO_2^{2+}	Diff. in O.D	O.D. Complex	O.D. UO_2^{2+}	Diff.in O.D.
0.1	.128	.008	.120	.092	.006	.086	.058	.004	.054
0.2	.240	.010	.230	.182	.008	.174	.125	.004	.121
0.3	.340	.012	.328	.256	.008	.248	.180	.005	.175
0.4	.376	.015	.371	.297	.009	.287	.205	.006	.200
0.5	.415	.018	.397	.318	.010	.308	.224	.006	.218
0.6	.375	.020	.355	.288	.012	.276	.195	.007	.188
0.7	.325	.022	.303	.244	.014	.230	.170	.008	.162
0.8	.236	.024	.208	.173	.015	.158	.120	.008	.112
0.9	.135	.025	.110	.093	.018	.075	.060	.010	.050

TABLE -29

TEMPERATURE = 30±1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-5-SULPHOSALICYLATE SYSTEM AT pH 3.3 KEEPING THE TOTAL VOLUME CONSTANT (50 Ml.) OF EACH SOLUTION BY THE ADDITION OF 50 PERCENT ALCOHOL, IONIC STRENGTH = 0.1M(KNO_3). INITIAL (UO_2^{2+} + 5-SSA)CONCENTRATION=$4x10^{-3}$M

(Fig. 28)

	Wave length = 460 mμ			Wave length = 500 mμ		
x	O.D. mixture	O.D. UO_2^{2+}	Diff.in O.D.	O.D. mixture	O.D. UO_2^{2+}	Diff.in OD
0.1	.087	.004	.083	.055	.002	.053
0.2	.159	.004	.155	.093	.003	.090
0.3	.205	.005	.200	.122	.004	.118
0.4	.236	.006	.230	.143	.005	.138
0.5	.258	.008	.250	.161	.006	.155
0.6	.238	.010	.228	.148	.008	.140
0.7	.214	.013	.201	.130	.010	.120
0.8	.170	.018	.152	.100	.012	.088
0.9	.102	.018	.084	.064	.014	.050

TABLE -30

TEMPERATURE = 30±1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-5-SULPHOSALICYLATE SYSTEM AT pH 3.80 KEEPING THE TOTAL VOLUME CONSTANT (50 ML) OF EACH SOLUTION BY THE ADDITION OF 50 % ALCOHOL. IONIC STRENGTH=0.1M(KNO_3). INITIAL(UO_2^{2+}+5-SSA)CONCENTRATION=$4x10^{-3}$M

(FIG. 28)

	Wave length=460 mμ			Wave length=500 mμ			Wave length = 520 mμ		
x	O.D. Mixture	O.D. UO_2^{2+}	Diff. in O.D.	O.D. Mixture	O.D. UO_2^{2+}	Diff. in O.D	O.D. Mixture.	O.D. UO_2^{2+}	Diff. in O.D.
0.1	.138	.005	.133	.074	.004	.070	.044	.004	.040
0.2	.252	.006	.246	.144	.006	.138	.078	.004	.074
0.3	.353	.008	.345	.207	.007	.200	.114	.005	.109
0.4	.417	.009	.408	.246	.008	.238	.135	.005	.130
0.5	.450	.010	.440	.268	.010	.258	.152	.005	.147
0.6	.425	.015	.410	.252	.012	.240	.136	.006	.130
0.7	.366	.018	.348	.213	.013	.200	.117	.007	.110
0.8	.263	.020	.243	.152	.015	.137	.080	.008	.072
0.9	.152	.022	.130	.084	.016	.068	.048	.009	.039

TABLE -31

TEMPERATURE = 30 ± 1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-5-SULPHOSALICYLATE SYSTEM AT pH 4.3 KEEPING THE TOTAL VOLUME CONSTANT (50 ML.) OF EACH SOLUTION BY THE ADDITION OF 50 PERCENT ALCOHOL. IONIC STRENGTH = 0.1M(KNO_3). INITIAL (UO_2^{2+}+ 5-SSA) CONCENTRATION = 4×10^{-3}M

(FIG. 28)

	Wave length = 460 m µ			Wave length = 500 m µ			Wave length =520 m µ		
x	O.D. mixture	O.D. UO_2^{2+}	Diff. in O.D.	O.D. mixture.	O.D. UO_2^{2+}	Diff. in O.D.	O.X. mixture.	O.D. UO_2^{2+}	Diff. in O.D.
0.1	.203	.008	.195	.123	.006	.117	.065	.004	.061
0.2	.370	.010	.360	.233	.008	.225	.142	.004	.138
0.3	.512	.012	.500	.323	.008	.315	.188	.005	.183
0.4	.608	.015	.593	.369	.009	.360	.229	.005	.224
0.5	.658	.018	.640	.392	.010	.382	.246	.006	.240
0.6	.605	.020	.585	.365	.012	.353	.227	.007	.220
0.7	.492	.022	.470	.304	.014	.290	.174	.008	.167
0.8	.368	.024	.344	.217	.015	.202	.128	.008	.120
0.9	.222	.025	.197	.124	.018	.106	.081	.010	.071

TABLE -32

TEMPERATURE = $30 \pm 1^{\circ}C$

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN URANYL NITRATE AND 2.5×10^{-3}M IN SALICYLIC ACID WITH 0.1M KOH IN 50 % ALCOHOLIC MEDIUM. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 2, FIG.30)

ML.of 0.1M KOH	pH	ML.of 0.1M KOH	pH
0.0	3.18	5.4	5.07
0.4	3.31	5.8	5.12
0.8	3.42	6.2	5.21
1.2	3.53	6.6	5.33
1.6	3.64	7.0	5.50
2.0	3.74	7.4	5.75
2.4	3.85	7.8	6.10
2.8	3.96	8.2	6.70
3.2	4.12	8.4	7.40
3.6	4.28	8.6	7.95
4.0	4.45	8.8	8.60
4.4	4.65	9.0	9.37
4.8	4.85	9.2	10.20
5.0	4.95	9.6	10.96
5.2	5.02		

TABLE - 33

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 200 ML. SOLUTION OF 1.25×10^{-3}M IN URANYL NITRATE AND 1.25×10^{-3}M IN SALICYLIC ACID WITH 0.1M KOH IN 50 % ALCOHOLIC MEDIUM. IONIC STRENGTH=0.1(KNO_3)

(CURVE 3, FIG.30)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	3.37	5.6	5.22
0.4	3.48	6.0	5.30
0.8	3.59	6.4	5.40
1.2	3.69	6.8	5.55
1.6	3.79	7.2	5.72
2.0	3.89	7.6	5.95
2.4	4.01	8.0	6.56
2.8	4.13	8.4	7.30
3.2	4.27	8.6	7.80
3.6	4.44	8.8	8.40
4.0	4.67	9.0	9.10
4.4	4.87	9.2	9.90
4.8	5.01	9.6	10.80
5.0	5.10	10.0	11.20
5.2	5.15		

TABLE - 34

TEMPERATURE = 30 ± 1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN URANYL NITRATE AND 2.5×10^{-3}M IN 5-SULPHO-SALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 PERCENT ALCOHOLIC MEDIUM. IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 2, FIG.31)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.73	7.5	5.06
0.4	2.80	8.0	5.15
0.8	2.85	8.5	5.30
1.2	2.90	9.0	5.45
1.6	2.95	9.5	5.68
2.0	3.02	10.0	6.00
2.5	3.09	10.4	6.60
3.0	3.16	10.6	7.35
3.5	3.27	10.8	8.20
4.0	3.39	11.0	8.65
4.5	3.50	11.2	9.37
5.0	3.64	11.4	10.20
5.5	3.85	11.6	10.70
6.0	4.08	11.8	10.94
6.5	4.42	12.0	11.14
7.0	4.76		

TABLE - 35

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 200 ML. SOLUTION OF 1.25×10^{-3}M IN URANYL NITRATE AND 1.25^{3}M IN 5-SULPHO-SALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE IN 50 % ALCOHOLIC MEDIUM

IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 3, FIG.31)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	3.00	7.0	4.90
0.4	3.05	7.5	5.16
0.8	3.10	8.0	5.30
1.2	3.15	8.5	5.42
1.6	3.20	9.0	5.53
2.0	3.25	9.5	5.75
2.4	3.30	10.0	6.01
2.8	3.35	10.4	6.60
3.2	3.40	10.6	7.23
3.6	3.48	10.8	7.75
4.0	3.57	11.0	8.45
4.6	3.72	11.2	8.98
5.0	3.84	11.4	9.75
5.5	4.05	11.6	10.25
6.0	4.28	11.8	11.65
6.5	4.60	12.0	10.95

(iii) URANYL CHELATES OF 1-HYDROXY - 2- NAPHTHALDEHYDE

POTENTIOMETRIC STUDIES

TABLE - 36

TEMPERATURE = 28 ± 1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}M$ IN 1-HYDROXY-2-NAPHTHALDEHYDE WITH 0.1M POTASSIUM HYDROXIDE IN 50 PERCENT ALCOHOLIC MEDIUM. IONIC STRENGTH = 0.1M(KNO_3)
(CURVE O, FIG.32)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	5.53	1.6	8.27
0.1	6.66	1.8	8.42
0.2	7.00	2.0	8.60
0.3	7.18	2.2	8.82
0.4	7.30	2.4	9.25
0.6	7.52	2.5	9.64
0.8	7.67	2.6	10.44
1.0	7.84	2.7	10.78
1.2	8.01	2.8	11.00
1.4	8.12	3.0	11.24

TABLE -37

TEMPERATURE = 28 ± 1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN URANYL NITRATE AND 5×10^{-3}M IN 1-HYDROXY-2-NAPHTHALDEHYDE WITH 0.1M POTASSIUM HYDROXIDE IN 50 PERCENT ALCOHOLIC MEDIUM. IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 1, FIG.32)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	3.26	5.8	6.00
0.4	3.53	6.0	6.70
0.8	3.74	6.2	7.15
1.0	3.85	6.4	7.50
1.4	4.00	6.6	7.70
1.8	4.13	6.8	7.90
2.2	4.26	7.2	8.20
2.6	4.35	7.6	8.50
3.0	4.40	8.0	8.76
3.4	4.44	8.6	9.13
3.8	4.47	9.0	9.60
4.2	4.51	9.2	9.80
4.6	4.55	9.4	10.22
5.0	4.62	9.6	10.70
5.4	4.80	9.8	11.00
5.6	5.16	10.0	11.26

TABLE -38

TEMPERATURE = 28 ± 1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}$M IN URANYL NITRATE AND $1.0x10^{-2}$M IN 1-HYDROXY-2-NAPHTHALDEHYDE WITH 0.1M POTASSIUM HYDROXIDE IN 50 PERCENT ALCOHOLIC MEDIUM, IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 2, FIG.32)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	3.10	5.6	7.88
0.4	3.32	6.0	8.10
0.8	3.53	6.5	8.30
1.2	3.72	7.0	8.50
1.6	3.90	7.5	8.65
2.0	4.08	8.0	8.70
2.4	4.20	8.5	8.76
2.8	4.30	9.0	8.81
3.2	4.37	9.5	8.89
3.6	4.40	10.0	9.00
4.0	4.45	10.5	9.10
4.4	4.56	11.0	9.25
4.8	4.90	11.4	9.57
5.0	5.50	11.6	9.80
5.1	6.05	11.8	10.25
5.2	7.20	12.2	10.98
5.4	7.70	12.4	11.25

TABLE -39

TEMPERATURE = 28 ± 1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}$M IN URANYL NITRATE AND $1.5x10^{-2}$M IN 1-HYDROXY-2-NAPHTHALDEHYDE WITH 0.1M KOH IN 50 PERCENT ALCOHOLIC MEDIUM. IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 3, FIG.32)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	3.06	6.4	8.08
0.5	3.25	7.0	8.32
1.0	3.45	7.5	8.50
1.5	3.68	8.2	8.70
2.0	3.93	9.0	8.80
2.5	4.10	10.0	8.96
3.0	4.20	11.0	9.17
3.5	4.26	11.5	9.25
4.0	4.34	12.0	9.30
4.5	4.50	12.5	9.45
4.8	4.81	13.0	9.90
5.0	5.48	13.2	10.20
5.1	6.45	13.4	10.50
5.2	7.00	13.6	10.83
5.4	7.30	13.8	11.20
5.6	7.55	14.0	11.32
6.0	7.82		

TABLE -40

TEMPERATURE =28 ± 1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5x10^{-3}M IN URANYL NITRATE AND 2.5x10^{-3}M IN 1-HYDROXY-2-NAPHTHALDEHYDE WITH 0.1M POTASSIUM HYDROXIDE IN 50 PERCENT ALCOHOLIC MEDIUM. IONIC STRENGTH = 0.1M (KNO_3)

(Curve 1', FIG. 32)

ML.OF 0.1M KOH	pH	ML.OF 0.1M KOH	pH
0.0	3.50	5.8	6.35
0.4	3.73	6.0	6.85
0.8	3.93	6.2	7.05
1.2	4.12	6.4	7.30
1.6	4.25	6.8	7.65
2.0	4.40	7.2	7.96
2.4	4.50	7.6	8.22
2.8	4.55	8.0	8.48
3.2	4.58	8.4	8.80
3.6	4.60	8.6	9.04
4.0	4.63	9.0	9.40
4.4	4.66	9.4	10.00
4.8	4.75	9.6	10.50
5.2	4.90	9.8	10.85
5.4	5.25	10.0	11.08
5.6	5.82	10.2	11.30

TABLE -41

TEMPERATURE = 28 ± 1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL NITRATE 1-HYDROXY-2-NAPHTHALDEHYDE MIXTURES KEEPING THE TOTAL VOLUME CONSTANT (50 ML.) OF EACH SOLUTION BY THE ADDITION OF 50 PERCENT ALCOHOL IONIC STRENGTH = 0.1M(KNO_3). INITIAL (UO_2^{2+} + 1-HYDROXY-2-NAPHTHALDEHYDE) CONCENTRATION = $2x10^{-3}M$

(FIG. 33)

	At pH 3.3		At pH 3.8	
x	λ =450 mμ O.D. mix	λ =470 m μ O.D. mix	λ =450 m μ O.D. mix	λ =470 m μ O.D. mix
0.1	.040	.035	.075	.062
0.2	.060	.050	.130	.101
0.3	.080	.063	.170	.130
0.4	.088	.073	.190	.150
0.5	.100	.079	.210	.170
0.6	.085	.074	.196	.155
0.7	.075	.061	.175	.135
0.8	.059	.055	.136	.108
0.9	.042	.040	.079	.070

TABLE -42

TEMPERATURE = 28 ± 1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL NITRATE-HYDROXY-2-NAPHTHALDEHYDE MIXTURES KEEPING THE TOTAL VOLUME CONSTANT (50 ML.) OF EACH SOLUTION BY THE ADDITION OF 50 PERCENT ALCOHOL. IONIC STRENGTH = 0.1M (KNO_3)

INITIAL (UO_2^{2+} + 1-HYDROXY-2-NAPHTHALDEHYDE)CONCENTRATION = $2x10^{-3}$M

(FIG. 33)

	At pH 4.3		At pH 4.8	
x	λ =450 m μ O.D.mixture	λ =470 m μ O.D.mixture	λ =450 m μ O.D. mixture	λ =470 m μ O.D. mixture
0.1	.180	.135	.270	.202
0.2	.270	.215	.401	.301
0.3	.325	.275	.480	.362
0.4	.401	.300	.520	.392
0.5	.415	.320	.540	.415
0.6	.370	.285	.460	.330
0.7	.350	.270	.430	.300
0.8	.260	.220	.330	.240
0.9	.176	.140	.260	.165

PART IV

CHELATES OF URANIUM (VI) WITH CATECHOL

CHAPTER I : RESULTS AND DISCUSSION
Uranyl chelates of catechol

CHAPTER II: EXPERIMENTAL
Uranyl chelates of catechol

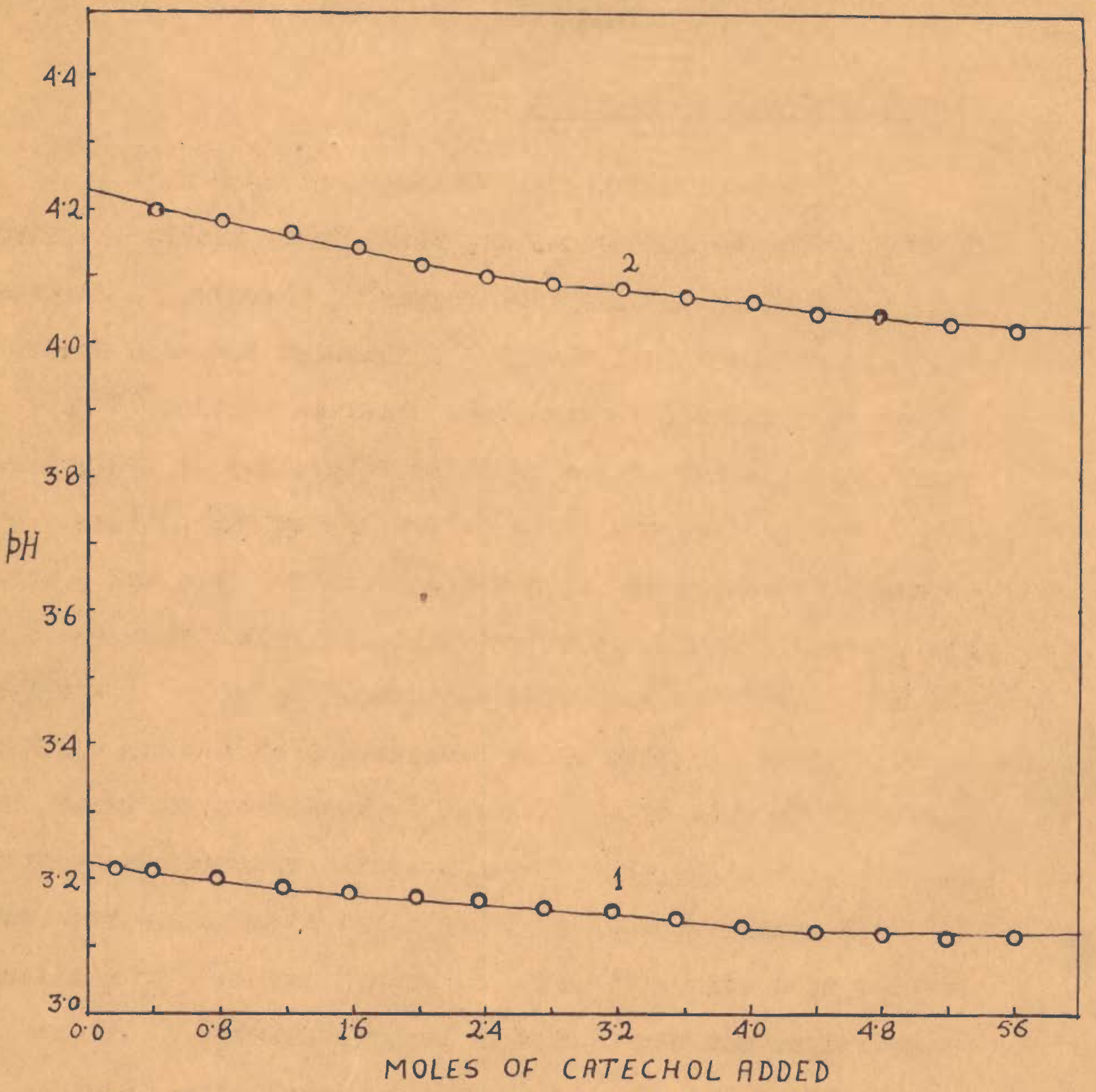


Fig. 34. Potentiometric titrations of 20 ml. of 2.5×10^{-2} M uranyl nitrate with 0.25 M. Catechol solution in the presence of 0 (Curve 1) and 1 (Curve 2) moles of potassium hydroxide per mole of uranyl ion.

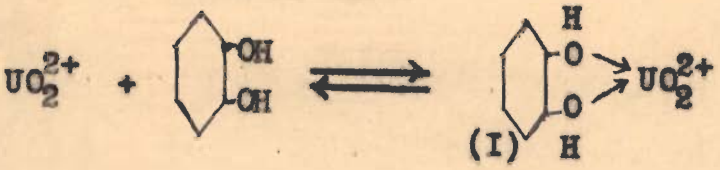
CHAPTER - I

URANYL CHELATES OF CATECHOL

Catechol, o-dihydroxy benzene, gives a five membered ring on chelation. It, thus, forms stable chelates with a number of cations like copper[89], chromium[90], aluminium[91], zirconium[92] and thorium[93]. Although catechol derivatives of uranium (VI) have been reported earlier[94-97], a quantitative study of the equilibria involved in their formation does not appear to be undertaken by the earlier workers. Rosenheim and co-workers[95] in 1931 isolated a number of uranyl complexes of catechol. Recently Shnaiderman and Galinker[96] have reported the formation of a 1:1 complex up to a pH of 5, above which interaction of the 1:1 chelate with another mole of the ligand has been shown to occur. More recently, Misra et al.[97] have, however, reported the formation of a 1:2 complex below pH 5 in a 1:2 uranyl-catechol system. In view of a strong tendency of uranyl ion and its chelates to hydrolyze and polymerize in aqueous solutions, it was considered of interest to carry out a systematic physicochemical study of the above system. Attempts were also made to determine stability and polymerization constants of the chelates.

RESULTS AND DISCUSSION

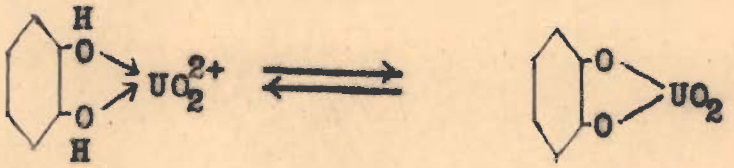
Curves 1 and 2 (Fig.34) show that pH of the uranyl nitrate solution falls by the addition of catechol indicating chelation of the type:



(I)

(i)

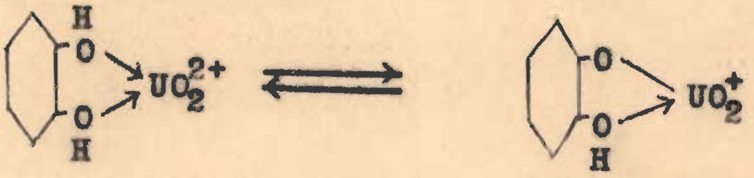
This chelation by the donation of lone pair of electrons from the hydroxy oxygen atoms of the ligand makes the hydrogen atoms more labile and acidic. Protons of both the phenolic groups of catechol may then either dissociate simultaneously :



(II)

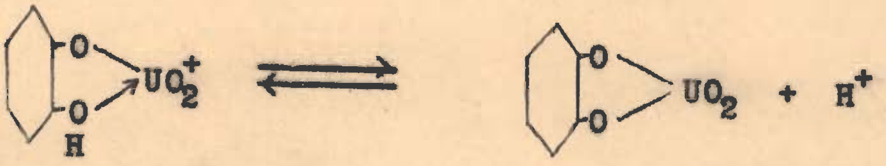
(ii)

or may ionize in two overlapping steps:



(III)

(iii)



(iv)

In view of the hydrolyzable nature of the uranyl ions at pH > 3, formation of the hydroxo chelate species in the system also cannot be ruled out.

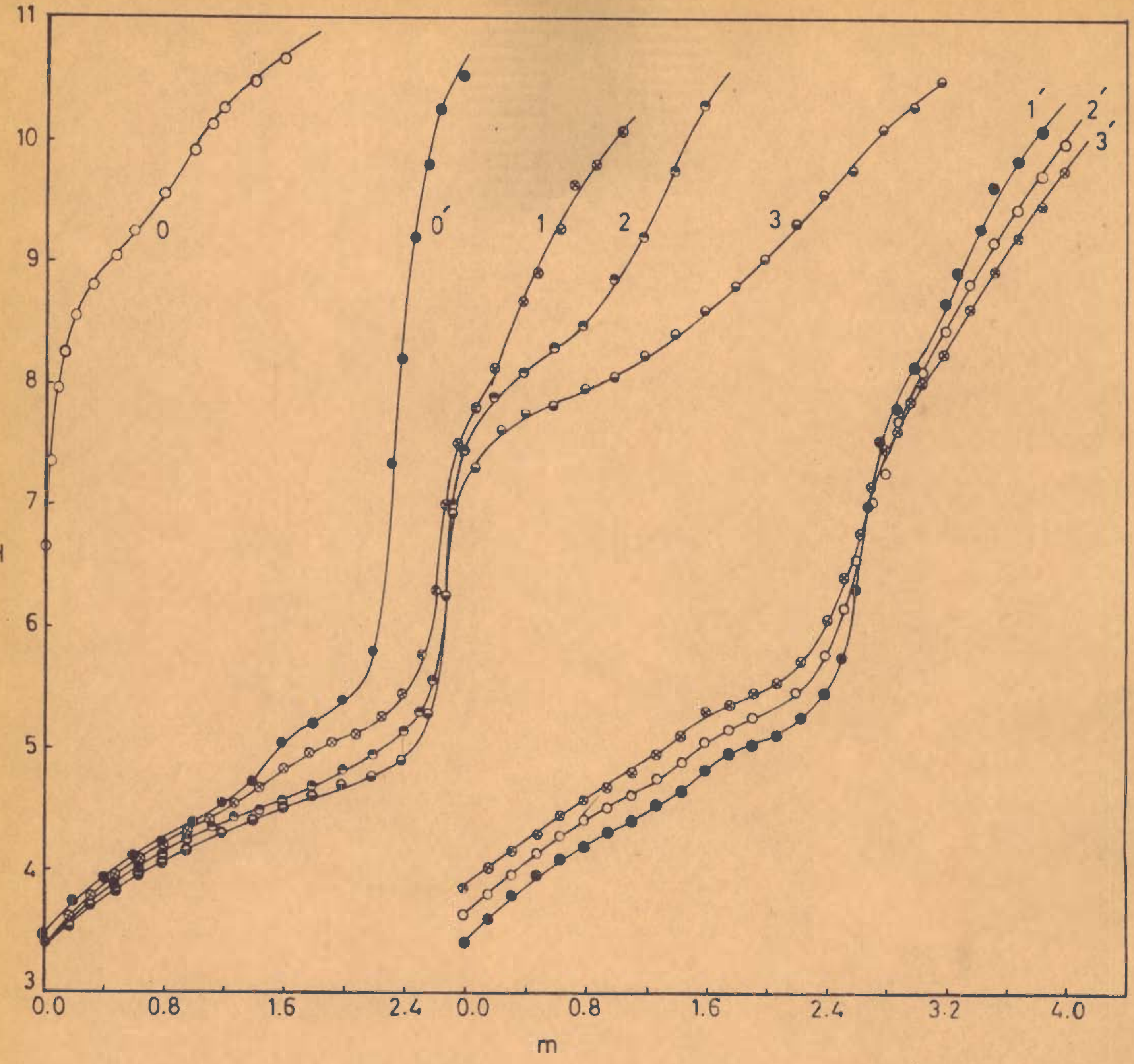


Fig.35. Potentiometric titrations of uranyl-catecholate chelate system with KOH(0.1N): Curves 1,2 and 3 represent titrations of 1:1, 1:2 and 1:3 uranyl nitrate-catechol mixtures respectively (T_M = 0.005M). Curves 0 and 0' represent titrations of catechol (0.005M) and uranyl nitrate (0.005M) respectively. Curves 1',2' and 3' represent titrations of equimolar mixtures of uranyl nitrate and catechol. Concentrations of uranyl nitrate: Curve 1', 5×10^{-3}M; Curve 2', 2.5×10^{-3}M; Curve 3', 1.25×10^{-3}M. m = moles of base added per mole of the metal ion. μ = 0.1M (KNO_3).

In order to study the above reaction, uranyl nitrate solution was titrated with potassium hydroxide solution in the presence of different molar concentrations of catechol. Curves 1,2 and 3 (Fig. 35) for the potentiometric titrations of reaction mixtures containing 1:1, 1:2 and 1:3 molar ratios of uranyl nitrate to catechol respectively with KOH exhibited a sharp inflexion at $m = 2\frac{2}{3}$. A similar nature of these curves in the acid medium with a common inflexion point indicated formation of a 1:1 complex only under the experimental conditions. This conclusion is supported by the work of Shnaiderman and Galinker[96]. Misra et al.[97] have, however, reported the formation of a 1:2 complex in the lower buffer region of the potentiometric curve obtained by the titration of a 1:2 mixture of uranyl acetate and catechol.

In view of the above and a red colour produced by the addition of catechol to uranyl nitrate solution, it was considered of interest to investigate the uranyl-catechol system spectrophotometrically. In figure 36 are presented the continuous variations data obtained at pH values of 3.7 and 4.5. In both cases, at each wave length studied (370-480 mμ), maximum absorbance was observed for solutions containing approximately equivalent amounts of catechol and the metal ion, thus, supporting the conclusion of the potentiometric study of the formation of 1:1 complex in acid medium.

Further confirmation of the stoichiometry of the chelate was obtained by the isolation of the precipitates obtained by the addition of $2\frac{2}{3}$ moles of KOH per mole of uranyl ion (moles of base required for the first inflexion point in potentiometric titrations) to the reaction mixtures containing 1:1, 1:2 and 1:3 molar ratio of uranyl nitrate to catechol. Analysis of the precipitated derivative, in all the three cases, corresponded to a combining ratio of uranyl to catechol of approximately 1:1, confirming the formation of a 1:1 complex in the lower buffer region of the potentiometric curves.

On the basis of reaction of the type (ii) alone, the potentiometric titration curves (Fig.35) would have exhibited an inflexion point at $m = 2.0$. The occurrence of inflexion points at $m = 2\frac{2}{3}$ indicated that (II) is not the final product of the reaction. Like uranyl-mandelate and -lactate chelate systems, in this case also, an extra consumption of $\frac{2}{3}$ mole of alkali per mole of the metal ion together with the establishment of the stoichiometry of 1:1 of the complex, appears to indicate polymerization of the metal chelate which involves the use of hydroxyl ions.

Mathematical Treatment of the Data

In view of the interesting nature of the potentiometric curves (Fig.35), it was considered worthwhile to carry out a mathematical analysis of the data. In order to investigate polymerization of the metal chelate, potentiometric titrations of equimolar mixtures of uranyl nitrate and catechol were carried out over a four-fold concentration range of the metal salt.

If H_2A represents catechol, considering reaction of the types (i-ii), which may be represented as:

$$UO_2^{2+} + H_2A \rightleftharpoons UO_2A + 2H^+$$

the equilibrium constant, K , for the reaction may be expressed as

$$K = \frac{[UO_2A]\ [H^+]^2}{[UO_2^{2+}]\ [H_2A]} \qquad (59)$$

In order to account for the amount of the hydrolyzed species of the uncomplexed uranyl ions present in the system, use was made of the value of the hydrolysis constant, K_2 , equal to $10^{-5.84}$, reported by Gustafson et al.[33], where K_2 is defined by equation (12) given in the uranyl-mandelate system.

From the usual material balance we obtain:

$$T_M = [UO_2] + 2\,[(UO_2\ OH)_2] + [UO_2A] \qquad (60)$$

$$T_{OH} + [H^+] = 2[(UO_2\ OH)_2] + 2[UO_2A] \qquad (61)$$

and

$$T_A = [H_2A] + [UO_2A] \qquad (62)$$

Charges on the metal species have been eliminated for the sake of clarity.

In the lower buffer region of the potentiometric curves, concentrations of HA^-, A^{2-} and OH^- were negligible as compared to those of the other species present in the system.

Elimination of $[UO_2A]$ between (60) and (61) gives

$$2T_M - T_{OH} - [H^+] = 2[UO_2] + 2[(UO_2\ OH)_2)] \qquad (63)$$

Combining equations (63) and (12) (see page26) and rearranging the terms in the form of a quadradic equation, we obtain

$$\frac{K_2}{[H^+]^2}[UO_2]^2 + [UO_2] - \left\{T_M - \frac{1}{2}(T_{OH} + [H^+])\right\} = 0 \qquad (64)$$

Concentration of the uncomplexed uranyl ions present in the system may, therefore, be given by

$$[UO_2] = \frac{-1 \pm \sqrt{1+4ac}}{2a} \qquad (64')$$

where

$$a = \frac{K_2}{[H^+]^2} \quad \text{and} \quad c = T_M - \frac{1}{2}(T_{OH} + [H^+])$$

After computation of $[UO_2]$, concentration of $[UO_2(OH)_2UO_2]$ may be determined from equation (12). Amount of the other species present in the solution may then be calculated algebraically from equations (60) and (62). The values of -log K, calculated from various points on the lower buffer region of potentiometric curves 1-3(Fig.35) are presented in table XXI.

Table XXI

Curve 1 and 1' (Fig.35), $T_A = T_M = 5x10^{-3}M$
Initial volume of reaction mixture = 50 ml.

KOH(ml.)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2
pH	3.51	3.61	3.71	3.79	3.87	3.94	4.01	4.08	4.14	4.20	4.25
-log K	6.40	6.41	6.44	6.42	6.44	6.41	6.39	6.36	6.35	(6.30	6.20)

Mean value of -log K = 6.40 ± 0.05
(   ) values not included in average.

Curve 2 (Fig.35), $T_A = 2T_M = 1.0x10^{-2}M$
Initial volume of reaction mixture = 50 ml.

KOH(ml.)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4
pH	3.46	3.56	3.65	3.73	3.80	3.86	3.93	3.99	4.06	4.12	4.18	4.24
-log K	6.40	6.39	6.40	6.42	6.42	6.40	6.42	6.42	6.44	6.43	6.44	6.43

Average value of -log K = 6.42±0.02

Curve 3 (Fig.35), $T_A = 3T_M = 1.5x10^{-2}M$

KOH(ml.)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4
pH	3.43	3.53	3.61	3.69	3.76	3.82	3.88	3.93	3.99	4.06	4.12	4.16
-log K	6.41	6.42	6.41	6.44	6.45	6.44	6.44	6.43	6.45	6.45	6.45	6.44

Average value of -log K = 6.43± 0.02

Constant values of -log K, obtained up to pH of about 4.2 (table XXI), indicated that the normal 1:1 chelate, $[UO_2A]$, is only formed under the experimental conditions, irrespective of the amount of catechol present in the system.

In order to investigate polymerization of the chelate, values of the equilibrium constants were determined over a four-fold concentration range. These values, calculated from the potentiometric data Of curves 2' and 3' (Fig.35) are given in table XXII.

Table XXII

Curve 2' (Fig. 35), $T_A = T_M = 2.5 \times 10^{-3}M$

Initial volume of reaction mixture = 100 ml.

KOH(ml.)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2
pH	3.71	3.80	3.89	3.97	4.05	4.14	4.21	4.27	4.34	4.40	4.45
-log K	6.56	6.56	6.57	6.55	6.56	6.53	6.53	6.52	6.51	(6.45	6.38)

Average value of -log K = 6.54 ± 0.03

( ) values not included in average.

Curve 3' (Fig.35), $T_A = T_M = 1.25 \times 10^{-3}M$

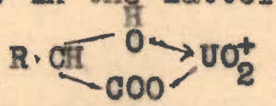
Initial volume of reaction mixture = 200 ml.

KOH(ml.)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
pH	3.93	4.00	4.07	4.15	4.22	4.30	4.37	4.45	4.52	4.58
-log K	6.68	6.67	6.66	6.67	6.63	6.65	6.63	6.65	6.62	(6.51)

Average value of -log K = 6.65 ± 0.03

( ) Values not included in average.

Comparison of the values of -log K, obtained in tables XXI and XXII shows that there is a gradual increase in the average values of -log K with a decrease in the total concentration of the metal salt. Such a trend is an indication of polymerization of the chelate.

It is considered of interest to compare this system with the corresponding mandelate and lactate systems (Part II, Chapter I). In the latter systems, the normal chelate species,  $R\cdot CH\begin{matrix}\overset{H}{O}\rightarrow\\ COO\nearrow\end{matrix}UO_2^+$, did not give any indication for polymerisation. They only appeared to polymerize through hydrolysis, i.e., through OH bridges. But in this system, polymerization of the normal chelate, UO_2A, indicated above, leads to the possibility of condensation through phenolic oxygen atoms of catechol. Such a behaviour is not abnormal in view of polymerization of the tiron derivatives of uranium (VI)[33] and thorium (IV). In these cases also polymerization of the chelates through phenolic oxygen atoms of the ligand has been reported.

Stability of the Chelate:

The stability constant, k, of the chelate UO_2A :

$$UO_2^{2+} + A^{2-} \rightleftharpoons UO_2A$$

may be defined as:

$$k = \frac{[UO_2A]}{[UO_2^{2+}][A^{2-}]} \qquad (65)$$

If K_{a_1} and K_{a_2} represent dissociation constants of catechol (H_2A), we have

$$K_{a_1} = \frac{[H^+][HA^-]}{[H_2A]} \qquad (66)$$

and

$$K_{a_2} = \frac{[H^+]\ [A^{2-}]}{[HA^-]} \qquad (67)$$

Combination of (65), (66), (67) and (59) gives

$$k = \frac{K}{K_{a_1}\ K_{a_2}} \qquad (68)$$

Substitution of the values of K (Average value from tables XXI and XXII is equal to 3.24×10^{-7}), K_{a_1} (6.31×10^{-10}) and K_{a_2} (1.18×10^{-12})$^{\text{ref.98}}$ in equation (68) gave a value of 4.35×10^{14} for the stability constant of the chelate.

Dimerization of the Chelate:

Polymerization of the chelate, indicated by the concentration dependence of pK (tables XXI and XXII), would possibly involve an intermediate formation of a dimer. Attempts were, therefore, made to analyze the titration data, in the range $m = 0$ to $m = 0.8$ which gives constant values of $-\log K$, on the basis of the reaction :

$$2UO_2^{2+} + 2H_2A \rightleftharpoons \underset{(IV)}{(UO_2A)_2} + 4H^+ \qquad (v)$$

The equilibrium constant, K_D, of the reaction may be expressed as

$$K_D = \frac{[(UO_2A)_2]\ [H^+]^4}{[UO_2^{2+}]^2\ [H_2A]^2} \tag{69}$$

Other pertinent equations are:

$$T_M = [UO_2]+2[(UO_2OH)_2]+[UO_2A]+2[(UO_2A)_2] \tag{70}$$

$$T_{OH} + [H^+] = 2\ [(UO_2\ OH)_2] + 2\ [UO_2A] + 4[(UO_2A)_2] \tag{71}$$

$$T_A = [H_2A] + [UO_2A] + 2\ [(UO_2A)_2] \tag{72}$$

Combination of (59), (69), (70) and (12) yields

$$\frac{T_M - [UO_2] - \dfrac{2.89\text{x}10^{-6}}{[H^+]^2}[UO_2]^2}{\dfrac{[UO_2]\ [H_2A]}{[H^+]^2}} = 2K_D \frac{[UO_2][H_2A]}{[H^+]^2} + K \tag{73}$$

In this case also, it may be shown that the concentration of the uncomplexed uranyl ions present in solution, $[UO_2]$, may be determined by using (64'). $[H_2A]$ may then be easily calculated with the help of equations (70) and (72).

It is evident from equation (73) that a plot on the left side of the equation (73) against the corresponding values of $[UO_2]\ [H_2A] \,/\, [H^+]^2$ should give a straight line of slope $2K_D$ and the intercept on Y-axis equal to K, if the chelate undergoes dimerization as postulated in reaction (v). Likewise it may be shown that a plot of the

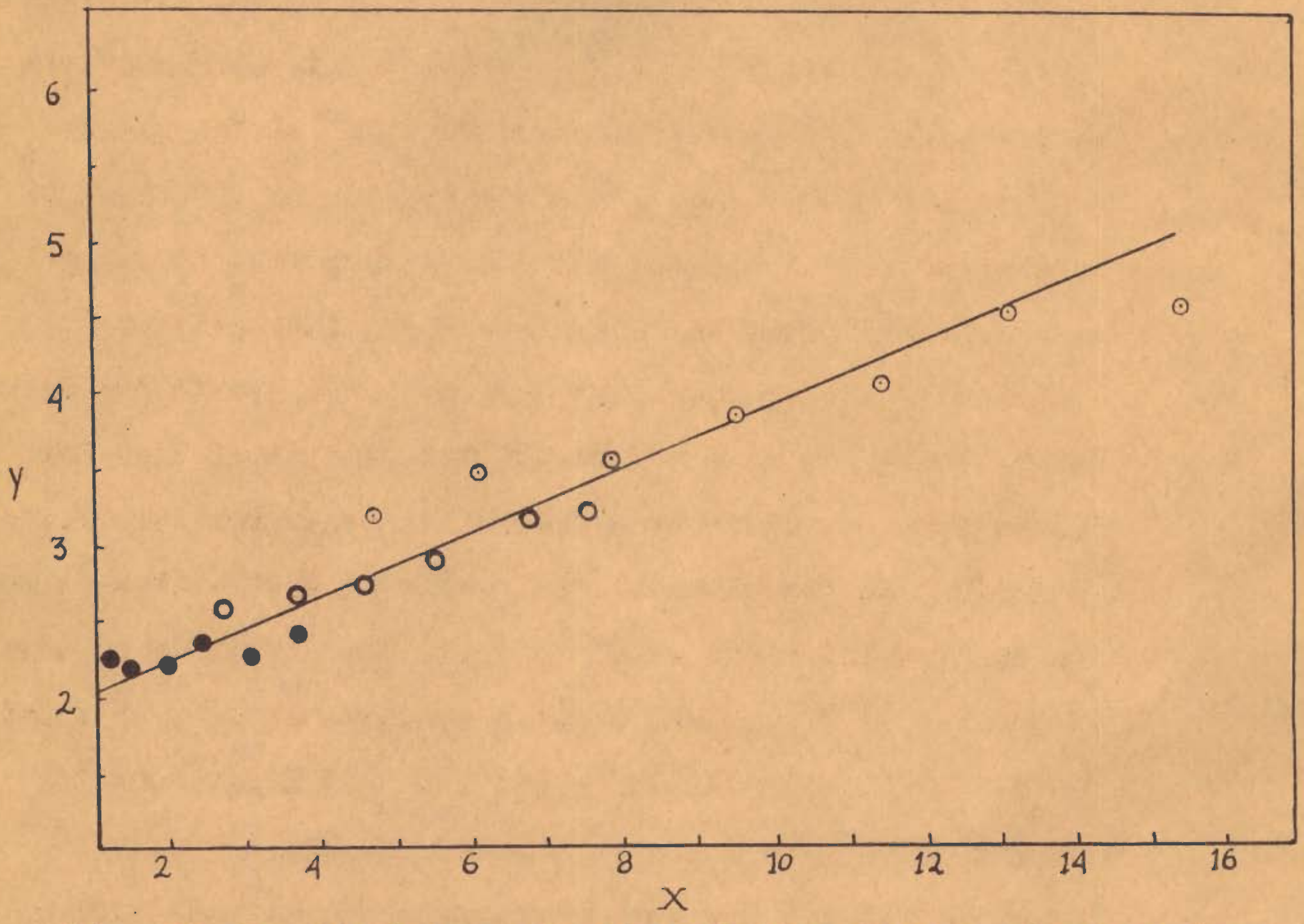


Fig. 37. Graphical demonstration of dimerization of mono-hydroxo-uranyl-catecholate chelate:

$$X = \frac{[UO_2]\ [H_2A]}{[H^+]^2} \times 10^2, \quad Y = \frac{\left\{T_M - [UO_2] - \frac{2.39\times10^{-6}}{[H^+]^2}\ [UO_2]^2\right\}}{[UO_2]\ [H_2A]\ /\ [H^+]^2} \times 10^{-7}$$

Concentrations: ⊙, 5×10^{-3}M; O, 2.5×10^{-3}M ; ●, 1.25×10^{-3}M

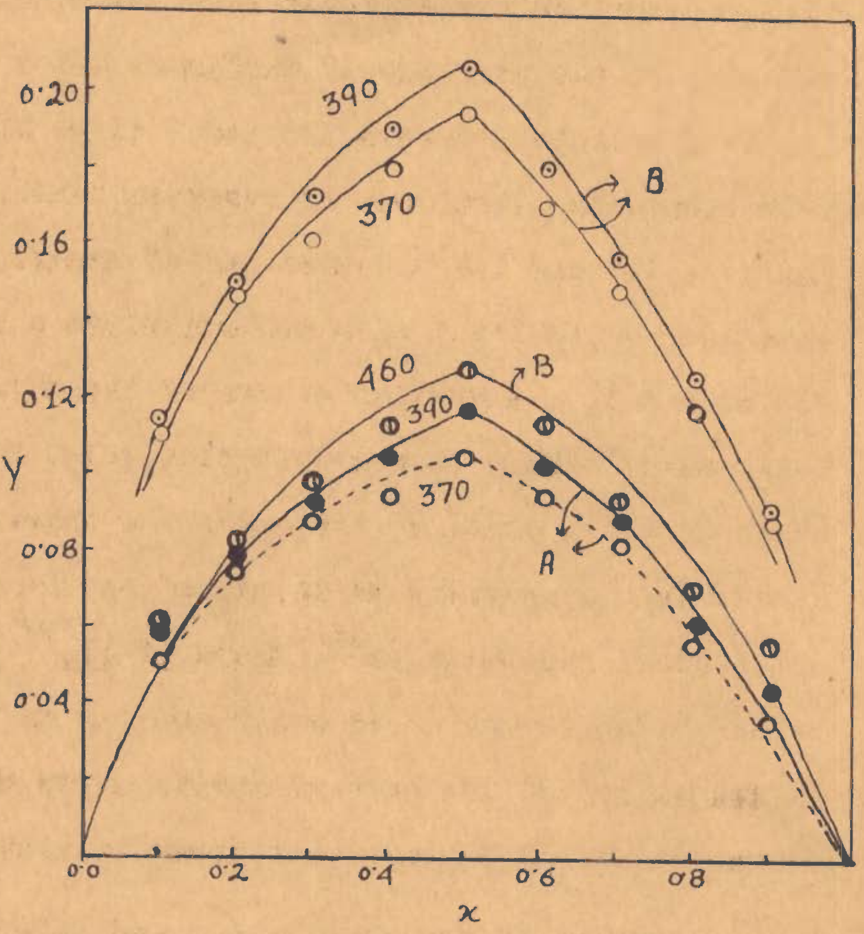


Fig. 36. Method of continuous variations applied to uranyl-catecholate system at different pH: (A) pH 3.7; (B) pH 4.5. $(T_A + T_M)$ for each solution = 0.004M; ionic strength = 0.1M(KNO_3). Abscissa x represents the added molar ratio $T_M/(T_M+T_A)$. Ordinate Y is the difference between the observed absorbance and that which would be by uranyl nitrate if no complexation reaction occurred.

values of the expression on the left side of equation (73) against the corresponding values $[UO_2]^2[H_2A]^2/[H^+]^4$ should yield a straight line, if a trimer is the predominant species present in the solution. A plot of the potentiometric data in the range m = 0 to m = 0.8, obtained over a four-fold concentration range (Fig.35) of the metal chelate, in accordance with equation (v) is presented in figure 37. A slight scattering of points seen in figure (37) probably indicates the presence of small amounts of other species in the system which have not been considered in the above treatment of the data. It was also found that the plots were sensitive to hydrogen ion concentration of the solution. An experimental pH error of 0.02 unit produced an appreciable shift of the points. Consideration of the formation of ternuclear chelate species showed much greater deviation from the linear plot. The best line shown in figure (37), however, gave a value of -log K = 6.68 and -log K_D = 10.00. The former value, compares well with a value -log K = 6.54 (curves 1', 2' and 3'; tables XXI and XXII), obtained when dimerization of the chelate is not considered.

<u>Hydrolysis of the Dimer:</u>

A gradual fall in the values of -log K calculated above m = 0.8 (tables XXI and XXII) and the occurrence of an inflexion point in curves 1-3 (Fig. 35) at m = $2\frac{2}{3}$ indicated hydrolysis of the chelate with the formation of hydroxo complexes in the system. If, in the initial stages of hydrolysis, the reaction is represented as :

$$(UO_2A)_2 + H_2O \rightleftharpoons \underset{(V)}{(UO_2A)_2(OH)^-} + H^+ \qquad (vi)$$

The hydrolysis constant, K_h, may then be expressed as:

$$K_h = \frac{[(UO_2A)_2(OH)^-]\ [H^+]}{[(UO_2A)_2]} \qquad (74)$$

Other pertinent equations are:

$$T_M = [UO_2] + 2[(UO_2OH)_2] + [UO_2A] + 2[(UO_2A)_2] + 2[(UO_2A)_2(OH)^-] \qquad (75)$$

$$T_{OH} + [H^+] = 2\ [(UO_2OH)_2] + 2[UO_2A] + 4[(UO_2A)_2] + 5[(UO_2A)_2(OH)] \qquad (76)$$

and

$$T_A = [H_2A] + [UO_2A] + 2[(UO_2A)_2] + 2[(UO_2A)_2(OH)] \qquad (77)$$

Elimination of $[(UO_2A)_2(OH)]$ between (74) and (75) gives

$$5T_M - 2T_{OH} - 2[H^+] = 5[UO_2] + 6[(UO_2OH)_2] + [UO_2A] + [(UO_2A)_2] \qquad (78)$$

In reaction mixtures containing an equimolar concentration of uranyl nitrate and catechol, since $T_A = T_M$, from equations (75) and (77) we obtain

$$[H_2A] = [UO_2] + 2[(UO_2OH)_2] \qquad (79)$$

Combining equations (12), (59), (69), (78) and (79) and rearranging the terms into the form of a polynomial gives

$$\frac{8K_2^2\ K_D}{[H^+]^8}[UO_2]^6 + \frac{8K_2\ K_D}{[H^+]^6}[UO_2]^5 + \frac{2K_D}{[H^+]^4}[UO_2]^4 + \frac{2K_2K}{[H^+]^4}[UO_2]^3 + \left(\frac{6K_2 + K}{[H^+]^2}\right)[UO_2]^2 + 5[UO_2] - \left\{5T_M - 2T_{OH} - 2[H^+]\right\} = 0 \qquad (80)$$

Knowing the values of K (tables XXI and XXII), K_D (Fig.36) and K_2 (expression 12), concentration of the uncomplexed uranyl ions in the solution can be determined by solving the above polynomial equation, using the Newton's method of successive approximations. Concentrations of the other species present in the system may then be calculated easily with the help of equations given above. The values of pK_h thus obtained from the potentiometric data of curves 1'-3' (Fig. 35) are presented in table XXIII.

Table XXIII

Curve 1' (Fig.35), $T_A = T_M = 5x10^{-3}M$

KOH(ml.)	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2
pH	4.34	4.40	4.46	4.53	4.60	4.67	4.75	4.83	4.92
$-\log K_h$	5.35	5.29	5.23	5.26	5.28	5.24	5.26	5.23	(5.15)

Average value of $-\log K_h = 5.29 \pm 0.06$

(   ) value not included in average.

Curve 2' (Fig.35); $T_A = T_M = 2.5\times10^{-3}M$

KOH(ml.)	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2
pH	4.54	4.60	4.67	4.74	4.82	4.89	4.98	5.06	5.14
-log K_h	5.53	5.50	5.54	5.50	5.50	5.43	5.48	5.44	(5.35)

Average value of -log K_h = 5.49±0.06
( ) value not included in average.

Curve 3' (Fig.35); $T_A = T_M = 1.25\times10^{-3}M$

KOH(ml.)	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2
pH	4.73	4.80	4.88	4.96	5.04	5.12	5.21	5.30	5.39
-log K_h	5.68	5.70	5.67	5.74	5.72	5.68	5.69	5.67	(5.55)

Average value of -log K_h = 5.69±0.05
( ) value not included in average.

The success thus obtained in calculating the equilibrium constant K_h seems to strengthen somewhat the validity of the original assumptions involved. Here also a gradual increase in the average values of -log K_h (Table XXIII) with the decrease of total concentration of UO_2^{2+} ions in solution confirms the polymerization of chelate.

A gradual fall in the values of -log K_h observed in table XXIII above 'm' values of about 1.6 indicates further hydrolysis of the chelate. Further, an inflexion point at $m = 2\frac{2}{3}$, exhibited by the potentiometric curves (Fig.35) may be accounted for on the basis of the reaction of the type:

$$3(UO_2A)_2(OH)^- + H_2O \rightleftharpoons \underset{(VI)}{2(UO_2A)_3\,(OH)_2^{2-}} + H^+ \qquad \text{(vii)}$$

An evidence for the formation of the chelate species of the type VI would be forthcoming from the calculation of the equilibrium constant of the reaction (vii) but unfortunately the formation of solid phase in the system warranted these calculations.

The ionic polynuclear chelate species bear a charge of minus two. In the solid state it would be associated with two unipositive radicals. An equimolar mixture of uranyl nitrate and catechol was, therefore, treated with $2\frac{2}{3}$ moles of ammonium hydroxide solution per mole of uranyl ion. Analysis of the precipitated compound, after a careful washing and drying, corresponded to a ratio of catechol to uranyl of 0.95 and that for ammonium to uranyl of 0.64. These experimentally determined combining ratios are in close agreement with the corresponding values of 1.0 and 0.67 respectively required for the compound $(NH_4)_2\ [(UO_2A)_3(OH)_2]$. This, thus, offers a direct evidence for the presence of the chelate species of the form VI in the system.

PART IV

CHAPTER - II

EXPERIMENTAL

URANYL CHELATES OF CATECHOL
POTENTIOMETRIC STUDIES

TABLE 1

TEMPERATURE = 25 ± 1°C

POTENTIOMETRIC TITRATION OF 20 ML. OF 2.5×10^{-2}M URANYL NITRATE SOLUTION WITH 2.5×10^{-1}M CATECHOL SOLUTION IN NITROGEN ATMOSPHERE

(Curve 1, Fig.34)

ML. OF 0.25M CATECHOL SOLN.	pH	ML. OF 0.25M CATECHOL SOLN.	pH
0.0	3.22	2.8	3.16
0.2	3.21	3.2	3.15
0.4	3.21	3.6	3.14
0.6	3.20	3.8	3.14
0.8	3.20	4.0	3.13
1.0	3.19	4.5	3.12
1.2	3.19	5.0	3.12
1.6	3.18	5.5	3.12
2.0	3.17	6.0	3.12
2.4	3.17		

TABLE - 2

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 20 ML. OF $2.5x10^{-2}$M URANYL WITH $2.5x10^{-1}$M CATECHOL IN PRESENCE OF 1 MOLE OF KOH IN NITROGEN ATMOSPHERE.(Curve 2, Fig. 34)

ML. OF 0.25M CATECHOL SOLN.	pH	ML. OF 0.25M CATECHOL SOLN.	pH
0.0	4.22	3.2	4.08
0.4	4.20	3.6	4.07
0.8	4.18	4.0	4.06
1.2	4.16	4.4	4.05
1.6	4.15	4.8	4.04
2.0	4.12	5.2	4.03
2.4	4.10	5.6	4.02
2.8	4.09	6.0	4.02

TABLE-3

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 100 ML. OF 2.5×10^{-3}M CATECHOL SOLUTION WITH 0.1M POTASSIUM HYDROXIDE. IONIC STRENGTH=0.1M(KNO_3)

(CURVE O, FIG.35)

ML. of 0.1M KOH	pH	ML. of 0.1M KOH	pH
0.0	6.66	1.5	9.25
0.1	7.34	2.0	9.56
0.2	7.94	2.5	9.92
0.5	8.54	2.8	10.13
0.8	8.80	3.0	10.26
1.2	9.06	3.5	10.47
1.4	9.17	4.0	10.67

TABLE -4

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}$ M IN URANYL NITRATE AND $5x10^{-3}$M IN CATECHOL WITH 0.1M KOH IN NITROGEN ATMOSPHERE. IONIC STRENGTH=0.1M(KNO_3)

(CURVE 1, FIG. 35)

ML. of 0.1M KOH	pH	ML. of 0.1M KOH	pH
0.0	3.41	4.4	4.94
0.4	3.61	4.8	5.02
0.6	3.71	5.2	5.10
0.8	3.79	5.6	5.26
1.0	3.87	6.0	5.47
1.2	3.94	6.3	5.75
1.4	4.01	6.5	6.30
1.6	4.08	6.7	7.00
1.8	4.14	6.9	7.52
2.0	4.20	7.2	7.82
2.4	4.30	7.5	8.13
2.8	4.40	8.0	8.65
3.0	4.46	8.2	8.90
3.2	4.53	8.6	9.27
3.4	4.60	8.8	9.63
3.6	4.67	9.0	9.73
3.8	4.75	9.2	9.83
4.0	4.83	9.6	10.08

TABLE -5

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN URANYL NITRATE AND 1×10^{-2}M IN CATECHOL WITH 0.1M POTASSIUM HYDROXIDE IN NITROGEN ATMOSPHERE

IONIC STRENGTH = 0.1M (KNO_3)

(CURVE 2, FIG.35)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	3.38	4.5	4.68
0.4	3.56	5.0	4.82
0.6	3.65	5.5	4.95
0.8	3.73	6.0	5.15
1.0	3.80	6.3	5.30
1.2	3.87	6.5	5.55
1.4	3.93	6.8	6.95
1.6	3.99	7.0	7.48
1.8	4.06	7.5	7.90
2.0	4.12	8.0	8.08
2.2	4.18	8.5	8.30
2.4	4.24	9.0	8.47
2.8	4.34	9.5	8.87
3.2	4.42	10.0	9.20
3.6	4.48	10.5	9.75
4.0	4.55	11.0	10.30

TABLE - 6

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN URANYL NITRATE AND 1.5×10^{-2}M IN CATECHOL WITH 0.1M POTASSIUM HYDROXIDE IN NITROGEN ATMOSPHERE.

IONIC STRENGTH = 0.1M(KNO_3)

(CURVE 3, FIG.35)

Ml.of 0.1M KOH	pH	Ml.of 0.1M KOH	pH
0.0	3.35	7.2	7.30
0.4	3.53	7.6	7.60
0.8	3.69	8.0	7.74
1.2	3.82	8.5	7.82
1.6	3.93	9.0	7.95
2.0	4.06	9.5	8.05
2.4	4.16	10.0	8.24
3.0	4.29	10.5	8.40
3.5	4.40	11.0	8.58
4.0	4.53	11.5	8.80
4.5	4.60	12.0	9.05
5.0	4.68	12.5	9.37
5.5	4.75	13.0	9.58
6.0	4.90	13.5	9.78
6.4	5.30	14.0	10.12
6.6	6.25	14.5	10.30
6.8	7.00	15.0	10.50

TABLE -7

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN URANYL NITRATE AND 2.5×10^{-3}M IN CATECHOL WITH 0.1M POTASSIUM HYDROXIDE IN NITROGEN ATMOSPHERE. IONIC STRENGTH = 0.1M (KNO_3). (Curve 2', Fig.35)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	3.62	4.4	5.14
0.4	3.80	4.8	5.24
0.6	3.89	5.0	5.29
0.8	3.97	5.5	5.46
1.0	4.05	6.0	5.77
1.2	4.14	6.3	6.17
1.4	4.21	6.5	6.54
1.6	4.27	6.8	7.02
1.8	4.34	7.0	7.25
2.0	4.40	7.2	7.68
2.4	4.50	7.6	8.07
2.8	4.60	8.0	8.43
3.0	4.67	8.4	8.80
3.2	4.74	8.8	9.15
3.4	4.82	9.2	9.40
3.6	4.89	9.6	9.70
3.8	4.98	10.0	9.95
4.0	5.06	10.4	10.15

TABLE -8

TEMPERATURE = 25±1°C

POTENTIOMETRIC TITRATION OF 200 ML. SOLUTION OF 1.25×10^{-3}M IN URANYL NITRATE AND 1.25×10^{-3}M IN CATECHOL WITH 0.1M POTASSIUM HYDROXIDE IN NITROGEN ATMOSPHERE. IONIC STRENGTH = 0.1M(KNO_3)

(Curve 3', Fig.35)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	3.85	4.4	5.38
0.4	4.00	4.8	5.47
0.6	4.07	5.2	5.56
0.8	4.15	5.6	5.73
1.0	4.22	6.0	6.05
1.2	4.30	6.3	6.40
1.4	4.37	6.6	6.76
1.6	4.45	6.8	7.15
1.8	4.52	7.0	7.45
2.0	4.57	7.2	7.62
2.2	4.63	7.4	7.85
2.4	4.68	7.6	8.00
2.6	4.73	8.0	8.26
2.8	4.80	8.4	8.60
3.0	4.88	8.8	8.90
3.2	4.96	9.2	9.20
3.4	5.04	9.6	9.45
3.6	5.12	10.0	9.75
4.0	5.30		

TABLE - 9

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-CATECHOLATE COMPLEX AT pH 3.7 KEEPING THE TOTAL VOLUME CONSTANT (50 Ml) OF EACH SOLUTION. IONIC STRENGTH = 0.1M(KNO_3). INITIAL (UO_2^{2+}+CATECHOL)CONCENTRATION= $4x10^{-3}$M

(Fig. 36)

	Wage length =370 mμ			Wave length = 390 mμ		
x	O.D. complex	O.D. UO_2^{2+}	Diff in O.D.	O.D. Complex	O.D. UO_2^{2+}	Diff. in O.D.
0.1	.055	.005	.050	.064	.007	.057
0.2	.080	.006	.074	.089	.008	.081
0.3	.095	.008	.087	.107	.014	.093
0.4	.105	.009	.094	.124	.020	.104
0.5	.115	.010	.105	.139	.023	.116
0.6	.110	.015	.095	.129	.028	.101
0.7	.100	.018	.082	.119	.032	.087
0.8	.080	.025	.055	.098	.037	.061
0.9	.068	.032	.036	.085	.042	.043

TABLE - 10

TEMPERATURE = 25 ± 1°C

JOB'S METHOD OF CONTINUOUS VARIATIONS APPLIED TO URANYL-CATECHOLATE COMPLEX AT pH 4.5 KEEPING THE TOTAL VOLUME CONSTANT (50 ML.) OF EACH SOLUTION. IONIC STRENGTH = 0.1M(KNO_3) INITIAL (UO_2^{2+} + CATECHOL) CONCENTRATION = 4×10^{-3}M

(Fig. 36)

x	O.D. complex	O.D. UO_2^{2+}	Diff. in O.D.	O.D. complex	O.D. UO_2^{2+}	Diff. in O.D.
Wave length = 370 mμ				Wave length = 390 mμ		
0.1	.120	.01	.110	.126	.012	.114
0.2	.157	.012	.145	.165	.015	.150
0.3	.175	.015	.160	.192	.020	.172
0.4	.200	.020	.180	.216	.025	.191
0.5	.222	.025	.197	.235	.028	.207
0.6	.198	.030	.168	.212	.034	.178
0.7	.170	.032	.138	.185	.039	.146
0.8	.156	.038	.118	.170	.045	.125
0.9	.130	.042	.088	.145	.055	.090
Wave length = 460 mμ				Wave length = 480 mμ		
0.1	.066	.006	.060	.062	.005	.057
0.2	.085	.006	.079	.080	.005	.075
0.3	.104	.007	.097	.092	.005	.087
0.4	.120	.008	.112	.102	.007	.095
0.5	.138	.010	.128	.116	.009	.107
0.6	.126	.013	.113	.097	.010	.087
0.7	.106	.015	.091	.086	.012	.074
0.8	.085	.016	.069	.075	.014	.061
0.9	.073	.018	.055	.068	.015	.053

PREPARATIVE STUDIES

PREPARATION OF URANYL CATECHOL DERIVATIVES UNDER DIFFERENT CONDITIONS

(1) Reaction of Uranyl Nitrate with $2\frac{2}{3}$ moles of caustic potash in presence of different amounts of catechol:

A solution of uranyl nitrate was treated with caustic potash ($2\frac{2}{3}$ moles) in presence of different amounts of catechol solution (1 to 3 moles). The reaction mixture was stirred well when a dark brown precipitate was obtained. It was left for an hour at room temperature (30°C) and then filtered. The precipitate was washed with water several times and dried in vacuum and analysed. The results are given in table 11.

Table - 11

Ml. of uranyl nitrate 0.1 M	Ml. of catechol 0.5M	Ml. of KOH 1M	Percentage of UO_2^{2+} in ppt.	Percentage of catechol in ppt.	Ratio of uranyl to catechol.
40	8	10.65	64.37	20.8	1.27
40	16	14.65	64.30	20.4	1.28
40	24	18.65	63.30	22.5	1.20

Precipitation of the uranyl mono-catecholate derivative was also carried out by the addition of ammonium Hydroxide (10.65 ml, 1M), instead of caustic potash, to the uranyl nitrate solution (0.1M, 40 ml.) containing catechol (0.5M, 8.0 ml.). The precipitate was washed, dried and analyzed.

UO_2^{2+} = 62.1 %, catechol = 24.8 %, NH_4^+ = 2.64 %

Ratio of UO_2^{2+} to catechol = 1.042, Ratio of NH_4 to uranyl = 0.64

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PART V

SUMMARY

A
SUMMARY OF THE
CONCLUSIONS
FROM
THE PRESENT INVESTIGATIONS

CHELATES OF URANIUM(VI) WITH OXYGEN DONAR LIGANDS AND A STUDY OF THEIR STABILITY AND POLYMERIZATION

The investigations presented in this thesis were undertaken to study the hydrolytic behaviour of uranyl chelates, in view of the interesting reports appeared in recent years [J. Am. Chem. Soc. 76 , 4726(1954); J. Phys. Chem. 64 , 1224(1960); J. Am. Chem. Soc. 82 , 1526(1960); J. Inorg. Nucl. Chem. 26, 1924(1964)] on the hydrolysis and polymerization of uranyl ion and its chelates in aqueous solutions. For this purpose, the interaction of uranyl ion with the following ligands was studied:

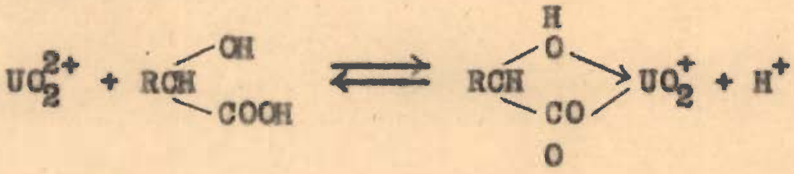
1. α-hydroxy carboxylic acids - mandelic and lactic acids.
2. Malonic acid.
3. o-hydroxy acids-salicylic, 5-sulphosalicylic, 1-hydroxy-2-naphthoic and 2-hydroxy-3-naphthoic acids.
4. 1-hydroxy-2-naphthaldehyde.
5. Catechol.

URANYL CHELATES OF MANDELIC AND LACTIC ACIDS:

Potentiometric titrations of uranyl nitrate with

KOH in the presence of an equimolar concentration of mandelic acid showed a sharp inflexion at $m = 2\frac{2}{3}$, where 'm' represents moles of KOH added per mole of the metal ion. This inflexion point has been interpreted on the basis of the formation of chelate species of the type $(UO_2HA)_3(OH)_2$. The 1:1 combining ratio of uranyl to ligand remains unaffected in the presence of an excess of mandelic acid. Verification of this conclusion has been made by spectrophotometry, using Job's method of continuous variations.

By a mathematical analysis of the potentiometric data for the titrations of uranyl-mandelate and -lactate systems, the reaction in the initial stages has been shown to proceed as

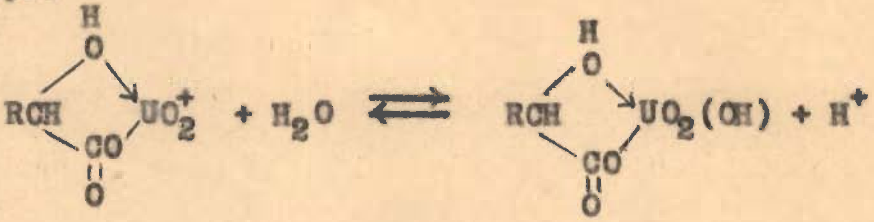


where R represents methyl or a phenyl group. Formation constant of the chelate has been found to be $10^{2.48}$. This value of 'k' has been shown to be independent of concentration of the metal chelate indicating that the above complex is present in solution mainly as a monomer.

HYDROLYSIS AND POLYMERIZATION :

In the calculation of formation constants of uranyl-mandelate and -lactate chelates, constant values of log k could be obtained up to 'm' value of about 0.4

(pH about 3.40), above which a gradual rise in the values of logk was observed. This has been explained on the basis of an occurrence of a reaction of the type:



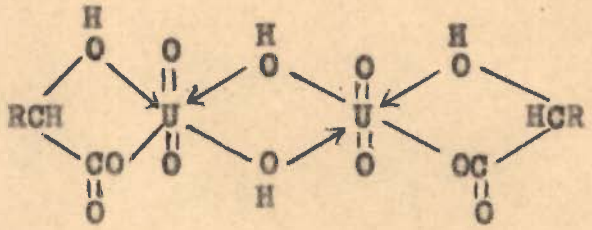
Values of hydrolysis constant, $K_h = \frac{[UO_2(OH)HA][H^+]}{[UO_2HA]}$, of the metal chelates were determined with the help of the material balance equations. Constant values of pK_h could be obtained up to about m = 1.0, above which a gradual fall in the pK_h values was observed indicating the occurrence of some side reaction which has not been considered in the above treatment. Determination of the hydrolysis constant over a four-fold concentration range showed a gradual increase in the values of pK_h with a decrease in concentration of the metal chelate indicating condensation of the monohydroxo 1:1 complex to form chelate species of higher molecular weight.

DIMERIZATION CONSTANT:

By applying a standard slope intercept relationship in the range m = 0.6 - 1.0, the metal chelate has been shown to dimerize in accordance with the reaction

$$2\ UO_2HA + 2H_2O \rightleftharpoons (UO_2(OH)HA)_2 + 2H^+$$

Values of the dimerization constant, $K_d = \frac{[(UO_2(OH)HA)_2]\ [H^+]^2}{[UO_2\ HA]^2}$ for the uranyl-mandelate and -lactate derivatives were found to be $10^{-4.94}$ and $10^{-5.13}$ respectively. A probable structure of binuclear chelate species has been suggested as



where R = $-CH_3$ in case of lactic acid

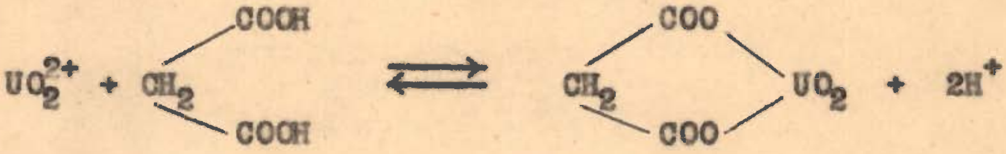
= $-C_6H_5$ in case of mandelic acid.

HYDROLYSIS OF DIMER

A gradual fall in the values of pK_h, calculated above 'm' values of about 1.0, is probably an indication of a further hydrolysis of the metal chelate. Beyond m = 1.0, mathematical analysis of the potentiometric data could not be made due to a greater complexity in the system caused by the overlapping of the successive hydrolytic and polymerization reactions.

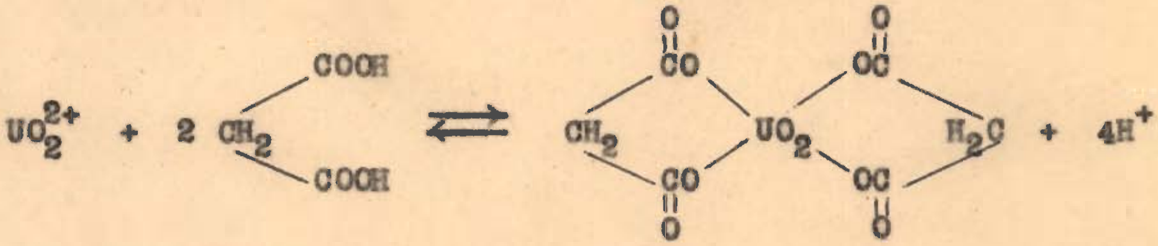
URANYL CHELATES OF MALONIC ACID

Complexation reactions of uranyl ion with malonic acid have been studied by potentiometry. The titration of an equimolar mixture of uranyl nitrate and malonic acid showed an inflexion point at m = 2. This is in accord with the reaction:



Beyond the inflexion point, the metal chelate was found to decompose into uranium hydroxide and the free ligand anions.

Potentiometric curve, for the titration of uranyl nitrate in the presence of two moles of malonic acid, approached an inflexion point at about m = 4. Formation of a 1:2 complex in accordance with the reaction;

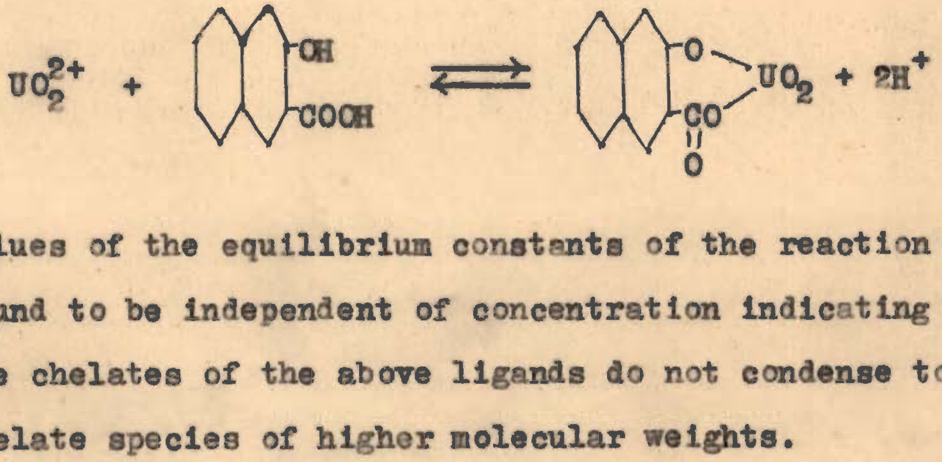


has been shown to take place. Beyond the inflexion point, the chelate started decomposition when a yellow precipitate, resembling uranium hydroxide, began to separate out from the reaction mixture.

Since the above chelates remained in solution below pH5, attempts were made to determine their formation constants, employing the algebraic and Bjerrum's methods. The values of these constants for the 1:1 and 1:2 chelates were found to be $\log k_1 = 5.78$ and $\log k_2 = 4.27$ respectively. The above values of the formation constants were independent of concentration indicating that the metal chelates do not polymerize under the experimental conditions employed.

URANYL CHELATES OF o-HYDROXY CARBOXYLIC ACIDS

A quantitative study of the interaction of uranyl ion with salicylic, 5-sulphosalicylic, 1-hydroxy-2-naphthoic and 2-hydroxy-3-naphthoic acids has been carried out by potentiometric titrations in 50 per cent alcoholic medium. In all the cases, formation of chelate species having metal to ligand ratio of 1:1 has been shown. This conclusion was verified by the Job's method of continuous variations. By a mathematical analysis of the potentiometric data, it has been shown that two hydrogen ions are liberated per mole of the metal ion. The chelation reaction in the case of uranyl-2-hydroxy-3-naphthoate system, for example, may be represented as



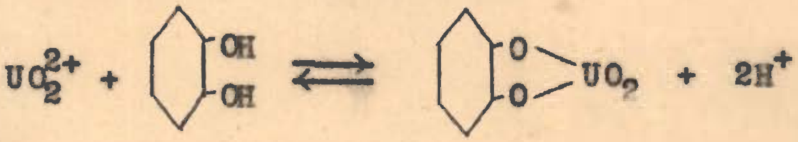
Values of the equilibrium constants of the reaction were found to be independent of concentration indicating that the chelates of the above ligands do not condense to give chelate species of higher molecular weights.

INTERACTION OF URANYL ION WITH 1-HYDROXY-2-NAPHTHALDEHYDE

Addition of a solution of 1-hydroxy-2-naphthaldehyde to uranyl nitrate produced a brilliant orange colour. In this case also, since the free ligand and the metal chelates were insoluble in aqueous medium, complex reactions were studied in 50 per cent alcohol. Formation of complexes having 1:1 and 1:2 molar ratios of uranyl to ligand has been established. Mathematical analysis of the potentiometric data above pH 3.5 could not be made due to the formation of a solid phase in the system.

INTERACTION OF URANYL ION WITH CATECHOL

Potentiometric titrations of uranyl nitrate with KOH in the presence of an increasing molar concentration of catechol (catechol to UO_2^{2+} ratio > 1) showed a sharp inflexion at $m = 2\frac{2}{3}$. On the basis of a mathematical treatment of the titration data, in the initial stages, the reaction has been shown to proceed as:



Average value of the equilibrium constant K of the reaction, calculated in the range m = 0-0.8 over a fourfold concentration range of the metal chelate was found to be 3.24×10^{-7} giving a value of 4.35×10^{14} for the stability constant of the chelate.

The value of pK was found to increase with a decrease in concentration of the metal chelate indicating polymerization of the complex. With the help of a standard slope intercept relationship, the chelate has been shown to dimerize in accordance with the reaction:

$$2\,UO_2^{2+} + 2H_2A \rightleftharpoons (UO_2A)_2 + 4H^+$$

The dimerization constant K_D ($K_D = \dfrac{[(UO_2A)_2]\,[H^+]^4}{[UO_2^{2+}]^2\,[H_2A]^2}$) was found to be 10^{-10}.

HYDROLYSIS OF DIMER:

A gradual fall observed in the calculation of pK beyond m = 0.8 has been explained on the basis of the occurrence of the reaction:

$$(UO_2A)_2 + H_2O \rightleftharpoons (UO_2A)_2(OH^-) + H^+$$

Value of the hydrolysis constant ($K_h = \dfrac{[(UO_2A)_2(OH^-)]\,[H^+]}{[(UO_2A)_2]}$) was found to be $10^{-5.29}$. Again constant values of K_h could be obtained up to 'm' values of about 1.6 above which a gradual fall in the values of pK_h was observed indicating further hydrolysis in the system.

A further mathematical analysis of the data could not be made due to the formation of a solid phase in the system. The inflexion point at m = $2\frac{2}{3}$ shown by the potentiometric curves has, however, been explained on the basis of the formation of the chelate species of the type $(UO_2A)_3(OH)_2$. Verification of this conclusion has been made by the isolation and analysis of the precipitate obtained by the addition of $2\frac{2}{3}$ moles of ammonium hydroxide to the reaction mixture containing an equimolar concentration of uranyl nitrate and catechol.

LIST OF PUBLICATIONS

1. Stability and polymerization of Uranyl Mandelate and Lactate Chelates. J. Less-Common Metals, Vol.12, No.3, pp.221-230 (1967).

2. Potentiometric studies of uranyl ion with malonic acid. J. Less-common Metals. (communicated).

3. Uranyl Chelates of 1-Hydroxy-2-Naphthoic and 2-Hydroxy-3-Naphthoic acids. Bulletin of Chemical Society of Japan (communicated).

4. Study of Salicylic and 5-Sulphosalicylic acids derivative of uranyl ion. Journal of Indian Chemical Society (communicated).

5. Uranyl Chelates of 1-Hydroxy-2-Naphthaldehyde. Journal fur praktische Chemie (communicated).

6. Stability and polymerization of uranyl catecholate chelates. Journal fur praktische Chemie(in press).