A THESIS ON

A PHYSICO-CHEMICAL STUDY OF NORMAL AND MIXED-LIGAND CHELATES OF OXOVANADIUM (IV) WITH OXYGEN AND NITROGEN DONOR LIGANDS

By

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CERTIFICATE

This is to certify that the thesis entitled ' A Physico-Chemical Study of Normal and Mixed-Ligand Chelates of Oxovanadium (IV) with some Oxygen and Nitrogen Donor Ligands' which is being submitted by Sri Kishan Lal for the award of the Degree of Doctor of Philosophy to the University of Roorkee, is a record of bonafide research work carried out by him under my supervision and guidance.

Sri Kishan Lal has worked for a period equivalent to 24 months in the Department of Chemistry of this University. The results embodied in the thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

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PART I

GENERAL INTRODUCTION

GENERAL INTRODUCTION

The main aim of the investigations presented in this thesis was to make a detailed study of mixed ligand chelates of oxovanadium (IV) with some oxygen and nitrogen donor complexing agents. For the determination of formation constants of these mixed ligand derivatives, an information was required about the simple chelates of VO^{2+} with the ligands involved in the present study. Although most of these simple chelates had been reported earlier, a survey of literature revealed that in some cases, e.g., catechol, chromotropic acid, mandelic and lactic acids, a more comprehensive study was desirable before an understanding of their nature could be claimed. In such cases, therefore, a systematic physico-chemical study was carried out for obtaining the data for the mixed ligand systems.

Although tartrate and malate complexes of VO(IV) have not been studied from the above point of view, interesting results obtained in the study of vanadyl-mandelate and -lactate systems led to extend this work to the corresponding tartrate and malate chelates. These have received a considerable importance in recent years, since in ammonia solution and in the solid state the complex $(NH_4)_2[VO(tart)](H_2O)$ is the only example of vanadyl complex known to exhibit, at room temperature, four distinct absorption bands in the ligand field region (1000-380 mμ).

In the study of the mixed ligand systems involving o-phenanthroline and 2,2'-dipyridyl as primary ligands, it was found that the successive reactions in the formation of mixed ligand chelates overlap. Determination of the formation constants of these complexes required a knowledge of equilibrium constants of the reactions associated with the formation of the simple VO-Phen and VO-Dipy chelates. Before investigating the formation of mixed ligand chelates, therefore, it was considered expedient to study the potentiometric data arising from the interaction of vanadyl ion with the above nitrogen donor ligands. Due to the special characteristics of systems described in this thesis and also dependent on the facilities available in our laboratories, the study has been based mainly on potentiometry.

Although the major interest of the investigations lay in the mixed ligand complexes, the subject matter of the thesis has been divided for convenience in two separate parts dealing with the simple chelates followed by mixed ligand derivatives.

SIMPLE CHELATES OF OXOVANADIUM (IV)

At least one ligand atom Is Oxygen:

Oxalate ion readily forms complexes[1-10] with oxovanadium (IV). These complexes are mainly of the types:

$VO(ox).xH_2O$, $M_2[VO(ox)_2](xH_2O)$ and $M_2[(VO)_2(ox)_3](xH_2O)$. Formation of the anhydrous compound $(NH_4)_2[(VO)_2(ox)_3]$ has recently been claimed[11]. A compound with the empirical formula $VO(ox)(H_2ox)(3H_2O)$ has been reported by Selbin and Holmes[12].

By using Job's method of continuous variations, the reaction of VO^{2+} with malonic acid has been reported[13] to produce a 1:1 complex. In alkaline solutions, malonato complexes of the general formula $M_2[VO(mal)_2].xH_2O$ have been isolated by Schramm[14]. These derivatives have been reported to give different coloured species when dehydrated in stages.

Tartrate complexes of VO(IV) have been a subject of research[15-24] since the earliest days of vanadium chemistry. Jørgensen[25] has suggested that in the complex ion $[VO(tart)]^{2-}$ all the four oxygen atoms of the tartrate ion are coordinated to the oxometal ion. Recently an interesting report[26], proclaiming the use of $(NH_4)_2[VO(tart)](H_2O)$ for the inhibition of cholesterol synthesis in brain tumors, has appeared.

Complexes of oxovanadium (IV) with other polybasic acids, viz., salicylic[27-29], phthalic[30], succinic[30], sebacic[30], citric[30-32], ascorbic[33] and picolinic[34] acids have been prepared by treating a suspension of the organic acid in carbon tetrachloride with $VOCl_3$ under anhydrous conditions. Mont and Martell[35] have studied the interaction of vanadyl ion with salicylic acid,5-sulphosalicylic acid titron, 5-sulpho-8-hydroxyquinoline and salicyl phosphate in aqueous medium. By using the potentiometric data of the systems, formation constants of the chelates have been determined. Stability constants of the vanadyl chelates of EDTA[36-38], HEDDA[39], HIMDA[39], chromotropic[40] and glycolic[41] acids have also been determined.

Salicyldehyde forms stable chelates[42-44] of the type $M_2[VO(Sal)_2](xH_2O)$. A complex with p-amino-salicyldehyde has also been synthesised[26]. Reactions of VO^{2+} with other hydroxyaldehydes (4-phenyl-, 5-chloro-, 5-bromo-, 3,5-dichloro-, and 3,5-dibromosalicyldehyde and β-hydroxynaphthaldehyde) and their imines have been recently reported[45].

Dutta and Lahiry[46] obtained a rose-coloured paramagnetic complex $[VOB_2]$ with benzehydroxamic acid (BH). They also reported[47,48] a cream-coloured hydrate $[VOQ_2]$ (H_2O) with quinaldinic acid (QH) and an isomeric olive-green aquo complex $[VOQ_2(H_2O)]$. Complexes of the type $[VOG_2]$ have been synthesised[49] with guanylalkyl-and guanylalkoxyalkylureas (GH).

Oxovanadium (IV) has been reported to form several complexes with β-diketones. Amongst these, the blue-green bis (acetylacetonate) oxovanadium (IV) complex has received an extensive attention. This compound was first prepared in 1876 by Guyard[50]. In 1900 the same compound was synthesised by Gach[51]. Morgan and Moss[52] formulated the complex as $[VO(acac)_2]$. Rosenheim and Mong[17] claimed it to be in a monohydrate form, $[VO(acac)_2(H_2O)]$. Again, in 1954 Jones[53] studied this complex and concluded that the original formulation without water molecule was correct. By using Bjerrum's method, Trujillo and Brito[54] obtained evidence for the formation of $VO(acac)^+$ and $[VO(acac)_2]$ complexes in aqueous solutions.

Recently, the vanadyl complexes of acetylacetone in aqueous and alcoholic solutions have been reported[55] to undergo slow oxidation by atmospheric oxygen. The oxidation reaction has been claimed to proceed rapidly with hydrogen peroxide. Other β-diketones which form complexes VO(IV) include: 3-cyanoacetylacetone[56]; 2-chloro-and 2-bromo-acetylacetone[57]; acetyl methylacetone[58]; benzoylacetone[59] and its 1:1 adducts with bases.

8-hydroxyquinoline has been reported[60] to form complexes having 1:1 and 1:2 ratios of vanadyl to ligand. Formation constants of these chelates have been determined by Bjerrum's method. Magnetic moment of $VO(oxine)_2$ has been measured[61,62] and the complex has been reported to form a stable pyridine adduct.

Complexes of VO(IV) with Schiff bases formed from β-diketones, ethylenediamine and salicyldehyde have received a considerable attention[63-68] in recent years. Amongst the complexes obtained from the Schiff bases derived from β-diketones, reference may be made of the complex bis (acetyl acetonepropylenediimino) oxovanadium (IV) which has been reported[69] to be the first compound of VO(IV) to have been successfully resolved into optical isomers. More recently, Sacconi and Campigli[70] have studied the interaction of Schiff bases formed from ring substituted salicyldehydes and N-substituted ethylenediamines. Complexes with the general formula $[X-SALen-N(R)R']_2VO$ have been synthesised. These complexes have been shown to have a five-coordinate structure.

The ligand atoms are nitrogen:

Vanadyl ion forms strong complexes[71] with o-phenanthroline and 2,2'-dipyridyl. They are of two general types. The first contains one ligand molecule per VO^{2+} entity. The second type includes complexes containing two molecules of ligand per mole of the oxometal ion. Sulphato derivatives of the above complexes have been synthesised by Selbin and Holmes[12,72]. The chloro-and bromo-derivatives have also been prepared[73]. By the interaction of vanadium tetrachloride with o-phenanthroline and 2,2'-dipyridyl (L), the complex VCl_4L has been obtained. This complex on hydrolysis has been reported[73] to yield $VOCl_2L$.

Complexes of biguanide and six different substituted biguanides have been reported[74]. These complexes have the general formula $[VO(big)_2(H_2O)]$.

Chelates of tetraphenylporphine[75-77] and its p-methyl-p-methoxy-, and p-chloro-[78] substituted derivatives have been studied and their infrared and visible spectra recorded. A phthalocyanine complex has also been reported[79].

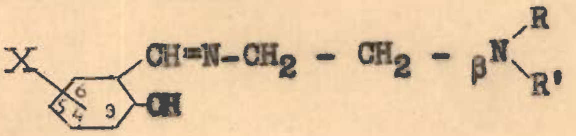
MIXED LIGAND CHELATES

The study of mixed ligand metal chelates has received considerable importance in recent years, since the formation of these derivatives offers an alternative reaction to hydrolysis and olation of the simple chelates in which some of the coordination positions of the central metal atom remain unfilled by the ligand molecule. In the Th-EDTA chelate, for example, the EDTA molecule occupies six coordination positions of the metal leaving the remaining two for hydrolysis and polymerization[80] reactions. In this case, therefore, bidentate ligands have been reported[81] to combine with the metal chelate giving stable mixed ligand derivatives.

When $VOC_2O_4.2H_2O$ complex is treated with neutral ligands such as dimethyl sulphoxide (DMSO) or antipyrine (Apy, 1-phenyl 2,3-dimethyl 5-pyrazolone), the two coordinated water molecules of the complex are replaced[82] by the ligand molecules giving $VOC_2O_4.2DMSO$ or $VOC_2O_4.2Apy$. By measuring molar conductance in acetonitride, these complexes have been shown to be nonelectrolytic in nature.

Mixed ligand chelates $[VO(C_{12} H_8N_2)C_2O4, VO(C_{10}H_8N_2) C_2O_4]$ containing o-phenanthroline or 2,2'-dipyridyl as one ligand and oxalic acid as another ligand have been synthesised by Selbin and Holmes[12].

Mixed ligand complexes of VO(IV) with Schiff bases of the general formula



formed from ring-substituted salicyldehydes and N-substituted ethylenediamines have been prepared by Sacconi and Campigili[70]. These complexes have been shown to have the formula [(X-SAL)(X-SALen-N(R)R']VO, where the substituents R and R' are alkyl groups (except when $R = R' = C_2H_5$), benzyl groups and the terminal amino group $-NR_2$ is $-N(CH_2)_4$ (pyrrolidino) or $-N(CH_2)_5$ (piperidino). They are deep red or violet in colour, except for those in which X = 5,6-benzo, which are green. These derivatives have been shown to have a hexacoordinate structure.

REFERENCES

1. J. Koppel and R.Goldman, Z.anorg. Chem., 36, 281(1903).

2. D.J. McAdam, Jr,,and C.A. Pierle, J. Am.Chem.Soc., 34, 606 (1912).

3. L.P. Ducret, Ann. chim (Paris), 6, 705(1951).

4. H. Hartman and H.L. Schlafer, Angew. Chem., 66 , 768 (1954).

5. R. Trujillo and F. Torres, Anales real soc. espan.fis.y quim 52B, 157 (1956).

6. V.L. Zolotavin and N.N. Kalugina, Zh. Neorgan. Khim., 1 , 703 (1956).

7. V.L. Zolotavin, Zh. Neorgan. Khim., 4 , 1254 (1959).

8. V.V. Zelentsov, Russ. J. Inorg. Chem., 7 , 670 (1962).

9. K.C. Satapathy, R. Parmar and B. Sahoo, Indian J. Chem., 1 , 402 (1963)

10. D.N. Sathyanarayana and C.C. Patel, J. Inorg. Nucl. Chem., 27 , 297 (1965).

11. D.N. Sathyanarayana and C.C. Patel, Bull. Chem. Soc. Japan, 37, 1736 (1964).

12. J. Selbin and L.H. Holmes, Jr., J. Inorg. Nucl. Chem., 24, 1111 (1962).

13. P.K. Bhattacharya and S.N. Banerji, Current Sci.(India), 29, 147 (1960).

14. N. Schramm, Z. anorg. allgem. Chem., 161, 231 (1927).

15. G.A. Barbieri, Atti Accad. Lincei, 23(2), 47 (1914).

16. G.A. Barbieri, Chem. Zentr. 2, 1427 (1914).

17. A. Rosenheim and H. Mong, Z. anorg. Chem., 148, 25,34 (1925).

18. B.C. Kar, J. Indian Chem. Soc., 25, 267 (1948).

19. B.C. Kar, and S.K. Roy, J. Indian Chem. Soc., 25, 397 (1948).

20. V.L. Zolotavin and T.A. Soboleva, Zh. Fiz. Khim., 28, 1950 (1954).

21. V.L. Zolotavin and N.I. Sintsov, J. Gen.Chem. USSR, 26, 33 (1956).

22. V.L. Zolotavin and T.A. Soboleva, Tr. Ural'sk. Politekhn. Inst., No.57, 50 (1956).

23. M. Ziegler, Naturwiss., 46, 492 (1959).

24. P.K. Bhattacharya, M.C. Saxena and S.N. Banerji, J. Indian Chem. Soc., 39, 240 (1962).

25. C.K. Jórgensen, Acta Chem. Scand., 11, 73 (1957).

26. J.B. Conn, U.S. Patent 3,076,830 (Feb. 5, 1963).

27. P.K. Bhattacharya and S.N. Banerji, J. Sci. Ind. Res. (India), 20B, 131 (1961)

28. A.K. Babko, A.I. Volkova, T.E. Getman and M.Kh. Pavlova, Ukr. Khim. Zh., 29, 1235 (1963).

29. A.I. Volkova and T.E. Getman, Ukr. Khim. Zh., 29, 1240 (1963).

30. S. Prasad and K.N. Upadhyaya, J. Indian Chem. Soc., 38, 163 (1961)

31. C. Heitner-Wirguin and D. Friedman, Bull. soc. chim. France, 970 (1958).

32. V.L. Zolotavin and N.N. Kalngina, J. Gen.Chem.USSR, 26, 1527 (1956).

33. A. Sobkowska and J. Minczewski, Roczniki Chem., 36, 17 (1962).

34. M. Paris and J.C. Merlin, Bull. soc. chim.France, 800 (1962).

35. G.E. Mont and A.E. Martell, J. Am. Chem. Soc., 88, 1387 (1966).

36. G. Schwarzenbach and J. Sandera, Helv. Chim. Acta, 36, 1089 (1953).

37. G. Schwarzenbach, R. Gut and G. Anderegg, Helv. Chim. Acta, 37, 937 (1954).

38. D.T. Sawyer and J.M. Mc Kinnie, J. Am. Chem. Soc., 82, 4191 (1960).

39. S. Chaberek, Jr., R.L. Gustafson, R.C. Courtney and A.E. Martell, J. Am. Chem. Soc., 81, 515 (1959).

40. S.M.F. Rehman and A.U. Malik, J. prakt. Chem., 21, 109 (1963).

41. S. Ahrland, Acta Chem.Scand., 7 , 485 (1953).

42. G.A. Barbieri, Atti Accad. Lincei 23 (2), 408 (1914).

43. M. Bobtelsky, C. Heitner and K.R.S. Ascher, Bull. soc. chim. France, [5] 19, 943 (1952).

44. G.P. Vishnevskaya, B.M. Kozyrev and P.G. Tishkev, Dekl. Akad. Nauk SSSR, 152, 644 (1963).

45. A.S. Pesis and E.V. Sokolova, Zh. Neorgan. Khim., 2518 (1963).

46. R.L. Dutta and S. Lahiry, J. Indian Chem. Soc., 39, 860 (1962).

47. R.L. Dutta and S. Lahiry, Chem. Ind. (London), 78 (1961).

48. R.L. Dutta and S. Lahiry, J. Indian Chem. Soc., 38, 1001 (1961).

49. R.L. Dutta and S. Lahiry, J. Indian Chem. Soc., 40, 863 (1963).

50. A. Guyard, Bull. soc. chim., 25, 350 (1876).

51. F. Gach, Monatsh., 21, 98 (1900).

52. G.T. Morgan and H.W. Moss, Proc. Chem. Soc., 28, 199 (1913).

53. M.M. Jones, J. Am. Chem. Soc., 76, 5995 (1954).

54. R. Trujillo and F. Brito, Anales real soc. espan. fis. yquim., 52B, 407 (1956).

55. T.R. Ortolano, J. Selbin and S.P. McGlynn, J. Chem. Phys., 41, 262 (1964).

56. J.P. Fackler, J. Chem. Soc., 1957 (1962).

57. R.W. Kluiber, U.S. Patent 3,014,939 (Dec.1961).

58. G.T. Morgan and H.W.Moss, J. Chem. Soc., 103, 78(1914).

59. R.D. Feltham, Thesis, University of California, UCRL-3867, 1957.

60. R.Trujillo and F. Brito, Anales real soc. espan.fis.y quim., 53B, 313 (1957)

61. H.J. Bielig and E. Bayer, Ann. Chem., 584, 96 (1953).

62. L.H. Holmes, Jr., Thesis, Louisiana State University, 1961.

63. E. Bayer, H.J. Bielig and K.H. Hausser, Ann. Chem., 584, 116 (1953).

64. H.J. Bielig and E. Bayer, Ann. Chem., 580, 135(1953).

65. P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl and H. Thielert, J. prakt. Chem., 149, 217 (1937).

66. P. Pfeiffer, H. Thielert and H. Glaser, J. prakt. Chem., 152, 145 (1939).

67. J. Selbin, H.R. Manning and G. Cessac, J. Inorg. Nucl. Chem., 25, 1253 (1963).

68. K. Ueno and A.E. Martell, J. Phys. Chem., 60, 1270 (1956).

69. K. Ramaiah, F.E. Anderson and D.F. Martin, Inorg. Chem., 3, 296 (1964).

70. L. Sacconi and U. Campigli, Inorg. Chem., 5, 606 (1966).

71. R. Trujillo and F. Brito, Anales real soc. espan.fis. y. quin., 53B, 249 (1957).

72. J. Selbin, L.H. Holmes, Jr., and S.P. McGlynn, J. Inorg. Nucl. Chem., 25, 1359 (1963).

73. R.J.H. Clark, J. Chem. Soc., 1377 (1963).

74. P. Ray, Chem. Rev., 61, 313 (1961).

75. J.T. Horeczy, B.N. Hill, A.E. Walters, H.G.Schutze and W.H. Bonner, Anal. Chem., 27, 1899 (1955).

76. W.H. Bonner, Jr., U.S. Patent 2,740,794 (April 3, 1956);

77. K. Ueno and A.E. Martell, J. Phys. Chem., 60, 934 (1956).

78. J.M. Goldstein, W.M. McNabb. and J.F. Hazel, J.Am. Chem. Soc., 78, 3543 (1956).

79. P. George and D.H. Irvine, Nature, 173, 1148 (1954).

80. R. Bogucki and A.E.Martell, J. Am. Chem. Soc., 80, 4170 (1958).

81. G.H. Carey, R.F. Bogucki and A.E. Martell, Inorg. Chem., 3 1288 (1964).

82. D.N. Sathyanarayana and C.C. Patel, J. Inorg. Nucl. Chem., 28, 2277 (1966).

PART II

SIMPLE CHELATES OF OXOVANADIUM (IV)

Section I- Oxovanadium (IV) Chelates of Catechol.

Section II- Oxovanadium (IV) Chelates of Chromotropic acid.

Section III- Oxovanadium (IV) Chelates of Mandelic and Lactic acids.

Section IV- Oxovanadium (IV) Chelates of Tartaric and Malic acids.

Section V Oxovanadium (IV) Chelates of Iminodiacetic acid.

Section VI- Oxovanadium (IV) Chelates of o-Phenanthroline and 2,2'-Dipyridyl.

SECTION I

OXOVANADIUM (IV) CHELATES OF CATECHOL

Catechol, o-dihydroxy benzene, gives a 5-membered ring on chelation. It, therefore, forms stable complexes with a number of metals like copper[1-3], chromium[4], zinc[5,6], nickel[6-8], cobalt[6-8], bismuth[9,10], aluminium[11], iron[12], zirconium[13,14], thorium[15] and uranium[16].

Oxovanadium (IV) has also been reported[17-20] to form strong chelates with catechol. Rosenheim and Mong[17] isolated vanadyl derivatives of catechol of formulae $M_2[VO(cat)_2]$ $(H_2cat)(xH_2O)$ from alkaline solutions of vanadyl sulphate containing an excess of the ligand. Recently a continuous variation study[18] of $VOSO_4$ with catechol revealed a violet 1:2 complex and a violet-black 1:3 complex. In the latter complex, the third molecule of the ligand has been reported to be loosely held and is claimed to be catechol of crystallization. In another study Trujillo and Cabrera[19], by treating vanadyl sulphate with caustic soda (3 moles) in the presence of an excess of catechol, showed the formation of complexes having vanadyl to catechol combining ratios of 1:1 and 1:2. More recently, Shnaiderman[20] by a photometric study of systems containing VO(IV) and polyhydroxy-benzenes, viz. catechol, pyrogallol and gallic acid, showed the formation of 1:1

complexes in the pH range 4-5 above which complexes containing 2 moles of the ligands per mole of VO(IV) have been reported to be formed.

In view of the above, it was considered desirable to carry out a systematic physico-chemical study of the interaction of VO^{2+} with catechol under the experimental conditions employed for the investigation of the mixed-ligand chelates. Attempts were also made to determine formation constants of the complexes formed in the system.

RESULTS AND DISCUSSION

Curve 1 (Fig.1), for the potentiometric titration of an equimolar mixture of vanadyl sulphate and catechol, exhibits a sharp inflexion at m = 3, where 'm' represents moles of potassium hydroxide added per mole of the metal ion. For the formation of a normal 1:1 chelate in accordance with the reaction:

...(i)

(I)

two moles of KOH per mole of the metal salt are required. An occurrence of inflexion point at m = 3 and the non-precipitation of the metal hydroxide in the system indicated that one of the water molecules of the aquo chelate (I) undergoes dissociation. The hydrolytic

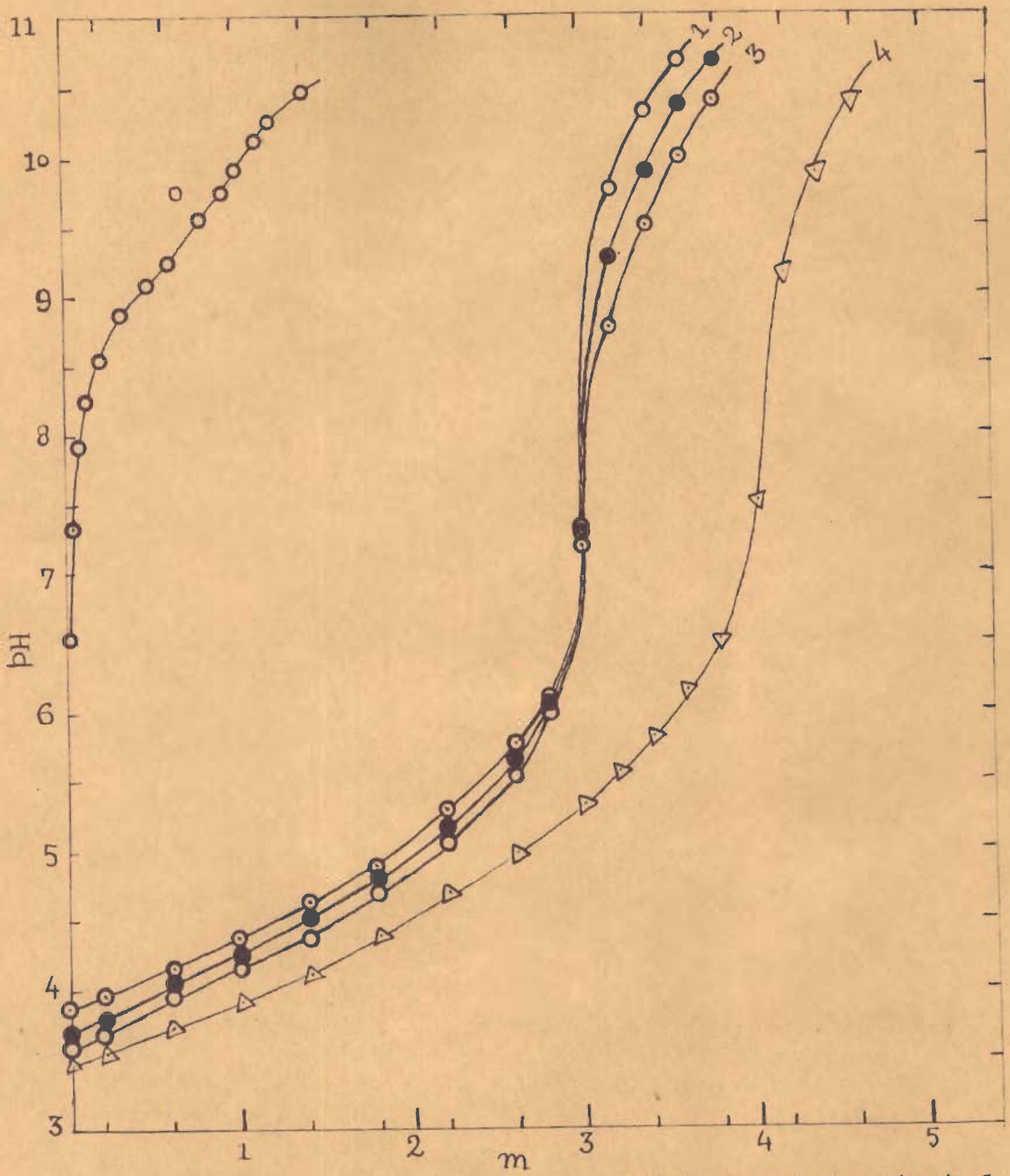
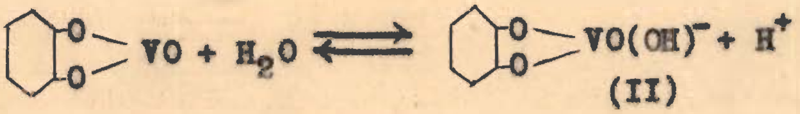


Fig.1. Potentiometric titrations of 1:1 vanadyl-catechol chelate systems with KOH(0.1N). Concentrations: curve 1, $5x10^{-3}M$; curve 2, $2.5x10^{-3}M$; curve 3, $1.25x10^{-3}M$. Curve 4, represents similar titration of 1:2 vanadyl-catechol system, $T_M = 5x10^{-3}M$. Ionic strength = 0.1M (KCl). m = moles of base added per mole of the metal ion. In the lower buffer regions portion of the curves for the neutralization of HCl present in VO(IV) soln. has been eliminated. Curve 0 represents titration of Catechol with KOH

reaction may, thus, be represented as:



(II) ..(ii)

The failure to obtain a titration breaks at m = 2 suggests that the formation of the hydroxo complex(II) starts before the formation of the normal 1:1 chelate(I) is completed. In the above equations and generally throughout this thesis, the water molecules of hydration have been omitted for the sake of simplicity.

In order to investigate the presence of polynuclear chelate species in the system[21], potentiometric titrations of 1:1 mixtures of vanadyl sulphate and catechol were carried out over a four-fold concentration range. The effect of concentration on the potentiometric data, illustrated by curves 1-3 (Fig.1) for the above titrations is so slight that no polymerization of the metal chelate seems to occur. The spread of the lower buffer regions seen in these curves can be accounted for entirely on the basis of variation of the concentration of hydrogen ions as a function of concentration of the metal chelate. Beyond the cross-over of the curves at m = 3, the second buffer region is displaced to higher pH values with a corresponding increase in the concentration of the metal chelate. This shift may be explained on the basis of the free alkali present in the system(i.e., the spread is due to the fact that different quantities of KOH solution were required to produce the same 'm' value since the total concentration of the metal chelate differed considerably).

In view of the above interesting results of the interaction of one mole of catechol with one mole of vanadyl ion and to verify the conclusion of the formation of mononuclear chelate species only in the system, it was considered worthwhile to carry out a mathematical analysis of the potentiometric titration data. The method used for the determination of equilibrium constants is outlined below:

If H_2A represents catechol, complexation reaction at initial stages of the titration may be represented as:

$$VO^{2+} + H_2A \rightleftharpoons VOA + 2H^{+} \qquad \text{...(i)}$$

Equilibrium constant K_1 may be expressed as:

$$K_1 = \frac{[VOA]\,[H^{+}]^2}{[VO^{2+}]\,[H_2A]} \qquad \text{... (1)}$$

Although the hydrolytic behaviour of vanadyl ions is not fully known, however, taking the values of K_{h_1} and K_{h_2} reported by Rossotti and Rossotti[22] for the equilibria:

$$VO^{2+} + H_2O \rightleftharpoons VO[OH]^+ + H^+$$

$$K_{h_1} = \frac{[VO[OH]^+][H^+]}{[VO^{2+}]} = 10^{-6.0} \quad \ldots (2)$$

and $2VO^{2+} + 2H_2O \rightleftharpoons (VO[OH])_2^{2+} + 2H^+$

$$K_{h_2} = \frac{[(VO[OH])_2^{2+}][H^+]^2}{[VO^{2+}]^2} = 10^{-6.88} \ldots (3)$$

it may be shown that in solutions of pH less than 3.5, the amount of the hydrolyzed species of the uncomplexed vanadyl ions is negligible as compared to the concentrations of the other species present in the equilibrium mixture. But in this study, due to a little chelation between vanadyl ion and catechol below pH 3.5, it was considered necessary to account for the equilibria involved in the hydrolysis of free vanadyl ions present in the system. For this purpose, the values of hydrolysis constants defined by the equations 2 and 3, were employed.

If T_M represents 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 obtain the following equations for maintaining the material balance:

$$T_M = [VO^{2+}] + [VO[OH]^+] + 2[(VO[OH])^{2+}] + [VOA] \quad \ldots (4)$$

$$T_{OH} + \left[H^{+}\right] = \left[VO(OH)^{+}\right] + 2\left[(VO[OH])_2^{2+}\right] + 2\left[VOA\right] \quad \ldots(5)$$

and

$$T_A = \left[H_2A\right] + \left[VOA\right] \quad \ldots(6)$$

In the pH range studied, concentrations of HA^-, A^{2-} and OH^- were negligible as compared to those of the other species present in the reaction mixture.

Elimination of $\left[VO[OH]^{+}\right]$, $\left[(VO[OH])_2^{2+}\right]$ and $\left[VOA\right]$ between equations 2-5 gives,

$$\frac{2\times10^{-6.88}}{\left[H^{+}\right]^{2}}\left[VO^{2+}\right]^{2} + \left(2+\frac{10^{-6.0}}{\left[H^{+}\right]}\right)\left[VO^{2+}\right] - \left(2T_M - T_{OH} - \left[H^{+}\right]\right) = 0 \quad \ldots(7)$$

Concentration of free vanadyl ions present in the equilibrium mixture may, therefore, be given by the expression,

$$\left[VO^{2+}\right] = \frac{-b \pm \sqrt{b^2+4ac}}{2a} \quad \ldots(8)$$

where

$$a = \frac{2\times10^{-6.88}}{\left[H^{+}\right]^{2}}, \quad b = 2 + \frac{10^{-6.0}}{\left[H^{+}\right]} \text{ and}$$

$$c = 2T_M - T_{OH} - \left[H^{+}\right]$$

After computation of the equilibrium concentration of free metal ions, concentrations of the other species present in solution may then be determined algebraically from equations 4-6. The values of the equilibrium constant K_1, calculated from various points of curves 1-3 (Fig.1), are presented in Table I.

Table I

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

m	0.20	0.28	0.36	0.44	0.52	0.60	0.76	0.92
pH	3.70	3.75	3.82	3.87	3.93	3.98	4.06	4.10
$-\log K_1$	5.87	5.87	5.86	5.85	5.86	5.85	(5.79	5.64)*

Average value of $-\log K_1$ = 5.86±0.01
*Values not included in the average.

Curve 2 (Fig.1), $T_A = T_M = 2.5x10^{-3}M$

m	0.20	0.28	0.36	0.44	0.60	0.76
pH	3.84	3.91	3.97	4.02	4.07	4.16
$-\log K_1$	5.88	5.88	5.88	5.87	(5.72	5.69)*

Average value of $-\log K_1$ = 5.88±0.0
* Values not included in the average.

Curve 3 (Fig.1), $T_A = T_M = 1.25x10^{-3}M$

m	0.12	0.20	0.28	0.44
pH	3.92	3.98	4.02	4.10
$-\log K_1$	5.85	5.85	(5.79	5.46)*

Average value of $-\log K_1$ = 5.85±0.0
*Values not included in the average

From the above table it is evident that the relatively constant values of $-\log K_1$ could be obtained up to a pH of about four only regardless of the initial concentration of the reaction mixture. It is also obvious from Table I that the value of the equilibrium constant is independent of concentration of the metal chelate indicating that the complex is present in solution mainly as a monomer under the experimental conditions employed.

On the basis of the mathematical treatment, given above, attempts were also made to calculate the value of equilibrium constant K_1, from the potentiometric data of curve 4 (Fig.1) for the titration of vanadyl sulphate with KOH in the presence of two moles of catechol. The results of these calculations are presented in table II.

Table II

Curve 4 (Fig.1), $T_A = 2T_M = 1.0\times10^{-2}$M

m	0.28	0.36	0.44	0.52	0.60	0.68	0.76
pH	3.60	3.66	3.70	3.74	3.78	3.82	3.86
$-\log K_1$	5.85	5.85	5.83	5.81	5.79	5.79	5.78

Average value of $-\log K_1 = 5.81 \pm 0.04$

In this case also constant values of $-\log K_1$ could be obtained up to a pH of about four only. This similarity together with a close agreement in the values of the equilibrium constant, given in Tables I and II, indicated that even in the presence of an excess of catechol a normal 1:1 chelate is the only complex formed in solutions of pH$<$4.

Stability of 1:1 Chelate

The stability constant, K_{MA}, of the 1:1 Metal chelate may be defined as:

$$K_{MA} = \frac{[VOA]}{[VO^{2+}][A^{2-}]} \qquad \ldots (9)$$

If K_{a_1} and K_{a_2} represent the first and second dissociation constants of catechol, it may be shown that:

$$K_{MA} = \frac{K_1}{K_{a_1} \cdot K_{a_2}} \qquad \ldots (10)$$

where K_1 represents the equilibrium constant defined by expression (1).

Substitution of the values of K_1 (from tables I and II average value of $pK_1 = 5.85$), Ka_1 $(10^{-9.2})^{ref.23}$ and $Ka_2(10^{-11.93})^{ref.23}$ in the above expression corresponded to a value of 15.28 for log K_{MA}.

Hydrolysis of 1:1 Chelate.

A gradual fall in the values of $-\log K_1$ above pH of about four (table I), calculated from the potentiometric titration data of the 1:1 vanadyl sulphate-catechol system (curves 1-3, fig.1) together with a single inflexion point at $m = 3$, indicated that the normal 1:1 chelate (I) undergoes hydrolysis with the formation of a hydroxo complex and there is some overlap between the two successive reactions. The hydrolytic reaction may be represented as:

$$VOA + H_2O \rightleftharpoons VO(OH)A^- + H^+ \qquad \text{... (ii)}$$

The hydrolysis constant, K_h, may be expressed as:

$$K_h = \frac{[VO(OH)A^-]\,[H^+]}{[VOA]} \qquad \text{... (11)}$$

The overall reaction in the system may be written as:

$$VO^{2+} + H_2A + H_2O \rightleftharpoons VO(OH)A^- \; + 3H^+$$

The equilibrium constant for the above reaction may be given by

$$K_H = \frac{[VO(OH)A^-][H^+]^3}{[VO^{2+}]\,[H_2A]} \qquad \text{... (12)}$$

Other pertinent equations are,

$$T_M = [VO^{2+}] + [VO(OH)^+] + 2[(VO[OH])_2^{2+}] + [VOA] + [VO(OH)A^-] \qquad \text{... (13)}$$

$$T_{OH} + [H^+] = [VO(OH)^+] + 2[(VO[OH])_2^{2+}] + 2[VOA] + 3[VO(OH)A^-] \qquad \text{... (14)}$$

$$T_A = [H_2A] + [VOA] + [VO(OH)A^-] \qquad \text{... (15)}$$

Here also, in the pH range studied, concentrations of HA^-, A^{2-} and OH^- were negligible as compared to those of the other species present in the system.

Elimination of $\left[VO(OH)A^-\right]$ between equations 13 and 14 gives

$$3T_M - T_{OH} - \left[H^+\right] = 3\left[VO^{2+}\right] + 2\left[VO(OH)^+\right] + 4\left[(VO[OH])_2^{2+}\right] + \left[VOA\right] \qquad \ldots (16)$$

Combination of equations 1-3 and 16 gives,

$$3T_M - T_{OH} - \left[H^+\right] = 3\left[VO^{2+}\right] + \frac{2x10^{-6.0}}{\left[H^+\right]}\left[VO^{2+}\right] + \frac{4x10^{-6.88}}{|H^+|^2}\left[VO^{2+}\right]^2$$

$$+ \frac{K_1\left[H_2A\right]}{\left[H^+\right]^2}\left[VO^{2+}\right] \qquad \ldots (17)$$

In a 1:1 reaction mixture, since $T_A = T_M$, from equations 13 and 15 we obtain

$$\left[H_2A\right] = \left[VO^{2+}\right] + \left[VO[OH]^+\right] + 2\left[(VO[OH])_2^{2+}\right] \qquad ..(18)$$

Combination of (17) and (18) and rearrangement of the terms into the form of a polynomial yield :

$$a\left[VO^{2+}\right]^3 + b\left[VO^{2+}\right]^2 + c\left[VO^{2+}\right] - d = 0 \qquad \ldots (19)$$

where

$$a = \frac{2K_1x10^{-6.88}}{\left[H^+\right]^4}, \quad b = \frac{4x10^{-6.88}}{\left[H^+\right]^2} + \frac{K_1x10^{-6.0}}{\left[H^+\right]^3} + \frac{K_1}{\left[H^+\right]^2},$$

$$c = 3 + \frac{2x10^{-6.0}}{\left[H^+\right]} \quad \text{and} \quad d = 3T_M - T_{OH} - \left[H^+\right]$$

Knowing the value of K_1(from tables I and II), equilibrium concentration of free vanadyl ions present in the solution could be determined by solving equation 19 with the help of Newton's method[24] of successive approximations using I.B.M. 1620 computer. Concentrations of the other species present in the equilibrium mixture could then be calculated from the above equations. The values K_h and K_H could thus be determined. Here also, in order to detect polymerization of the hydroxo chelate (II), these constants were determined over a four-fold concentration range of the metal chelate. The results of these calculations, obtained from the potentiometric data of curves 1-3 (Fig.1) are given in table III.

Table III

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

m	1.24	1.40	1.56	1.72	1.80	1.88	2.04	2.20
pH	4.31	4.41	4.50	4.62	4.68	4.73	4.86	5.05
$-\log K_h$	5.02	5.07	5.04	5.09	5.12	5.08	5.09	5.18
$-\log K_H$	10.87	10.92	10.89	10.94	10.96	10.93	10.94	11.03

Average value of $-\log K_h = 5.09 \pm 0.69$ and

$-\log K_H = 10.93 \pm 0.10$

Curve 2 (Fig.1), $T_A = T_M = 2.5\times10^{-3}M$

m	1.24	1.40	1.56	1.72	1.80	1.88	2.04	2.20
pH	4.45	4.54	4.63	4.73	4.80	4.86	5.01	5.14
$-\log K_h$	5.19	5.14	5.17	5.13	5.13	5.16	5.16	5.13
$-\log K_H$	11.05	11.00	10.99	11.01	11.02	11.01	11.09	11.08

Average value of $-\log K_h = 5.15\pm0.04$ and

$-\log K_H = 11.03\pm0.06$

Curve 3 (Fig.1), $T_A = T_M = 1.25\times10^{-3}M$

m	1.08	1.24	1.40	1.56	1.72	1.80	1.88	2.04
pH	4.46	4.52	4.62	4.74	4.83	4.87	4.95	5.12
$-\log K_h$	4.91	4.85	4.96	5.15	5.14	5.11	5.17	5.18
$-\log K_H$	10.83	10.75	10.85	11.00	10.99	10.96	11.05	11.12

Average value of $-\log K_h = 5.06\pm0.12$ and

$-\log K_H = 10.94\pm0.18$

Again, it is evident from the above table that the values of pK_h and pK_H are almost independent of the concentration of the metal chelate indicating that the monohydroxo complex also does not polymerize under the experimental conditions employed.

By the use of the equilibrium constants presented in tables I-III and the equations given in the mathematical treatment of the data, it was possible to determine the distribution of the chelate species I and II as a function of the total metal chelate concentration and pH of the reaction mixture

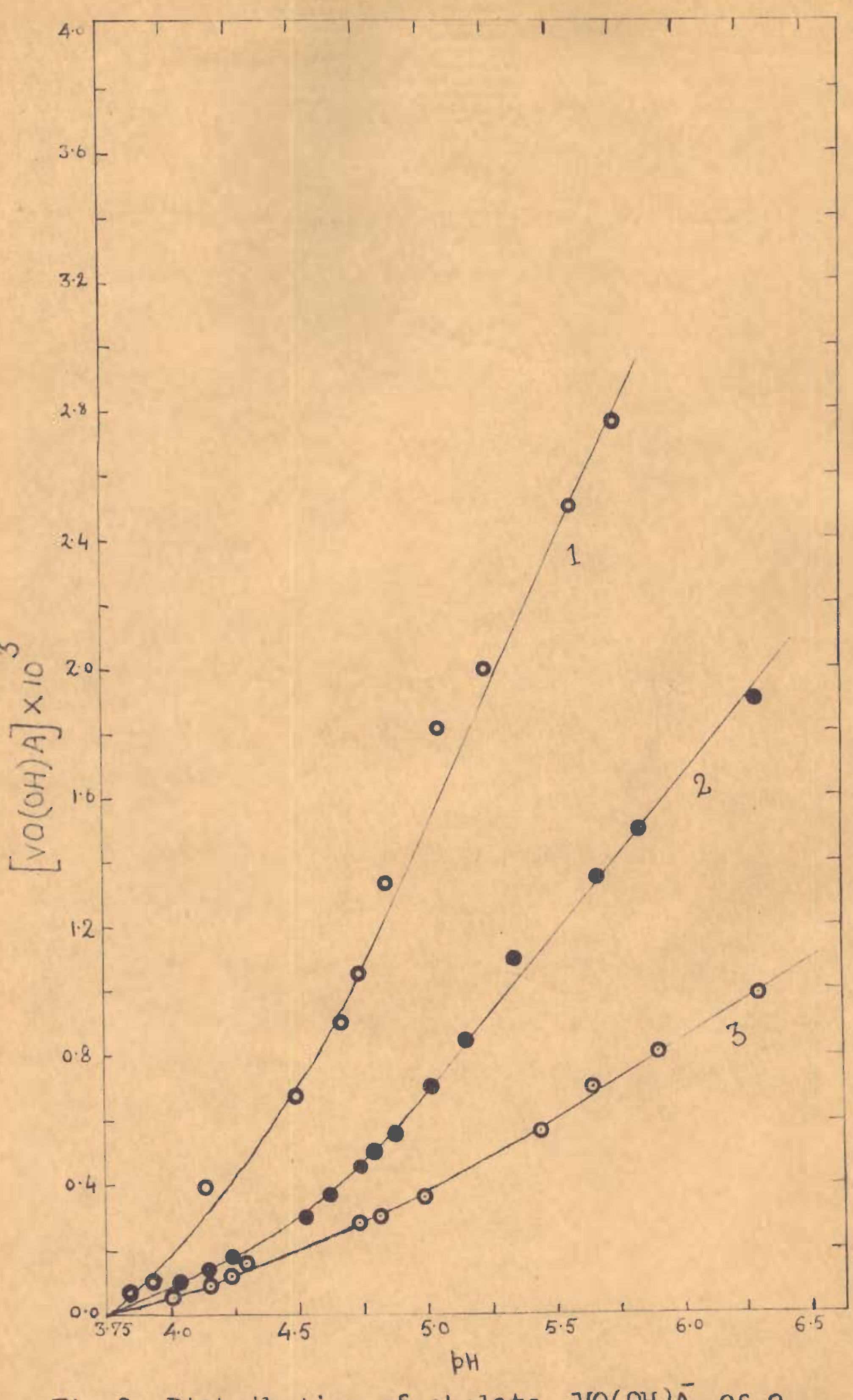


Fig.3. Distribution of chelate, $VO(OH)\bar{A}$, as a function of pH in 1:1 vanadyl-catechol system (curves 1,2 & 3, Fig.1).
Curve 1, $T_M = 5 \times 10^{-3}M$,
Curve 2, $T_M = 2.5 \times 10^{-3}M$,
Curve 3, $T_M = 1.25 \times 10^{-3}M$.

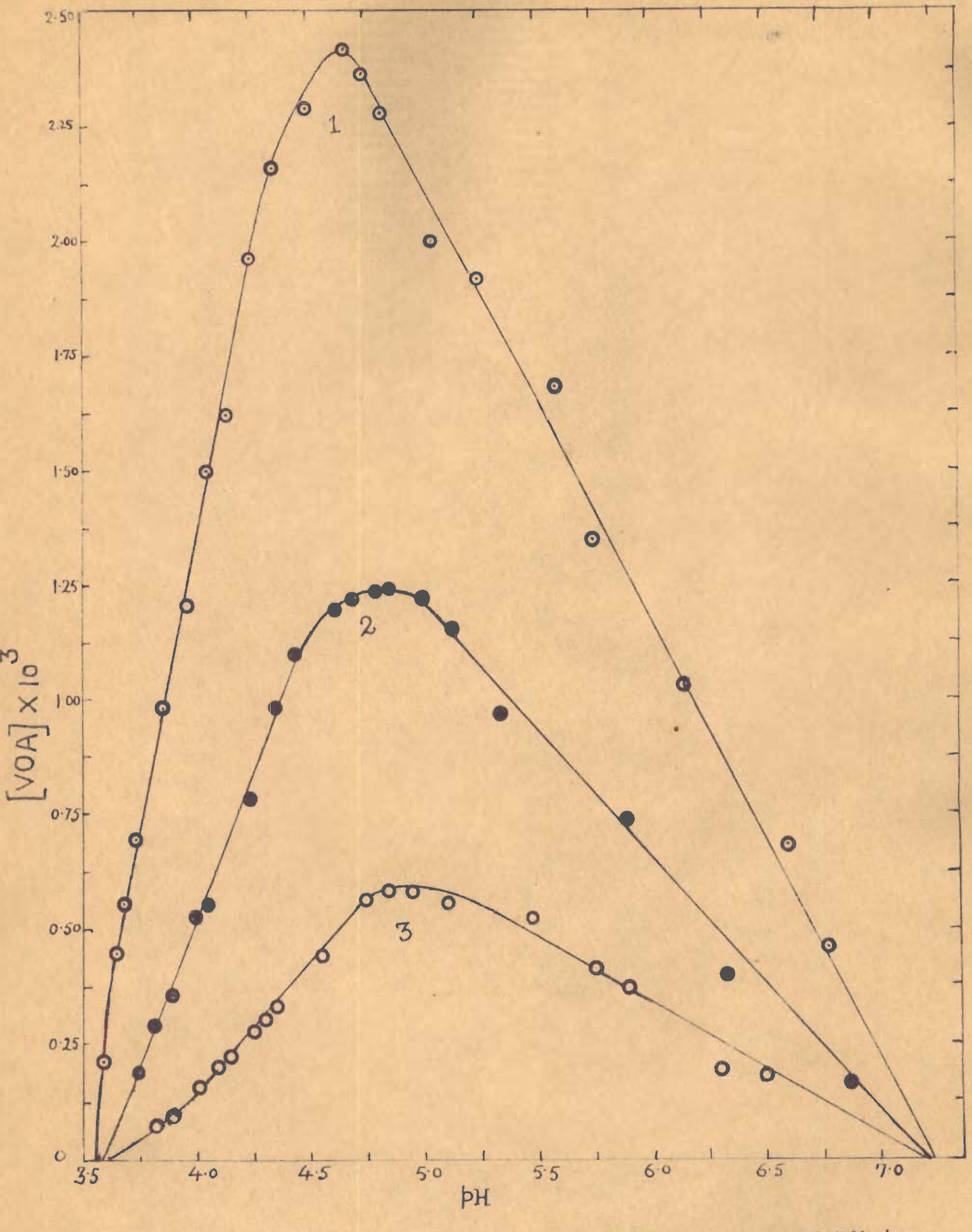
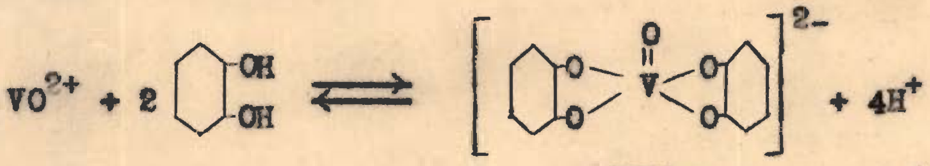


Fig.2. Distribution of chelate, VOA, as a function of pH in 1:1 vanadyl-catechol system. (Curves 1,2 & 3, Fig.1) Curve 1, $T_M = 5\times10^{-3}$M, Curve 2, 2.5×10^{-3}M, Curve 3, 1.25×10^{-3}M.

containing an equimolar concentration of vanadyl sulphate and catechol. Figure 2 thus shows that formation of the normal 1:1 chelate starts from a pH of about 3.6. Concentration of the complex becomes maximum around pH 4.7, above which reaction (ii) becomes more significant (Fig.3), the concentration of VOA, therefore, falls and ultimately as the system approaches a pH$\sim$7, the complex is completely converted into the hydroxo chelate $VO(OH)A^-$.

Interaction of one Mole of Vanadyl Sulphate with two Moles of Catechol:

Curve 4 (Fig.1) for the potentiometric titration of vanadyl sulphate with KOH in the presence of two moles of catechol is throughout lower than the curve 1 for a similar titration of vanadyl sulphate in the presence of one mole of catechol. The lowering, however, increases above pH of about 4 and a sharp inflexion occurs at m = 4. Inflexion point at m=4 is in accord with the reaction:



(III) ... (iii)

The above conclusion is supported by a spectrophotometric study reported by Bhattacharya and Banerji[18]. The relatively constant values of pK_1, the equilibrium constant for the formation of a normal 1:1 chelate, obtained up to a pH of about 4 (table II), indicated that the 1:1 complex (I) is the predominant metal chelate species present in the system below pH of 4. The lowering in curve 4 (cf. curve 1, fig.1) up to this pH may, thus, be accounted for on the basis of the formation of 1:1 metal chelate formed as a function of total concentration of catechol present in the system. Above pH of 4, the 1:1 complex begins to combine with another mole of catechol present in the system with the formation of a 1:2 complex. Since the hydrolysis of the normal 1:1 complex takes place in the same pH range (table III) in which formation of 1:2 complex occurs, a portion of the former may be converted into the monohydroxo complex (II) which by raising the pH of the solution by the addition of alkali, in the presence of an excess of catechol, is gradually converted into the 1:2 complex. Thus, three chelate species, viz., VOA, $VO(OH)A^-$ and VOA_2^{2-}, appear to exist in the system. A single inflexion point at m = 4 indicates that the successive reactions for the formation of various chelate species in the system overlap.

Determination of Equilibrium Constants

Reaction for the formation of 1:2 complex may be represented as:

$$VOA + H_2A \rightleftharpoons VOA_2^{2-} + 2H^+$$

Equilibrium constant K_2, of the reaction may be expressed as:

$$K_2 = \frac{[VOA_2^{2-}][H^+]^2}{[VOA][H_2A]} \qquad \ldots (20)$$

K, the equilibrium constant of the overall reaction,

$$VO^{2+} + 2H_2A \rightleftharpoons VOA_2^{2-} + 4H^+$$

may be defined as:

$$K = \frac{[VOA_2^{2-}][H^+]^4}{[VO^{2+}][H_2A]^2} \quad \ldots (21)$$

Assuming that only mononuclear metal chelate species are formed in the system, the following equations for material balance in solution may be readily deduced:

$$T_M = [VO^{2+}] + [VO(OH)^+] + 2[(VO(OH))_2^{2+}] + [VOA] + \\ + [VO(OH)A^-] + [VOA_2^{2-}] \quad \ldots (22)$$

$$T_{OH} + [H^+] = [VO(OH)^+] + 2[(VO(OH))_2^{2+}] + 2[VOA] + \\ + 3[VO(OH)A^-] + 4[VOA_2^{2-}] \quad \ldots (23)$$

and

$$T_A = [H_2A] + [VOA] + [VO(OH)A^-] + 2[VOA_2^{2-}] \quad .. (24)$$

Elimination of $[VOA_2^{2-}]$ between (23) and (24) gives,

$$2T_A - T_{OH} - [H^+] = 2[H_2A] - [VO(OH)^+] - 2[(VO(OH))_2^{2+}] - \\ [VO(OH)A] \quad \ldots (25)$$

Combination of equations 2,3,12 and 25 gives,

$$[H_2A] = \frac{2T_A - T_{OH} - [H^+] + \frac{K_{h1}}{[H^+]}[VO^{2+}] + 2\frac{K_{h2}}{[H^+]^2}[VO^{2+}]^2}{2 - \frac{K_H}{[H^+]^3}[VO^{2+}]} \quad \ldots (26)$$

Again, combining equations 1-3, 12, 22 and 23 we get,

$$4T_M - T_{OH} - [H^+] = 4[VO^{2+}] + 3\frac{K_{h_1}}{[H^+]}[VO^{2+}] + \frac{6K_{h_2}}{[H^+]^2}[VO^{2+}]^2 +$$

$$\frac{2K_1[H_2A]}{[H^+]^2}[VO^{2+}] + \frac{K_H[H_2A]}{[H^+]^3}[VO^{2+}] \qquad \ldots (27)$$

Now substituting the value of $[H_2A]$ from equation 26 in equation 27 and then rearranging the terms into the form of a polynomial we have,

$$a[VO^{2+}]^3 + b[VO^{2+}]^2 + c[VO^{2+}] + d = 0 \qquad \ldots (28)$$

where

$$a = \frac{2xK_{h_2}}{[H^+]^4}\left[\frac{K_H}{[H^+]} - K_1\right],$$

$$b = \frac{K_{h_1}}{[H^+]^3}\left[\frac{K_H}{[H^+]} - K_1\right] + \frac{2}{[H^+]^2}\left[\frac{K_H}{[H^+]} - 3\,K_{h_2}\right]$$

$$c = \frac{1}{[H^+]^2}\left[\frac{K_H}{[H^+]} + K_1\right]\left[T_{OH} + [H^+] - 4T_M\right] - \frac{3K_{h_1}}{[H^+]} - 4,$$

and

$$d = 4T_M - T_{OH} - [H^+]$$

Knowing the values of K_{h_1}, K_{h_2} (from equations 2 and 3) and the equilibrium constants K_1 and K_H (from tables I-III), computati of the equilibrium concentration of the free vanadyl ions, present in solution, could be made by solving equation 28. Concentrations of the other species present in the equilibrium mixture could then be calculated with the help of the above equations and the values of pK and pK_2 could, thus, be determined from various points of the titration curve. The results of these calculations are presented in table IV.

Table IV

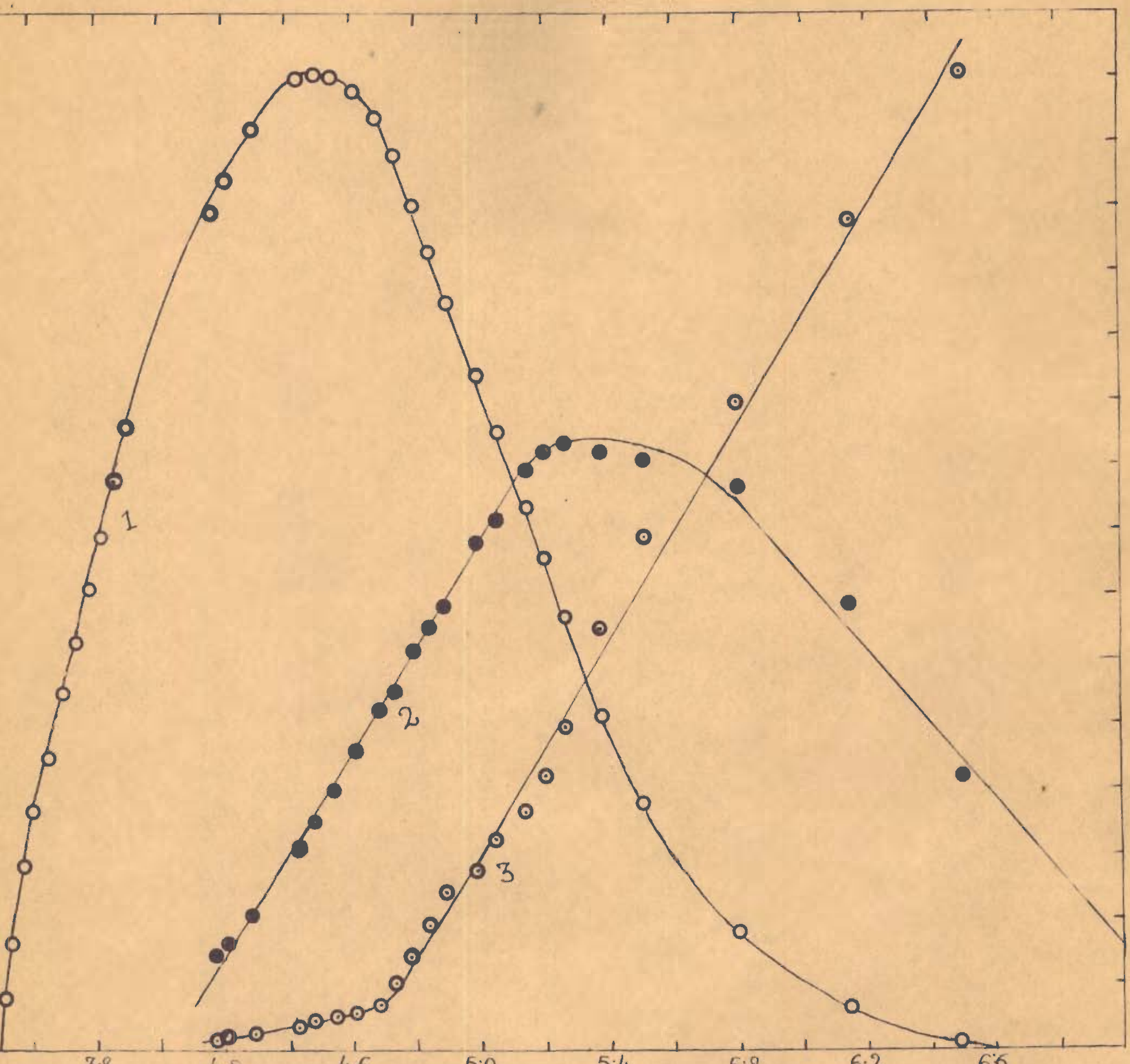
Curve 4 (Fig.1): $T_A = 2T_M = 1.0 \times 10^{-2}$M.

m	1.40	1.56	1.72	1.88	2.04	2.20	2.36	2.52
pH	4.17	4.25	4.34	4.43	4.53	4.66	4.79	4.89
pK_2	8.01	8.06	8.22	8.17	8.09	8.15	8.15	8.02
pK	13.86	13.91	14.07	14.03	13.95	14.01	14.01	13.88

Average value of pK = 13.96 ± 0.11 and pK_2 = 8.11 ± 0.06

In this connection it may be pointed out that since the hydrogen ion concentration appears as the fourth power in the expression for the equilibrium constant (equation 21), an experimental error of only ±0.02 pH unit would give an appreciable deviation in the values of the equilibrium constants. The accuracy of the values of these constants, given in Table IV, is, therefore, limited to about ±0.15 pK units.

After computation of the equilibrium constants, distribution of the various chelate species as a function of pH of the solution could be determined. This has been



.4. Distribution of chelate species VOA, VO(OH)A$^-$ and VOA$_2^{2-}$ (curves 1,2 & 3 respectively) as a function of pH in a 1:2 vanadyl-catechol chelate system(curve 4, Fig.1).

presented in Figure 4.

Stability of 1:2 Chelate

Formation constant K_{MA_2} of the 1:2 complex and the overall stability constant K'_{MA_2} of the metal chelate may be defined as:

$$K_{MA_2} = \frac{[VOA_2^{2-}]}{[VOA]\,[A^{2-}]} \qquad \ldots (29)$$

and

$$K'_{MA_2} = \frac{[VOA_2^{2-}]}{[VO^{2+}]\,[A^{2-}]^2} \qquad \ldots (30)$$

Using the equations 20, 21 and the expressions for K_{a_1} and K_{a_2}, the dissociation constants of catechol, it may be shown that,

$$K_{MA_2} = \frac{K_2}{K_{a_1}\,K_{a_2}} \qquad \ldots (31)$$

and

$$K'_{MA_2} = \frac{K}{K_{a_1}^2\,K_{a_2}^2} \qquad \ldots (32)$$

Substitution of the values of K_2 and K (from table IV) and the dissociation constants of the ligand, reported by Heureux and Martell[23], thus, gave the values of $\log K_{MA_2}$ and $\log K'_{MA_2}$ equal to 13.02 and 28.30 respectively.

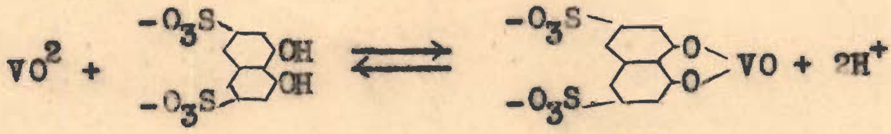
SECTION II

OXOVANADIUM (IV) CHELATES OF CHROMOTROPIC ACID

Although chromotropic acid (1,8-dihydroxynaphthalene 3,6-disulphonate, DNS) complexes of oxovanadium(IV) have been reported earlier[25-27], a survey of literature revealed that a quantitative study of the equilibria involved in the interaction of VO^{2+} with DNS has not been carried out. In order to have an understanding of the nature of these simple chelates, therefore, it was considered worthwhile to carry out a mathematical analysis of the potentiometric data arising from the interaction of VO^{2+} with DNS. For a comparison of the stabilities of these simple complexes with those of the mixed ligand chelates, attempts were made to determine formation constants of the complexes under the experimental conditions employed in the study of mixed-ligand systems.

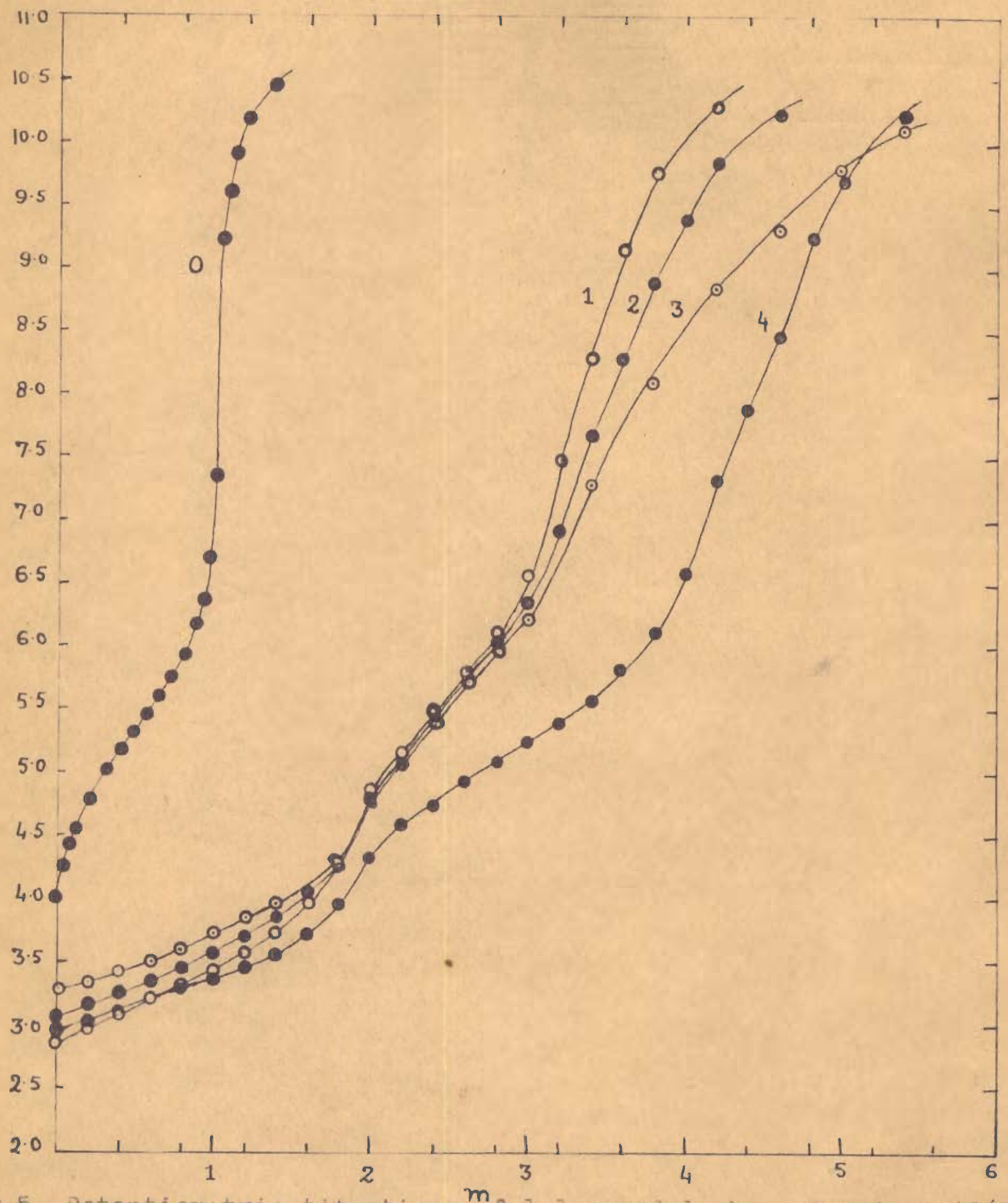
RESULTS AND DISCUSSION

Curve 1 (Fig.5), for the potentiometric titration of an equimolar mixture of vanadyl sulphate and chromotropic acid (disodium salt, DNS) with KOH, exhibits sharp inflexion points at m = 2 and m = 3. An inflexion point at m =2 is in accord with the reaction:



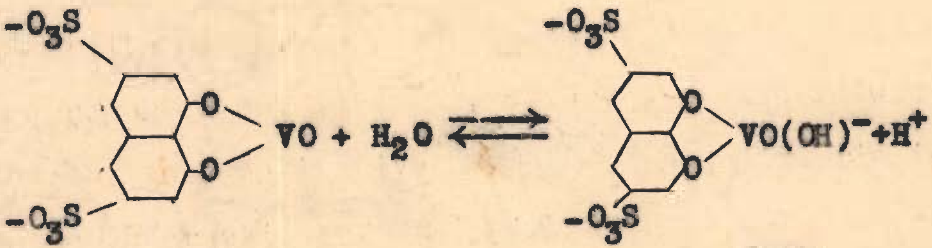
...(i)

(I)



g.5. Potentiometric titrations of 1:1 vanadyl-chromotropic acid(DNS) elate systems with KOH(0.1N). Concentrations: curve 1, $5x10^{-3}$M; curve 2, 5x10^{-3}M; curve 3, $1.25x10^{-3}$M. Curve 4, represents similar titration of 2 vanadyl-DNS system, curve 0, represents titration of DNS with KOH. nic strength=0.1M(KCl). m=moles of base added per mole of the metal n. In the lower buffer regions portion of the curves for the neutrazation of HCl present in VO(IV) soln. has been eliminated.

The occurrence of a buffer region in the range m = 2 to 3 indicates a reaction of the type:



...(ii)

(II)

In order to verify the above conclusions, attempts were made to determine the equilibrium constant K_1 of reaction (i) from the potentiometric data of the lower buffer region and K_h, the hydrolysis constant of the chelate, represented by reaction (ii), from the data of the upper buffer region of the curve.

If H_2A^{2-} represents chromotropic acid, the equilibrium constant K_1 may be defined as:

$$K_1 = \frac{[VOA^{2-}][H^+]^2}{[VO^{2+}][H_2A^{2-}]} \qquad \ldots(33)$$

and the hydrolysis constant K_h may be expressed as:

$$K_h = \frac{[VO(OH)A^{3-}][H^+]}{[VOA^{2-}]} \qquad \ldots(34)$$

By using the mathematical treatment of data presented by equations 1-8 in the vanadyl catechol system, the values of K_1 , obtained from various points on the lower buffer region of curve 1 (Fig.5) are given in table V.

Table V

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

m	0.20	0.40	0.60	0.80	1.00	1.20	1.40
pH	2.97	3.08	3.19	3.30	3.43	3.56	3.71
$-\log K_1$	4.08	4.07	4.08	4.08	4.11	4.11	4.10

Average value of $-\log K_1 = 4.09\pm0.02$

Hydrolysis Constant:

The hydrolysis constant K_h, defined by (34), may be determined with the help of the material balance equations:

$$T_M = [VOA^{2-}] + [VO(OH)A^{3-}] \qquad \ldots (35)$$

$$T_{OH} + [H^+] = [VO(OH)A^{3-}] \qquad \ldots (36)$$

and

$$T_A = [VOA^{2-}] + [VO(OH)A^{3-}] \qquad \ldots (37)$$

Values of K_h, calculated from the potentiometric data of the upper buffer region of curve 1 (Fig.5) are presented in table VI.

Table VI

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

m	2.2	2.3	2.4	2.5	2.6
pH	5.17	5.32	5.50	5.65	5.82
$-\log K_h$	5.66	5.68	5.67	5.65	5.64

Average value of $-\log K_h = 5.66 \pm 0.02$

The success thus achieved in obtaining constant values of the equilibrium constants (tables V and VI) clearly shows that a normal 1:1 metal complex(I) is the only chelate species formed in the lower buffer region of the curve and in the upper buffer region the complex(I) undergoes hydrolysis in accordance with reaction (ii).

Having established the nature of the chelation reactions occurring in the system, it was considered of interest to investigate polymerization of the chelates formed in the solution. Titrations of 1:1 mixtures of vanadyl sulphate and chromotropic acid were, therefore, carried out at various concentrations of the metal salt. Values of the constants K_1 and K_h, determined from the titration data of these curves (curves 2 and 3, Fig.5), are listed in tables VII and VIII respectively.

Table VII

Curve 2 (Fig.5), $T_A = T_M = 2.5\times10^{-3}M$

m	0.2	0.4	0.6	0.8	1.0	1.2	1.4
pH	3.15	3.25	3.35	3.46	3.58	3.71	3.86
$-\log K_1$	4.05	4.05	4.06	4.07	4.09	4.10	4.10

Average value of $-\log K_1 = 4.07\pm0.03$

Curve 3 (Fig.5), $T_A = T_M = 1.25\times10^{-3}M$

m	0.2	0.4	0.6	0.8	1.0	1.2	1.4
pH	3.34	3.42	3.50	3.60	3.71	3.84	3.97
$-\log K_1$	4.02	4.00	3.98	3.98	3.99	4.01	3.97

Average value of $-\log K_1 = 3.99\pm0.03$

Table VIII

Curve 2 (Fig.5), $T_A = T_M = 2.5\times10^{-3}M$

m	2.2	2.3	2.4	2.5	2.6
pH	5.10	5.29	5.50	5.67	5.80
$-\log K_h$	5.70	5.65	5.68	5.67	5.62

Average value of $-\log K_h = 5.66\pm0.04$

Curve 3 (Fig.5), $T_A = T_M = 1.25\times10^{-3}M$

m	2.2	2.3	2.4	2.5	2.6
pH	5.06	5.25	5.44	5.66	5.78
$-\log K_h$	5.64	5.61	5.61	5.59	5.60

Average value of $-\log K_h = 5.61\pm0.03$

It is evident from tables V-VIII that the values of pK_1 and pK_h are almost independent of concentration of the metal chelate, indicating that both the species, the normal 1:1 chelate (I) and the monohydroxo complex(II), do not polymerize to any significant extent under the experimental conditions employed.

Stability of 1:1 Chelate

After determining equilibrium constant K_1 of reaction (i) (tables V and VII), formation constant of the chelate:

$$K_{MA} = \frac{[VOA^{2-}]}{[VO^{2+}][A^{4-}]} \qquad \ldots (38)$$

may be determined from the expression

$$K_{MA} = \frac{K_1}{K_{a_1} K_{a_2}} \qquad \ldots (39)$$

where K_{a_1} and K_{a_2} represent the dissociation constants of the ligand (H_2A^{2-}), defined by

$$K_{a_1} = \frac{[HA^{3-}][H^+]}{[H_2A^{2-}]} \qquad \ldots (40)$$

and

$$K_{a_2} = \frac{[A^{4-}][H^+]}{[HA^{3-}]} \qquad \ldots (41)$$

Substitution of the values of K_1 (from tables V and VII average value of $pK_1 = 4.05$), K_{a_1} ($10^{-5.34}$) and

K_{a_2} $(10^{-15.60})^{ref.23}$ in (39) gives a value of log K_{MA} equal to 16.89.

Analysis of the Potentiometric data of Curve 4 (Fig.5) :

Curve 4 (Fig.5) for the titration of a reaction mixture containing 1:2 molar ratio of vanadyl sulphate to chromotropic acid is throughout lower than the curve 2 for the corresponding titration of a 1:1 mixture of vanadyl sulphate and chromotropic acid, and shows inflexion points at m = 2 and m = 4. A similar nature of this curve with curve 2 in the range m = 0 to 2 is indicative of the formation of a 1:1 chelate (I) (reaction i) in the system.

In order to verify the above conclusion, attempts were made to calculate the equilibrium constant K_1 from the potentiometric data of the lower buffer region of curve 4 by using the mathematical treatment employed in the 1:1 vanadyl sulphate-chromotropic acid system. The results of these calculations are given in table IX.

Table IX

Curve 4 (Fig.5), $T_A = 2\ T_M = 5 \times 10^{-3}M$

m	0.2	0.4	0.6	0.8	1.0	1.2	1.4
pH	3.03	3.12	3.18	3.26	3.35	3.45	3.56
$-\log K_1$	4.06	4.09	4.05	4.05	4.06	4.08	4.09

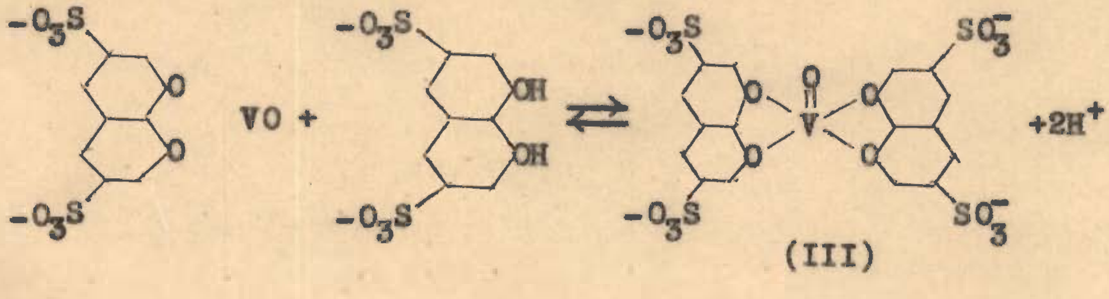
Average value of $-\log K_1 = 4.07 \pm 0.02$

The relatively constant values of pK_1(cf. table VII), observed in Table IX, showed that even in the presence of an excess of the ligand only a 1:1 metal chelate(I) is formed in the lower buffer region of the curve. An inflexion point at m = 2 thus indicated the complete conversion of vanadyl ions in the system into the normal 1:1 metal chelate (I).

Beyond m = 2, lowering in the curve (cf. curve 2) becomes more significant. In the range m = 2 to 4, the curve may be interpreted in two different ways:

I. As this portion of the curve (m = 2-4) appears to be a composite of the upper buffer region of curve 2 for the titration of 1:1 chelate system and the curve 0 for the titration of the free ligand, a probable explanation may be based on the assumption of the formation of a hydroxo 1:1 complex of the type (II) (reaction ii) and the neutralization of free ligand (one mole) present in the system.

II. Lowering shown by the curve in the range m = 2 to 4 and an inflexion point at m = 4 may also be accounted for on the basis of the combination of 1:1 complex (I) with another mole of the ligand in accordance with the reaction:



(III)

In order to characterize the reactions occurring in the system, attempts were first made to analyse the potentiometric data of the upper buffer region of the curve on the basis of model I.

From the values of $10^{-5.34}$ and $10^{-15.60}$ for the dissociation constants of the phenolic protons of the ligand, it is evident that only one proton of the phenolic groups may dissociate under the experimental conditions (see curve 0, Fig.5). Therefore, taking into account the reaction:

$$H_2A^{2-} \rightleftharpoons HA^{3-} + H^+$$

from the material balance, we obtain

$$T_M = [VOA^{2-}] + [VO(OH)A^{3-}] \qquad \ldots(42)$$

$$T'_{OH} + [H^+] = [VO(OH)A^{3-}] + [HA^{3-}] \qquad \ldots(43)$$

$$T_A = [H_2A^{2-}] + [HA^{3-}] + [VOA^{2-}] + [VO(OH)A^{3-}] \qquad \ldots(44)$$

In equation 43, T'_{OH} represents the concentration of KOH added at any point in the titration beyond m = 2.

In reaction mixture containing a 1:2 initial molar ratio of vanadyl sulphate to chromotropic acid, since $T_A = 2\ T_M$, combination of equations 40 and 42-44 gives

$$[VO(OH)A^{3-}] = \overset{?}{T_{OH}} + [H^+] - T_M \Big/ \left(1 + \frac{[H^+]}{K_{a_1}} \right) \qquad \ldots(45)$$

Substitution of $[VO(OH)A^{3-}]$ from (45) in (42) yields

$$[VOA^{2-}] = T_M - T_{OH} - [H^+] + \frac{T_M}{\left(1 + \frac{[H^+]}{K_{a_1}}\right)} \quad \ldots(46)$$

Having determined the concentrations of the species VOA^{2-} and $VO(OH)A^{3-}$, the hydrolysis constant K_h may then be calculated. Values of K_h, obtained from the titration data in the range m = 2-4 are presented in table X.

Table X

Curve 4 (Fig.5), $T_A = 2T_M = 5 \times 10^{-3}$M

m	2.4	2.6	2.8	3.0	3.2	3.4	3.6
pH	4.74	4.93	5.08	5.22	5.38	5.57	5.76
$-\log K_h$	5.32	5.25	5.17	5.10	5.05	5.02	4.97

A gradual fall in the values of $-\log K_h$, observed in table X, indicated that the solution contained a greater concentration of hydrogen ions than that would be on the basis of postulate I. Potentiometric data were then treated in accordance with the model II as given below:

Interaction of 1:1 chelate, VOA^{2-}, with another mole of the ligand may be represented as

$$VOA^{2-} + H_2A^{2-} \rightleftharpoons \underset{(III)}{VOA_2^{6-}} + 2H^+ \quad \ldots \text{(iii)}$$

Equilibrium constant K_2 of the reaction may be expressed as:

$$K_2 = \frac{[VOA_2^{6-}]\,[H^+]^2}{[VOA^{2-}]\,[H_2A^{2-}]} \qquad \ldots (47)$$

Since dissociation of a phenolic proton of the ligand and the hydrolysis of VOA^{2-} (reaction ii) take place in the same pH range in which reaction (iii) is assumed to occur, taking into account these factors, from the material balance we obtain:

$$T_M = [VOA^{2-}] + [VO(OH)A^{3-}] + [VOA_2^{6-}] \qquad \ldots (48)$$

$$T'_{OH} + [H^+] = [HA^{3-}] + [VO(OH)A^{3-}] + 2[VOA_2^{6-}] \qquad \ldots (49)$$

$$T_A = [H_2A^{2-}]+[HA^{3-}]+[VOA^{2-}]+[VO(OH)A^{3-}]+2[VOA_2^{6-}] \qquad \ldots (50)$$

In a 1:2 $VOSO_4$ - chromotropic acid reaction mixture, since $T_A = 2T_M$, from equations 48 and 50 we obtain

$$[VOA^{2-}] + [VO(OH)A^{3-}] = [H_2A^{2-}]+[HA^{3-}] \qquad \ldots (51)$$

Again from (49) and (50) we get

$$T_A - T'_{OH} - [H^+] = [H_2A^{2-}]+[VOA^{2-}] \qquad \ldots (52)$$

Combination of (34), (40), (51) and (52) yields

$$\left[H_2A^{2-}\right] = \frac{\left(1 + \frac{K_h}{\left[H^+\right]}\right)\left(T_A - T_{OH}' - \left[H^+\right]\right)}{2 + \frac{1}{\left[H^+\right]}\left(K_{a_1} + K_h\right)} \qquad \ldots (53)$$

After computation of $\left[H_2A^{2-}\right]$, concentration of VOA^{2-} may be obtained from (52), and $\left[VO(OH)A^{3-}\right]$ may then be calculated from (34). Having determined $\left[VOA^{2-}\right]$ and $\left[VO(OH)A^{3-}\right]$, concentration of the 1:2 complex, $\left[VOA_2^{6-}\right]$, may be calculated from equation 48. Values of the equilibrium constant K_2, thus obtained from various points on the upper buffer region of curve 4 (Fig.5) are presented in table XI.

Table XI

Curve 4(Fig.5), $T_A = 2T_M = 5x10^{-3}M$

m	2.4	2.6	2.8	3.0	3.2	3.4	3.6
pH	4.74	4.93	5.08	5.22	5.38	5.57	5.76
$-\log K_2$	7.88	7.88	7.85	7.82	7.84	7.89	7.81

Average value of $-\log K_2 = 7.85 \pm 0.04$

The success thus obtained in calculating the equilibrium constant K_2 and the failure to obtain constant values of pK_h on the basis of model I (table X) strengthens the validity of postulate II. Formation of a 1:2 vanadyl-chromotropic acid chelate is, therefore, believed to occur in the system.

Stability of 1:2 Complex

Having established the formation of a 1:2 vanadyl-chromotropic acid chelate in the system, formation constant K_{MA_2} of the complex defined by

$$K_{MA_2} = \frac{\left[VOA_2^{6-}\right]}{\left[VOA^{2-}\right]\left[A^{4-}\right]} \qquad \ldots (54)$$

may be determined from the expression:

$$K_{MA_2} = \frac{K_2}{K_{a_1}\,K_{a_2}} \qquad \ldots (55)$$

Thus, substitution of the values of K_2 (Average value of pK_2 from table XI is equal to 7.85), K_{a_1} ($10^{-5.34}$) and Ka_2($10^{-15.60}$)$^{\text{ref.23}}$ yields a value of log K_{MA_2} equal to 13.09.

SECTION III

OXOVANADIUM (IV) CHELATES OF MANDELIC AND LACTIC ACIDS

Although complexes of vanadyl ion with glycolic, tartaric and citric acids have been known[28-32] since the earliest investigation of vanadium chemistry, chelates of mandelic acid (phenyl-glycolic acid) have, however, received little attention by the earlier workers. Before carrying out a study of the mixed-ligand systems involving mandelic and lactic acids as ligands, therefore, it was considered of interest to investigate the nature of the simple mandelate and lactate complexes of VO(IV) formed in aqueous solutions.

RESULTS AND DISCUSSION

VANADYL-MANDELATE CHELATES

Curve 0 (Fig.6) for the titration of mandelic acid with KOH shows a sharp inflexion at one equivalent of alkali indicating the neutralization of carboxylic proton of the acid. The α-hydroxy hydrogen atom of the ligand thus remains unaffected under the experimental conditions.

Curve 1 (Fig.6) for the titration of an equimolar mixture of vanadyl sulphate and mandelic acid shows a slight inflexion near $m = 2$ and a sharp inflexion at about $m = 3$. A hint of inflexion near $m = 2$ is indicative

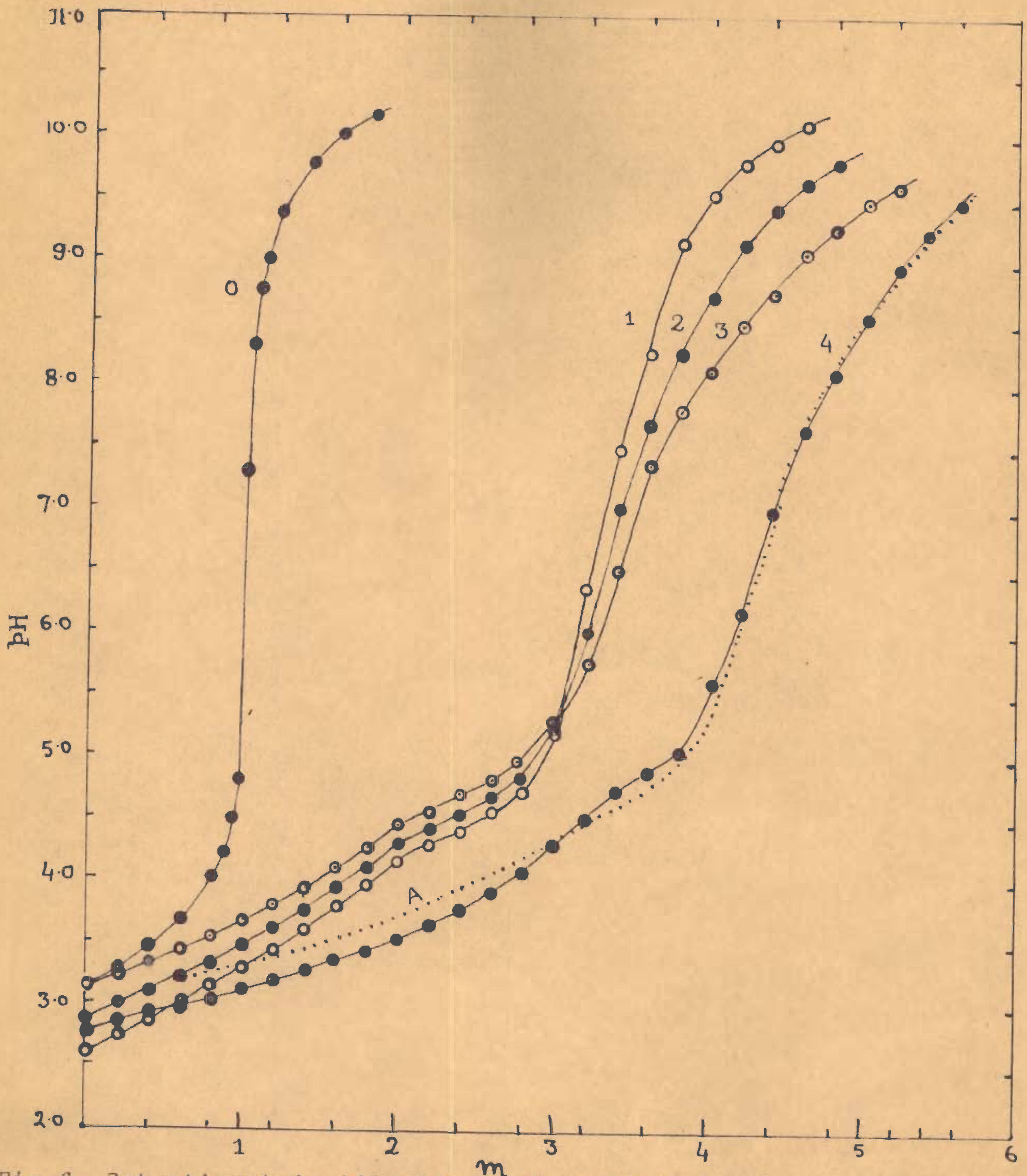
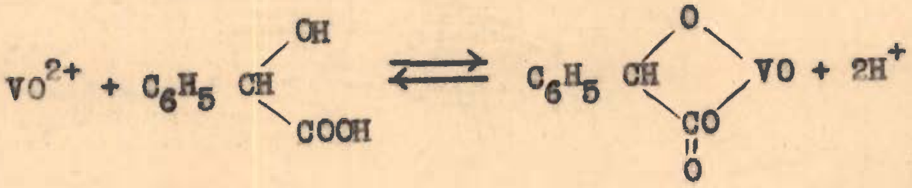


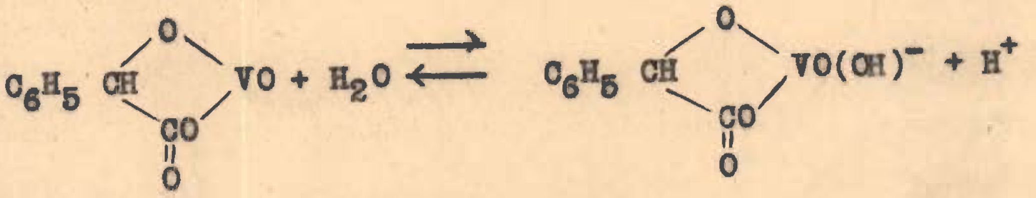
Fig.6. Potentiometric titrations of vanadyl-mandelate chelate systems with KOH(0.1N): Curve 0,2.5x10^{-3}M in mandelic acid; Curve 1, 5x10-^{3}M in VO(IV) and 5x10^{-3}M in mandelic acid; curve 2, 2.5x10^{-3}M in VO(IV) and 2.5x10^{-3}M in mandelic acid; Curve 3, 1.25x10^{-3}M in VO(IV) and 1.25x10^{-3}M in mandelic acid; Curve 4, 2.5x10^{-3}M in VO(IV) and 5.0x10^{-3}M in mandelic acid, Curve A, composite curve of 0 and 2. In the lower buffer regions portion of the curves for the neutralization HCl present in VO(IV) solution has been eliminated.

of a reaction of the type:



(i)

An inflexion point at about m = 3 is in accord with the reaction:



(ii)

In order to verify the above conclusions, attempts were first made to analyze the potentiometric data on the basis of reaction (i). If H_2A represents mandelic acid, dissociation of the carboxylic proton of the ligand may be represented as :

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

K_a, the dissociation constant of the acid may be expressed as

$$K_a = \frac{[HA^-]\,[H^+]}{[H_2A]} \qquad \ldots \quad (56)$$

From a plot of $-\log[H^+]$ against $\log\frac{[HA^-]}{[H_2A]}$ (Fig.7), obtained from the potentiometric data of curve O(Fig.6), the value of pK_a was found to be 3.39 as an intercept on the $-\log[H^+]$ axis. This value is in good agreement with

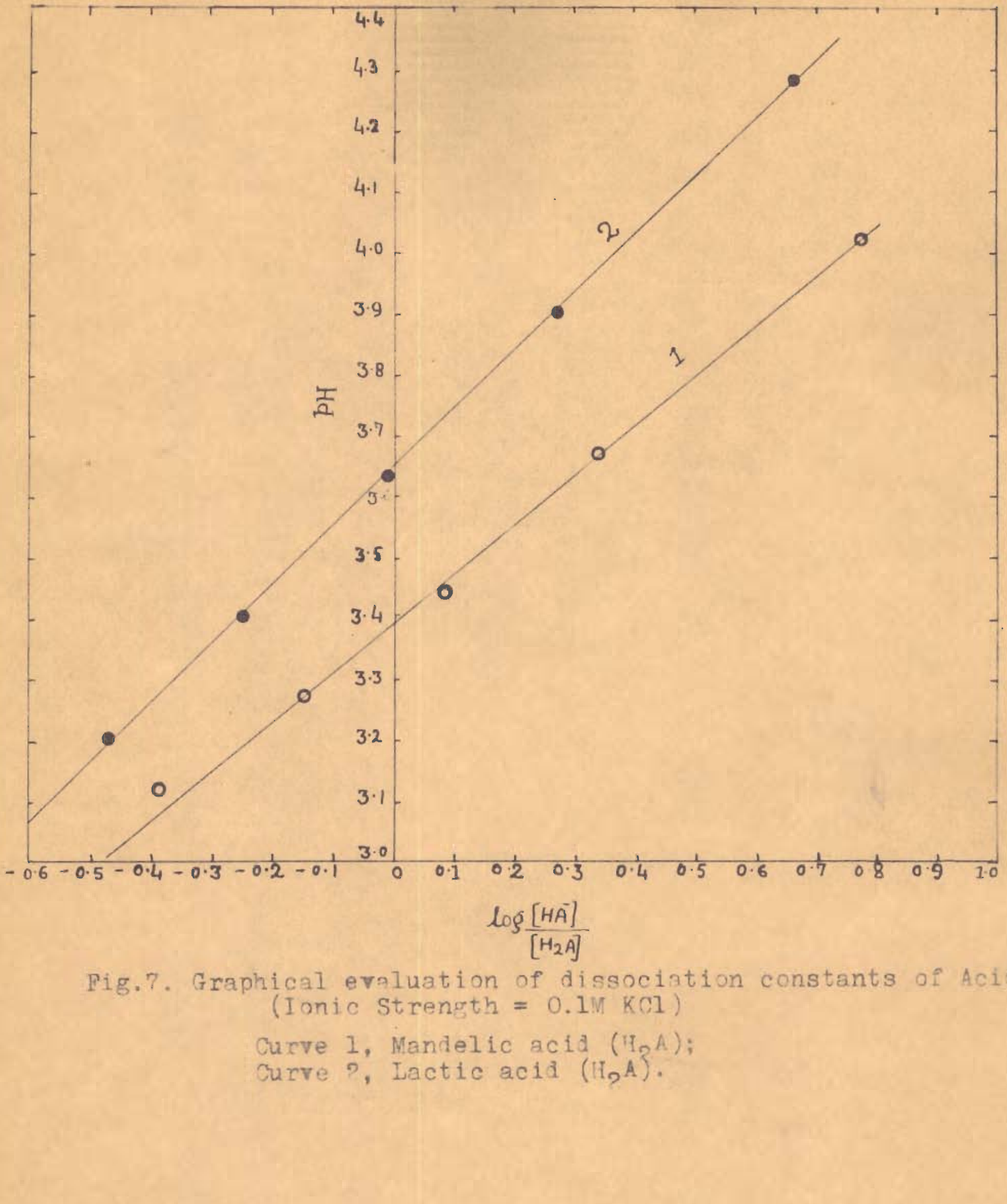


Fig.7. Graphical evaluation of dissociation constants of Acids.
(Ionic Strength = 0.1M KCl)

Curve 1, Mandelic acid (H_2A);
Curve 2, Lactic acid (H_2A).

a value of 3.41 reported by Bell and Waind[33].

The equilibrium constant K of reaction (i) may be defined as

$$K = \frac{[VOA]\,[H^+]^2}{[VO^{2+}]\,[H_2A]} \qquad \ldots (57)$$

From the material balance we obtain

$$T_M = [VO^{2+}] + [VOA] \qquad \ldots (58)$$

$$T_{OH} + [H^+] = [HA^-] + 2[VOA] \qquad \ldots (59)$$

$$T_A = [H_2A] + [HA^-] + [VOA] \qquad \ldots (60)$$

In the pH range studied, concentrations of A^{2-}, OH^- and the hydrolyzed species of vanadyl ions were negligible as compared to those of the other species present in the system.

Combination of (56), (59) and (60) gives

$$[H_2A] = \frac{2T_A - T_{OH} - [H^+]}{2 + \frac{K_a}{[H^+]}} \qquad \ldots (61)$$

After determining $[H_2A]$, concentrations of the species present in the system may be determined with the help of equations 58-60. Values of K thus obtained from various points of the titration curve are presented in table XII.

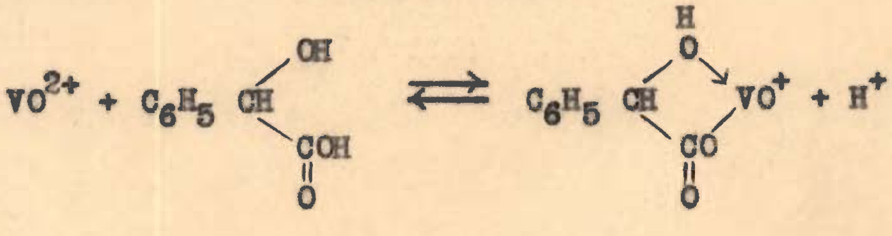
Table XII

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

m	0.2	0.4	0.6	0.8	1.0	1.2
pH	2.71	2.82	2.98	3.15	3.35	3.55
-log K	3.39	3.46	3.65	3.82	4.01	4.13

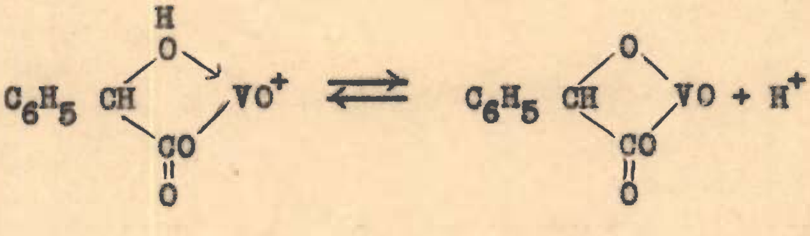
It is evident from table XII that the above mathematical treatment of the data did not give constant values of the equilibrium constant. A gradual increase observed in the values of pK indicated that the concentration of hydrogen ions in the system was less than that would be on the basis of reaction (i).

In view of the above, it was thought that the liberation of two hydrogen ions per mole of vanadyl ion (reaction i) might take place in two overlapping steps. The following reactions were therefore considered:



$$VO^{2+} + C_6H_5CH(OH)COOH \rightleftharpoons C_6H_5CH(OH)(COO)VO^{+} + H^{+}$$

(iii)



$$C_6H_5CH(OH)(COO)VO^{+} \rightleftharpoons C_6H_5CH(O)(COO)VO + H^{+}$$

(iv)

Formation constant K_{MHA} of the chelate $VOHA^+$ may be defined as

$$K_{MHA} = \frac{[VOHA^{+}]}{[VO^{2+}][HA^{-}]} \qquad \ldots (62)$$

In the initial stages of titration, considering reaction (iii) alone, from the material balance we obtain

$$T_M = [VO^{2+}] + [VOHA^{+}] \qquad \ldots (63)$$

$$T_{OH} + [H^{+}] = [HA^{-}] + [VOHA^{+}] \qquad \ldots (64)$$

$$T_A = [H_2A] + [HA^{-}] + [VOHA^{+}] \qquad \ldots (65)$$

Combination of (56), (64) and (65) yields

$$[HA^{-}] = \frac{K_a(T_A - T_{OH} - [H^{+}])}{[H^{+}]} \qquad \ldots (66)$$

From (64) and (66) we obtain

$$[VOHA^{+}] = \frac{1}{[H^{+}]}\left\{(T_{OH} + [H^{+}])\,(K_a + [H^{+}]) - K_a\,T_A\right\} \qquad \ldots (67)$$

Having obtained $[VOHA^{+}]$, concentration of the uncomplexed vanadyl ions in the solution may be determined algebraically from equation (63). Values of the formation constant K_{MHA} thus obtained from the potentiometric data of curve 1 (Fig.6) are given in table XIII.

Table XIII

Curve 1 (Fig.6), $T_A = T_M = 5\times10^{-3}M$

m	0.04	0.12	0.20	0.28	0.36	0.44
pH	2.62	2.67	2.71	2.78	2.81	2.86
$\log K_{MHA}$	3.40	3.40	3.47	3.44	(3.51	3.72)*

Average value of log K_{MHA} = 3.43 ± 0.04

* Values not included in the average.

Constant values of log K_{MHA} obtained in the range m = 0 to 0.28 showed the formation of complex of the $VOHA^+$ type in the system.

A gradual increase in the values of log K_{MHA}, observed in table XIII, at m > 0.28 indicated the occurrence of reaction of type (iv). If K represents equilibrium constant of reaction(iv), we have

$$K = \frac{[VOA]\ [H^+]}{[VOHA^+]} \qquad \ldots (68)$$

Other pertinent equations are

$$T_M = [VO^{2+}] + [VOHA^+] + [VOA] \qquad \ldots (69)$$

$$T_{OH} + [H^+] = [HA^-] + [VOHA^+] + 2[VOA] \qquad \ldots (70)$$

$$T_A = [H_2A] + [HA^-] + [VOHA^+] + [VOA] \qquad \ldots (71)$$

In a 1:1 vanadyl sulphate-mandelic acid system since $T_A = T_M$, combination of equations 56, 63 and 69-71 and rearranging the terms into the form of a quadratic equation we obtain

$$K_{MHA} K_a \left[VO^{2+}\right]^2 + (K_a + 2\left[H^+\right]) \left[VO^{2+}\right] - (2T_A - T_{OH} - \left[H^+\right]) X K_a = 0 \quad ...(72)$$

where

$$X = 1 + \frac{\left[H^+\right]}{K_a}$$

Concentration of the uncomplexed vanadyl ions in the system may, therefore, be determined by solving the above equation.

After computation of $\left[VO^{2+}\right]$, concentrations of the other species present in the system may be easily calculated with the help of equations given above. Values of K so obtained are listed in table XIV.

Table XIV

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

m	0.4	0.6	0.8	1.0	1.2
pH	2.82	2.98	3.15	3.35	3.55
-log K	3.69	3.67	3.62	3.63	3.60

Average value of -log K = 3.64 ± 0.03

The success thus obtained in calculating the equilibrium constants for reactions (iii) and (iv) showed that formation of VOA in the system takes place through an intermediate formation of a chelate of the $VOHA^+$ type.

Here it may be mentioned that the liberation of a second hydrogen ion (reaction iv) may also occur as

$$VOHA^+ + H_2O \rightleftharpoons VO(OH)HA + H^+ \qquad (v)$$

But formation of chelate species of the VO(OH)HA type may be considered less likely in view of the fact that the unchelated vanadyl ion itself does not hydrolyze below pH 3.5.

Having established the reactions taking place in the system, it was considered worthwhile to investigate polymerization of the chelate species. Titrations of equimolar mixtures of vanadyl sulphate and mandelic acid were, therefore, carried out at two more concentrations of the metal salt. Values of K_{MHA} and K, calculated from the potentiometric data of curves 2 and 3 (Fig.6) for titrations of 1:1 vanadyl sulphate-mandelic acid reaction mixtures having concentrations of 2.5×10^{-3}M and 1.25×10^{-3}M of vanadyl sulphate respectively are presented in tables XV and XVI.

Table XV

Curve 2 (Fig.6), $T_A = T_M = 2.5\times10^{-3}$M

m	0.04	0.12	0.20	0.28	0.36
pH	2.87	2.92	2.98	3.01	3.03
log K_{MHA}	3.48	3.47	3.44	(3.60	3.81)*

Average value of log K_{MHA} = 3.46±0.02

* Values not included in the average.

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

m	0.04	0.12	0.20	0.28
pH	3.14	3.18	3.21	3.24
log K_{MHA}	3.44	3.48	(3.61	3.85)*

Average value of logK_{MHA} = 3.46±0.02

* Values not included in the average.

Table XVI

Curve 2 (Fig.6), $T_A = T_M = 2.5 \times 10^{-3}$M

m	0.4	0.6	0.8	1.0	1.2
pH	3.04	3.17	3.32	3.50	3.68
-log K	3.67	3.64	3.63	3.65	3.62

Average value of -log K = 3.64 ± 0.03

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

m	0.4	0.6	0.8	1.0	1.2
pH	3.26	3.37	3.51	3.66	3.83
-log K	3.67	3.64	3.66	3.65	3.63

Average value -log K = 3.65±0.02

Concentration independence of equilibrium constants seen in tables XIII-XVI showed that the chelate species do not polymerize under the experimental conditions employed.

Analysis of Curve 4(Fig.6) for the titration of a 1:2 Vanadyl Sulphate - Mandelic acid system with KOH:

The curve shows a hint of inflexion at m = 3 and a sharp inflexion at about m = 4. These inflexion points may be accounted for on the basis of the formation of a 1:1 complex (cf. curve 1, fig.6) and the neutralization of free ligand (one mole) present in the system. In order to verify this interpretation, a calculated curve 'A' was obtained by the addition of abscissae of curves 0 and 2 (Fig.6). The resulting composite curve A (shown by dotted line in figure 6) was similar to the experimental curve with a sharp inflexion at about m = 4, thus indicating that there is no combination of the 1:1 vanadyl-mandelic acid chelate with another mole of the ligand under the experimental conditions. Lowering of the lower buffer region in the experimental curve, as compared with the composite curve, may be accounted for on the basis of mass action.

VANADYL-LECTATE CHELATES:

RESULTS AND DISCUSSION

Potentiometric titrations of vanadyl sulphate in the presence of lactic acid gave curves essentially similar to those obtained in the vanadyl-mandelate system. In this case also, from the nature of potentiometric curves,

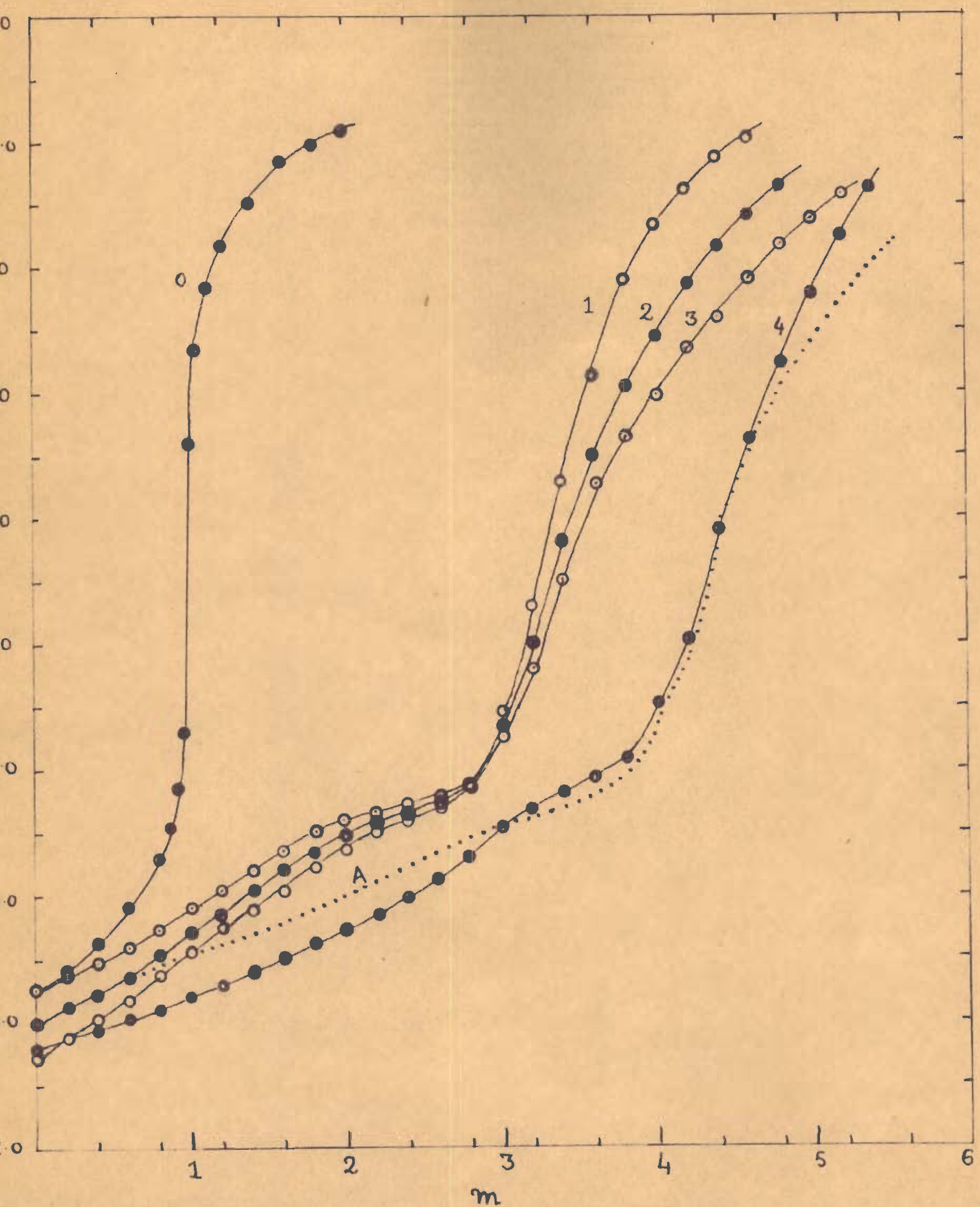
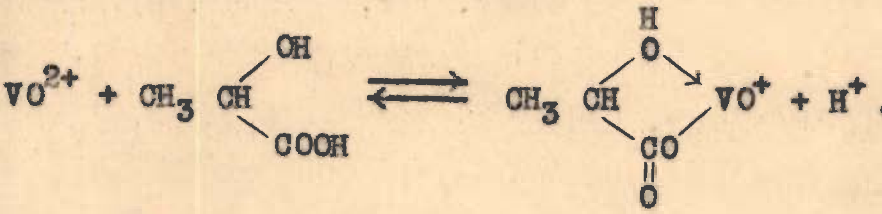
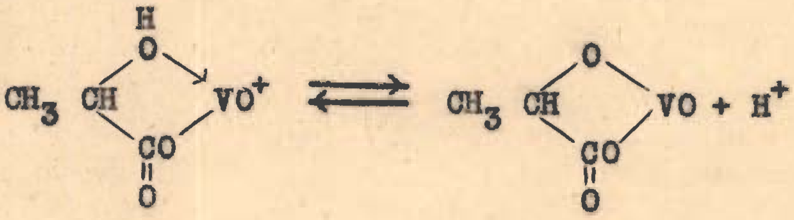


Fig.8. Potentiometric titrations of vanadyl-lactate chelate systems with KOH(0.1N): Curve 0, $2.5\text{x}10^{-3}$M in lactic acid; 1, $5\text{x}10^{-3}$M in VO(IV) and 5x10-3M in lactic acid; 2, 2.5x10-3M in VO(IV) and $2.5\text{x}10^{-3}$M in lactic acid; 3, $1.25\text{x}10^{-3}$M in VO(IV) and $1.25\text{x}10^{-3}$M in lactic acid; 4, 2.5x10-3M in VO(IV) and $5.0\text{x}10^{-3}$M in lactic acid; A, composite curve of 0 and 2. In the lower buffer regions portion of the curves for the neutralization of HCl present in VO(IV) solution has been eliminated. m=moles of KOH added per mole of the metal ion.

only a 1:1 metal chelate appears to be formed under the experimental conditions. From an analogy of this system with vanadyl-mandelate system, reactions occurring in the lower buffer region of curves 1,2 and 3 (Fig.8) may be represented as:

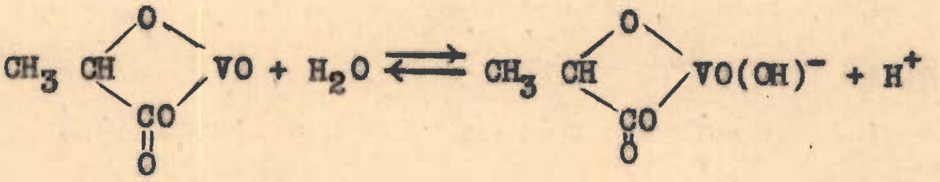


...(i)



... (ii)

In the upper buffer region (m = 2 to 3) of curves1-3(Fig.8) a probable reaction:



... (iii)

appears to take place.

Formation of the VOA type of chelate in two overlapping steps, represented by reactions (i) and (ii), has been established by a mathematical analysis of the data, employing a treatment similar to that presented in the vanadyl-mandelate system.

Dissociation constant of the carboxylic proton of lactic acid, determined from a plot of $-\log[H^+]$ against

$\log \frac{[HA^-]}{[H_2A]}$ (Fig.7), corresponded to a value of pK_a equal to 3.65. This value is comparable with a value of 3.74 reported by Cannan and Kibrick[34]. Values of the formation constant K_{MHA} of chelate $VOHA^+$ and the equilibrium constant K for reaction (ii), calculated over a four-fold concentration range from the potentiometric data of curves 1-3 (Fig.8), are listed in tables XVII and XVIII respectively.

Table XVII

Curve 1 (Fig.8), $T_A = T_M = 5x10^{-3}$

m	0.04	0.12	0.20	0.28	0.36	0.44
pH	2.75	2.82	2.88	2.95	2.99	3.06
log K_{MHA}	3.15	3.14	3.17	3.19	(3.30	3.39)*

Average value of log K_{MHA} = 3.16±0.03
* Values not included in the average.

Curve 2 (Fig.8), $T_A = T_M = 2.5x10^{-3}M$

m	0.04	0.12	0.20	0.28	0.36	0.44
pH	3.01	3.06	3.12	3.19	3.25	3.29
log K_{MHA}	3.15	3.19	3.21	3.21	(3.28	3.42)*

Average value of log K_{MHA} = 3.19±0.02

* Values not included in the average.

Curve 3 (Fig.8), $T_A = T_M = 1.25 \times 10^{-3}M$

m	0.04	0.12	0.20	0.28	0.36	0.44
pH	3.25	3.31	3.36	3.42	3.47	3.51
log K_{MHA}	3.18	3.17	3.21	3.23	(3.32	3.49)*

Average value of log K_{MHA} = 3.20±0.03

* Values not included in the average.

Table XVIII

Curve 1 (Fig.8), $T_A = T_M = 5 \times 10^{-3}M$

m	0.4	0.6	0.8	1.0	1.2
pH	3.00	3.18	3.38	3.57	3.76
-log K	3.82	3.80	3.81	3.77	3.73

Average value of -log K = 3.77±0.05

Curve 2 (Fig.8), $T_A = T_M = 2.5 \times 10^{-3}M$

m	0.6	0.8	1.0	1.2	1.4
pH	3.37	3.54	3.72	3.88	4.09
-log K	3.84	3.83	3.81	3.74	3.75

Average value of -log K = 3.79±0.05

Curve 3 (Fig.8), $T_A = T_M = 1.25 \times 10^{-3}M$

m	0.6	0.8	1.0	1.2	1.4
pH	3.59	3.73	3.90	4.06	4.24
-log K	3.74	3.81	3.80	3.81	3.74

Average value of -log K = 3.78±0.03

SECTION IV

OXOVANADIUM (IV) CHELATES OF TARTARIC AND MALIC ACIDS

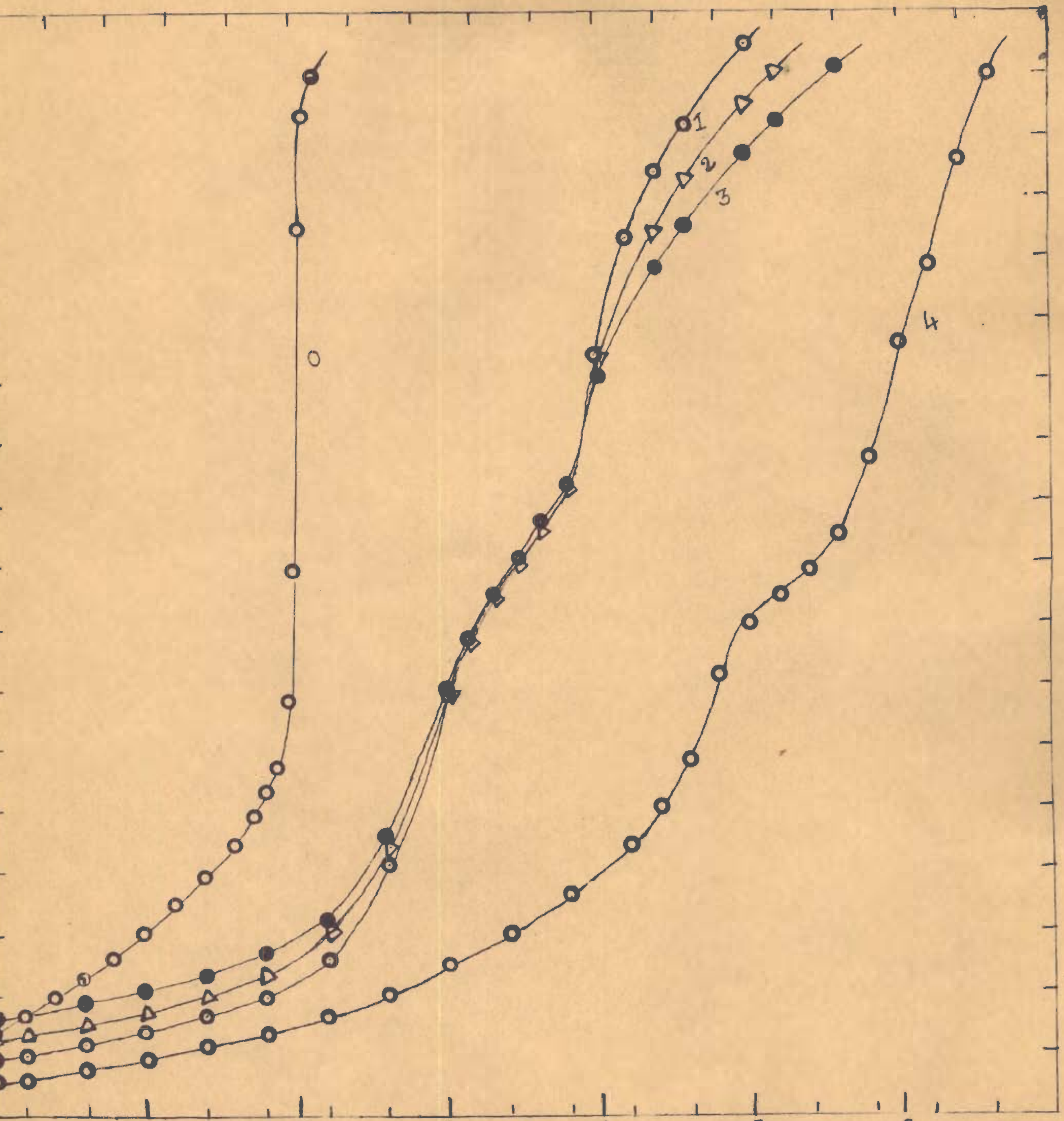
Although many papers[35-47] have appeared on the tartrate and malate complexes of oxovanadium (IV), a quantitative study of the equilibria involved in their formation does not appear to be undertaken by the earlier workers. In view of the interesting results obtained in the study of mandelate and lactate chelates of VO(IV), it was considered worthwhile to extend this work to the tartrate and malate complexes.

VANADYL-TARTRATE CHELATES

RESULTS AND DISCUSSION

Curve 0 (Fig.9) for the potentiometric titration of tartaric acid with KOH exhibits a sharp inflexion at two moles of alkali per mole of the acid indicating the neutralization of the carboxylic protons of the ligand. The alcoholic (OH) hydrogen atoms thus remain unaffected under the experimental conditions. A single inflexion at two equivalents of alkali shows that dissociation of the two carboxylic protons of tartaric acid takes place in two overlapping steps.

Curves 1-3 (Fig. 9) represent titrations of 1:1 mixtures of vanadyl sulphate and tartaric acid of concentrations $5x10^{-3}$, 2.5×10^{-3} and



g.9. Potentiometric titrations of vanadyl-tartrate chelate systems with H(0.1N): Curve 0, 5×10^{-3} M in tartaric acid; curve 1, 5×10^{-3} M in VO(IV) d 5×10^{-3} M in tartaric acid; curve 2, 2.5×10^{-3} M in VO(IV) and 2.5×10^{-3} M in rtaric acid; curve 3, 1.25×10^{-3} M in VO(IV) and 1.25×10^{-3} M in tartaric acid; rve 4, 5×10^{-3} M in VO(IV) and 1.0×10^{-2} M in tartaric acid. In the lower ffer regions portion of the curves for the neutralization HCl present in)(IV) soln. has been eliminated.

1.25×10^{-3}M respectively. These curves exhibit two inflexion points, one at m = 3 and the other at m = 4. Occurrence of an inflexion point at m = 3 indicates that either one of the α-hydroxy hydrogen atoms of the ligand dissociates as a result of chelation with vanadyl ion or that one water molecule of hydration of the oxo-metal ion undergoes dissociation to give a hydroxo complex. If H_4A represents tartaric acid having two ionizable carboxylic protons and two weakly acid alcoholic hydrogen atoms, formation of the above two alternative chelate species may be represented as:

$$VO^{2+} + H_4A \rightleftharpoons \underset{(A)}{VOHA^-} + 3H^+ \qquad \ldots(i)$$

$$\text{or} \quad VO^{2+} + H_4A \xrightleftharpoons{H_2O} \underset{(B)}{VO(OH)H_2A^-} + 3H^+ \qquad \ldots(ii)$$

The possibility of reaction (ii) may be considered less likely in view of the fact that the unchelated vanadyl ion itself does not undergo hydrolysis below pH 3.5.

Occurrence of a buffer region in the pH range 5.5-7.5 and an inflexion point at m = 4 shown by the curves indicate that either hydrogen atom of the second hydroxy group of the ligand dissociates and the tartrate ion acts as a quadridentate ligand as reported by Jørgensen[38] or a water molecule of vanadyl ion undergoes dissociation in which case the tartrate ion would behave as a tridentate ligand as shown by Feldman and coworkers[48] in the uranyl-tartrate chelates. The chelate species formed may thus be formulated as:

VOA^{2-} , $VO(OH)HA^{2-}$

(C) (D)

From the potentiometric data alone it is difficult to distinguish between the above two possibilities. However, the formation of (C), reported by Jørgensen, obtains support from the work of Selbin[49].

Determination of Equilibrium Constants

Dissociation Constants of Tartaric Acid:

Determination of equilibrium constants of the reactions involved in the interaction of vanadyl ion with tartaric acid required a knowledge of dissociation constants of carboxylic protons of tartaric acid under the experimental conditions employed in the present investigation. For this purpose, a procedure similar to that described by Speakman[50] is employed. The method is briefly outlined below.

If K_{a_1} and K_{a_2} represent the first and second dissociation constants of tartaric acid, we have:

$$K_{a_1} = \frac{[H_3\bar{A}][H^+]}{[H_4A]} \qquad \ldots (73)$$

and

$$K_{a_2} = \frac{[H_2A^{2-}]\,[H^+]}{[H_3A^-]} \qquad \ldots(74)$$

Other pertinent equations are :

$$T_A = [H_4A] + [H_3A^-] + [H_2A^{2-}] \qquad \ldots(75)$$

$$T_{OH} + [H^+] = [H_3A^-] + 2[H_2A^{2-}] \qquad \ldots(76)$$

In the lower buffer region of the titration curve (Curve 0, Fig.9), concentrations of HA^{3-}, A^{4-} and OH^- were negligible as compared to those of the other species present in the solution. Combination of (73)-(76) gives :

$$[H_2A^{2-}] = \frac{T_A - T_{OH} - [H^+]}{\dfrac{[H^+]^2}{K_{a_1}\,K_{a_2}} - 1} \qquad \ldots(77)$$

Elimination of $[H_3A^-]$ and $[H_2A^{2-}]$ between (74), (76) and (77) yields

$$\frac{[H^+]^2\left\{T_{OH} + [H^+]\right\}}{2T_A - T_{OH} - [H^+]} = \frac{[H^+]\left\{T_A - T_{OH} - [H^+]\right\}}{2T_A - T_{OH} - [H^+]}\,K_{a_1} + K_{a_1}\,K_{a_2} \qquad \ldots(78)$$

Hence a plot of $\dfrac{[H^+]^2\{T_{OH} + [H^+]\}}{2T_A - T_{OH} - [H^+]}$ as ordinate versus $\dfrac{[H^+]\{T_A - T_{OH} - [H^+]\}}{2T_A - T_{OH} - [H^+]}$ should give a straight line of slope

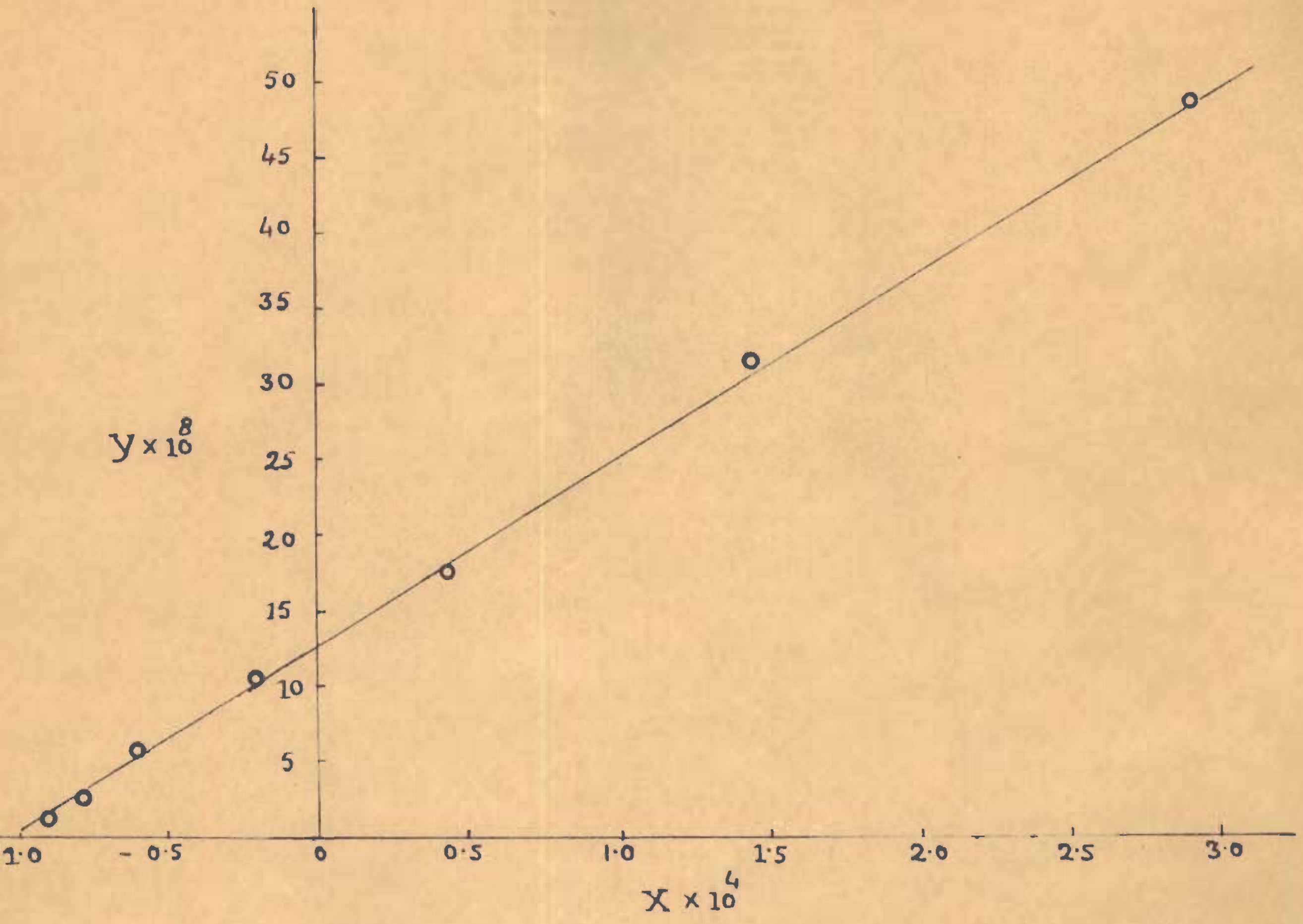


Fig.10. Graphical evaluation of dissociation constants of tartaric acid (H_4A) (Ionic Strength 0.1 KCl)

$$X = \frac{[H^+]\left(T_A - T_{OH} - [H^+]\right)}{\left(2T_A - T_{OH} - [H^+]\right)} \quad , \quad Y = \frac{[H^+]^2\left(T_{OH} + [H^+]\right)}{\left(2T_A - T_{OH} - [H^+]\right)}$$

K_{a_1} and intercept on $\dfrac{[H^+]^2\{T_{OH} + [H^+]\}}{2T_A - T_{OH} - [H^+]}$ axis equal to $K_{a_1} K_{a_2}$. Thus the values of pK_{a_1} and pK_{a_2} from the plot (Fig.10) obtained from the potentiometric data of curve O (Fig. 9) were found to be 2.90 and 3.99 respectively. These values are in close agreement with the literature[34] values of 2.88 and 3.94.

Equilibrium Constants:

Having determined acid dissociation constants of the ligand, equilibrium constants of the reactions were determined as follows:

Equilibrium constant K of reaction(i) may be defined as:

$$K = \frac{[VOHA^-]\,[H^+]^3}{[VO^{2+}][H_4A]} \qquad \ldots(79)$$

From the material balance we obtain

$$T_M = [VO^{2+}] + [VOHA^-] \qquad \ldots(80)$$

$$T_{OH} + [H^+] = [H_3A^-] + 2[H_2A^{2-}] + 3[VOHA^-] \qquad \ldots(81)$$

$$T_A = [H_4A] + [H_3A^-] + [H_2A^{2-}] + [VOHA^-] \quad \ldots(82)$$

In the pH range studied, concentrations of HA^{3-}, A^{4-} and OH^- were negligible as compared to those of the other species present.

Combination of equations (73),(74),(81), and (82) gives:

$$[H_4A] = \frac{3T_A - T_{OH} - [H^+]}{3 + \frac{2K_{a_1}}{[H^+]} + \frac{K_{a_1}K_{a_2}}{[H^+]^2}} \quad \ldots (83)$$

Concentration of the chelate species may be given by

$$[VOHA^-] = T_A - [H_4A]\left\{1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2}\right\} \quad \ldots (84)$$

After computation of $[VOHA^-]$, concentration of free vanadyl ions present in the solution may be determined from (80). Values of equilibrium constant K thus obtained from various points of the lower buffer region of curves 1-3 (Fig.9) are presented in table XIX.

Table XIX

Curve 1, (Fig.9), $T_A = T_M = 5x10^{-3}M$

m	0.28	0.44	0.60	0.76	0.92	1.08	1.24	1.40
pH	2.53	2.57	2.61	2.65	2.68	2.73	2.77	2.83
-log K	5.54	5.54	5.55	5.55	5.51	5.58	5.53	5.58

Average value of -log K = 5.55±0.03

Curve 2, (Fig.9), $T_A = T_M = 2.5x10^{-3}M$

m	0.28	0.44	0.60	0.76	0.92	1.08	1.24	1.40
pH	2.70	2.74	2.77	2.81	2.85	2.88	2.92	2.97
-log K	5.57	5.59	5.57	5.58	5.58	5.55	5.55	5.57

Average value of -log K = 5.57±0.02

Curve 3, (Fig.9), $T_A = T_M = 1.25\times10^{-3}M$

m	0.28	0.44	0.60	0.76	0.92	1.08	1.24
pH	2.87	2.91	2.94	2.96	3.01	3.05	3.09
-log K	5.50	5.56	5.59	5.52	5.55	5.56	5.56

Average value of -log K = 5.55±0.04

From the values of the equilibrium constant (table XIX) determined over a four-fold concentration range of the metal chelate, it is evident that the chelate is present in solution mainly as a monomer under the experimental conditions. A slight shift of the low buffer regions of curves 1-3 (Fig.9) with a variation in the concentration of the metal chelate may be accounted for on the basis of variation of the degree of dissociation of the acid forms as a function of concentration and no condensation of the metal chelate thus seems to occur.

Equilibrium Constant for Reaction in pH Range 5.5-7.5

If we consider formation of the VOA^{2-} type of chelate as reported by Jørgensen[38] and Selbin[49], the equilibrium constant K' of the reaction:

$$VOHA^- \rightleftharpoons VOA^{2-} + H^+$$

may be defined as:

$$K' = \frac{[VOA^{2-}]\,[H^+]}{[VOHA^-]} \qquad \ldots (85)$$

Other pertinent equations are

$$T_M = \left[VOHA^-\right] + \left[VOA^{2-}\right] \qquad \ldots (86)$$

$$T_{OH} + \left[H^+\right] - \left[OH^-\right] = \left[VOA^{2-}\right] \qquad \ldots (87)$$

The results of these calculations are given in table XX.

Table XX

Curve 1 (Fig.9), $T_A = T_M = 5x10^{-3}$

m	3.16	3.32	3.48	3.64	3.80
pH	5.87	6.23	6.55	6.77	7.22
-log K'	6.59	6.56	6.58	6.52	6.58

Average value of -log K' = 6.57±0.02

Curve 2 (Fig.9), $T_A = T_M = 2.5x10^{-3}M$

m	3.16	3.32	3.48	3.64	3.80
pH	5.86	6.21	6.49	6.77	7.16
-log K'	6.58	6.54	6.52	6.52	6.56

Average value of -log K' = 6.54±0.04

Curve 3 (Fig.9), $T_A = T_M = 1.25x10^{-3}M$

m	3.16	3.32	3.48	3.64	3.80
pH	5.87	6.28	6.54	6.85	7.17
-log K'	6.59	6.61	6.57	6.60	6.57

Average value of -log K' = 6.59±0.02

Constant values of K', independent of concentration, showed that the mononuclear 1:1 complex, VOA^{2-}, is the only complex formed in the system under the experimental conditions.

The above conclusions of the formation of $VOHA^-$ type of chelate in acid solution and the production of VOA^{2-} type of complex are supported by the preparative work carried out by Conn[36] and Jørgensen[38].

Analysis of Curve 4 (Fig.9)

The potentiometric titration for a solution containing 1:2 molar ratio of vanadyl sulphate to tartaric acid corresponded to a curve (curve 4, Fig.9) which would be predicted for a mixture of the 1:1 chelate and free ligand. Formation of a 1:2 complex therefore does not appear to take place. This conclusion has been confirmed by the calculation of equilibrium constant K (reaction i) in a manner similar to that used in the 1:1 system. The results obtained from various points in the lower buffer region of the curve are presented in table XXI.

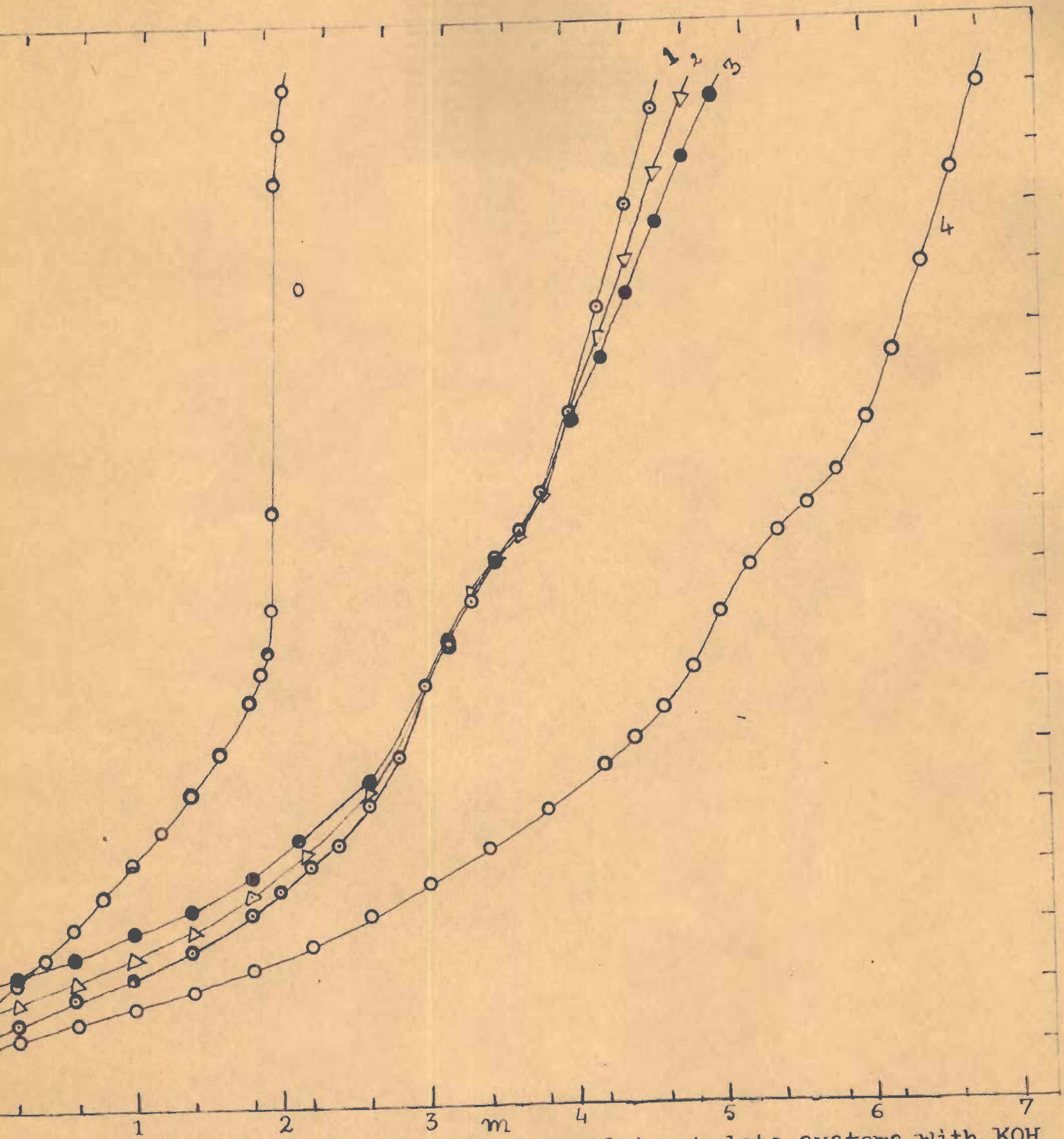
Table XXI

Curve 4, (Fig.9), $T_A = 2T_M = 1.0x10^{-2}M$

m	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
pH	2.36	2.39	2.43	2.47	2.51	2.55	2.58	2.62	2.68
-log K	5.39	5.36	5.38	5.40	5.42	5.44	5.41	5.42	5.44

Average value of -log K = 5.41±0.03

The value of -log K in the above table is comparable with a value of 5.56 obtained in table XIX. The success thus obtained in calculating the equilibrium constant K from the potentiometric data of the curve strengthened the



Potentiometric titrations of vanadyl-malate chelate systems with KOH
: Curve 0 , 5x10^{-3}M in malic acid; curve 1, 5x10^{-3}M in VO(IV) and
M in malic acid; curve 2, 2.5x10^{-3}M in VO(IV) and 2.5x10^{-3}M in malic
curve 3, 1.25x10^{-3}M in VO(IV) and 1.25x10^{-3}M in malic acid; curve 4,
M in VO(IV) and 1.0x10^{-2}M in malic acid. In the lower buffer regions
on of the curves for the neutralization of HCl present in VO(IV) soln.
een eliminated.

above conclusion.

VANADYL-MALATE CHELATES

RESULTS AND DISCUSSION

An inflexion point at two equivalents of alkali, shown by curve O(Fig.11) for the titration of malic acid indicated that the dissociation of the two carboxylic protons of malic acid overlap to give a single low pH buffer system. Acid dissociation constants of the ligand (H_3A),

$$K_{a_1} = \frac{[H_2A^-][H^+]}{|H_3A|} \qquad \ldots (88)$$

$$K_{a_2} = \frac{[HA^{2-}][H^+]}{[H_2A^-]} \qquad \ldots (89)$$

were determined by the slope intercept method described in the vanadyl-tartrate system. The values of pK_{a_1} and pK_{a_2} were found (Fig.12) to be 3.29 and 4.97 respectively.

Potentiometric titrations of vanadyl sulphate in the presence of malic acid yielded curves essentially similar to those obtained in the vanadyl-tartrate system. The first inflexion point at m = 3 observed in curve 1 (Fig.11) is in accord with the reaction:

$$VO^{2+} + H_3A \rightleftharpoons VOA^- + 3H^+ \qquad \ldots (i)$$

However, calculations of equilibrium constant K of the

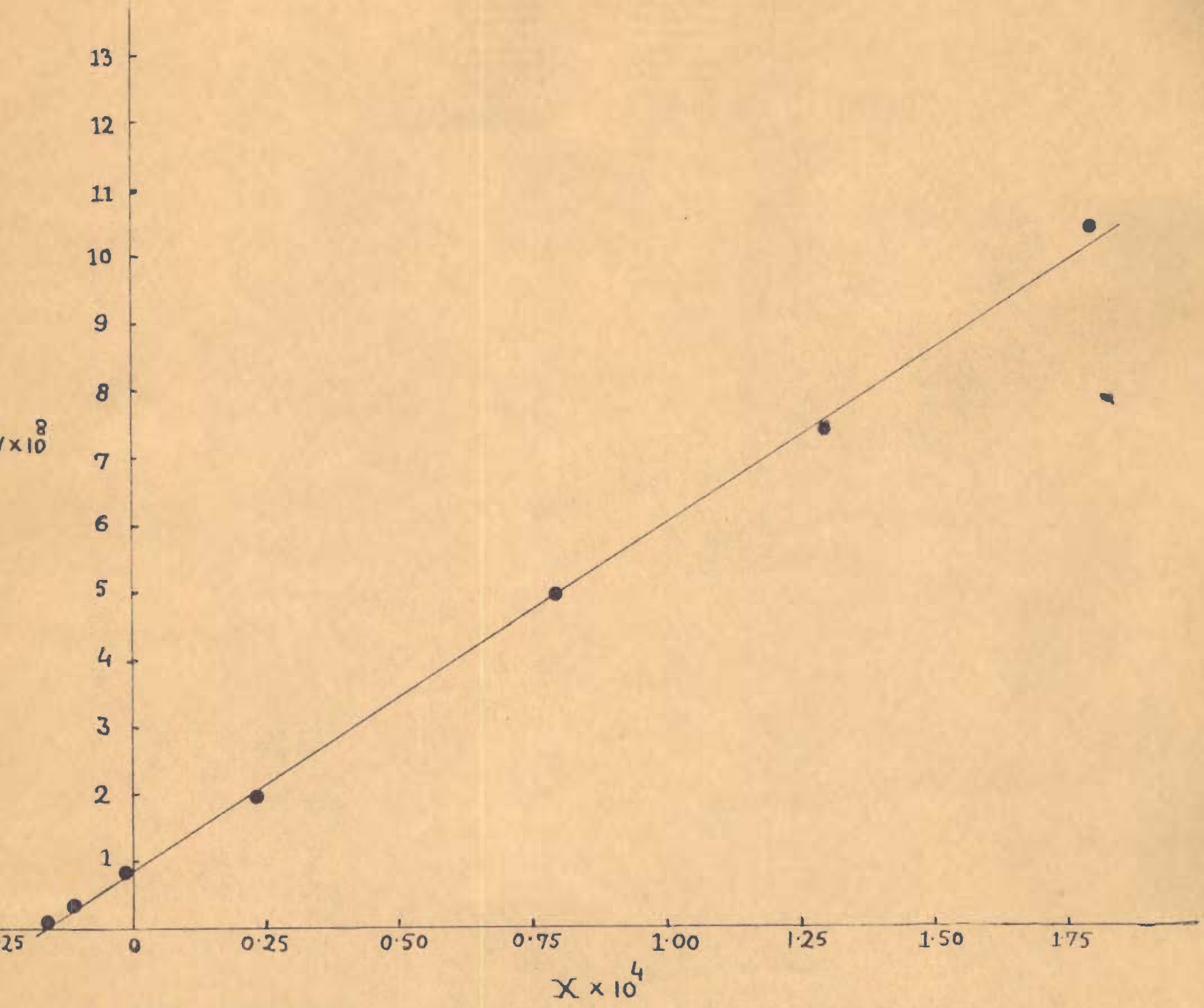


Fig.12. Graphical evaluation of dissociation constants of Malic acid (H_3A). (Ionic Strength 0.1M KCL)

$$X = \frac{[H^+]\left(T_A - T_{OH} - [H^+]\right)}{\left(2T_A - T_{OH} - [H^+]\right)}, \quad Y = \frac{[H^+]^2\left(T_{OH} + [H^+]\right)}{\left(2T_A - T_{OH} - [H^+]\right)}$$

above reaction, using mathematical equations 79-84 given in the vanadyl-tartrate system, did not give constant values as is evident from table XXII given below.

Table XXII

Curve 1 (Fig.11), $T_A = T_M = 5.0 \times 10^{-3} M$

m	0.20	0.44	0.60	0.76	0.92	1.00	1.08	1.24
pH	2.69	2.80	2.87	2.95	3.05	3.08	3.13	3.21
-log K	6.32	6.47	6.56	6.68	6.85	6.89	6.98	7.07

A gradual increase in the values of -log K observed in the above table indicated that the concentration of hydrogen ions in the system was less than that would be on the basis of the liberation of three hydrogen ions per mole of vanadyl ion as represented in reaction (i). Attempts were, therefore, made to treat the potentiometric data on the basis of the formation of VOA^- in two overlapping steps:

$$VO^{2+} + H_3A \rightleftharpoons VOHA + 2H^+ \qquad \ldots (ii)$$

and

$$VOHA \rightleftharpoons VOA^- + H^+ \qquad \ldots (iii)$$

Equilibrium constants K_1 and K_2 for reactions (ii) and (iii) may be defined as :

$$K_1 = \frac{[VOHA][H^+]^2}{[VO^{2+}][H_3A]} \qquad \ldots (90)$$

$$K_2 = \frac{[VOA^-][H^+]}{[VOHA]} \qquad \ldots (91)$$

If K_{MHA} represents formation constant of the chelate VOHA, we have

$$K_{MHA} = \frac{[VOHA]}{[VO^{2+}][HA^{2-}]} \qquad \ldots (92)$$

In the initial stages of the titration , if concentration of the chelate VOA^- is negligibly small, from the usual material balance we obtain

$$T_M = [VO^{2+}] + [VOHA] \qquad \ldots (93)$$

$$T_{OH} + [H^+] = [H_2A^-] + 2[HA^{2-}] + 2[VOHA] \qquad \ldots (94)$$

$$T_A = [H_3A] + [H_2A^-] + [HA^{2-}] + [VOHA] \quad .. (95)$$

Combination of (88), (89), (94), and (95) yields

$$[H_3A] = \frac{2T_A - T_{OH} - [H^+]}{2 + \dfrac{K_{a_1}}{[H^+]}} \qquad \ldots (96)$$

Elimination of $[H_2A^-]$ and $[HA^{2-}]$ between (88),(89) and (95) gives

$$[VOHA] = T_A - [H_3A]\left\{1 + \frac{K_{a_1}}{[H^+]} + \frac{K_{a_1}K_{a_2}}{[H^+]^2}\right\} \ldots (97)$$

After determining $[H_3A]$ and $[VOHA]$, concentration of the uncomplexed vanadyl ions in the system may be determined from equation (93). Equilibrium constants K_1 and K_{MHA} may then be determined. Values of these constants thus obtained over a four-fold concentration range of the metal chelate are presented in table XXIII.

Table XXIII

Curve 1 (Fig.11) $T_A = T_M = 5x10^{-3}M$

m	0.20	0.28	0.44	0.60	0.76	0.92	1.00	1.08	1.24	1.40
pH	2.69	2.72	2.80	2.87	2.95	3.05	3.08	3.13	3.19	3.30
$-\log K_1$	3.34	3.35	3.36	3.36	3.33	3.34	3.35	3.33	(3.27	3.15)*
$\log K_{MHA}$	4.92	4.91	4.90	4.90	4.93	4.92	4.91	4.93		

Average value of $-\log K_1 = 3.34 \pm 0.02$, $\log K_{MHA} = 4.92 \pm 0.01$

Curve 2 (Fig.11), $T_A = T_M = 2.5x10^{-3}M$

m	0.20	0.28	0.44	0.60	0.76	0.92	1.00	1.08	1.24	1.40
pH	2.89	2.92	2.99	3.07	3.13	3.21	3.26	3.30	3.36	3.46
$-\log K_1$	3.35	3.34	3.35	3.39	3.33	3.32	3.34	3.31	(3.23	3.15)*
$\log K_{MHA}$	4.91	4.92	4.91	4.87	4.93	4.94	4.92	4.95		

Average value of $-\log K_1 = 3.35 \pm 0.04$, $\log K_{MHA} = 4.92 \pm 0.03$

Curve 3 (Fig.11), $T_A = T_M = 1.25x10^{-3}M$

m	0.20	0.28	0.44	0.60	0.76	0.92	1.00	1.08	1.24	1.40
pH	3.10	3.12	3.19	3.26	3.32	3.41	3.46	3.50	3.54	3.63
$-\log K_1$	3.32	3.35	3.35	3.36	3.31	3.35	3.35	3.33	(3.24	3.06)*
$\log K_{MHA}$	4.94	4.91	4.91	4.90	4.95	4.91	4.91	4.93		

Average value of $-\log K_1 = 3.34 \pm 0.02$, $\log K_{MHA} = 4.92 \pm 0.03$

* Values not included in the average

It is evident from the above table that constant values of the equilibrium constants could be obtained in the range m = 0 to m = 1.1 indicating that in this region only the VOHA type of chelate is formed in the system.

A gradual fall in the values of $-\log K_1$ seen in table XXII above 'm' values of about 1.1 indicated that the protonated complex VOHA undergoes acid dissociation giving species of the type VOA^- as represented by reaction (iii). This conclusion was verified by a mathematical treatment of the data outlined below.

Considering reactions (ii) and (iii), from the material balance we obtain

$$T_M = [VO^{2+}] + [VOHA] + [VOA^-] \qquad \ldots(98)$$

$$T_{OH} = [H^+] = [H_2A^-] + 2[HA^{2-}] + 2[VOHA] + 3[VOA^-] \qquad \ldots(99)$$

$$T_A = [H_3A] + [H_2A^-] + [HA^{2-}] + [VOHA] + [VOA^-] \qquad \ldots(100)$$

In an equimolar mixture of vanadyl sulphate and malic acid, since $T_A = T_M$, combination of equations 88-90 and 98-100 and rearranging the terms into the form a quadratic we obtain

$$\frac{K_1}{[H^+]^2 X}[VO^{2+}]^2 + \frac{Y}{X}[VO^{2+}] - (3T_A - T_{OH} - [H^+]) = 0 \qquad \ldots(101)$$

where

$$X = 1 + \frac{K_{a_1}}{[H^+]} + \frac{K_{a_1}\ K_{a_2}}{[H^+]^2} \quad \text{and } Y = 3 + \frac{2K_{a_1}}{[H^+]} + \frac{K_{a_1}K_{a_2}}{[H^+]^2}$$

Concentration of the uncomplexed vanadyl ions in the system may, therefore, be determined by solving the above equation.

Having determined $[VO^{2+}]$, concentration of the other species present in the system may be determined with the help of equations 88-90 and 98-100. Values of the equilibrium constant K_2 thus obtained over a fourfold concentration range of the metal chelate are presented in table XXIV

Table XXIV

Curve 1 (Fig.11), $T_A = T_M = 5x10^{-3}M$

m	1.24	1.40	1.56	1.72	1.80	2.00	2.2	2.4	2.6
pH	3.19	3.30	3.42	3.55	3.61	3.79	3.98	4.21	4.51
$-\log K_2$	7.51	7.57	7.57	7.56	7.52	7.49	7.45	7.47	7.49

Average value of $-\log K_2 = 7.51 \pm 0.06$

Curve 2 (Fig.11), $T_A = T_M = 2.5x10^{-3}M$

m	1.24	1.40	1.56	1.72	1.80	1.96	2.20	2.36	2.60
pH	3.36	3.46	3.58	3.69	3.79	3.90	4.13	4.34	4.65
$-\log K_2$	7.64	7.50	7.66	7.59	7.59	7.59	7.57	7.62	7.64

Average value of $-\log K_2 = 7.60 \pm 0.06$

Curve 3 (Fig.11), $T_A = T_M = 1.25\times10^{-3}M$

m	1.24	1.40	1.56	1.72	1.80	1.96	2.2	2.36	2.60
pH	3.54	3.63	3.70	3.84	3.90	4.03	4.22	4.40	4.70
$-\log K_2$	7.70	7.66	7.52	7.62	7.61	7.61	7.56	7.59	7.58

Average value of $-\log K_2 = 7.60\pm0.10$

The success thus achieved in obtaining constant values of the equilibrium constant is an evidence for the formation of the normal 1:1 chelate, VOA^-, through an intermediate formation of a protonated complex VOHA. It is also evident from tables XXIII and XXIV that the values of the equilibrium constants are almost independent of concentration of the metal salt indicating that the chelate species do not condense to give complex species of higher molecular weight.

Hydrolysis of Vanadyl-Malate Chelate

Appearance of a buffer region between m = 3 and m =4 in curves 1-3 (Fig.11) with an inflexion point at m = 4 is in accord with a reaction of the type

$$VOA^- + H_2O \rightleftharpoons VO(OH)A^{2-} + H^+ \qquad \text{... (iv)}$$

Hydrolysis constant, K_h , of the chelate may, therefore, be expressed as:

$$K_h = \frac{[VO(OH)A^{2-}][H^+]}{[VOA^-]} \qquad \text{... (102)}$$

Values of K_h calculated by making use of the usual material balance equations are listed in table XXV.

Table XXV

Curve 1 (Fig.11), $T_A = T_M = 5.0 \times 10^{-3}M$

m	3.16	3.32	3.48	3.64	3.80
pH	5.82	6.26	6.57	6.77	7.12
pK_h	6.54	6.59	6.60	6.52	6.57

Average value of $pK_h = 6.56 \pm 0.04$

Curve 2 (Fig.11), $T_A = T_M = 2.5 \times 10^{-3}M$

m	3.16	3.32	3.48	3.64	3.80
pH	5.86	6.28	6.56	6.75	7.11
pK_h	6.58	6.60	6.53	6.50	6.51

Average value of $pK_h = 6.54 \pm 0.06$

Curve 3 (Fig.11), $T_A = T_M = 1.25 \times 10^{-3}M$

m	3.16	3.32	3.48	3.64	3.80
pH	5.80	6.21	6.54	6.78	7.11
pK_h	6.52	6.54	6.59	6.53	6.51

Average value of $pK_h = 6.54 \pm 0.05$

Analysis of Curve 4 (Fig.11)

Potentiometric titration of vanadyl sulphate in the presence of two moles of malic acid (curve 4, Fig.11) showed inflexion points at m = 5 and 6. As the curve is a composite of curves 0 and 1 for the titration of free ligand and 1:1 vanadyl-malate chelate system respectively, combination of the 1:1 metal chelate with another mole of malic acid does not appear to take place.

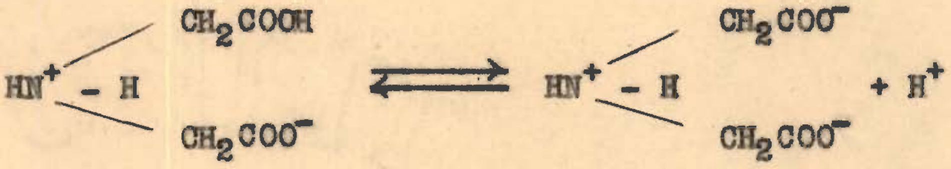
SECTION V

OXOVANADIUM (IV) CHELATES OF IMINODIACETIC ACID

In view of the success achieved in determining equilibrium constants of the reactions associated with the formation of vanadyl-tartrate and and -malate complexes, it was considered of interest to extend this work to the chelates of iminodiacetic acid, a terdentate ligand.

RESULTS AND DISCUSSION

A sharp inflexion exhibited by curve 0 (Fig. 13) at one mole of KOH per mole of the ligand showed that one proton of iminodiacetic acid (IMDA) is strongly acidic and the other proton remains unaffected in acid solutions.



By plotting $-\log[H^+]$ vs. $\log \frac{[HA^-]}{[H_2A]}$ (Fig.14), the first dissociation constant pK_{a_1} of the ligand was found to be 2.67. This value is comparable with a value of 2.54 reported by Chaberek and Martell[51].

Curves 1-3 (Fig.13) for the titrations of equimolar mixtures of vanadyl sulphate and iminodiacetic acid over a four-fold concentration range of the metal

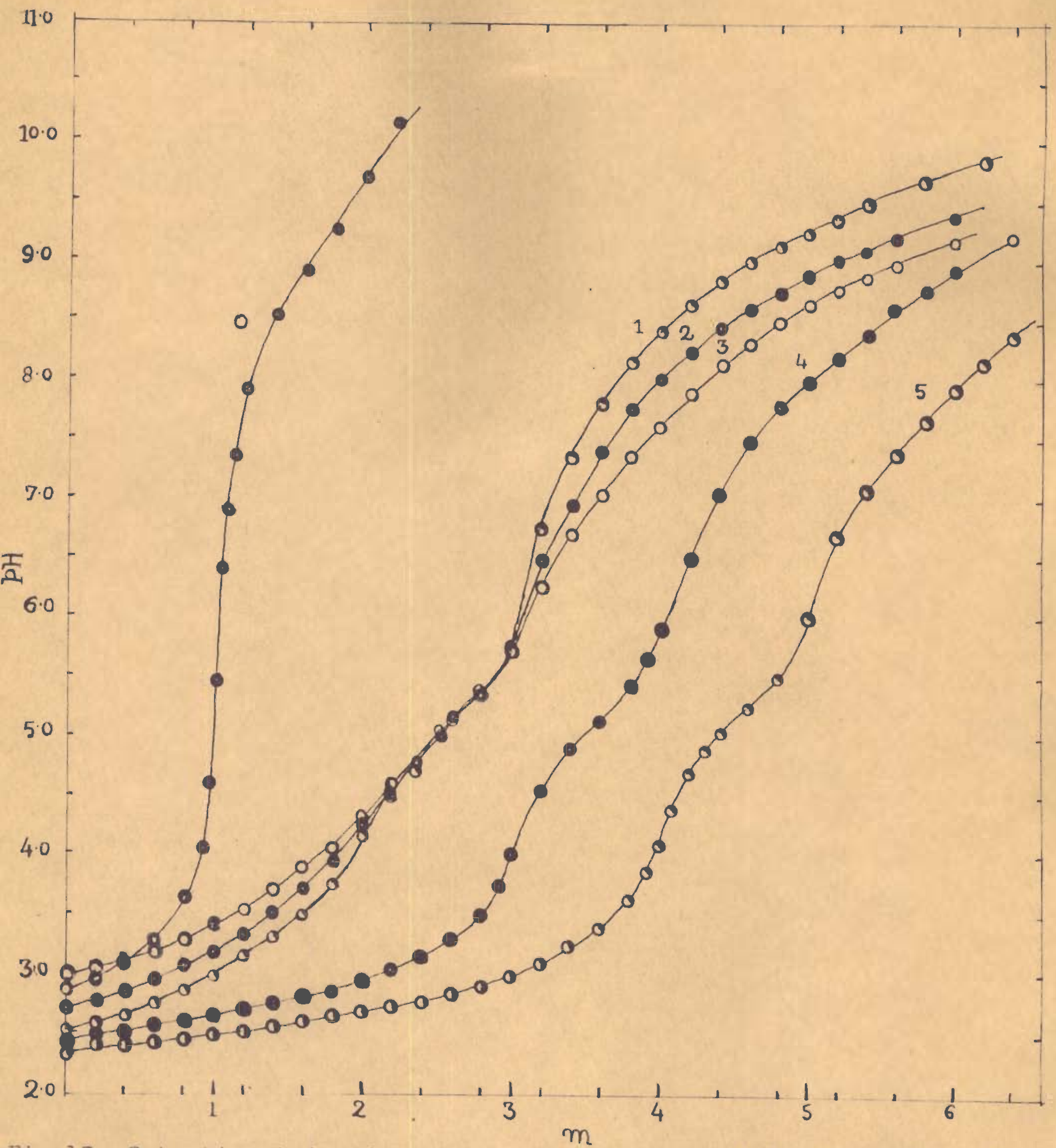


Fig.13. Potentiometric titrations of 1:1 vanadyl-iminodiacetic acid (IMDA) systems with KOH(0.1N). Concentrations: Curve 1, 5×10^{-3}M; Curve 2, 2.5×10^{-3}M; Curve 3, 1.25×10^{-3}M; Curve 4 and 5, represent similar titrations of 1:2 and 1:3 vanadyl-IMDA system, Curve 0 represents titration of IMDA with KOH. Ionic strength=0.1M(KCl). m=moles of base added per mole of the metal ion. In the lower buffer regions portion of the curves for the neutralization of HCl present in VO(IV) soln. has been eliminated.

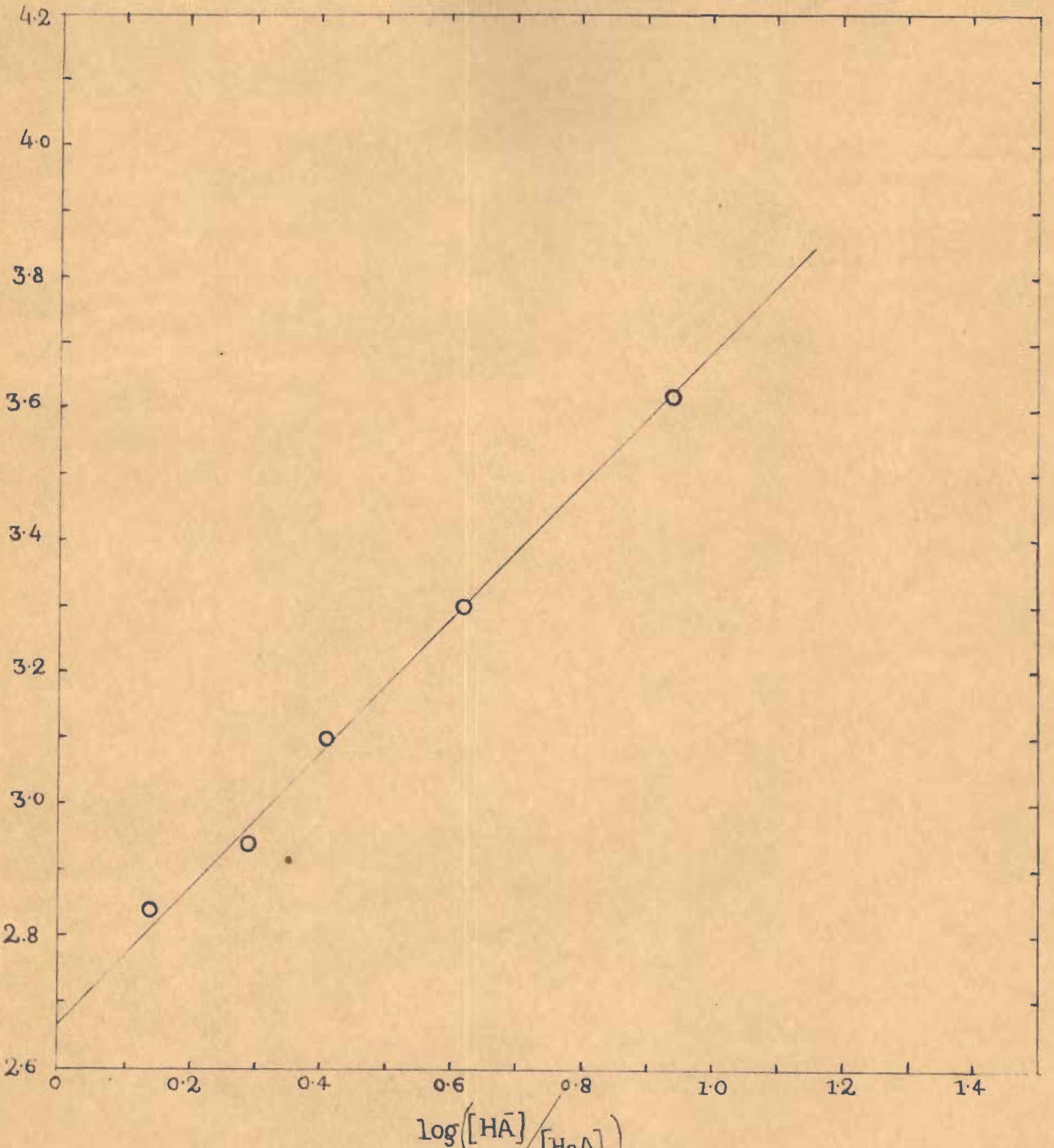
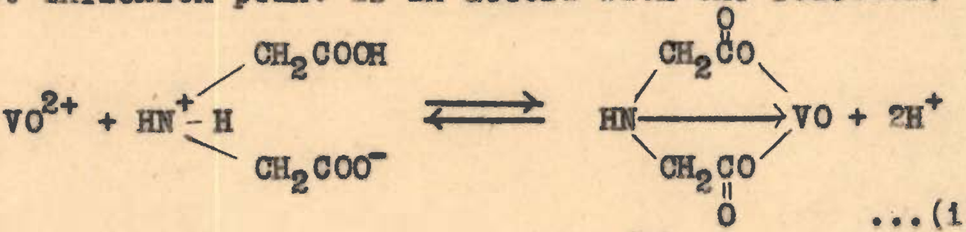


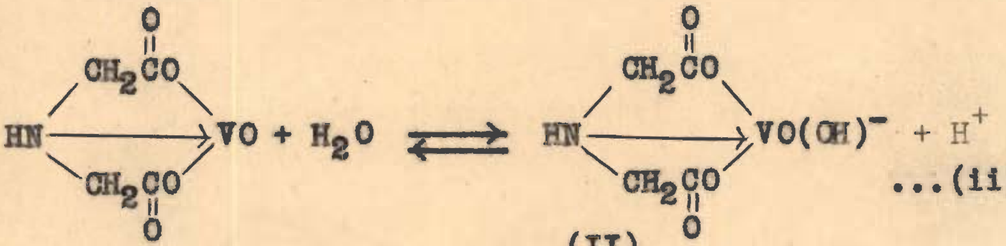
Fig.14. Graphical evaluation of dissociation constants of Iminodiacetic acid (H_2A). (Ionic Strength = 0.1M KCl)

salt, exhibit inflexion points at m = 2 and 3. The first inflexion point is in accord with the reaction:



(I) ...(i)

Occurrence of a buffer region between m = 2 and 3 in these curves showed a hydrolytic reaction of the type:



(II) ...(ii)

Curves 4 and 5 for the titration of vanadyl sulphate in the presence of 2 and 3 moles of iminodiacetic acid are similar in nature to curve 1. In fact curve 4 is a composite of the potentiometric curves 0 and 2. Formation of a 1:2 VO-IMDA chelate, therefore, does not appear to take place in the system under the experimental conditions.

Equilibrium and Formation Constants

Equilibrium constant of reaction (i) may be given by

$$K = \frac{[VOA]\,[H^+]^2}{[VO^{2+}]\,[H_2A]}$$

Values of K determined from various points of the lower buffer region of curves 1-3 (Fig.13) by making use of the usual material balance equations, are presented in table XXVI.

Table XXVI

Curve 1 (Fig.13), $T_A = T_M = 5\times10^{-3}M$

m	0.2	0.4	0.6	0.8	1.0	1.2	1.4
pH	2.58	2.64	2.75	2.85	2.97	3.12	3.29
pK	3.08	3.08	3.03	3.01	3.01	3.02	2.96

Average value of pK = 3.03±0.05

Curve 2 (Fig.13), $T_A = T_M = 2.5\times10^{-3}M$

m	0.2	0.4	0.6	0.8	1.0	1.2	1.4
pH	2.77	2.85	2.94	3.04	3.16	3.32	3.50
pK	2.96	2.97	2.98	2.97	2.97	3.00	2.95

Average value of pK = 2.97±0.03

Curve 3 (Fig.13), $T_A = T_M = 1.25\times10^{-3}M$

m	0.2	0.4	0.6	0.8	1.0	1.2
pH	3.01	3.08	3.17	3.27	3.39	3.53
pK	3.01	2.97	2.98	2.97	2.96	2.92

Average value of pK = 2.96 ± 0.05

The relatively constant values of pK, independent of concentration, thus obtained, showed that a mononuclear 1:1 complex (I) is the only chelate species formed in the system.

Having determined the equilibrium constant of reaction (i), formation constant K_{MA} of the chelate which may be defined as

$$K_{MA} = \frac{[VOA]}{[VO^{2+}][A^{2-}]}$$

was determined from the expression :

$$K_{MA} = \frac{K}{K_{a_1} K_{a_2}}$$

Substitution of the values of K ($10^{-2.99}$ table XXVI), K_{a_1} ($10^{-2.67}$) and K_{a_2} ($10^{-9.12}$)ref.51 gave a value of $10^{8.80}$ for the formation constant of the chelate.

Hydrolysis Constant

Values of the equilibrium constant K_h of reaction (ii), obtained from the potentiometric data of the upper buffer region of curve 1-3 (Fig.13) are presented in table XXVII.

TABLE XXVII

Curve 1 (Fig.13), $T_A = T_M = 5\times10^{-3}M$

m	2.20	2.28	2.36	2.44	2.52	2.60
pH	4.48	4.58	4.70	4.84	5.00	5.17
pK_h	5.05	4.99	4.94	4.96	4.96	5.00

Average value of pK_h = 4.98 ± 0.07

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Curve 2 (Fig.13), $T_A = T_M = 2.5\times10^{-3}M$

m	2.20	2.28	2.36	2.44	2.52	2.60
pH	4.52	4.60	4.72	4.87	5.06	5.19
pK_h	5.09	4.98	4.95	4.96	5.02	5.01

Average value of $pK_h = 5.00 \pm 0.09$

Curve 3 (Fig.13), $T_A = T_M = 1.25\times10^{-3}M$

m	2.20	2.28	2.36	2.44	2.52	2.60
pH	4.47	4.61	4.75	4.83	5.04	5.16
pK_h	5.00	4.97	4.97	4.91	4.99	4.97

Average value of $pK_h = 4.97 \pm 0.03$

It is interesting to note that the chelates of VO(IV) hydrolyse much more easily than those of any other metal of the first transition series. It is evident from the behaviour of the vanadyl chelates studied in the present investigation that they prefer combination with hydroxyl ions to a second mole of the ligand. The only exceptions to this behaviour are the very basic anions of catechol and chromotropic acid which can compete with the hydroxy ion to form stable 1:2 chelates. Tiron, a ligand similar to catechol, has also been reported to form a 1:2 complex.

SECTION VI

OXOVANADIUM(IV) CHELATES OF o-PHENANTHROLINE AND 2,2'— DIPYRIDYL

Although chelates of VO(IV) with o-Phenanthroline and 2,2'-dipyridyl have been studied earlier[52], it was considered desirable to analyse the potentiometric data arising from the interaction of vanadyl ion and these ligands, since the successive reactions involved in the formation of mixed-ligand chelates overlap.

RESULTS AND DISCUSSION

Interaction of VO^{2+} with one mole of o-phenanthroline hydro-chloride.

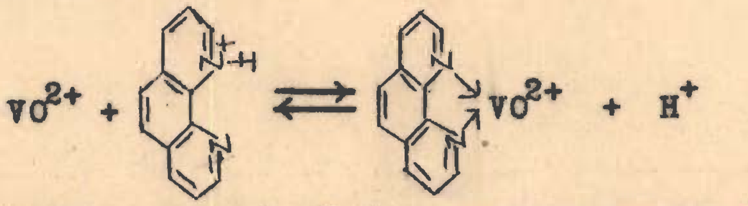
Curve 1 (Fig.15) for the titration of o-phenanthroline hydrochloride, showed a sharp inflexion at one equivalent of KOH indicating that the ligand acts as a monobasic acid. Acid dissociation constant K_a of the ligand was found to be 10^{-5} which is in close agreement with the literature value[53] of $10^{-5.02}$.

Curve 3 (Fig.15) for the titration of vanadyl sulphate in the presence of an equimolar concentration of o-phenanthroline hydrochloride approaches an inflexion point at about $m = 3$. A single inflexion point in the curve indicated that the reactions for the formation of a normal 1:1 chelate and its hydrolysis overlap. It is of course likely that at higher pH values the 1:1 complex may disproportionate into a 1:2 complex and vanadyl

Fig.15. Potentiometric titrations of the normal chelate systems of Oxovanadium(IV) having o-phenanthroline hydrochloride (phen) and 2, 2'-dipyridyl hydrochloride(dipy) as ligands. Curve 1, phen; 2,dipy; 3,1:1 VO-phen; 4,1:1 VO-dipy. All solutions are 2.5x10^{-3}M in ligand at the start of the titration; m=moles of KOH added per mole of the metal ion. Arrows indicate appearance of a solid phase.

hydrous oxide. From the nature of the curve, it seems reasonable to assume that since precipitation did not occur in the system up to pH of about 5.9(vanadyl hydrous oxide is precipitated from vanadyl salt solution at pH of about 4.5), disproportionation reaction does not occur in the lower buffer region of the system. Since the chief purpose of this study was to obtain the reaction constants which could be used in calculating formation constants of the mixed-ligand chelates (part III), it was not considered necessary to analyse the potentiometric data of the upper buffer region of the curve or to study the formation of higher complexes.

In the initial stages of the titration, if the reaction be represented as



...(i)

equilibrium constant of the reaction may be given by:

$$K = \frac{[VOL^{2+}][H^+]}{[VO^{2+}]\ [HL^+]} \quad \text{... (103)}$$

where HL^+ represents protonated form of o-phenanthroline. Formation constant K_{ML} of the chelate may be expressed as

$$K_{ML} = \frac{[VOL^{2+}]}{[VO^{2+}]\ [L]} \quad \text{... (104)}$$

Values of log K_{ML} determined from various points of the lower buffer region of curve 3(Fig.15) by making use of the usual material balance equations, are given in table XXVIII.

Table XXVIII

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

m	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
pH	2.74	2.80	2.85	2.93	3.00	3.05	3.10	3.21
log K_{ML}	5.85	5.87	5.91	5.86	5.90	(6.19	6.68	6.98) *

Average value of log K_{ML} = 5.88 ± 0.03

* Values not included in the average.

The relatively constant values of log K_{ML} obtained between m = 0 and m = 0.4 indicated that in this region, i.e. upto pH of about 3, only the normal 1:1 chelate (I) is formed in the system.

Hydrolysis of the Chelate

A gradual rise in the values of log K_{ML} seen in table XXVIII at m > 0.4 (pH > 3) indicated that the normal 1:1 metal chelate is comparatively more stable below pH of about 3. As pH of the system is raised above this value, appreciable hydrolysis of the chelate sets in making the solution more acidic than it would be in the absence of hydrolytic effects. In the initial stages, if the hydrolysis reaction be represented as

$$VOL^{2+} + H_2O \rightleftharpoons VO(OH)L^{+} + H^{+} \qquad ...(ii)$$

Hydrolysis constant of the chelate may be expressed as

$$K_h = \frac{[VO(OH)L^+]\,[H^+]}{[VOL^{2+}]} \qquad \ldots (105)$$

Equilibrium constant for the overall reaction:

$$VO^{2+} + HL^+ + H_2O \rightleftharpoons VO(OH)L^+ + 2H^+$$

may be given by

$$K_H = \frac{[VO(OH)L^+]\,[H^+]^2}{[VO^{2+}]\,[HL^+]} \qquad \ldots (106)$$

From the material balance we obtain

$$T_M = [VO^{2+}] + [VOL^{2+}] + [VO(OH)L^+] \qquad \ldots (107)$$

$$T_{OH} + [H^+] = [L] + [VOL^{2+}] + 2\,[VO(OH)L^+] \qquad \ldots (108)$$

$$T_L = [HL^+] + [L] + [VOL^{2+}] + [VO(OH)L^+] \quad \ldots (109)$$

In an equimolar mixture of vanadyl sulphate and o-phenanthroline hydrochloride since $T_M = T_L$, combining equations 104, 107-109 and the expression for acid dissociation constant of the ligand and rearranging the terms into the form of a quadratic, we obtain

$$K_{ML}[VO^{2+}]^2 + \left(1 + \frac{2[H^+]}{K_a}\right)[VO^{2+}] - \left\{2T_M - T_{OH} - [H^+]\right\} \times \left(1 + \frac{[H^+]}{K_a}\right) = 0 \qquad \ldots (110)$$

Concentration of uncomplexed vanadyl ions in the system may, therefore, be calculated by solving the above equation.

After computation of $[VO^{2+}]$, concentration of other species in the system may be determined easily with the help of the material balance equations given above. Values of pK_H thus obtained are presented in table XXIX.

Table XXIX

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

m	0.6	0.8	1.0	1.2	1.4	1.6	1.8
pH	3.10	3.28	3.49	3.70	3.93	4.10	4.32
$-\log K_H$	3.04	3.06	3.05	3.03	3.02	(2.87	2.67)*

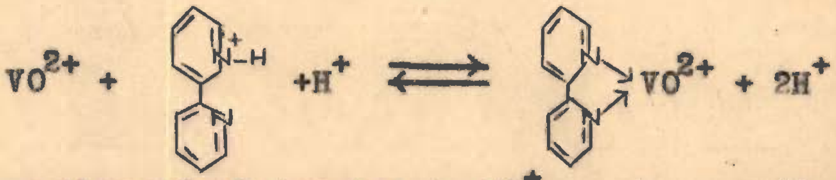
Average value of $-\log K_H = 3.04 \pm 0.02$
*Values not included in the average.

It is evident from the above table that the relative constancy in the values of the equilibrium constant could be obtained up to pH of about 4 above which a gradual fall in the values of pK_H is observed. This is an indication of a further hydrolysis of the chelate.

Interaction of VO^{2+} with one mole of 2,2'-dipyridyl dihydrochloride.

Curve 2(Fig.15) for the potentiometric titration of 2,2'-dipyridyl dihydrochloride showed a slight inflexion at one equivalent of KOH followed by a sharp inflexion at two equivalents of alkali. From the potentiometric data it is evident that one proton of the ligand is strongly acidic and is almost completely dissociated under the experimental conditions. The other proton is comparatively weakly acidic as is evidant from the value of its dissociation constant equal to 3.162×10^{-5} obtained from the titration data.

Titrations of vanadyl sulphate in the presence of 2,2'-dipyridyl hydrochloride (curve 4, Fig.15) gave a curve similar in nature to that obtained for the VO-phen chelate system. The curve approaches an inflexion point at about m = 4. A marked difference between the titration of this system and that of the VO-phen. chelate system is that in this case no precipitation occurred at any stage indicating that the hydroxo chelate species of VO-dipy. are soluble under the experimental conditions. In this case also, in the initial stages of the titration, the reaction may be represented as:



...(i)

In the mathematical treatment, HL^+ may be considered to be the ligand, since one proton of the ligand is completely dissociated in the solution. Beyond m = 1, therefore, the reaction may be expressed as

$$HL^+ + VO^{2+} \rightleftharpoons VOL^{2+} + H^+ \qquad \text{...(ii)}$$

Values of formation constant K_{ML} of the chelate VOL^{2+}, calculated from the potentiometric data of curve 4 (Fig.15), are presented in table XXX.

Table XXX

Curve 4 (Fig.15), $T_M = T_L = 2.5 \times 10^{-3}M$

m	1.0	1.1	1.2	1.3	1.4	1.5	1.6
pH	2.81	2.86	2.92	3.00	3.07	3.12	3.18
log K_{ML}	5.04	5.09	5.10	5.08	(5.18	5.26	5.63)*

Average value of log K_{ML} = 5.08 ± 0.02

*(   ) Values not included in the average.

Like VO-phen chelate system, here also it is evident from table XXX that constant values of the formation constant could be obtained up to pH of about 3 only above which a gradual rise in the values of log K_{ML} is observed probably on account of hydrolytic effects in the system. Thus the normal 1:1 chelate, VOL^{2+} appears to be comparatively more stable below pH of about 3.

Hydrolysis Constant:

In the initial stages, if the hydrolytic reaction be represented as

$$VOL^{2+} + H_2O \rightleftharpoons VO(OH)L^{+} + H^{+} \quad ...(iii)$$

or, if the overall reaction for the formation of $VO(OH)L^{+}$ type of chelate be expressed as

$$VO^{2+} + HL^{+} + H_2O \rightleftharpoons VO(OH)L^{+} + 2H^{+} \quad ... (iv)$$

the values of equilibrium constant K_H of reaction (iv), determined with the help of the usual material balance equations (see page 85), are presented in table XXXI.

Table XXXI

Curve 4 (Fig.15), $T_A = T_M = 2.5\times10^{-3}M$

m	1.6	1.7	1.8	1.9	1.0	1.1	1.2	1.4
pH	3.18	3.27	3.37	3.46	3.56	3.63	3.72	3.88
$-\log K_H$	3.43	3.42	3.37	3.38	3.37	(3.30	3.27	3.12)*

Average value of $-\log K_H = 3.39 \pm 0.04$

* Values not included in the average.

As observed in the VO-phen. chelate system, here also, a gradual fall in the values of pK_H seen in table XXXI above pH of about 3.6 is probably due to a further hydrolysis of the chelate. Since the object of this study was to determine the equilibrium constants of reactions which could be used in the determination of formation constants of mixed-ligand chelates having 2,2'-dipyridyl as a primary ligand (Part III) analysis of the potentiometric data at pH values greater than 3.5 was not considered necessary.

PART III

MIXED-LIGAND CHELATES OF OXOVANADIUM (IV)

Section I- Mixed-ligand Chelates of Oxovanadium(IV) with o-Phenanthroline and Oxygen donor Bidentate Ligands

Section II- Mixed-Ligand Chelates of Oxovanadium(IV) with 2,2'-Dipyridyl and Oxygen donor Bidentate Ligands.

SECTION I

MIXED-LIGAND CHELATES OF OXOVANADIUM (IV) WITH o-PHENANTHROLINE AND SOME DIHYDRIC PHENOLIC COMPOUNDS

In view of the strong chelation of vanadyl ion with o-phenanthroline and 2,2'-dipyridyl and a fairly high stability of the hydroxo derivatives of the 1:1 vanadyl chelates of these ligands, they are expected to form mixed-ligand chelates. Attempts were, therefore, made to study the interaction of vanadyl sulphate with o-phenanthroline and 2,2'-dipyridyl as primary chelating agents in the presence of some oxygen donor ligands ~~such~~ such as catechol, tiron, chromotropic acid, etc. as secondary chelating agents.

RESULTS AND DISCUSSION

In figures 16, 17, and 18, curve 3 represents potentiometric titrations of vanadyl sulphate with KOH in the presence of an equimolar concentration of catechol, tiron and chromotropic acid respectively. These curves may be interpreted on the basis of the formation of normal 1:1 chelates and their conversion into the corresponding monohydroxo chelate species (see VO-catechol and VO-DNS systems). Since precipitation does not occur in these systems at any stage of titration, the hydroxy complexes of these chelates appear to be stable over a wide range of pH.

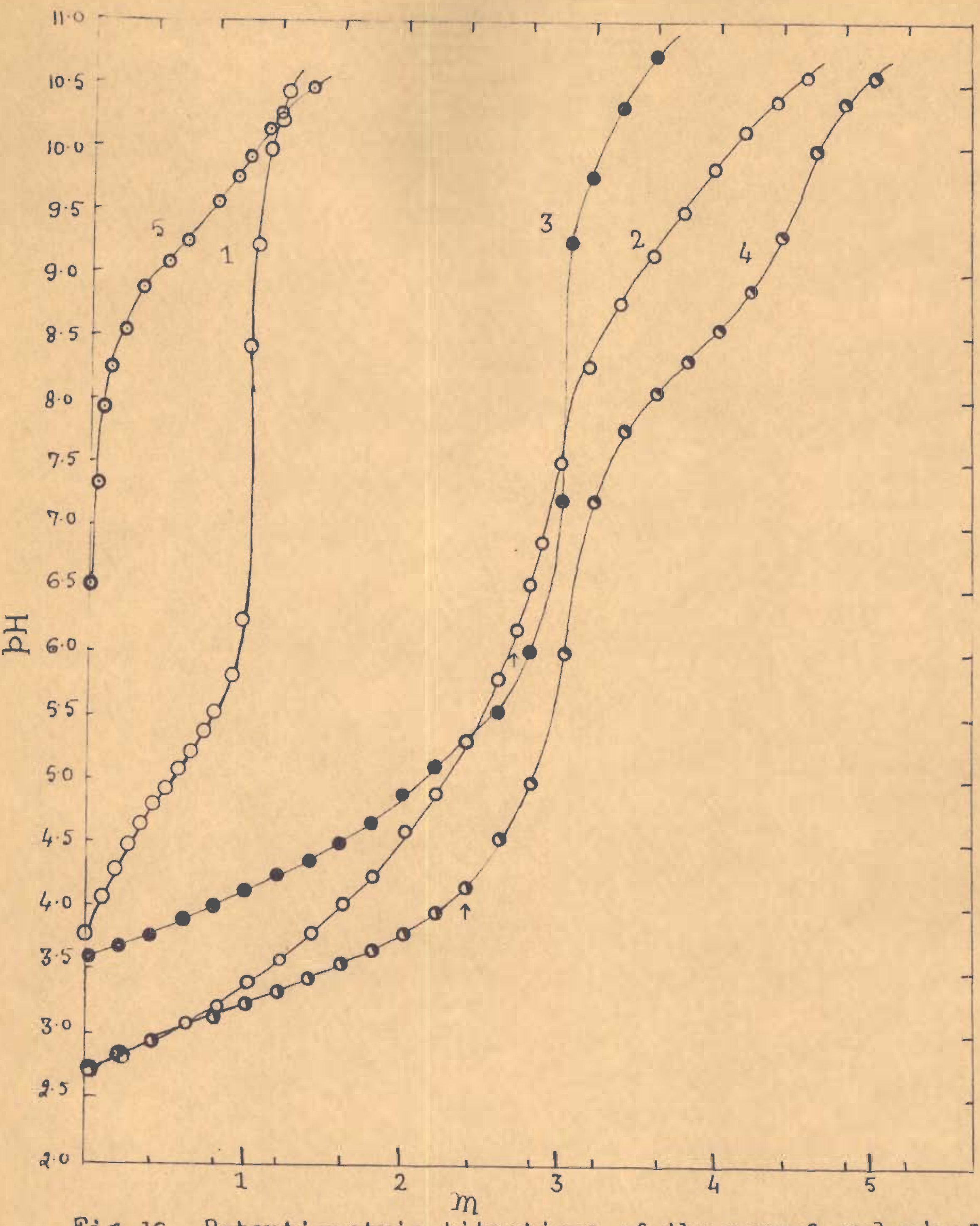


Fig.16. Potentiometric titrations of the normal and mixed ligand chelate systems of oxovanadium(IV) having o-phenanthroline hydrochloride(phen.) and catechol as ligands: Curve 1, phen.; 2, 1:1 VO-phen.; 3, 1:1 VO-catechol; 4, 1:1:1 VO-phen.-catechol; 5, catechol. All solutions are 2.5×10^{-3}M in ligand at the start of titration; m = moles of KOH added per mole of the metal ion. Arrows indicate appearance of a solid phase.

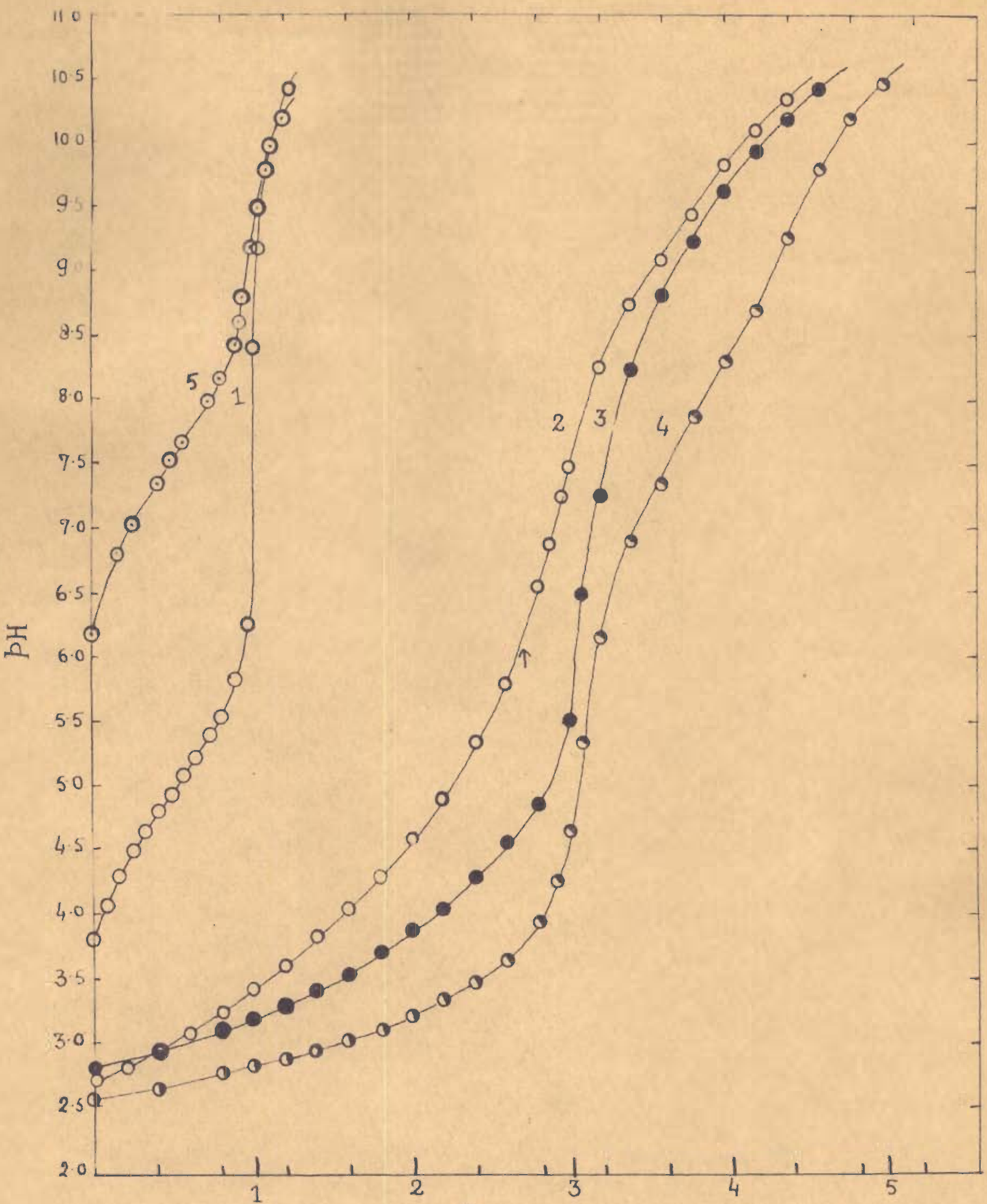


Fig.17. Potentiometric titrations of the normal and mixed ligand chelate systems of oxovanadium(IV) having o-phenanthroline hydrochloride(phen.) and tiron as ligands: Curve 1, phen.; 2, 1:1 VO-phen.; 3, 1:1 VO-tiron; 4, 1:1:1 VO-phen.-tiron; 5, tiron. All solutions are 2.5×10^{-3} M in ligand at the start of titration; m = moles of KOH added per mole of the metal ion. Arrows indicate appearance of a solid phase.

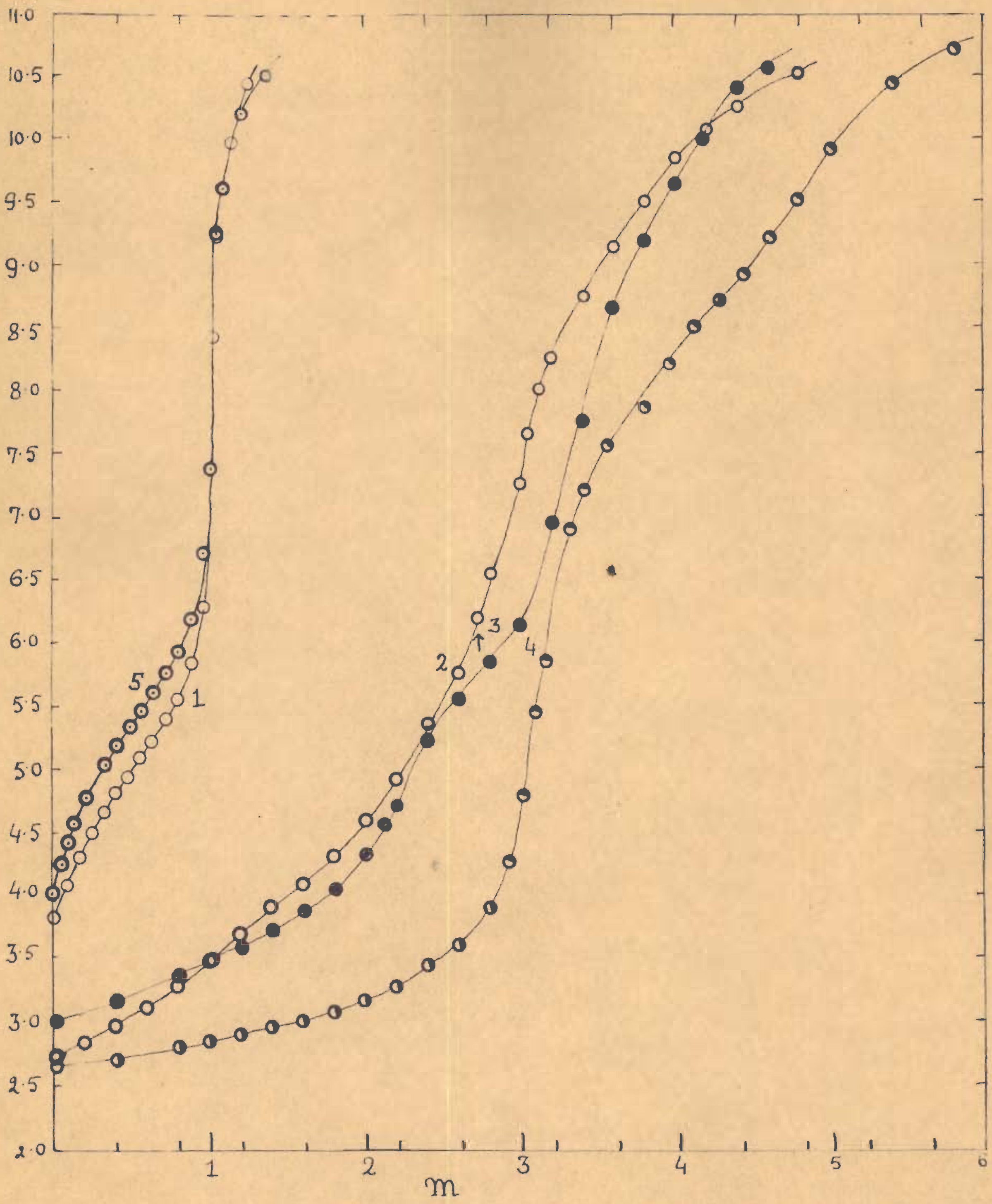


Fig.18. Potentiometric titrations of the normal and mixed ligand chelate systems of oxovanadium(IV) having o-phenanthroline hydrochloride(phen.) and chromotropic acid(DNS) as ligands: Curve 1, phen.; 2, 1:1 VO-phen.; 3, 1:1 VO-DNS; 4, 1:1:1 VO-phen.-DNS; 5, DNS. All solutions are 2.5×10^{-3} M in ligand at the start of titration; m = moles of KOH added per mole of the metal ion. Arrows indicate appearance of a solid phase.

Potentiometric data of lower buffer regions of the curves obtained by the titration of 1:1:1 VO-phen-secd. ligand systems with KOH were treated in accordance with the following different postulates:

I. Formation of a mixture of two simple chelate compounds.

$$VO^{2+} + HL^{+} \rightleftharpoons VOL^{2+} + H^{+}$$

and

$$VO^{2+} + H_2A \rightleftharpoons VOA + 2H^{+}$$

where HL^{+} represents protonated form of o-phenanthroline (primary ligand) and H_2A represents a secondary ligand.

II. Formation of a simple 1:1 chelate between the metal ion and a ligand which has a stronger tendency for complex formation. The other ligand may remain unbound in the solution.

III(A) Combination of the metal ion with both ligands simultaneously to form a mixed-ligand chelate in a single step.

$$VO^{2+} + HL^{+} + H_2A \rightleftharpoons VOLA + 3H^{+}$$

(B) Formation of a mixed-ligand chelate in two overlapping steps.

$$VO^{2+} + HL^{+} \overset{-H^{+}}{\rightleftharpoons} VOL^{2+} \overset{H_2A}{\rightleftharpoons} VOLA + 2H^{+}$$

On the basis of model I, potentiometric curve for the titration of mixed-ligand system would be expected to lie between curves 2 and 3 for the separate titrations of the simple 1:1 chelates of the two ligands. But in all the three cases, curve 4 (Figs. 16,17 and 18) lies below curves 2 and 3. Possibility of the formation of a mixture of simple chelates of the two ligands present in the system may, therefore, be ruled out. The above conclusion obtains support from the fact that in the 1:1:1 VO-Phen-catechol system, a precipitate was observed at pH of about 4. A mixture of the 1:1 chelates of vanadyl sulphate with o-phenanthroline and catechol would have given a soluble system at relatively low pH ($pH \leqslant 5.9$).

In each case a considerable lowering shown by curve 4 as compared with the curves which would be obtained by the titration of a simple 1:1 chelate system and the free ligand rules out the postulate II as well.

In view of the above arguments, formation of a mixed-ligand chelate, VOLA, seems to be the only explanation for the unique nature of the curve (curve 4, Figs.16-18) for the titration of the 1:1:1 VO-phen-secd. ligand system. It now remains to be established whether the mixed-ligand chelate is formed in a single step:

$$VO^{2+} + HL^{+} + H_2A \rightleftharpoons VOLA + 3H^{+}$$

or it is formed in two overlapping steps.

$$VO^{2+} + HL^{+} \xrightleftharpoons{-H^{+}} VOL^{2+} \xrightleftharpoons{H_2A} VOLA + 2H^{+}$$

From the potentiometric data and the stability constants determined for the chelates VOL^{2+} and VOLA, it was found that in the initial stages of the titration of 1:1:1 VO-phen-secondary ligand system, concentration of the mixed-ligand chelate was much smaller than that of VOL^{2+}. In fact in the VO-phen-catechol system (Fig.16), lowering of curve 4 (cf. curves 2 and 3), which is a measure of the mixed-ligand chelate formation, occurs beyond m = 0.4. Between m = 0 and m = 0.4, curve 4 remains identical with curve 2 (Fig.16) indicating that no mixed-ligand chelate is formed in this buffer region of the system. Formation of mixed-ligand chelate, therefore, appears to take place in two overlapping steps, rather than in a single step. Although in the mixed-ligand systems involving tiron (curve 4, Fig.17) and chromotropic acid (curve 4, Fig.18) as secondary ligands, lowering in the potentiometric curves (cf. curves 2 and 3) occurs from the beginning of the titration, probably due to a higher stability of the chelates of these ligands as compared to that of the corresponding chelates of catechol, in these cases also, by a mathematical analysis of the potentiometric data it was found that at the initial stages of the titration, the concentration of VO-phen.$^{2+}$ chelate was much larger than that of VO-phen-catechol, thus indicating the formation of the mixed-ligand chelate through an intermediate formation of a simple chelate of the type VO-phen^{2+}.

Determination of Equilibrium Constants

As shown in the VO-phen system, formation of 1:1

VO-phen. chelate may be represented as:

$$VO^{2+} + L \rightleftharpoons VOL^{2+} \qquad \text{... (i)}$$

Formation of the mixed-ligand chelate may be represented by the reaction

$$VOL^{2+} + H_2A \rightleftharpoons VOLA + 2H^{+} \qquad \text{... (ii)}$$

Overall reaction for the formation of VOLA may be expressed as:

$$VO^{2+} + HL^{+} + H_2A \rightleftharpoons VOLA + 3H^{+} \qquad \text{... (iii)}$$

If K and K' represent equilibrium constants of reactions (ii) and (iii), we have

$$K = \frac{[VOLA]\,[H^{+}]^{2}}{[VOL^{2+}]\,[H_2A]} \qquad \text{... (111)}$$

and

$$K' = \frac{[VOLA]\,[H^{+}]^{3}}{[VO^{2+}]\,[HL^{+}][H_2A]} \qquad \text{... (112)}$$

In a 1:1:1 reaction mixture of vanadyl sulphate, o-phenanthroline hydrochloride and a secondary ligand, from the material balance, we obtain

$$T_M = [VO^{2+}] + [VOL^{2+}] + [VOLA] \qquad \text{... (113)}$$

$$T_{OH} + [H^{+}] = [L] + [VOL^{2+}] + 3[VOLA] \qquad \text{... (114)}$$

$$T_L = [HL^{+}] + [L] + [VOL^{2+}] + [VOLA] \qquad \text{... (115)}$$

$$T_A = [H_2A] + [VOLA] \qquad \text{... (116)}$$

In the lower buffer system, concentration of HA^-, A^{2-} and OH^- were negligible as compared to those of the other species present. As shown before (see page 84) hydrolysis of 1:1 VO-phen.chelate was also considered to be negligible below pH 3. Charges on the mixed-ligand chelate species have been eliminated for the sake of generalization.

Combination of (113)-(116) and the expressions for the formation constant K_{ML} of VOL^{2+} and the acid dissociation constant of HL^+ and re-arranging the terms into the form of a quadratic yield

$$2K_{ML}\left[VO^{2+}\right]^2 + \left\{2 + \frac{3\left[H^+\right]}{K_a}\right\}\left[VO^{2+}\right] - \left\{3T_M - T_{OH} - \left[H^+\right]\right\} \times \left(1 + \frac{\left[H^+\right]}{K_a}\right) = 0 \quad ...(117)$$

Concentration of the uncomplexed vanadyl ions may, therefore, be given by

$$\left[VO^{2+}\right] = \frac{-b \pm \sqrt{b^2 + 4\ ac}}{2a}$$

where

$$a = 2K_{ML}, \quad b = 2 + \frac{3\left[H^+\right]}{K_a} \text{ and}$$

$$c = \left(3T_M - T_{OH} - \left[H^+\right]\right)\left(1 + \frac{\left[H^+\right]}{K_a}\right)$$

Having determined $\left[VO^{2+}\right]$, concentration of the other species present in the reaction mixture may be easily calculated with the help of the equations given above. Values of the equilibrium constants K and K', thus obtained from various points of the lower buffer region of curve 4 (Fig.17) for the mixed-ligand system having tiron as a secondary ligand, are presented in table XXXII.

Table XXXII

Curve 4 (Fig.17), $T_A = T_M = T_L = 2.5 \times 10^{-3}$M

m	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
pH	2.61	2.66	2.72	2.77	2.83	2.89	2.96	3.03
pK	2.85	2.84	2.87	2.85	2.85	2.84	2.85	2.83
pK'	1.97	1.96	2.00	1.97	1.97	1.96	1.96	1.95

Average value of pK = 2.85 ± 0.02 ,

pK'= 1.97 ± 0.03

Very similar results were obtained for the mixed-ligand system involving chromotropic acid as a secondary ligand. In fact virtually the same values, 2.85 and 1.97, were obtained for pK and pK' from the potentiometric data of curve 4 (Fig.18).

Equations 113-115 and 117 hold at pH ⩽ 3 of the reaction mixture, since hydrolysis of VOL^{2+} has been considered negligible in deriving the above equations. But the potentiometric curve for the titration of a mixed-ligand system having catechol as a secondary ligand (curve 4, Fig.16) lies above pH 3. Therefore, considering hydrolysis of the chelate VOL^{2+}, as shown in the interaction of vanadyl sulphate with o-phenanthroline (see page 84), equations 113–115 become

$$T_M = [VO^{2+}] + [VOL^{2+}] + [VO(OH)L^{+}] + [VOLA] \quad \ldots(118)$$

$$T_{OH} + [H^{+}] = [L] + [VOL^{2+}] + 2[VO(OH)L^{+}] + 3[VOLA] \quad \ldots(119)$$

$$T_A = [HL^{+}] + [L] + [VOL^{2+}] + [VO(OH)L^{+}] + [VOLA] \quad \ldots(120)$$

From the above relationships it may be shown that

$$\left\{2K_{ML}\,K_a[H^{+}] + K_H\right\}[VO^{2+}]^2 + [H^{+}](2K_a + 3[H^{+}]) \times [VO^{2+}] - (3T_M - T_{OH} - [H^{+}])(K_a + [H^{+}])[H^{+}] = 0$$

Concentration of the uncomplexed vanadyl ion may therefore be calculated by solving the above quadratic equation. Concentrations of other species present in the system may, therefore, be easily evaluated. Values of the equilibrium constant thus obtained for VO-phen-catechol system are listed in table XXXIII.

TABLE XXXIII

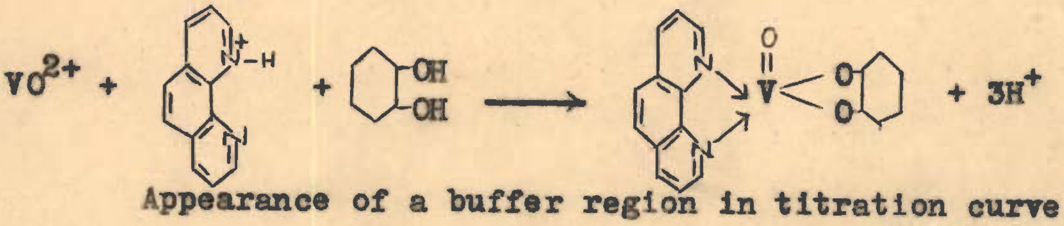
Curve 4 (Fig.16), $T_A = T_M = T_L = 2.5\times10^{-3}M$

m	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
pH	3.00	3.12	3.24	3.34	3.44	3.55	3.66	3.78
pK	4.44	4.44	4.47	4.45	4.43	4.44	4.44	4.45
pK'	3.56	3.56	3.59	3.57	3.55	3.56	3.56	3.57

Average value of pK = 4.44 ± .03, pK'=3.56 ± .03

In this system due to the appearance of a solid phase near pH 4, calculations could not be made beyond m = 2. The lower solubility of the mixed-ligand chelate of catechol (VOLA) as compared to that of the corresponding derivatives of tiron and chromotropic acid ($VOLA^{2-}$), is probably on account of the fact that the former complex is a nonelectrolyte whereas molecules of the latter two complexes carry a charge of minus two. Formation of the mixed-ligand chelate of o-phenanthroline and catechol at higher pH values than that of the corresponding derivatives of sulphonated catechols shows that the sulphonate groups in tiron and chromotropic acid have an effect of increasing reactivity of the aromatic hydroxyl groups in the coordination with VO^{2+}. This is also evident from the titration curves of the 1:1 VO-secondary-ligand chelate systems (Curve 3, Figs. 16-18).

A sharp inflexion at m = 3 in the potentiometric curve for the titration of the mixed-ligand systems (curve 4, Figs. 16-18), discussed above, may be explained on the basis of the complete neutralization of a proton of o-phenanthroline hydrochloride and two phenolic protons of the secondary ligand liberated as a result of chelation. Considering catechol as a secondary ligand, for example, the overall reaction may be represented as:



Appearance of a buffer region in titration curve 4, (Figs. 16-18) in alkaline solutions (m>3) indicated an appreciable hydrolysis of the mixed-ligand chelate.

Stability Constants of Mixed-Ligand Chelates

Having determined equilibrium constants for the reactions envisaged in postulate III, formation constants of the mixed-ligand chelates which may be defined as

$$K_{MLA} = \frac{[VOLA]}{[VOL^{2+}][A^{2-}]}$$

may be determined with the help of expression

$$K_{MLA} = \frac{K}{K_{a_1} K_{a_2}}$$

where K is the equilibrium constant of reaction

$$VOL^{2+} + H_2A \rightleftharpoons VOLA + 2H^+$$

K_{a_1} and K_{a_2} represent the first and second acid dissociation constants of the secondary ligand.

The overall stability constant of the mixed-ligand chelate:

$$K'_{MLA} = \frac{[VOLA]}{[VO^{2+}][L][A^{2-}]}$$

may be evaluated from the expression

$$K'_{MLA} = \frac{K'}{K_{a_1} K_{a_2} K_a}$$

where K' represents equilibrium constant of the overall reaction

$$VO^{2+} + HL^{+} + H_2A \rightleftharpoons VOLA + 3H^{+}$$

Thus by substituting the values of K and K' (from table XXXII and XXXIII) and the dissociation constants of the ligands (given in table XXXIV), stability constants of the mixed-ligand chelates could be determined. These constants and the values of the formation constants(K_{ML}) of the simple 1:1 chelates of VO^{2+} with secondary ligands, calculated from the potentiometric data of curve 3 (Figs. 16-18), are tabulated below:

Table XXXIV

Secd. Ligand	$-\log K_{a_1}$	$-\log K_{a_2}$	$\log K_{MA}$	$\log K_{MLA}$	$\log K'_{MLA}$
Catechol	9.20	11.93(23)	15.28	16.69	22.57
Tiron	7.56	12.48(54)	16.61	17.19	23.07
Chromotropic acid	5.34	15.60(23)	16.89	18.09	23.97

It is evident from table XXXIV that the stabilities of the simple and mixed-ligand chelates of the above three ligands are in the following order:

chromotropic acid > tiron > catechol

This is to be expected in view of a decreasing order in the basicities of these ligands. Anion of DNS being the most basic in character, forms strongest complexes whereas the anion of catechol the least basic of the above three

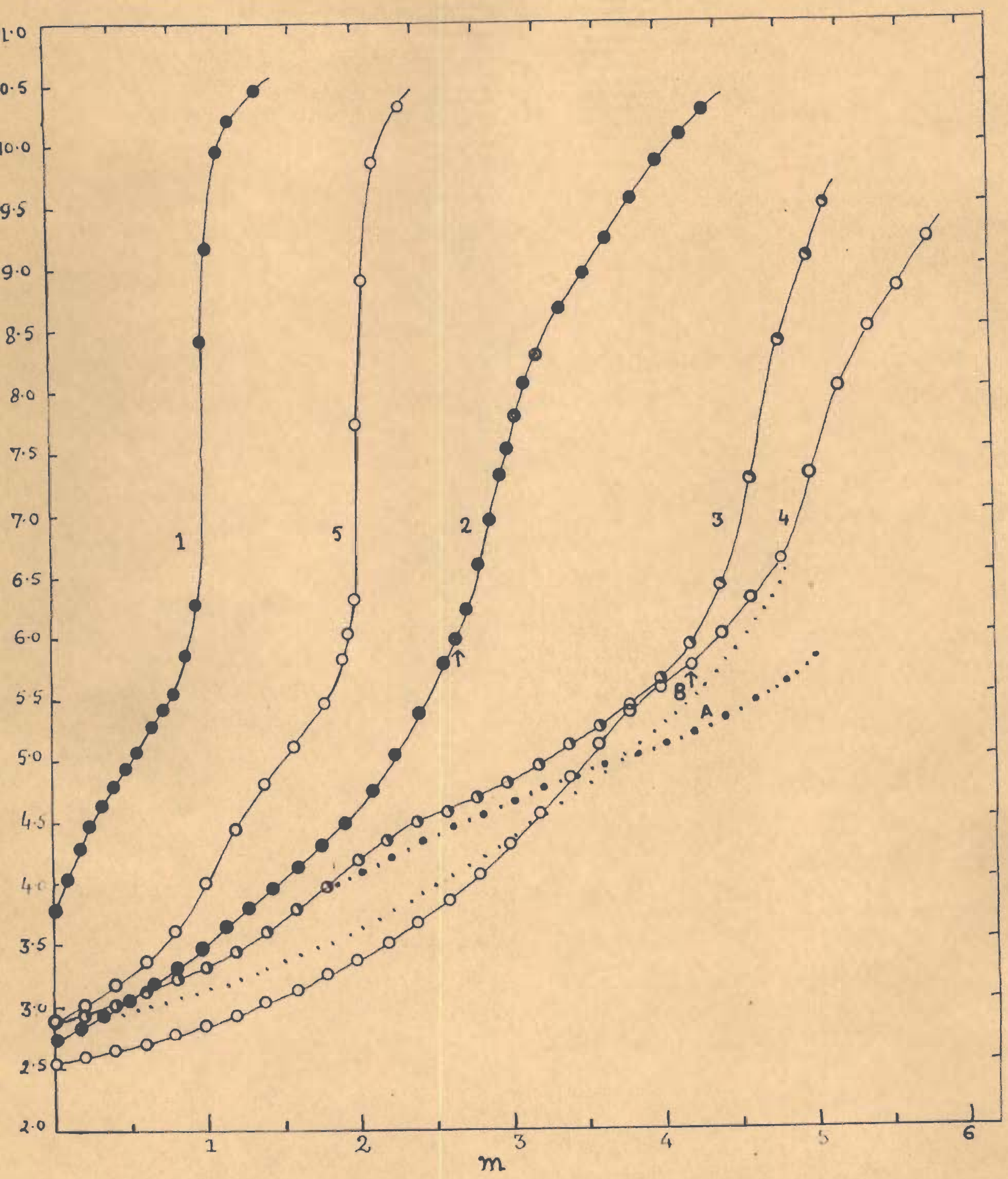


Fig.24. Potentiometric titrations of the normal and mixed ligand chelate systems of oxovanadium(IV) having o-phenanthroline hydrochloride(Phen) and phthalic acid(Ph.A) as ligands: 1,Phen; 2,1:1 VO-Phen; 3,1:1 VO-Ph.A; 4,1:1:1 VO-Phen-Ph.A; 5,Ph.A. A,composite curve of 1 & 3; B,composite curve of 2 & 5. All solutions are 2.5×10^{-3}M in ligand at the start of titration; m = moles of KOH added per mole of the metal ion. Arrows indicate appearance of a solid phase.

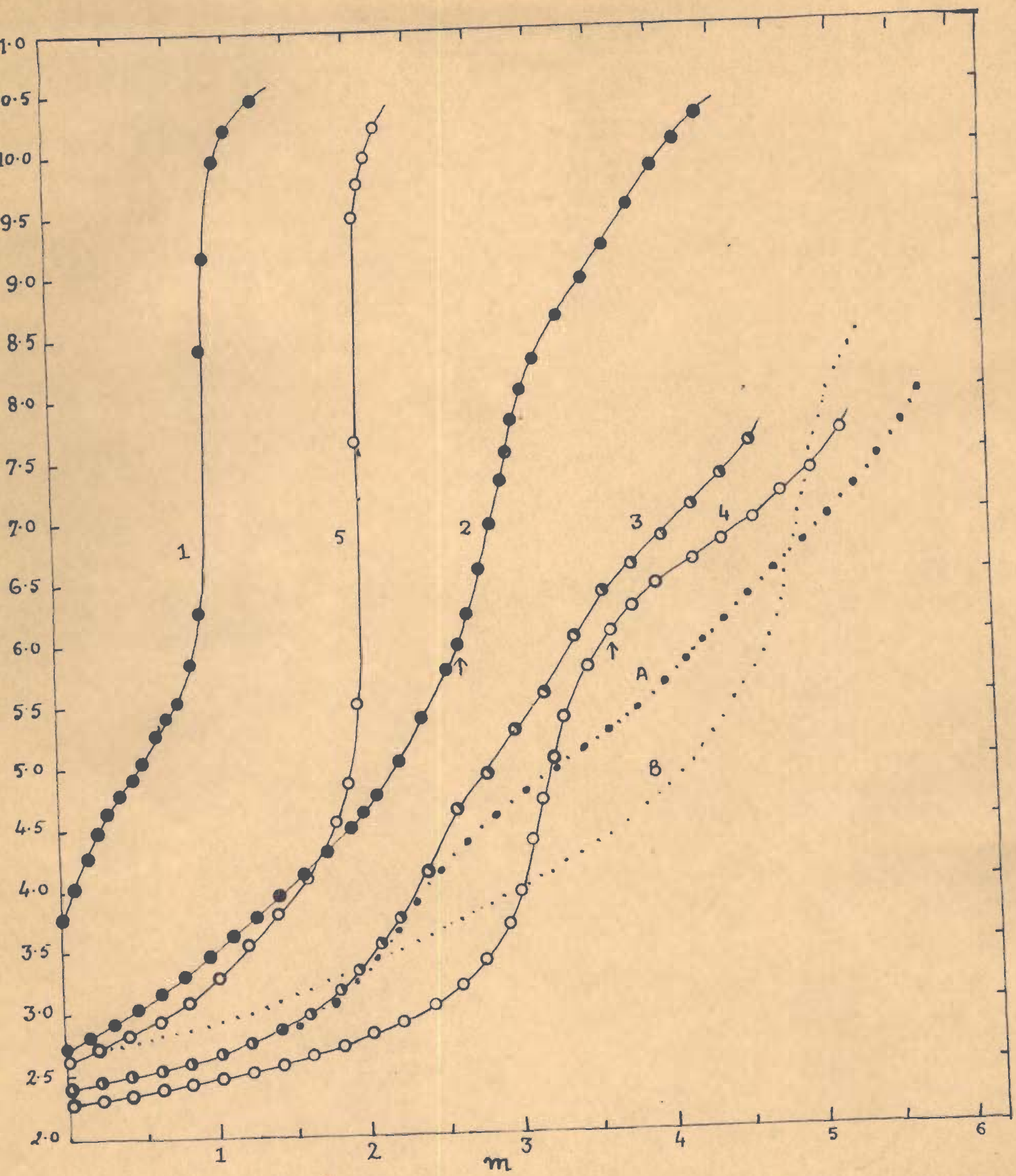


Fig.23. Potentiometric titrations of the normal and mixed ligand chelate systems of oxovanadium(IV) having o-phenanthroline hydrochloride(Phen) and oxalic acid(Ox.A) as ligands: 1,Phen; 2,1:1 VO-Phen; 3,1:1 VO-Ox.A; 4,1:1:1 VO-Phen-Ox.A; 5,Ox.A. A, composite curve of 1 & 3; B,composite curve of 2 & 5. All solutions are 2.5×10^{-3}M in ligand at the start of titration; m = moles of KOH added per mole of the metal ion. Arrows indicate appearance of a solid phase.

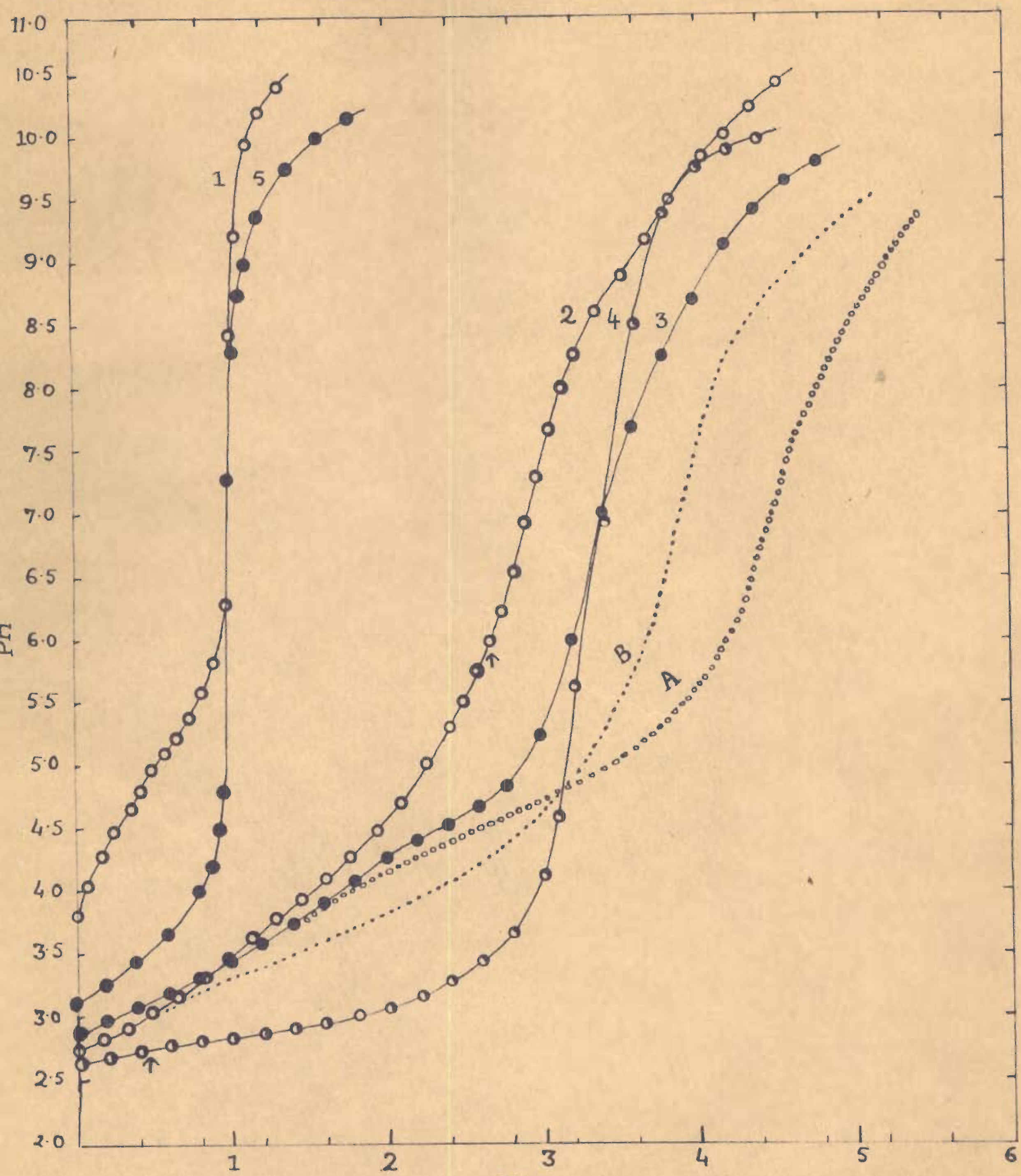


Fig.22. Potentiometric titrations of the normal and mixed ligand chelate systems of oxovanadium(IV) having o-Phenanthroline hydrochloride(phen) and mandelic acid(MA) as ligands: Curve 1, Phen; 2, 1:1 VO-phen; 3, 1:1 VO-MA; 4, 1:1:1 VO-phen-MA; 5, MA; A, composite curve of 1 and 3; B, composite curve of 2 and 5. All solutions are 2.5×10^{-3}M in ligand at the start of the titration; m=moles of KOH added per mole of the metal ion. Arrows indicate appearance of a solid phase.

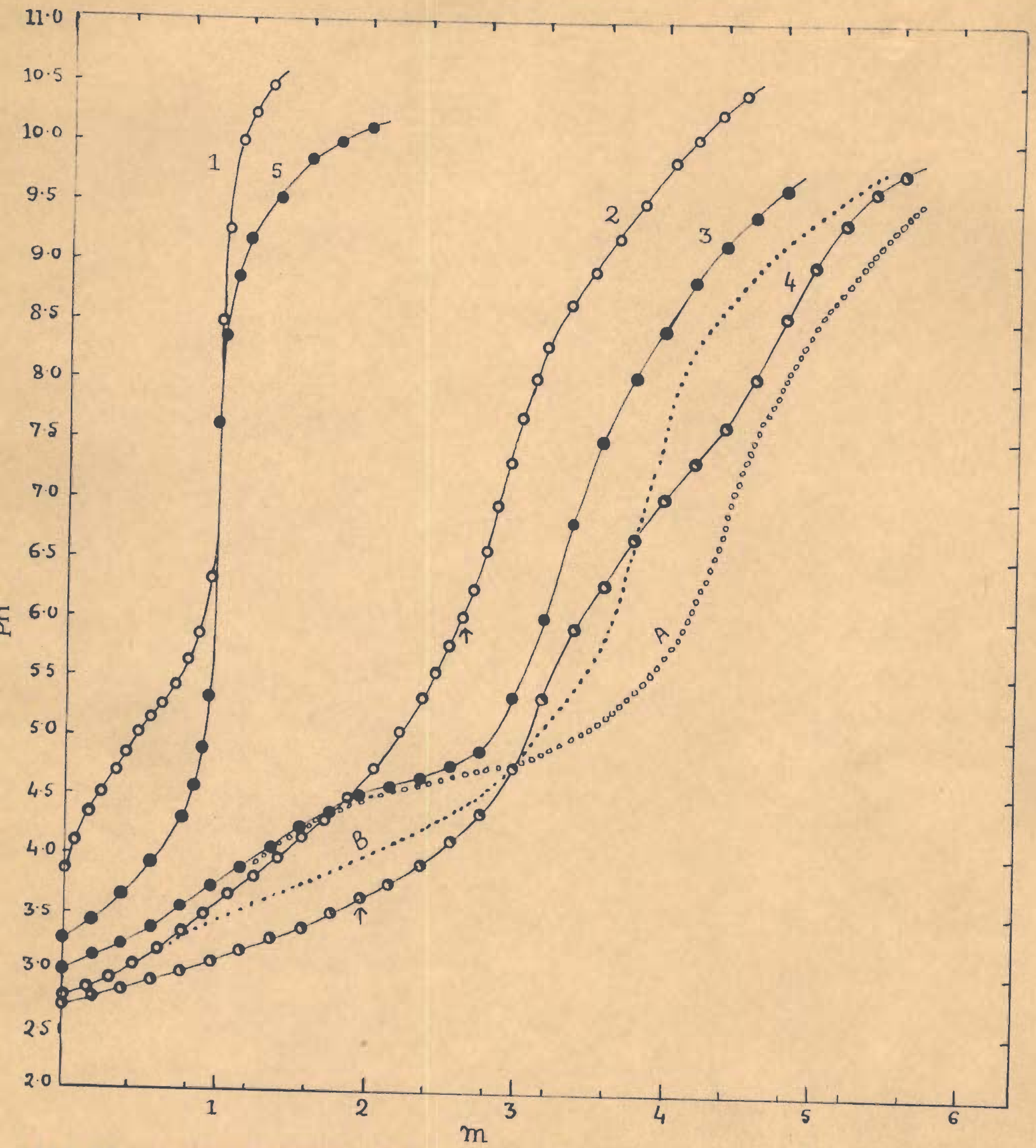


Fig.21. Potentiometric titrations of the normal and mixed ligand chelate systems of oxovanadium(IV) having o-Phenanthroline hydrochloride(phen) and lactic acid(LA) as ligands: Curve 1, Phen; 2, 1:1 VO-phen;3,1:1 VO-LA; 4, 1:1:1 VO-phen-LA. 5, LA; A, composite curve of 1 and 3; B, composite curve of 2 and 5. All solutions are 2.5x10^{-3}M in ligand at the start of the titration; m=moles of KOH added per mole of the metal ion. Arrows indicate appearance of a solid phase.

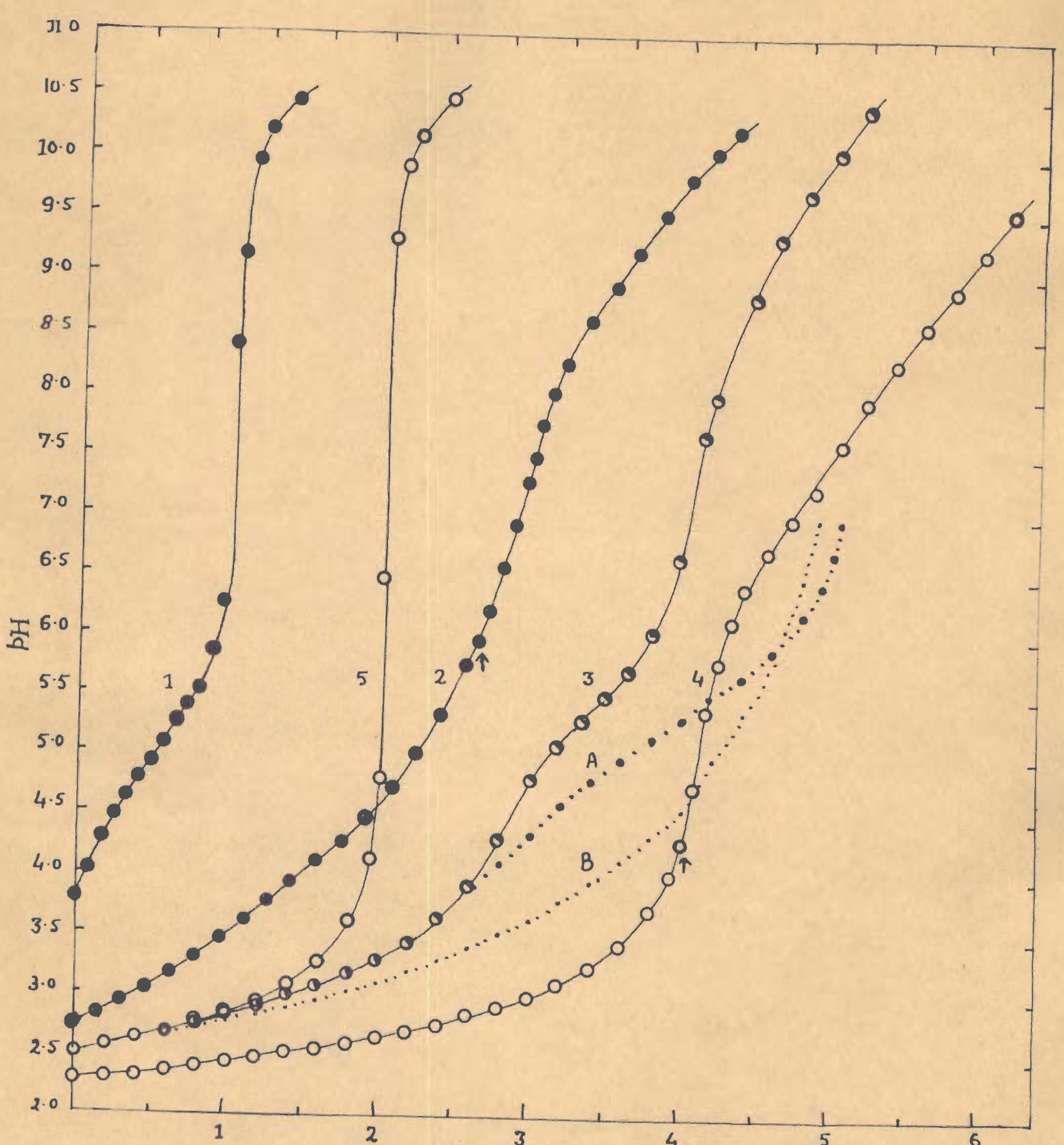


Fig. 20. Potentiometric titrations of the normal and mixed-ligand chelate systems of oxovanadium(IV) having o-phenanthroline hydrochloride (Phen) and sulphosalicylic acid (SSA) as ligands: 1, Phen; 2, 1:1 VO-Phen; 3, 1:1 VO-SSA; 4, 1:1:1 VO-Phen-SSA; 5, SSA. A, composite curve of 1 & 3; B, composite curve of 2 & 5. All solutions are 2.5×10^{-3}M in ligand at the start of titration; m = moles of KOH added per mole of the metal ion. Arrows indicate appearance of a solid phase.

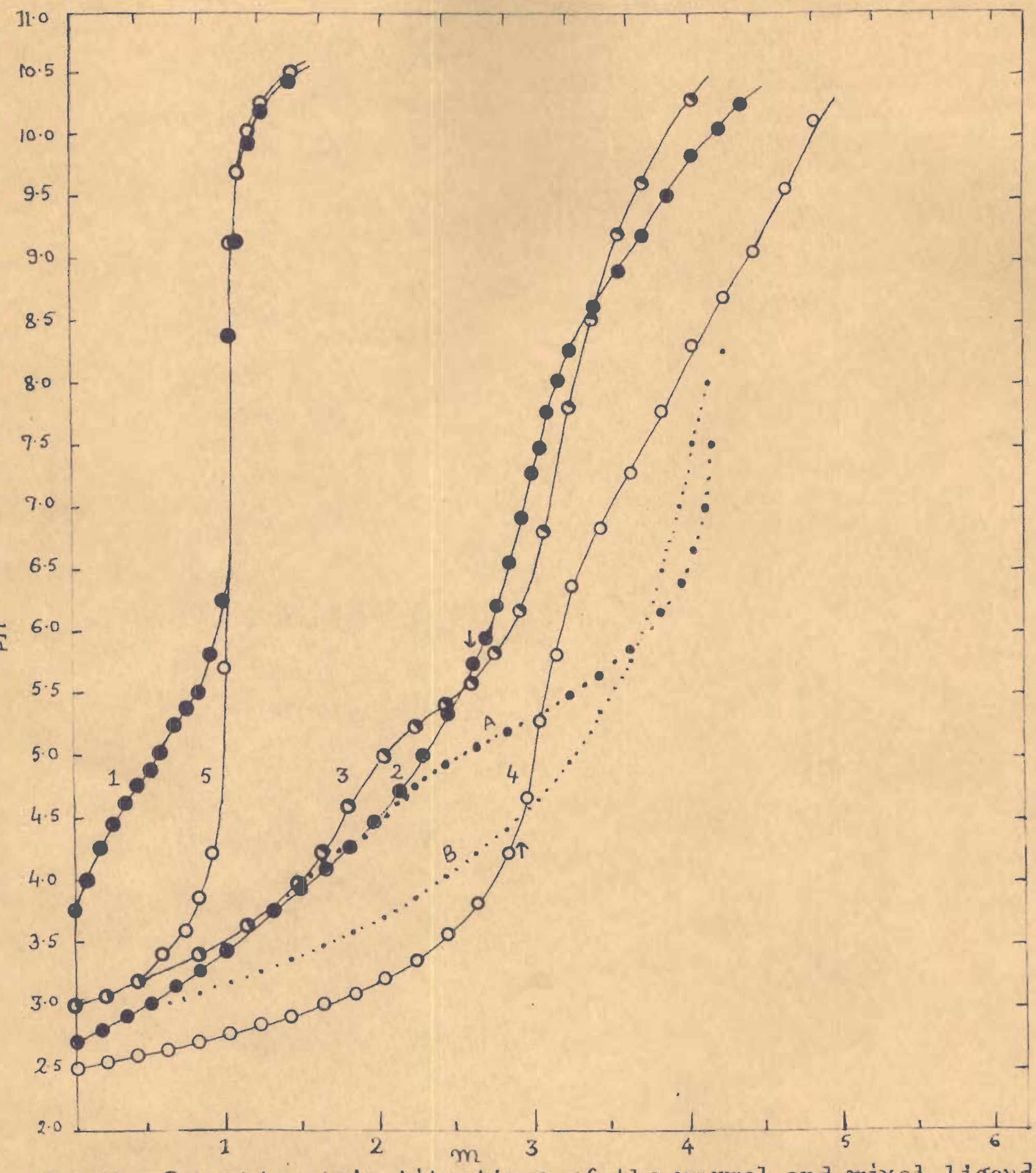


Fig.19. Potentiometric titrations of the normal and mixed ligand chelate systems of oxovanadium(IV) having o-phenanthroline hydrochloride(Phen.) and salicylic acid(SA) as ligands: 1, Phen.; 2, 1:1 VO-Phen; 3, 1:1 VO-SA; 4, 1:1:1 VO-Phen-SA; 5, SA. A, composite curve of 1 & 3; B, composite curve of 2 & 5. All solutions are 2.5×10^{-3}M in ligand at the start of titration; m = moles of KOH added per mole of the metal ion. Arrows indicate appearance of a solid phase.

ligands, gives weakest complexes. The anion of tiron being of intermediate basicity forms chelates which are stronger than those of catechol and weaker than the corresponding complexes of chromotropic acid. It is interesting to note an unexpectedly higher stability of the above mixed-ligand derivatives as compared to that of the corresponding simple 1:1 chelates.

MIXED-LIGAND CHELATES OF OXOVANADIUM(IV) WITH o-PHENTHROLINE AND ORGANIC CARBOXYLIC ACIDS.

Like VO-phen-dihydric phenol systems, here also, the potentiometric data of the lower buffer region of the titration curves were treated in accordance with the three different postulates described on page 91.

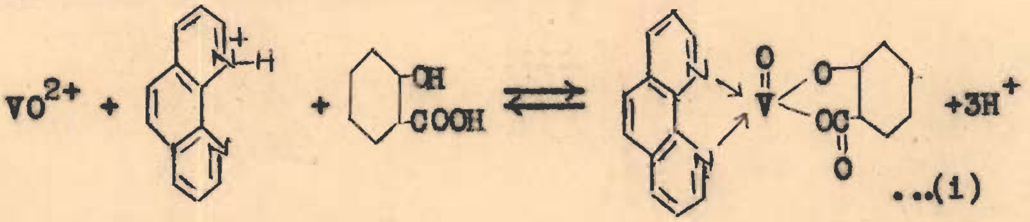
In all these cases, since the curve for the titration of mixed-ligand system, (Figs. 19-24, curve 4) is throughout lower than curves 2 and 3, for the titrations of 1:1 chelate systems of the primary and secondary ligands, possibility of the formation of a mixture of two simple chelates of the two ligands (postulate I) may, therefore, be easily ruled out.

In order to test the postulate II and to characterize the reactions occurring in the mixed-ligand systems, two calculated curves, shown by the dotted lines in the figures, were obtained. Curve A was obtained by the addition of the abscissas of curves 1 and 3 (Figs. 19-24) for the potentiometric titrations of o-phenanthroline hydrochloride and the 1:1 VO-secd. ligand chelate system respectively with KOH. In a similar manner horizontal addition of curves 2 and 5 for the titration of 1:1 VO-phen chelate and free secondary ligand respectively yielded the curve B. These composite curves were compared with the experimental curve 4 (Figs. 19-24) for the titration of mixed ligand system.

VO-phen-SA: VO-phen-SSA: VO-phen-LA: VO-phen-MA Systems.

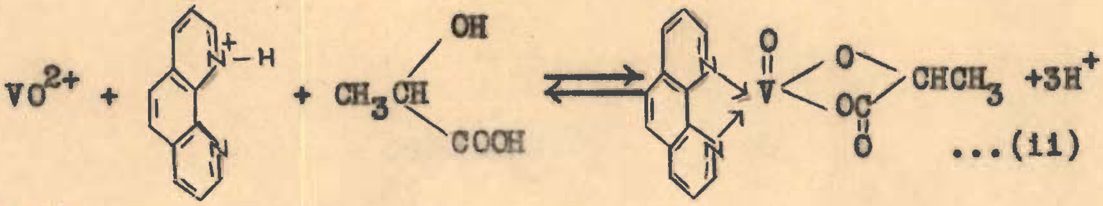
Potentiometric titrations of the mixed ligand systems involving salicylic (SA), 5-sulpho-salicylic (SSA), lactic (LA) and mandelic (AA) acids as secondary ligands (Figs. 19-22, curve 4) yielded analogous curves indicating reactions of a similar nature. Comparison of the calculated curves A and B with the experimental curve 4 shows that the latter curve neither resembles in nature with curve A nor with the curve B. Curve A (Figs.19, 21 and 22) shows inflexion points at 'm' values of about 2 and 4. Curve B approaches an inflexion between m = 3.5 and 4.0. The experimental curve, on the other hand, exhibits a sharp inflexion at m = 3. Formation of a simple 1:1 metal chelate of either of the two ligands present in the system (postulate II) may, therefore, be ruled out.

An inflexion point at m = 3 exhibited by curve 4 (Fig. 19) is in accord with the reaction



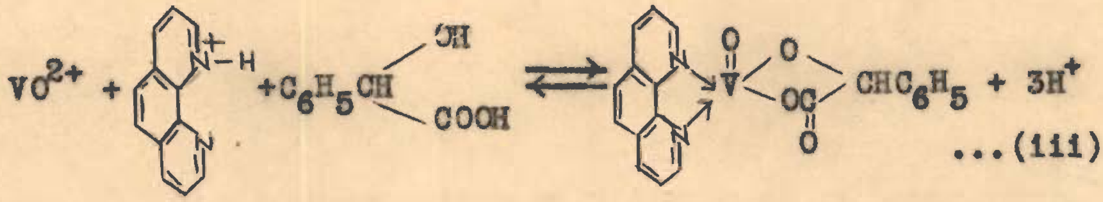
...(i)

In the 1:1:1 VO-phen-LA (Fig.21) and VO-phen-MA(Fig.22) systems, the reactions may be represented as



...(ii)

and



...(iii)

An inflexion point at m = 4 shown by the titration curve for the 1:1:1 VO-phen-SSA system (Fig.20) may be interpreted on the basis of the liberation of three protons in accordance with a reaction of the type (i), and consumption of one mole of alkali per mole of the ligand by the strongly acidic sulphonic acid group present in 5-sulphosalicylic acid.

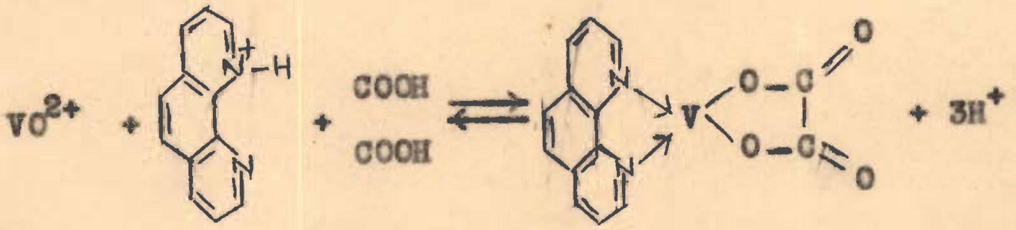
The appearance of a solid phase at relatively low pH in the above mixed-ligand systems offers a direct evidence for the formation of mixed-ligand chelates.

As indicated before (see page 93) in these systems also by an analysis of the potentiometric data, it was found that in the beginning of the above titrations, concentration of the simple 1:1 VO-phen chelate was much higher than that of the mixed-ligand complexes. This fact and a single inflexion point exhibited by the curves showed that the formation of a VOLA type of chelate takes place through the formation of a 1:1 VO-phen chelate i.e. mixed ligand chelate is formed in accordance with the model III B.

VO-phen-Oxalic acid; VO-phen-Phthalic acid.

As shown in the mixed ligand systems involving α-hydroxy carboxylic acids* as secondary ligands, in these cases also the experimental curve 4 (Figs. 23,24) showed a different nature than would be expected on the basis of the formation of a simple 1:1 chelate of either of the two ligands present in the solution. In fig.23, for example, curve A, obtained by the addition of abscissae of curves 1 and 3, shows a start of inflexion at about m = 2. Curve B, a composite of curves 2 and 5, exhibits an inflexion point at about m = 5. The experimental curve, on the other hand, showed a sharp inflexion at about m = 3. This, therefore, rules out the postulate II.

As indicated in the VO-phen-SA system, one would expect an inflexion point at m = 3 in curve 4 (Fig.23) on the basis of the formation of a chelate of the type VO-phen-oxalate. The overall reaction may thus be represented as



... (*)

This conclusion obtains support from the work of Selbin and Holmes[55] who have isolated a compound $VO(C_{12}H_8N_2)C_2O_4$.

Titration curve for the 1:1:1 VO-phen-phthalic acid system showed a poorly defined sloping inflexion. A slight lowering of the lower buffer region observed in the curve as compared with the composite curve B is probably indicative of the formation of a weak mixed-ligand chelate. The complex appears to be hydrolyze almqst immediately as pH of the system is raised to a value of about 5.5.

Stability Constants

In the mixed ligand systems involving α-hydroxy carboxylic acid as a second ligand, from the material balance, we obtain

$$T_M = [VO^{2+}] + [VOL^{2+}] + [VOLA] \qquad \ldots (121)$$

$$T_L = [HL^+] + [L] + [VOL^{2+}] + [VOLA] \qquad \ldots (122)$$

$$T_A = [H_2A] + [HA^-] + [VOLA] \qquad \ldots (123)$$

and

$$T_{OH} + [H^+] = [VOL^{2+}] + [HA^-] + [L] + 3[VOLA] \qquad \ldots (124)$$

In solutions of pH up to about 3, concentrations of $VO(OH)L^+$, VOA and A^{2-} were negligible as compared to those of other species present. Combination of equations 121-124 and the expression for the acid dissociation constants of the ligands yields

$$K_{ML}(2Y-1)[VO^{2+}]^2+(3XY-X-Y)[VO^{2+}]-(3T_M - T_{OH} - [H^+])XY = 0 \qquad \ldots (125)$$

where

$$X = 1 + \frac{[H^+]}{K_a} \text{ and } Y = 1 + \frac{[H^+]}{K_{a_1}}$$

(K_{a_1} represents dissociation constant of carboxylic proton of α-hydroxy carboxylic acid)

Concentration of free vanadyl ions in the system may, therefore, be determined by solving the above quadratic equation.

After computation of $[VO^{2+}]$, concentration of other species present in the system, may be easily evaluated. Values of the formation constants obtained for the mixed ligand chelates having salicylic, 5-sulphosalicylic acids as secondary ligands are presented in tables XXXV, and XXXVI respectively.

Table XXXV

Curve 4(Fig.19), $T_A = T_M = T_L = 2.5 \times 10^{-3} M$

$pK_a = 5.00$, $pK_{a_1} = 2.88$, $pK_{a_2} = 13.40^{\overset{\text{ref.}}{(56)}}$

m	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
pH	2.57	2.62	2.67	2.73	2.79	2.85	2.92	3.01
$\log K_{MLA}$	13.31	13.33	13.36	13.34	13.35	13.37	13.37	13.32
$\log K'_{MLA}$	19.19	19.21	19.24	19.22	19.23	19.25	19.25	19.20

Average value of $\log K_{MLA} = 13.34 \pm 0.03$ and

$\log K'_{MLA} = 19.22 \pm 0.03$

Table XXXVI

Curve 4 (Fig.20), $T_A = T_M = T_L = 2.5\times10^{-3}M$

$pK_a = 5.00$, $pK_{a_2} = 2.50$, $pK_{a_3} = 11.59^{(ref.56)}$

m	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6
pH	2.48	2.52	2.57	2.62	2.67	2.72	2.79	2.86
$\log K_{MLA}$	11.73	11.76	11.73	11.73	11.74	11.78	11.75	11.75
$\log K'_{MLA}$	17.61	17.64	17.61	17.61	17.62	17.66	11.63	17.63

Average value of $\log K_{MLA} = 11.75 \pm 0.03$ and $\log K'_{MLA} = 17.63 \pm 0.03$

In the mixed ligand system involving 5-sulphosalicylic acid (H_3A) as a secondary ligand, H_2A^- was considered to be the chelating agent in the mathematical treatment given above, since the proton of the sulphonic acid group was completely dissociated under the experimental conditions.

Values of the equilibrium constant for reaction (iii), calculated from the potentiometric data of curve 4 (Fig.21) are given in table XXXVII.

Table XXXVII

Curve 4, (Fig.21), $T_A = T_M = T_L = 2.5\times10^{-3}M$

$pK_a = 5.00$, $pK_{a_1} = 3.64$

m	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
pH	2.83	2.91	2.99	3.08	3.16	3.27	3.34	3.48
$-\log K$	4.03	3.98	3.94	3.94	3.93	4.00	4.04	4.04
$-\log K'$	3.15	3.10	3.06	3.06	3.04	3.12	3.16	3.16

Average value of $-\log K = 3.99 \pm 0.05$,
$-\log K' = 3.11 \pm 0.05$

In the mixed-ligand system involving mandelic acid as a secondary ligand, it was not possible to determine the reaction constants, since a precipitate was formed almost in the beginning of the titration.

In the 1:1:1 VO-phen-oxalic acid system dissociation of both the protons of oxalic acid has to be taken into consideration. Equations 123 and 124 then become

$$T_A = [H_2A] + [HA^-] + [A^{2-}] + [VOLA] \qquad \ldots (126)$$

and

$$T_{OH} + [H^+] = [VOL^{2+}] + [L] + [HA^-] + 2[A^{2-}] + 3[VOLA] \qquad ..(127)$$

With the help of the above equations and the expression for the formation constant K_{ML} and acid dissociation constants of the ligands, it may be shown that

$$K_{ML}\,(2Y-Z)[VO^{2+}]^2 + \left\{X(3Y-Z)-Y\right\}[VO^{2+}] - \left\{3T_M - T_{OH} - [H^+]\right\} \times XY = 0$$

where

$$X = 1 + \frac{[H^+]}{K_a}, \quad Y = 1 + \frac{[H^+]}{K_{a_1}} + \frac{[H^+]^2}{K_{a_1}K_{a_2}} \quad \text{and}$$

$$Z = 2 + \frac{[H^+]}{K_{a_2}}$$

Concentration of uncomplexed vanadyl ion may, therefore, be determined by solving the above quadratic equation. Other species may then be evaluated easily. Values of formation constant of the 1:1:1 VO-phen-oxalic acid chelate obtained from the data of curve 4(Fig.23) are listed in table XXXVIII.

Table XXXVIII

$pK_a = 5.00$, $pK_{a_1} = 1.91$, $pK_{a_2} = 3.89$

m	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
pH	2.29	2.33	2.37	2.41	2.46	2.51	2.57	2.63
$\log K_{MLA}$	5.38	5.34	5.33	5.36	5.32	5.33	5.31	5.35
$\log K'_{MLA}$	11.26	11.22	11.21	11.24	11.20	11.21	11.19	11.23

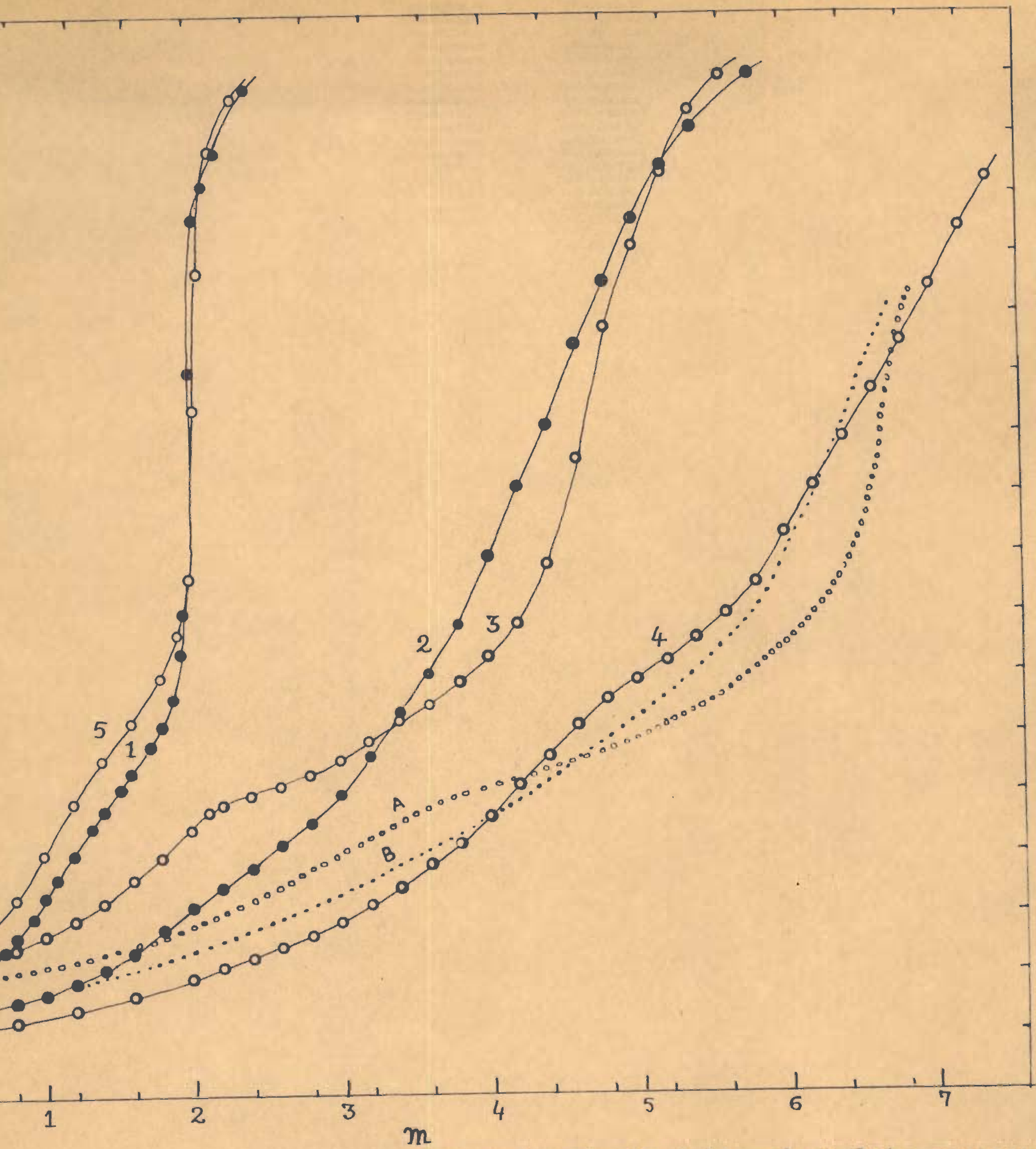
Average value of $\log K_{MLA} = 5.34 \pm 0.03$,

$\log K'_{MLA} = 11.22 \pm 0.03$.

From tables XXXV, XXXVI and XXXVIII, it is evident that the stabilities of the mixed-ligand chelates of VO-phen with salicylic, 5-sulphosalicylic and oxalic acids as secondary ligands, are in the following order

SA > SSA > Ox. acid

The anion of salicylic and 5-sulphosalicylic acids being strongly basic, form complexes of high stability. Oxalic acid, although gives a five membered ring on chelation, forms a mixed-ligand chelate of low stability on account of a lower basicity of the oxalate ion.



Potentiometric titrations of normal and mixed ligand chelate systems
vandium(IV) having 2, 2'-dipyridyl hydrochloride(dipy) and phthalic
Ph.A) as ligands: curve 1, dipy; 2, 1:1 VO-dipy; 3, 1:1 VO-Ph.A;
:1 VO-dipy-Ph.A; 5, Ph.A; A, composite curve of 1 and 3; B, composite
of 2 and 5. All solutions are 2.5×10^{-3}M in ligand at the start of the
ion; m=moles of KOH added per mole of the metal ion.

.32. Potentiometric titrations of the normal and mixed ligand chelates oxovanadium(IV) having 2, 2'-dipyridyl hydrochloride(dipy) and oxalic id (Ox.A) as ligands: Curve 1, dipy; 2, 1:1 VO-dipy; 3, 1:1 VO-Ox.A; 1:1:1 VO-dipy-Ox.A; 5, Ox.A; A, composite curve of 1 and 3; B, composite rve of 2 and 5, All solutions are 2.5×10^{-3}M in ligand at the start of the trations: m=moles of KOH added per mole of the metal ion. Arrows indicate pearance of a solid phase.

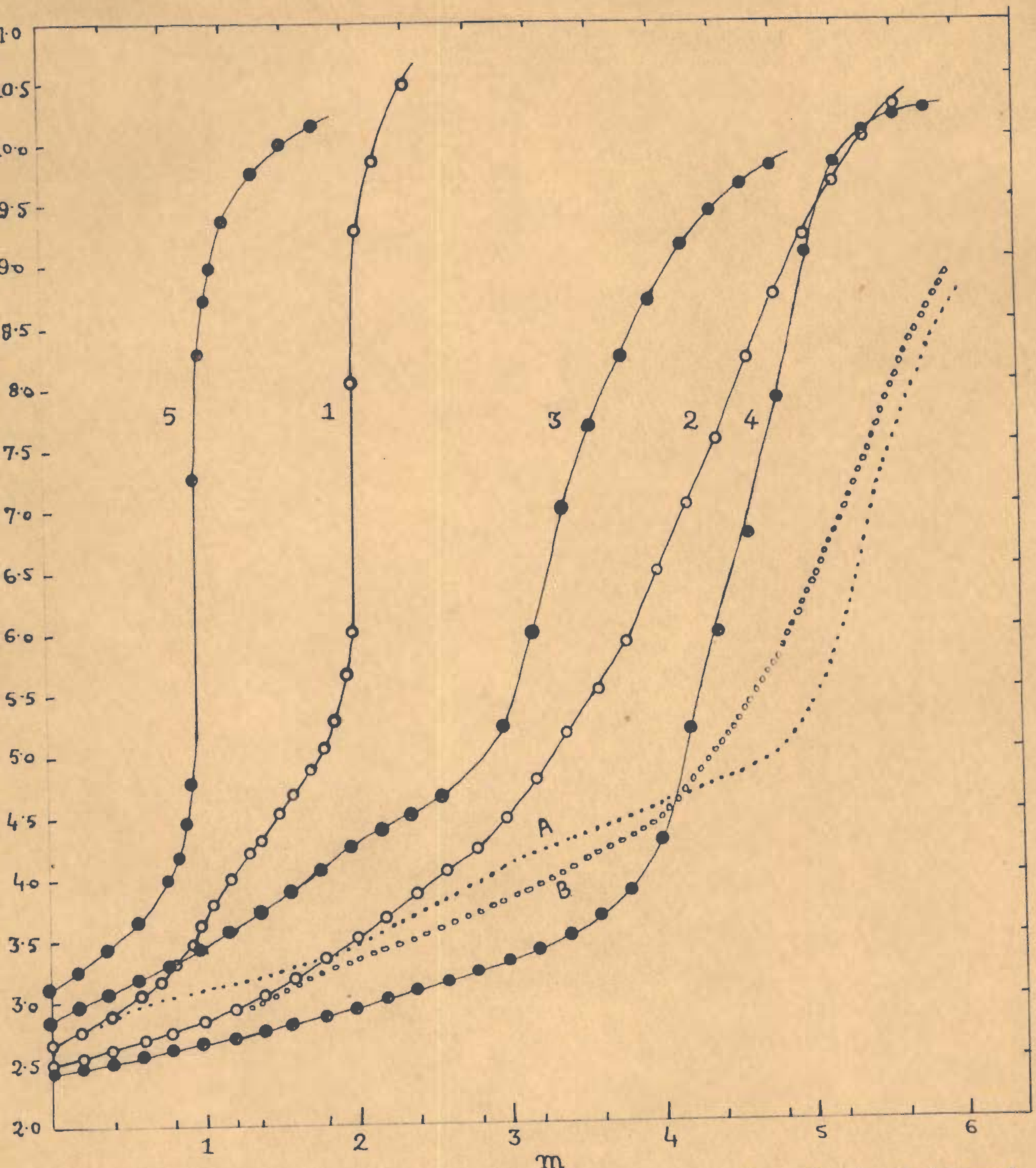


Fig.31. Potentiometric titrations of the normal and mixed ligand chelates of oxovanadium(IV) having 2,2'-dipyridyl hydrochloride (dipy) and mandelic acid(MA) as ligands: Curve 1, dipy; 2,1:1 VO-dipy; 3, 1:1 VO-MA; 4, 1:1:1 VO-dipy-MA;5,MA; A, composite curve of 1 and 3; B, composite curve of 2 and 5. All solutions are 2.5x10^{-3}M in ligand at the start of the titration; m=moles of KOH added per mole of the metal ion.Arrows indicate appearance of a solid phase.

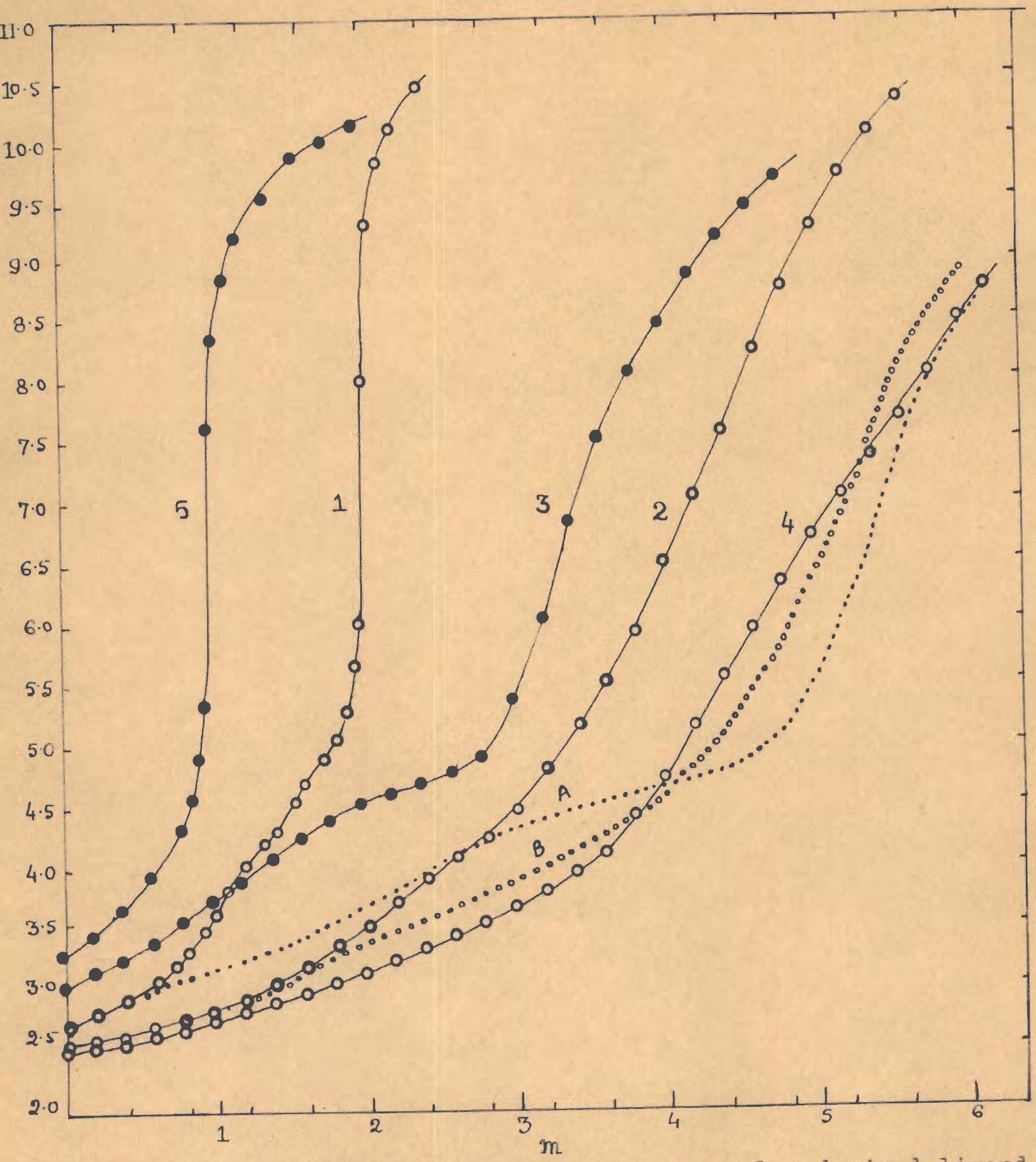
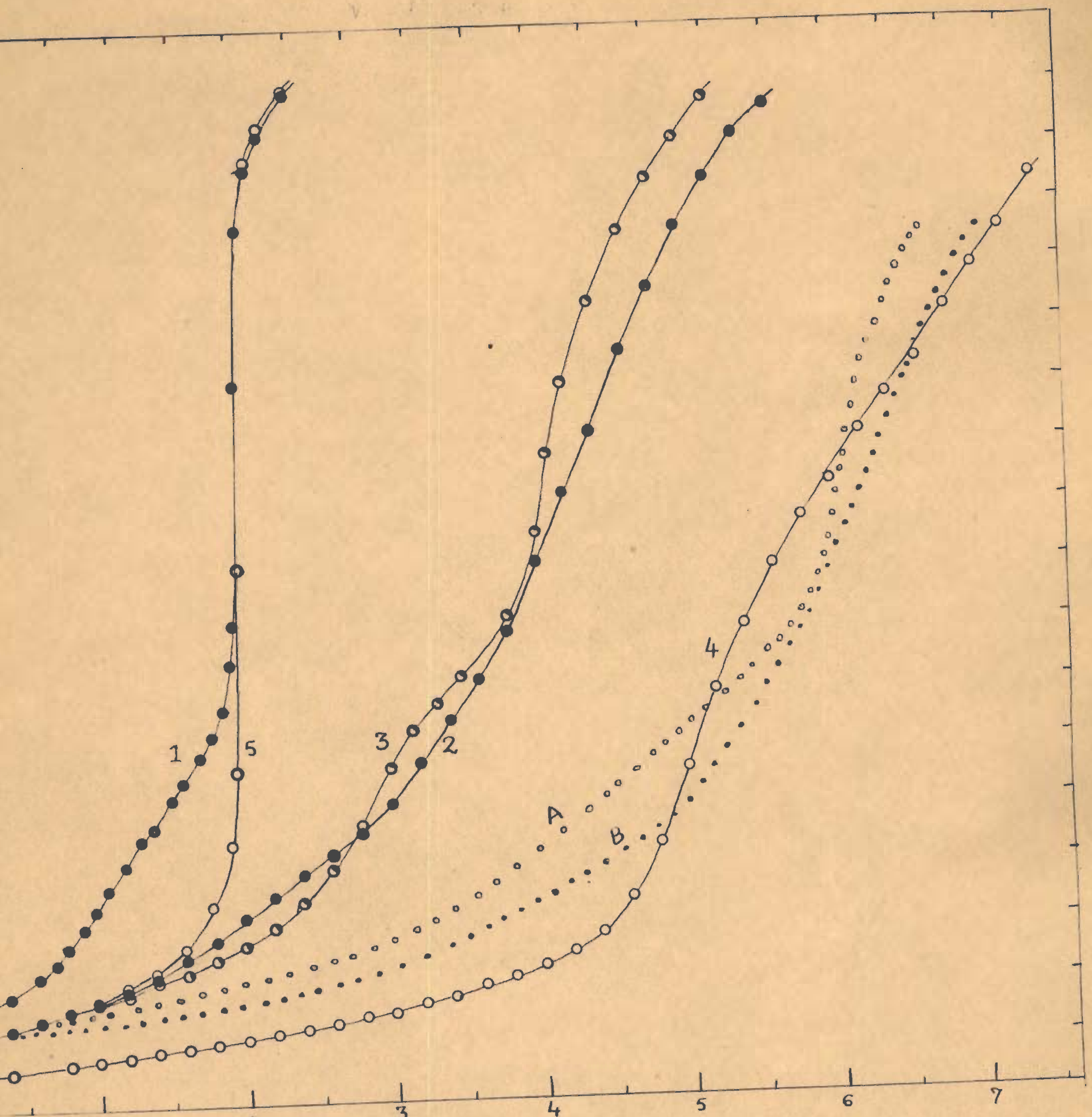


Fig.30. Potentiometric-titrations of the normal and mixed ligand chelates of oxovanadium(IV) having 2,2'-dipyridyl hydrochloride (dipy) and lactic acid (LA) as ligands: Curve 1, dipy; 2, 1:1 VO-dipy; 3, 1:1 VO-LA; 4, 1:1:1 VO-dipy-LA; 5, LA; A, composite curve of 1 and 3; B, composite curve of 2 and 5. All solutions are 2.5x10^{-3}M in ligand at the start of the titration; m=moles of KOH added per mole of the metal ion.



29. Potentiometric-titrations of the normal and mixed ligand chelates
oxovanadium(IV) having 2,2'-dipyridyl hydrochloride(dipy) and sulpho-
icylic acid (SSA) as ligands: curve 1, dipy; 2, 1:1 VO-dipy; 3,1:1 VO-
; 4, 1:1:1 VO-dipy-SSA; 5, SSA; A, composite curve of 1 and 3; B,comp-
te curve of 2 and 5. All solutions are 2.5x10^{-3}M in ligand at the start
the titration; m=moles of KOH added per mole of the metal ion.

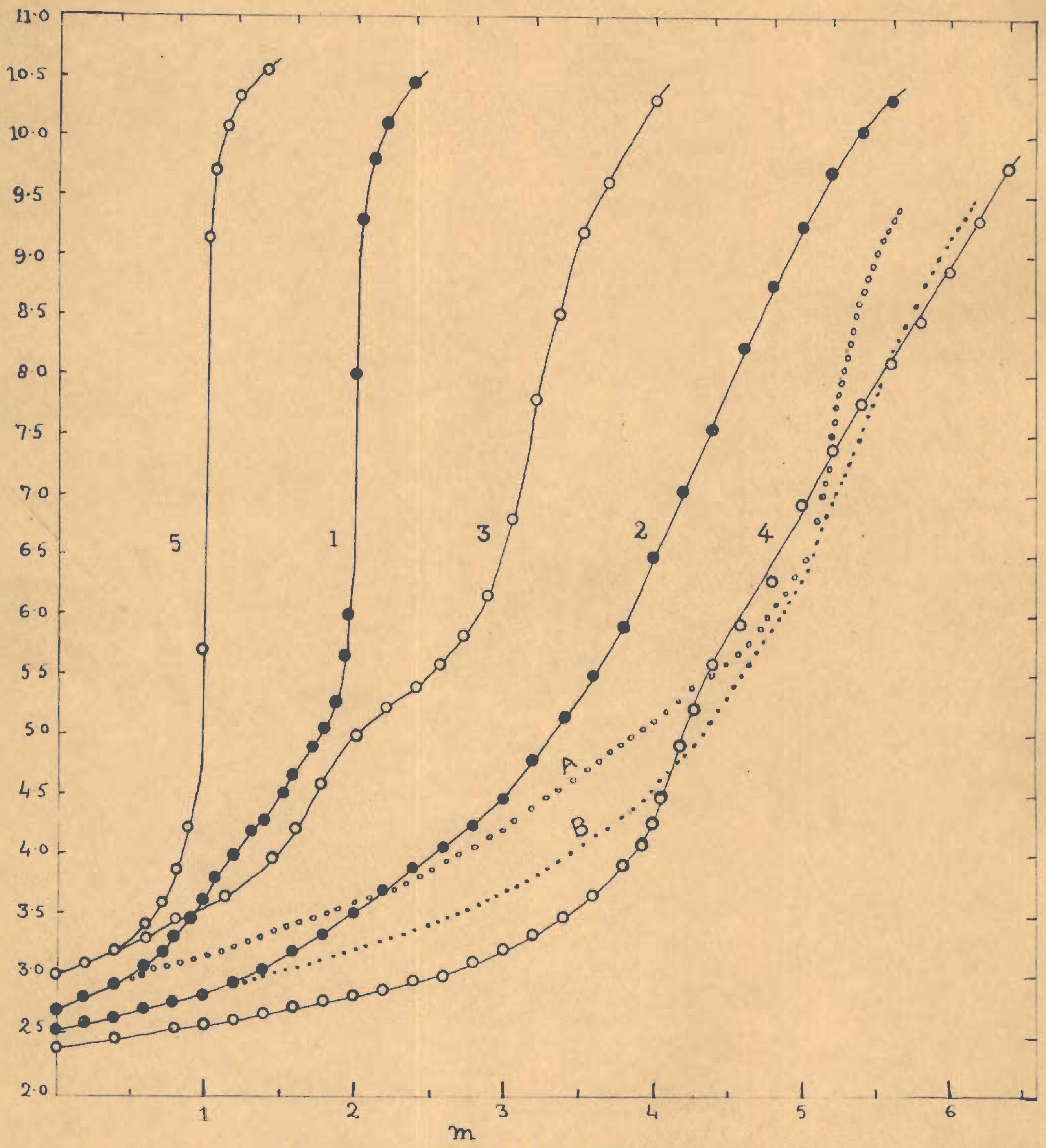


Fig.28. Potentiometric titrations of normal and mixed ligand chelate systems of oxovanadium(IV) having 2,2'-dipyridyl hydrochloride(dipy) and salicylic acid(SA) as ligands: Curve 1,dipy;2,1:1 VO-dipy; 3, 1:1 VO-SA;4, 1:1:1 VO-dipy-SA; 5, SA: A, composite curve of 1 and 3; B, composite curve of 2 and 5. All solutions are $2.5x10^{-3}$M in ligand at the start of the titration; m=moles of KOH added per mole of the metal ion.

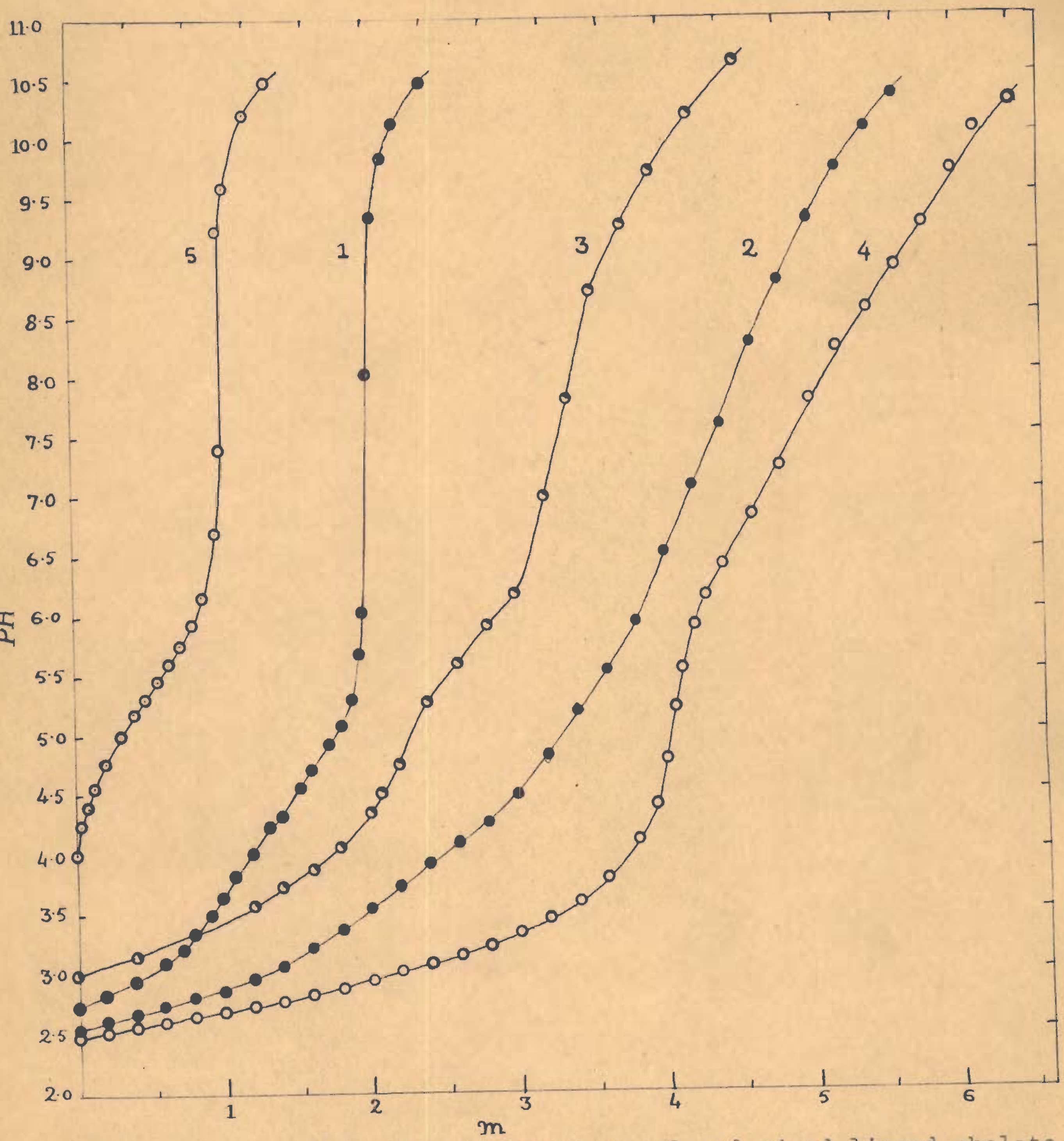


Fig.27. Potentiometric titrations of normal and mixed ligand chelate systems of oxovanadium(IV) having 2,2'-dipyridyl hydrochloride(dipy) and chromotropic acid(DNS) as ligands: Curve 1, dipy; 2,1:1 VO-dipy; 3,1:1 VO-DNS; 4,1:1:1 VO-dipy-DNS; 5,DNS. All solutions are 2.5x10^{-3}M in ligand at the start of titration; m=moles of KOH added per mole of the metal ion.

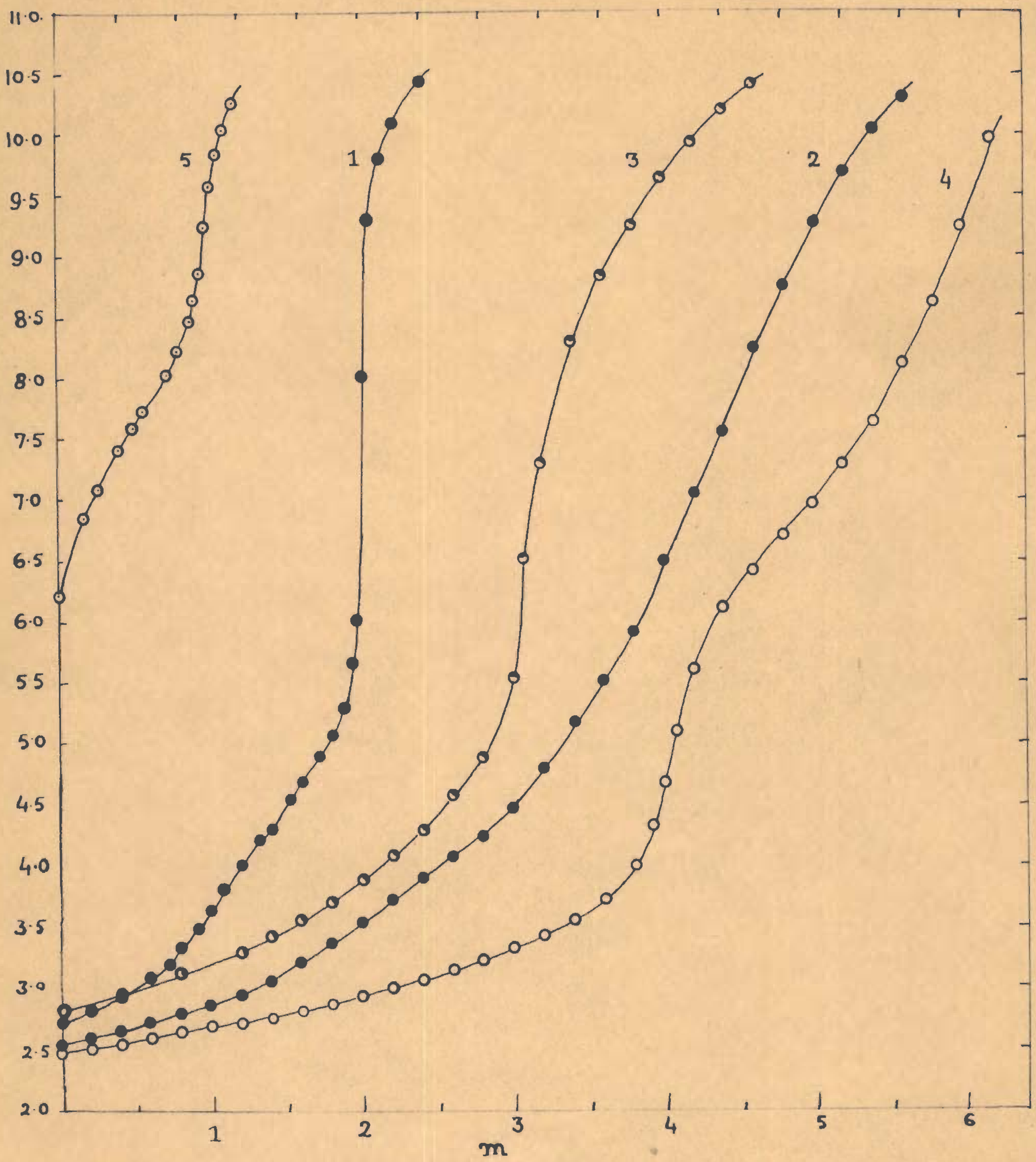


Fig.26. Potentiometric titration of normal and mixed ligand chelate systems of oxovanadium(IV) having 2,2'-dipyridyl hydrochloride (dipy) and tiron as ligands: curve 1, dipy; 2, 1:1 VO-dipy; 3, 1:1 VO-tiron; 4, 1:1 VO-dipy-tiron; 5, tiron. All solutions are 2.5×10^{-3}M in ligand at the start of titration; m=moles of KOH added per mole of the metal ion.

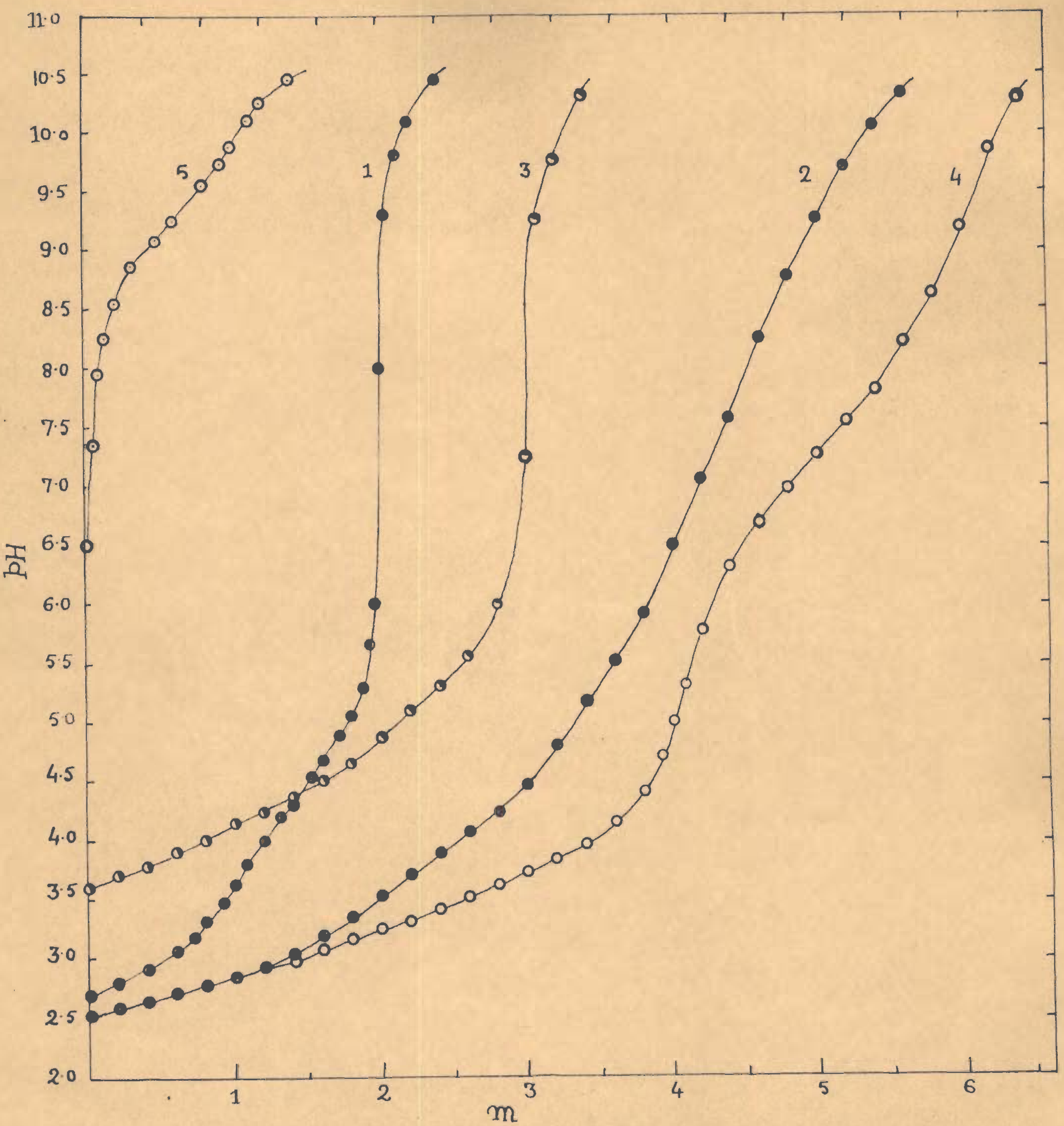


Fig.25. Potentiometric titrations of the normal and mixed ligand chelate systems of oxovanadium(IV) having 2,2'-dipyridyl hydrochloride(dipy) and catechol as ligands: curve 1, dipy; 2, 1:1 VO-dipy; 3, 1:1 VO-catechol; 4, 1:1:1 VO-dipy-catechol; 5, catechol. All solutions are 2.5x10^{-3}M in ligand at the start of titration; m=moles of KOH added per mole of the metal ion.

SECTION II

MIXED LIGAND CHELATES OF OXOVANADIUM (IV) WITH 2,2'-DIPYRIDYL AND OXYGENDONOR BIDENTATE LIGANDS

Potentiometric titrations of mixed ligand systems involving 2,2'-dipyridyl as a primary ligand corresponded to the curves (Curve 4, Figs. 25-33) essentially similar to those obtained for the corresponding 1:1:1 VO-Phen-Secd. ligand systems. As indicated in the 1:1 VO-dipy system (See page 87), here also, HL^+ was considered to be the ligand, since one proton of dipyridyl dihydrochloride is strongly acidic and is completed ionized under the experimental conditions.

Formation constants of the mixed ligand chelates were determined with the help of the mathematical treatment presented in the analogous VO-Phen-Secd. ligand systems. The results of these calculations are tabulated below:

Table -XXXIX

System: VO-Dipy-Catechol.

Curve 4 (Fig.25), $T_A=T_M=T_L = 2.5x10^{-3}M$

m	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2
pH	3.14	3.23	3.32	3.42	3.51	3.61	3.72	3.84
log K_{MLA}	16.89	16.88	16.90	16.93	16.90	16.91	16.91	16.93

Average value of log K_{MLA} = 16.91 ± 0.02

System: VO-Dipy-Tiron

Curve 4 (Fig.26), $T_A=T_M=T_L = 2.5x10^{-3}M$

m	1.0	1.4	1.8	2.2	2.6	3.0	3.4
pH	2.64	2.74	2.86	2.98	3.12	3.30	3.54
logK_{MLA}	17.20	17.17	17.19	17.18	17.18	17.17	17.17

Average value of log K_{MLA} = 17.18 ± 0.02

System: VO-Dipy-DNS

Curve 4 (Fig.27), $T_A = T_M = T_L = 2.5\times10^{-3}M$

m	1.0	1.4	1.8	2.2	2.6	3.0	3.4
pH	2.66	2.77	2.88	3.01	3.15	3.33	3.59
$\log K_{MLA}$	17.98	17.97	18.01	17.97	17.98	17.96	17.94

Average value of $\log K_{MLA} = 17.97 \pm 0.04$

System: VO-Dipy-SA

Curve 4 (Fig.28), $T_A = T_M = T_L = 2.5\times10^{-3}M$

m	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6
pH	2.62	2.68	2.74	2.79	2.86	2.92	2.99	3.07
$\log K_{MLA}$	13.18	13.13	13.12	13.19	13.15	13.19	13.20	13.19

Average value of $\log K_{MLA} = 13.17 \pm 0.03$

System : VO-Dipy-SSA

Curve 4 (Fig.29), $T_A = T_M = T_L = 2.5\times10^{-3}M$

m	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6
pH	2.56	2.61	2.66	2.72	2.78	2.83	2.90	2.97
$\log K_{MLA}$	11.37	11.35	11.36	11.32	11.31	11.39	11.38	11.39

Average value of $\log K_{MLA} = 11.36 \pm 0.03$

PART IV

EXPERIMENTAL

EXPERIMENTAL

GENERAL DESCRIPTION

A stock solution of vanadyl sulphate ($VOSO_4.4H_2O$) was standardized by titrating with a standard solution of potassium permanganate using phosphoric acid as a catalyst[57] and ferroin as an indicator. In order to prevent oxidation[58-65] of vanadyl ions, known volume of a standard solution of hydrochloric acid (one mole) was added to the vanadyl sulphate solution.

Catechol, tiron (disodium catechol-3,5-disulphonate) and chromotropic acid (1,8-dihydroxy-naphthalene-3,6-disulphonate) were of Merk (G.R.) quality. Lactic, tartaric, malic, salicylic, 5-sulphosalicylic, oxalic, phthalic and iminodiacetic acids were of B.D.H. reagent grade quality. Mandelic acid (B.D.H.) was purified by recrystallisation. o-Phenanthroline hydrochloride and 2,2'-dipyridyl were of Merk (G.R.) products. Potassium chloride was of B.D.H., Analar quality.

Aqueous solutions of the ligands were prepared by direct weighing and their strengths were checked by potentiometric titrations with a standard KOH solution. To the 2,2'-dipyridyl solution two moles of hydrochloric acid were added in order to start the titrations with the amine dihydrochloride. The solution of KOH was standardized against potassium hydrogen phthalate.

pH measurements were carried out, using a Cambridge pH-meter (NO 317044) equipped with calomel and glass electrodes, standardized against standard buffer solutions.

Known volumes of vanadyl sulphate, potassium chloride and the ligand solutions were pipetted into a titration cell. Conductivity water was added to provide the desired volume and ionic strength (0.1M). The reaction mixture was then titrated with standard KOH solution (0.1N). The pH of the solutions were read after each addition of small increments of KOH solution and lapse of sufficient time for the attainment of equilibrium. All titrations were repeated at least two times and agreement between the pH-readings of the different titrations was usually within ± 0.02 units. The solutions were stirred continuously by bubbling nitrogen through them. Before and after each titration the pH-meter was checked against buffer solutions of known pH.

TABLE -1

TEMPERATURE = 30±1°C

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

(Curve O, Figure 1)

Ml. of 0.1M KOH	pH	Ml. of 0.1M KOH	pH
0.0	6.50	1.5	9.25
0.1	7.34	2.0	9.56
0.2	7.94	2.3	9.76
0.3	8.26	2.5	9.92
0.4	8.40	2.8	10.13
0.5	8.54	3.0	10.26
0.8	8.80	3.3	10.38
1.2	9.06	3.5	10.47

TABLE - 2

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5x10^{-3}M IN VANADYL SULPHATE, 5x10^{-3}M IN HCl AND 5x10^{-3}M IN CATECHOL WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 1, Figure 1)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.65	6.0	4.41
0.4	2.79	6.4	4.50
0.8	2.91	6.8	4.62
1.2	3.06	7.2	4.73
1.6	3.22	7.6	4.86
2.0	3.43	8.0	5.05
2.4	3.56	8.4	5.25
2.8	3.66	8.8	5.44
3.2	3.75	9.2	5.75
3.6	3.87	9.6	6.10
4.0	3.98	9.8	6.40
4.4	4.06	10.0	7.20
4.8	4.10	10.2	9.25
5.2	4.18	10.4	9.70
5.6	4.31	11.0	10.30

TABLE -3

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl AND 2.5×10^{-3}M IN CATECHOL WITH 0.1M POTASSIUM HYDROXIDE SOLUTION, IONIC STRENGTH=0.1(KCl)

(Curve 2, Figure 1)

ML. of 0.1M KOH	pH	ML. of 0.1M KOH	pH
0.0	2.92	4.8	6.30
0.4	3.18	4.9	6.42
0.8	3.45	5.0	7.25
1.2	3.71	5.1	8.26
1.6	3.91	5.2	9.10
2.0	4.07	5.3	9.45
2.4	4.25	5.4	9.70
2.8	4.45	5.5	9.92
3.2	4.63	5.6	10.10
3.6	4.85	5.8	10.45
4.0	5.14	6.0	10.70
4.4	5.55	7.0	11.00

TABLE -4

TEMPERATURE =30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 1.25×10^{-3}M IN VANADYL SULPHATE, 1.25×10^{-3}M IN HCl AND 1.25×10^{-3}M IN CATECHOL WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M(KCl)

(Curve 3, Figure 1)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	3.20	4.4	5.67
0.4	3.41	4.8	6.30
0.8	3.63	5.0	7.35
1.2	3.82	5.1	8.25
1.6	4.02	5.2	8.65
2.0	4.15	5.3	9.00
2.4	4.31	5.4	9.25
2.8	4.52	5.5	9.50
3.2	4.74	5.6	9.70
3.6	4.95	5.8	10.10
4.0	5.30	6.0	10.40

TABLE -5

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}$M IN VANADYL SULPHATE, $5x10^{-3}$M IN HCl AND $1x10^{-2}$M IN CATECHOL WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 4, Figure 1)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.65	7.6	4.53
0.4	2.78	8.0	4.66
0.8	2.92	8.4	4.79
1.2	3.04	8.8	4.89
1.6	3.18	9.2	5.05
2.0	3.33	9.6	5.20
2.4	3.43	10.0	5.37
2.8	3.52	10.4	5.50
3.2	3.60	10.8	5.71
3.6	3.70	11.2	5.90
4.0	3.78	11.6	6.18
4.4	3.86	12.0	6.50
4.8	3.91	12.4	7.00
5.2	3.97	12.6	7.82
5.6	4.08	13.0	9.15
6.0	4.17	13.4	9.85
6.4	4.25	13.8	10.25
6.8	4.34	14.2	10.55
7.2	4.43	15.0	10.95

TABLE -6

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF $2.5x10^{-3}$M CHROMOTROPIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M(KCl)

(Curve O, Figure 5)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	4.02	2.0	5.93
0.1	4.25	2.2	6.18
0.2	4.42	2.3	6.38
0.3	4.55	2.4	6.70
0.5	4.78	2.5	7.34
0.8	5.02	2.6	9.24
1.0	5.18	2.7	9.60
1.2	5.30	2.8	9.72
1.4	5.46	3.0	10.20
1.6	5.59	3.2	10.36
1.8	5.75	3.4	10.48

TABLE -7

TEMPERATURE=30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}$M IN VANADYL SULPHATE, $5x10^{-3}$M IN HCl AND $5x10^{-3}$M IN CHROMOTROPIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH =0.1M(KCl)

(Curve 1, Figure 5)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.37	6.5	3.97
0.5	2.46	7.0	4.29
1.0	2.54	7.5	4.86
1.5	2.64	8.0	5.17
2.0	2.75	8.5	5.50
2.5	2.85	9.0	5.82
3.0	2.97	9.5	6.11
3.5	3.08	10.0	6.55
4.0	3.19	10.5	7.49
4.5	3.30	11.0	8.29
5.0	3.43	11.5	9.15
5.5	3.56	12.0	9.79
6.0	3.71	13.0	10.30

TABLE = 8

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl AND 2.5×10^{-3}M IN CHROMOTROPIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M (KCl)

(Curve 2, Figure 5)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.66	7.0	4.34
0.5	2.73	7.5	4.83
1.0	2.81	8.0	5.10
1.5	2.89	8.5	5.50
2.0	2.98	9.0	5.80
2.5	3.06	9.5	6.03
3.0	3.15	10.0	6.35
3.5	3.25	10.5	6.92
4.0	3.35	11.0	7.68
4.5	3.46	11.5	8.30
5.0	3.58	12.0	8.90
5.5	3.71	12.5	9.40
6.0	3.86	13.0	9.86
6.5	4.06	14.0	10.24

TABLE -9

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 1.25×10^{-3}M IN VANADYL SULPHATE, 1.25×10^{-3}M IN HCl, AND 1.25×10^{-3}M IN CHROMOTROPIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M (KCl)

(Curve 3, Figure 5)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.94	4.5	5.78
0.5	3.06	5.0	6.24
1.0	3.20	5.5	7.28
1.5	3.34	6.0	8.10
2.0	3.50	6.5	8.85
2.5	3.71	7.0	9.35
3.0	3.97	7.5	9.82
3.5	4.31	8.0	10.10
4.0	5.06	9.0	10.45

TABLE -10

TEMPERATURE =30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl AND 5×10^{-3}M IN CHROMOTROPIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION, IONIC STRENGTH = 0.1M(KCl)

(Curve 4, Figure 5)

ML.OF 0.1M KOH	pH	ML.OF 0.1M KOH	pH
0.0	2.61	8.0	4.60
0.5	2.68	8.5	4.74
1.0	2.75	9.0	4.93
1.5	2.83	9.5	5.08
2.0	2.89	10.0	5.22
2.5	2.96	10.5	5.38
3.0	3.03	11.0	5.57
3.5	3.12	11.5	5.76
4.0	3.18	12.0	6.10
4.5	3.26	12.5	6.64
5.0	3.35	13.0	7.32
5.5	3.45	13.5	7.88
6.0	3.56	14.0	8.48
6.5	3.72	14.5	9.26
7.0	3.96	15.0	9.70
7.5	4.30	16.0	10.22

TABLE -11

TEMPERATURE=30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5x10^{-3}M
IN MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION
IONIC STRENGTH = 0.1M (KCl)
(Curve O, Figure 6)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	3.12	2.6	8.32
0.5	3.27	2.7	8.76
1.0	3.44	2.8	9.00
1.5	3.67	3.0	9.40
2.0	4.02	3.5	9.78
2.2	4.20	4.0	10.02
2.4	4.81	4.5	10.16
2.5	7.28	5.0	10.24

TABLE - 12

TEMPERATURE = 30 ± 1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN VANADYL SULPHATE, 5×10^{-3}M IN HCl AND 5×10^{-3}M IN MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 1, Figure 6)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.30	7.5	4.15
0.5	2.36	8.0	4.28
1.0	2.42	8.5	4.38
1.5	2.48	9.0	4.55
2.0	2.54	9.5	4.69
2.5	2.60	10.0	5.33
3.0	2.71	10.5	6.37
3.5	2.82	11.0	7.49
4.0	2.98	11.5	8.26
4.5	3.15	12.0	9.16
5.0	3.35	12.5	9.54
5.5	3.55	13.0	9.80
6.0	3.67	13.5	9.96
6.5	3.79	14.0	10.10
7.0	3.95	15.0	10.35

TABLE -13

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl AND 2.5×10^{-3}M IN MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M (KCl)

(Curve 2, Figure 6)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.58	8.5	4.51
1.0	2.68	9.0	4.67
2.0	2.79	9.5	4.80
2.5	2.86	10.0	5.30
3.0	2.98	10.5	6.00
3.5	3.04	11.0	7.03
4.0	3.17	11.5	7.70
4.5	3.32	12.0	8.26
5.0	3.50	12.5	8.72
5.5	3.68	13.0	9.18
6.0	3.77	13.5	9.46
6.5	3.93	14.0	9.66
7.0	4.10	14.5	9.82
7.5	4.29	15.0	9.95
8.0	4.40	16.0	10.15

TABLE -14

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 1.25×10^{-3}M
IN VANADYL SULPHATE, 1.25×10^{-3}M IN HCl AND 1.25×10^{-3}M
IN MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE
SOLUTION. IONIC STRENGTH = 0.1M (KCl)
(Curve 3, Figure 6)

ML.OF 0.1M KOH	pH	ML.OF 0.1M KOH	pH
0.0	2.88	4.5	4.82
0.5	2.98	5.0	5.31
1.0	3.09	5.5	6.50
1.5	3.22	6.0	7.80
2.0	3.37	6.5	8.53
2.5	3.66	7.0	9.08
3.0	3.97	7.5	9.50
3.5	4.26	8.0	9.75
4.0	4.55	9.0	9.90

TABLE -15

TEMPERATURE = 30 ± 1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF $2.5x10^{-3}$M IN VANADYL SULPHATE, $2.5x10^{-3}$M IN HCl AND $5x10^{-3}$M IN MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION, IONIC STRENGTH = 0.1M (KCl)

(Curve 4, Figure 6)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.54	9.0	3.89
1.0	2.62	9.5	4.06
2.0	2.72	10.0	4.28
2.5	2.77	10.5	4.50
3.0	2.83	11.0	4.72
3.5	2.89	11.5	4.88
4.0	2.96	12.0	5.04
4.5	3.02	12.5	5.60
5.0	3.10	13.0	6.17
5.5	3.17	13.5	7.00
6.0	3.26	14.0	7.65
6.5	3.34	14.5	8.12
7.0	3.42	15.0	8.55
7.5	3.52	15.5	8.98
8.0	3.63	16.0	9.25
8.5	3.75	17.0	9.50

TABLE -16

TEMPERATURE=30±1°C
POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION
IONIC STRENGTH = 0.1M (KCl)
(Curve 0, Figure 8)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	3.20	2.6	8.34
0.5	3.40	2.8	8.84
1.0	3.63	3.0	9.16
1.5	3.90	3.5	9.50
2.0	4.28	4.0	9.84
2.2	4.54	4.5	9.95
2.4	5.30	5.0	10.10
2.5	7.60	6.0	10.25

TABLE -17

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

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN VANADYL SULPHATE, 5×10^{-3}M IN HCl AND 5×10^{-3}M IN LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH=0.1M(KCl)

(Curve 1, Figure 8)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.38	7.5	4.55
0.5	2.44	8.0	4.61
1.0	2.50	8.5	4.70
1.5	2.57	9.0	4.78
2.0	2.65	9.5	4.91
2.5	2.73	10.0	5.46
3.0	2.88	10.5	6.30
3.5	3.00	11.0	7.28
4.0	3.18	11.5	8.12
4.5	3.38	12.0	8.88
5.0	3.57	12.5	9.34
5.5	3.76	13.0	9.64
6.0	3.87	13.5	9.86
6.5	4.03	14.0	9.98
7.0	4.22	15.0	10.05

TABLE - 18

TEMPERATURE = 30 ± 1°C
POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl AND 2.5×10^{-3}M IN LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION, IONIC STRENGTH = 0.1M (KCl)
(Curve 2, Figure 8)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.61	8.0	4.55
0.5	2.68	8.5	4.61
1.0	2.76	9.0	4.70
1.5	2.84	9.5	4.87
2.0	2.92	10.0	5.36
2.5	3.00	10.5	6.00
3.0	3.12	11.0	6.80
3.5	3.27	11.5	7.50
4.0	3.37	12.0	8.04
4.5	3.54	12.5	8.44
5.0	3.72	13.0	8.85
5.5	3.88	13.5	9.16
6.0	4.09	14.0	9.40
6.5	4.22	14.5	9.85
7.0	4.33	15.0	10.03
7.5	4.46	16.0	10.10

TABLE -19

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 1.25×10^{-3}M IN VANADYL SULPHATE, 1.25×10^{-3}M IN HCl AND 1.25×10^{-3}M IN LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 3, Figure 8)

ML. OF 0.1M KOH	pH	ML.OF 0.1M KOH	pH
0.0	2.90	4.5	4.77
0.5	3.00	5.0	5.25
1.5	3.36	5.5	6.50
2.0	3.59	6.0	7.60
2.5	3.90	6.5	8.35
3.0	4.24	7.0	8.89
3.5	4.49	7.5	9.35
4.0	4.60	8.0	9.65

TABLE -20

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

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF $2.5\text{x}10^{-3}$M
IN VANADYL SULPHATE, $2.5\text{x}10^{-3}$M IN HCl AND $5\text{x}10^{-3}$M
IN LACTIC ACID WITH 0.1M DOTASSIUM HYDROXIDE
SOLUTION. IONIC STRENGTH = 0.1M (KCl)
(Curve 4, Figure 8)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.50	9.5	4.28
1.0	2.61	10.0	4.46
2.0	2.72	10.5	4.64
2.5	2.78	11.0	4.80
3.0	2.86	11.5	4.94
3.5	2.93	12.0	5.06
4.0	3.01	12.5	5.54
4.5	3.10	13.0	6.03
5.0	3.20	13.5	6.90
5.5	3.30	14.0	7.62
6.0	3.40	14.5	8.22
6.5	3.51	15.0	8.76
7.0	3.62	15.5	9.24
7.5	3.72	16.0	9.60
8.0	3.84	16.5	9.82
8.5	3.97	17.0	9.95
9.0	4.12	18.0	10.10

TABLE -21

TEMPERATURE = 30±1°C

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

(Curve 0, Figure 9)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.72	4.5	4.63
0.5	2.84	4.7	4.88
1.0	2.98	4.8	5.42
1.5	3.14	4.9	6.46
2.0	3.31	5.0	9.25
2.5	3.51	5.1	10.17
3.0	3.72	5.2	10.28
3.5	3.97	5.4	10.50
4.0	4.24	5.8	10.72
4.3	4.46	6.0	10.80

TABLE -22

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN VANADYL SULPHATE, 5×10^{-3}M IN HCl AND 5×10^{-3}M IN TARTARIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M (KCl)

(Curve 1, Figure 9)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.30	7.6	3.15
0.4	2.32	8.0	3.29
0.8	2.34	8.4	3.52
1.2	2.36	8.8	3.85
1.6	2.38	9.2	4.25
2.0	2.40	9.6	4.70
2.4	2.44	10.0	5.47
2.8	2.48	10.4	5.87
3.2	2.53	10.8	6.23
3.6	2.57	11.2	6.55
4.0	2.61	11.6	6.77
4.4	2.65	12.0	7.22
4.8	2.68	12.4	7.95
5.2	2.73	12.8	8.90
5.6	2.77	13.2	9.50
6.0	2.83	13.6	9.77
6.4	2.88	14.0	10.10
6.8	2.92	14.5	10.48
7.2	2.99	15.0	10.70

TABLE - 23

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl. and 2.5×10^{-3}M IN TARTARIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH=0.1M (KCl)

(Curve 2, Figure 9)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.48	5.0	5.48
0.4	2.52	5.2	5.86
0.8	2.57	5.4	6.21
1.2	2.61	5.6	6.49
1.4	2.65	5.8	6.77
1.6	2.70	6.0	7.16
2.0	2.77	6.2	7.95
2.4	2.85	6.4	8.50
2.8	2.92	6.6	9.05
3.2	3.02	6.8	9.30
3.6	3.23	7.0	9.70
4.0	3.53	7.2	9.89
4.4	4.01	7.4	10.15
4.8	4.85	8.0	10.57

TABLE - 24

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 1.25×10^{-3}M IN VANADYL SULPHATE, 1.25×10^{-3}M IN HCl and 1.25×10^{-3}M IN TARTARIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION, IONIC STRENGTH=0.1M (KCl)

(Curve 3, Figure 9)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.66	5.2	5.87
0.4	2.71	5.4	6.28
0.8	2.76	5.6	6.54
1.2	2.81	5.8	6.85
1.6	2.87	6.0	7.17
2.0	2.94	6.2	7.86
2.4	3.01	6.4	8.30
2.8	3.09	6.6	8.65
3.2	3.23	6.8	8.97
3.6	3.39	7.0	9.25
4.0	3.60	7.2	9.50
4.4	4.14	7.4	9.75
4.8	4.98	7.8	10.15
5.0	5.51	8.0	10.35

TABLE - 25

TEMPERATURE = 30 ± 1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN VANADYL SULPHATE, 5×10^{-3}M IN HCl AND 1×10^{-2}M IN TARTARIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M(KCl)

(Curve 4, Figure 9)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.16	12.0	3.82
1.0	2.21	12.5	3.99
2.0	2.27	13.0	4.22
3.0	2.36	13.5	4.52
4.0	2.43	14.0	4.90
5.0	2.51	14.5	5.60
6.0	2.58	15.0	6.02
7.0	2.68	15.5	6.24
8.0	2.82	16.0	6.43
9.0	3.02	16.5	6.70
9.5	3.13	17.0	7.35
10.0	3.24	17.5	8.30
10.5	3.37	18.0	8.95
11.0	3.51	18.5	9.80
11.5	3.66	19.0	10.50

TABLE - 26

TEMPERATURE - 30±1°C

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

(Curve 0, Figure 11)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.88	4.3	5.20
0.5	3.08	4.5	5.38
1.0	3.26	4.7	5.62
1.5	3.50	4.8	6.15
2.0	3.78	4.9	6.96
2.5	4.04	5.0	9.70
3.0	4.36	5.1	10.12
3.5	4.62	5.3	10.50
4.0	4.94	5.5	10.90

TABLE -27

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN VANADYL SULPHATE, 5×10^{-3}M IN HCl AND 5×10^{-3}M IN MALIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH=0.1M(KCl)

(Curve 1, Figure 11)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.36	7.2	3.65
0.4	2.40	7.6	3.84
0.8	2.44	8.0	4.00
1.2	2.50	8.4	4.14
1.6	2.55	8.8	4.35
2.0	2.59	9.2	4.63
2.4	2.63	9.6	5.00
2.8	2.67	10.0	5.50
3.2	2.72	10.4	5.82
3.6	2.80	10.8	6.26
4.0	2.87	11.2	6.57
4.4	2.95	11.6	6.77
4.8	3.05	12.0	7.12
5.2	3.13	12.4	7.70
5.6	3.19	12.8	8.28
6.0	3.30	13.2	8.95
6.4	3.42	13.6	9.67
6.8	3.55	14.0	10.35

TABLE - 28

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $2.5x10^{-3}M$ IN VANADYL SULPHATE, $2.5x10^{-3}M$ IN HCl AND $2.5x10^{-3}M$ IN MALIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION, IONIC STRENGTH = 0.1M (KCl)

(Curve 2, Figure 11)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.58	4.8	5.08
0.4	2.66	5.0	5.50
0.8	2.75	5.2	5.86
1.2	2.82	5.4	6.28
1.6	2.92	5.6	6.56
2.0	3.07	5.8	6.75
2.4	3.21	6.0	7.11
2.8	3.36	6.2	7.65
3.2	3.58	6.4	8.10
3.6	3.83	6.6	8.60
4.0	4.13	6.8	9.02
4.4	4.52	7.0	9.75

TABLE-29

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 1.25×10^{-3}M IN VANADYL SULPHATE, 1.25×10^{-3}M IN HCl AND 1.25×10^{-3}M IN MALIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH=0.1M (KCl)

(Curve 3 Figure 11)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.86	5.0	5.50
0.4	2.94	5.2	5.80
0.8	3.02	5.4	6.21
1.2	3.06	5.6	6.54
1.6	3.12	5.8	6.78
2.0	3.26	6.0	7.11
2.4	3.41	6.2	7.65
2.8	3.54	6.4	7.95
3.2	3.70	6.6	8.40
3.6	3.96	6.8	8.92
4.0	4.22	7.0	9.35
4.4	4.61	7.2	9.80
4.8	5.15	7.4	10.25

TABLE -30

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}M$ IN VANADYL SULPHATE, $5x10^{-3}M$ IN HCl AND $1x10^{-2}M$ IN MALIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION, IONIC STRENGTH = 0.1M (KCl)

(Curve 4, Figure 11)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.30	13.5	5.05
1.0	2.39	14.0	5.31
2.0	2.48	14.5	5.64
3.0	2.59	15.0	6.10
4.0	2.70	15.5	6.50
5.0	2.83	16.0	6.76
6.0	2.98	16.5	6.99
7.0	3.15	17.0	7.25
8.0	3.34	17.5	7.70
9.0	3.58	18.0	8.25
10.0	3.85	18.5	9.00
11.0	4.14	19.0	9.76
12.0	4.46	19.5	10.50
13.0	4.83	20.0	11.00

TABLE -31

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN IMINODIACETIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION, IONIC STRENGTH = 0.1M (KCl)

(Curve O, Fig. 13)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.84	2.7	6.89
0.5	2.94	2.8	7.35
1.0	3.10	3.0	7.90
1.5	3.30	3.5	8.53
2.0	3.62	4.0	8.88
2.3	4.04	4.5	9.25
2.4	4.60	5.0	9.70
2.5	5.46	5.5	10.16
2.6	6.39	6.0	10.40

TABLE -32

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF 5×10^{-3}M IN VANADYL SULPHATE, 5×10^{-3}M IN HCl AND 5×10^{-3}M IN IMINODIACETIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH= 0.1M(KCl)

(Curve 1, Fig.13)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.38	8.5	4.77
1.0	2.43	9.0	5.17
2.0	2.49	9.5	5.34
2.5	2.53	9.8	5.50
3.0	2.58	10.0	5.88
3.5	2.64	10.5	6.75
4.0	2.75	11.0	7.34
4.5	2.85	11.5	7.80
5.0	2.97	12.0	8.14
5.5	3.12	12.5	8.38
6.0	3.29	13.0	8.65
6.5	3.47	13.5	8.83
7.0	3.75	14.0	9.00
7.3	3.86	15.0	9.26
7.5	4.16	16.0	9.46
7.7	4.30	17.0	9.67
8.0	4.48	18.0	9.85

TABLE -33

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML.SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl AND 2.5×10^{-3}M IN IMINODIACETIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION, IONIC STRENGTH=0.1M(KCl)

(Curve 2, Fig. 13)

ML.OF 0.1M KOH	pH	ML.OF 0.1M KOH	pH
0.0	2.55	8.5	4.79
1.0	2.60	9.0	5.19
2.0	2.66	9.5	5.35
2.5	2.71	9.8	5.47
3.0	2.77	10.0	5.86
3.5	2.85	10.5	6.50
4.0	2.94	11.0	6.95
4.5	3.04	11.5	7.43
5.0	3.16	12.0	7.75
5.5	3.32	12.5	8.02
6.0	3.50	13.0	8.26
6.5	3.70	13.5	8.40
7.0	3.96	14.0	8.61
7.3	4.11	15.0	8.90
7.5	4.26	16.0	9.12
7.7	4.39	17.0	9.30
8.0	4.52	18.0	9.50

TABLE - 34

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML SOLUTION OF 1.25×10^{-3}M IN VANADYL SULPHATE, 1.25×10^{-3}M IN HCl AND 1.25×10^{-3}M IN IMINODIACETIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M(KCl)

(Curve 3, Fig. 13)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.67	4.5	5.16
0.5	2.78	5.0	5.75
1.0	2.89	5.5	6.70
1.5	3.01	6.0	7.35
2.0	3.17	6.5	7.87
2.5	3.39	7.0	8.30
3.0	3.66	7.5	8.64
3.5	4.08	8.0	8.85
3.8	4.30	8.5	9.10
4.0	4.47	9.0	9.28
4.3	4.83	10.0	9.40

TABLE -35

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 50 ML. SOLUTION OF $5x10^{-3}M$ IN VANADYL SULPHATE, $5x10^{-3}M$ IN HCl AND $1.0x10^{-2}M$ IN IMINODIACETIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M (KCl)

(Curve 4, Fig. 13)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.33	10.0	3.85
1.0	2.37	10.2	4.15
2.0	2.42	10.5	4.59
2.5	2.45	11.0	4.95
3.0	2.48	11.5	5.13
3.5	2.52	12.0	5.35
4.0	2.57	12.5	5.71
4.5	2.61	13.0	6.35
5.0	2.65	13.5	7.07
5.5	2.69	14.0	7.51
6.0	2.75	14.5	7.81
6.5	2.81	15.0	7.99
7.0	2.89	15.5	8.19
7.5	2.96	16.0	8.47
8.0	3.05	16.5	8.61
8.5	3.15	17.0	8.75
9.0	3.29	18.0	8.97
9.5	3.49	19.0	9.23
9.8	3.69	20.0	9.45

TABLE -36

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

POTENTIOMETRIC TITRATION OF 50 ML SOLUTION OF 5×10^{-3}M IN VANADYL SULPHATE, 5×10^{-3}M IN HCl AND 1.5×10^{-2} IN IMINODIACETIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M(KCl)

(Curve 5, Fig. 13)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.20	12.5	4.11
1.0	2.25	12.7	4.39
2.0	2.30	13.0	4.71
3.0	2.35	13.3	4.91
4.0	2.42	13.5	5.01
5.0	2.49	14.0	5.25
6.0	2.57	14.5	5.49
7.0	2.69	15.0	5.83
8.0	2.73	15.5	6.69
8.5	2.79	15.7	7.07
9.0	2.85	16.0	7.39
9.5	2.92	16.5	7.65
10.0	3.01	17.0	7,95
10.5	3.11	17.5	8.17
11.0	3.24	18.0	8.37
11.5	3.41	18.5	8.57
12.0	3.63	19.0	8.75
12.3	3.85	20.0	8.97

TABLE -37

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN o-PHENANTHROLINE HYDROCHLORIDE WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M(KCl)

(Curve 1, Figure 15)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	3.80	1.8	5.38
0.2	4.06	2.0	5.58
0.4	4.28	2.2	5.82
0.6	4.48	2.3	6.07
0.8	4.64	2.4	6.27
1.0	4.79	2.5	8.40
1.2	4.92	2.6	9.20
1.4	5.08	2.8	9.96
1.6	5.22	3.0	10.22

TABLE -38

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M 2,2'-DIPYRIDYL HYDROCHLORIDE WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M (KCl)

(Curve 2, Figure 15)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.70	3.8	4.54
0.5	2.80	4.0	4.68
1.0	2.92	4.3	4.88
1.5	3.08	4.5	5.06
1.8	3.18	4.7	5.30
2.0	3.31	4.8	5.66
2.3	3.48	4.9	6.00
2.5	3.64	5.0	8.02
2.7	3.80	5.1	9.30
3.0	4.00	5.3	9.80
3.3	4.21	5.5	10.10
3.5	4.35	6.0	10.46

TABLE -39

TEMPERATURE =30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE AND 2.5×10^{-3}M IN o-PHENANTHROLINE HYDROCHLORIDE WITH 0.1M POTASSIUM HYDROXIDE SOLUTION, IONIC STRENGTH = 0.1M (KCl)

(Curve 3, Figure 15)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.74	6.4	5.75
0.4	2.82	6.6	5.94
0.8	2.94	6.8	6.20
1.2	3.04	7.0	6.56
1.6	3.15	7.2	6.90
2.0	3.28	7.4	7.26
2.4	3.45	7.6	7.66
2.8	3.62	7.8	7.99
3.2	3.78	8.0	8.25
3.6	3.94	8.4	8.60
4.0	4.10	8.8	8.88
4.4	4.27	9.2	9.18
4.8	4.47	9.6	9.50
5.2	4.72	10.0	9.84
5.6	5.03	10.4	10.02
6.0	5.35	11.0	10.30

TABLE -40

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl AND 2.5×10^{-3}M IN 2,2'-DIPYRIDYL HYDROCHLORIDE WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH=0.1M(KCl)

(Curve 4, Figure 15)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.32	9.0	4.06
1.0	2.40	9.5	4.24
2.0	2.46	10.0	4.46
2.5	2.53	10.5	4.80
3.0	2.57	11.0	5.18
3.5	2.63	11.5	5.50
4.0	2.70	12.0	5.89
4.5	2.75	12.5	6.50
5.0	2.81	13.0	7.05
5.5	2.92	13.5	7.56
6.0	3.04	14.0	8.25
6.5	3.18	14.5	8.75
7.0	3.37	15.0	9.26
7.5	3.56	15.5	9.70
8.0	3.72	16.0	10.05
8.5	3.88	17.0	10.50

TABLE -41

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl AND 2.5×10^{-3}M IN CATECHOL WITH 0.1M POTASSIUM HYDROXIDE SOLUTION.

IONIC STRENGTH=0.1M(KCl)

(Curve 3, Figure 16)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.65	7.5	4.88
0.5	2.81	8.0	5.10
1.0	2.98	8.5	5.36
1.5	3.20	9.0	5.63
2.0	3.43	9.5	6.22
2.5	3.60	9.8	6.50
3.0	3.70	10.0	7.25
3.5	3.80	10.2	9.25
4.0	3.98	10.5	9.75
4.5	4.07	11.0	10.30
5.0	4.15	11.5	10.70
5.5	4.23	12.0	10.95
6.0	4.35	12.5	11.10
6.5	4.50	13.0	10.21
7.0	4.65	14.0	10.35

TABLE -42

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

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5x10^{-3}M IN VANADYL SULPHATE, 2.5x10^{-3}M IN HCl, 2.5x10^{-3}M IN o-PHENANTHROLINE HYDROCHLORIDE AND 2.5x10^{-3}M IN CATECHOL WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M(KCl)

(Curve 4, Figure 16)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.42	8.5	4.15
0.5	2.48	9.0	4.54
1.0	2.54	9.5	5.00
1.5	2.60	9.8	5.35
2.0	2.66	10.0	6.00
2.5	2.74	10.2	6.50
3.0	2.84	10.5	7.20
3.5	2.92	11.0	7.75
4.0	3.00	11.5	8.06
4.5	3.12	12.0	8.30
5.0	3.24	12.5	8.54
5.5	3.34	13.0	8.86
6.0	3.44	13.5	9.29
6.5	3.55	14.0	9.98
7.0	3.66	14.5	10.36
7.5	3.78	15.0	10.58
8.0	3.96	16.0	10.70

TABLE -43

TEMPERATURE=30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl AND 2.5×10^{-3}M IN TIRON WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 3, Figure 17)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.60	7.5	3.94
0.5	2.65	8.0	4.08
1.0	2.70	8.5	4.34
1.5	2.76	9.0	4.64
2.0	2.82	9.5	4.91
2.5	2.88	9.8	5.15
3.0	2.95	10.0	5.55
3.5	3.03	10.2	6.50
4.0	3.11	10.5	7.25
4.5	3.18	11.0	7.85
5.0	3.26	11.5	8.35
5.5	3.35	12.0	9.25
6.0	3.46	12.5	9.65
6.5	3.58	13.0	10.20
7.0	3.74	14.0	10.75

TABLE -44

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl, 2.5×10^{-3}M IN o- PHENANTHROLINE HYDROCHLORIDE AND 2.5×10^{-3}M IN TIRON WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH =0.1M (KCl)

(Curve 4, Figure 17)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.40	9.0	3.65
1.0	2.45	9.5	3.94
2.0	2.52	9.8	4.27
2.5	2.57	10.0	4.65
3.0	2.61	10.2	5.34
3.5	2.66	10.5	6.16
4.0	2.72	11.0	6.92
4.5	2.77	11.5	7.34
5.0	2.83	12.0	7.90
5.5	2.89	12.5	8.32
6.0	2.96	13.0	8.70
6.5	3.03	13.5	9.26
7.0	3.11	14.0	9.82
7.5	3.21	14.5	10.22
8.0	3.32	15.0	10.44
8.5	3.47	16.0	10.60

TABLE -45

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M TIRON WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M (KCl). (Curve 5, Figure 17)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	6.20	2.2	8.44
0.2	6.55	2.3	8.62
0.4	6.82	2.4	8.83
0.6	7.06	2.5	9.20
1.0	7.38	2.6	9.52
1.2	7.54	2.7	9.80
1.4	7.68	2.8	9.98
1.8	7.99	2.9	10.07
2.0	8.18	3.0	10.20

TABLE - 46

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl, 2.5×10^{-3}M IN o-PHENANTHROLINE HYDROCHLORIDE AND 2.5×10^{-3}M IN CHROMOTROPIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M (KCl)

(Curve 4, Figure 18)

ML.OF 0.1M KOH	pH	ML.OF 0.1M KOH	pH
0.0	2.43	9.0	3.60
0.5	2.46	9.5	3.91
1.0	2.50	9.8	4.25
1.5	2.54	10.0	4.80
2.0	2.58	10.2	5.38
2.5	2.62	10.5	6.50
3.0	2.65	11.0	7.20
3.5	2.70	11.5	7.65
4.0	2.73	12.0	8.00
4.5	2.77	12.5	8.28
5.0	2.83	13.0	8.58
5.5	2.88	13.5	8.85
6.0	2.96	14.0	9.20
6.5	3.03	14.5	9.51
7.0	3.09	15.0	9.90
7.5	3.20	15.5	10.15
8.0	3.28	16.0	10.44
8.5	3.45	17.0	10.75

TABLE - 47

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl AND 2.5×10^{-3}M IN SODIUM SALICYLATE WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M(KCl)

(Curve 3, Figure 19)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	3.00	6.0	5.40
0.5	3.09	6.5	5.62
1.0	3.19	7.0	6.00
1.5	3.30	7.3	6.25
2.0	3.41	7.5	6.60
2.5	3.56	7.7	7.00
3.0	3.74	8.0	7.80
3.5	3.92	8.5	8.71
4.0	4.23	9.0	9.38
4.5	4.65	9.5	9.90
5.0	5.00	10.0	10.30
5.5	5.23	11.0	10.85

TABLE -48

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl, 2.5×10^{-3}M IN o-PHENANTHROLINE HYDROCHLORIDE AND 2.5×10^{-3}M IN SODIUM SALICYLATE WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH= 0.1M (KCl)

(Curve 4, Figure 19)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.52	7.0	4.22
0.5	2.57	7.3	4.66
1.0	2.62	7.5	5.28
1.5	2.67	7.7	5.85
2.0	2.73	8.0	6.36
2.5	2.79	8.5	6.82
3.0	2.85	9.0	7.26
3.5	2.92	9.5	7.76
4.0	3.01	10.0	8.30
4.5	3.10	10.5	8.68
5.0	3.22	11.0	9.06
5.5	3.37	11.5	9.56
6.0	3.56	12.0	10.10
6.5	3.83	13.0	10.54

TABLE -49

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M SALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 5, Figure 19)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	3.00	2.0	3.88
0.2	3.03	2.2	4.24
0.4	3.07	2.3	4.90
0.8	3.15	2.4	5.72
1.0	3.20	2.5	9.14
1.2	3.32	2.6	9.70
1.4	3.41	2.7	9.88
1.6	3.50	2.8	10.06
1.8	3.60	3.0	10.28

TABLE-50

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5x10^{-3}M IN VANADYL SULPHATE, 2.5x10^{-3}M IN HCl AND 2.5x10^{-3}M IN SULPHO-SALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 3, Figure 20)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.52	8.5	5.41
1.0	2.64	9.0	5.67
2.0	2.77	9.5	6.05
3.0	2.90	10.0	6.75
4.0	3.07	10.2	7.40
4.5	3.20	10.5	8.00
5.0	3.31	11.0	8.65
6.0	3.67	11.5	9.25
6.5	3.94	12.0	9.70
7.0	4.32	12.5	10.04
7.5	4.80	13.0	10.38
8.0	5.15	14.0	10.90

TABLE - 51

TEMPERATURE = 30 ± 1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF $2.5x10^{-3}M$ IN VANADYL SULPHATE, $2.5x10^{-3}M$ IN HCl, $2.5x10^{-3}M$ IN o-PHENANTHROLINE HYDROCHLORIDE AND $2.5x10^{-3}M$ IN SULPHOSALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH= = 0.1M (KCl)

(Curve 4, Fig.20)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.19	11.5	3.47
1.0	2.22	12.0	3.78
2.0	2.26	12.3	4.05
3.0	2.31	12.5	4.31
4.0	2.37	12.7	4.78
5.0	2.44	13.0	5.64
5.5	2.48	13.5	6.40
6.0	2.52	14.0	6.80
6.5	2.57	14.5	7.19
7.0	2.62	15.0	7.60
7.5	2.67	15.5	8.00
8.0	2.72	16.0	8.30
8.5	2.79	16.5	8.61
9.0	2.86	17.0	8.90
9.5	2.94	17.5	9.24
10.0	3.03	18.0	9.60
10.5	3.14	19.0	10.20
11.0	3.28	20.0	10.58

TABLE -52

TEMPERATURE=30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5x10^{-3}M SULPHOSALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M(KCl)

(Curve 5, Figure 20)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.52	4.4	3.57
0.5	2.58	4.6	4.06
1.0	2.64	4.8	4.76
1.5	2.70	4.9	6.48
2.0	2.77	5.0	9.30
2.5	2.86	5.1	9.93
3.0	2.96	5.2	10.08
3.5	3.10	5.4	10.18
4.0	3.30	6.0	10.48

TABLE -53

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl, 2.5×10^{-3}M IN o-PHENANTHROLINE HYDROCHLORIDE AND 2.5×10^{-3}M IN LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 4, Figure 21)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.48	9.0	4.10
1.0	2.57	9.5	4.35
2.0	2.66	10.0	4.73
2.5	2.71	10.5	5.34
3.0	2.76	11.0	5.86
3.5	2.83	11.5	6.26
4.0	2.91	12.0	6.66
4.5	2.99	12.5	7.00
5.0	3.08	13.0	7.32
5.5	3.18	13.5	7.62
6.0	3.27	14.0	8.04
6.5	3.38	14.5	8.54
7.0	3.48	15.0	9.00
7.5	3.61	15.5	9.34
8.0	3.74	16.0	9.60
8.5	3.90	17.0	9.90

TABLE -54

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl, 2.5×10^{-3}M IN o-PHENANTHROLINE HYDROCHLORIDE AND 2.5×10^{-3}M IN MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 4, Figure 22)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.44	8.0	3.18
1.0	2.52	8.5	3.30
2.0	2.60	9.0	3.46
2.5	2.64	9.5	3.68
3.0	2.69	10.0	4.14
3.5	2.74	10.2	4.60
4.0	2.79	10.5	5.64
4.5	2.81	10.7	6.26
5.0	2.83	11.0	6.96
5.5	2.86	11.5	8.52
6.0	2.90	12.0	9.42
6.5	2.95	12.5	9.76
7.0	3.01	13.0	9.90
7.5	3.08	14.0	10.00

TABLE -55

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF $2.5x10^{-3}$M IN VANADYL SULPHATE, $2.5x10^{-3}$M IN HCl AND $2.5x10^{-3}$M IN OXALIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 3, Figure 23)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.23	8.5	4.12
1.0	2.30	9.0	4.62
2.0	2.36	9.5	4.86
2.5	2.40	10.0	5.24
3.0	2.44	10.5	5.54
3.5	2.48	11.0	6.00
4.0	2.54	11.5	6.36
4.5	2.60	12.0	6.56
5.0	2.67	12.5	6.80
5.5	2.76	13.0	7.04
6.0	2.86	13.5	7.30
6.5	2.98	14.0	7.54
7.0	3.16	14.5	7.75
7.3	3.30	15.0	8.94
7.5	3.42	15.5	9.68
7.7	3.56	16.0	10.10
8.0	3.74	17.0	10.40

TABLE - 56

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl, 2.5×10^{-3}M IN o-PHENANTHROLINE HYDROCHLORIDE AND 2.5×10^{-3}M IN OXALIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH=0.1M (KCl)

(Curve 4, Figure 23)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.13	10.0	4.00
1.0	2.18	10.2	4.35
2.0	2.23	10.5	4.90
2.5	2.26	11.0	5.61
3.0	2.29	11.5	5.95
3.5	2.33	12.0	6.22
4.0	2.37	12.5	6.45
4.5	2.41	13.0	6.60
5.0	2.46	13.5	6.75
5.5	2.51	14.0	6.88
6.0	2.57	14.5	7.15
6.5	2.63	15.0	7.33
7.0	2.71	15.5	7.65
7.5	2.77	16.0	8.15
8.0	2.90	16.5	8.60
8.5	3.03	17.0	8.94
9.0	3.20	17.5	9.50
9.5	3.51	18.0	9.85
9.8	3.75	19.0	10.40

TABLE - 57

TEMPERATURE = 30±1°C
POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M OXALIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION
IONIC STRENGTH = 0.1M(KCl)
(Curve 5, Figure 23)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.65	4.0	4.12
0.4	2.73	4.4	4.40
0.8	2.80	4.8	5.09
1.2	2.88	4.9	5.52
1.6	2.97	5.0	7.63
2.0	3.10	5.1	9.48
2.4	3.25	5.2	9.75
2.8	3.43	5.3	9.97
3.2	3.64	5.4	10.10
3.6	3.85	6.0	10.60

TABLE -58

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF $2.5x10^{-3}$M IN VANADYL SULPHATE, $2.5x10^{-3}$M IN HCl AND $2.5x10^{-3}$M IN POTASSIUM HYDROGEN PHTHALATE WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH =0.1M(KCl)

(Curve 3, Figure 24)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.86	6.5	4.54
0.5	2.94	7.0	4.64
1.0	3.03	7.5	4.77
1.5	3.12	8.0	4.92
2.0	3.22	8.5	5.10
2.5	3.32	9.0	5.24
3.0	3.44	9.5	5.42
3.5	3.60	10.0	5.64
4.0	3.78	10.5	5.90
4.5	3.96	11.0	6.40
4.8	4.09	11.5	7.27
5.0	4.22	12.0	8.38
5.1	4.27	12.5	9.05
5.3	4.33	13.0	9.68
5.5	4.39	13.5	10.18
6.0	4.46	14.0	10.46

TABLE -59

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF $2.5x10^{-3}$M IN VANADYL SULPHATE, $2.5x10^{-3}$M IN HCl, $2.5x10^{-3}$M IN o-PHENANTHROLINE HYDROCHLORIDE AND $2.5x10^{-3}$M IN POTASSIUM HYDROGEN PHTHALATE WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 4, Figure 24)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.56	9.2	5.24
1.0	2.66	9.6	5.41
2.0	2.78	10.0	5.56
3.0	2.92	10.4	5.72
4.0	3.11	10.8	5.88
4.4	3.20	11.2	6.06
4.8	3.30	11.6	6.36
5.2	3.42	12.0	6.62
5.6	3.53	12.4	7.10
6.0	3.66	12.6	7.46
6.4	3.82	12.8	7.76
6.8	3.98	13.2	8.20
7.2	4.16	13.6	8.54
7.6	4.36	14.0	8.82
8.0	4.59	14.4	9.20
8.4	4.82	14.8	9.48
8.8	5.04	15.0	9.58

TABLE -60

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M PHTHALIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 5, Figure 24)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.91	4.0	5.09
0.4	3.00	4.4	5.36
0.8	3.12	4.8	5.82
1.2	3.25	4.9	6.30
1.6	3.40	5.0	7.72
2.0	3.61	5.1	8.84
2.4	3.91	5.2	9.60
2.8	4.35	5.4	9.86
3.2	4.62	5.6	10.10
3.6	4.85	6.0	10.45

TABLE - 61

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl, 2.5×10^{-3}M IN 2,2'-DIPYRIDYL HYDROCHLORIDE AND 2.5×10^{-3}M IN CATECHOL WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH=0.1M(KCl)

(Curve 4, Figure 25)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.34	10.0	3.72
1.0	2.40	10.5	3.84
2.0	2.48	11.0	3.97
2.5	2.53	11.5	4.14
3.0	2.58	12.0	4.41
3.5	2.64	12.5	4.99
4.0	2.70	13.0	5.78
4.5	2.76	13.5	6.30
5.0	2.83	14.0	6.68
5.5	2.92	14.5	6.98
6.0	2.99	15.0	7.26
6.5	3.08	15.5	7.54
7.0	3.14	16.0	7.84
7.5	3.23	16.5	8.22
8.0	3.32	17.0	8.62
8.5	3.42	17.5	9.18
9.0	3.51	18.0	9.88
9.5	3.61	19.0	10.50

Primary ligand : 2, 2'-Dipyridyl

Catechol (H_2A)	$VOL^{2+} + A^{2-} \rightleftarrows VOLA$	16.91*
Tiron (H_2A^{2-})	$VOL^{2-} + A^{4-} \rightleftarrows VOLA^{2-}$	17.18*
Chromotropic acid (H_2A^{2-})	$VOL^{2-} + A^{4-} \rightleftarrows VOLA^{2-}$	17.97*
Salicylic acid (H_2A)	$VOL^{2+} + A^{2-} \rightleftarrows VOLA$	13.17*
Sulphosalicylic acid (H_3A)	$VOL^{2+} + A^{3-} \rightleftarrows VOLA^{-}$	11.36*
Mandelic acid (H_2A)	$VOL^{2+} + H_2A \rightleftarrows VOLA + 2H^{+}$	3.53
	$VO^{2+} + HL^{+} + H_2A \rightleftarrows VOLA + 3H^{+}$	2.95
Lactic acid(H_2A)	$VOL^{2+} + H_2A \rightleftarrows VOLA + 2H^{+}$	3.98
	$VO^{2+} + HL^{+} + H_2A \rightleftarrows VOLA + 3H^{+}$	3.40
Oxalic acid (H_2A)	$VOL^{2+} + A^{2-} \rightleftarrows VOLA$	4.63*
	$VO^{2+} + L + A^{2-} \rightleftarrows VOLA$	9.71*

* Log K values.

It is interesting to note an unexpectedly higher stabilities of the above mixed ligand derivatives as compared to those of the corresponding simple 1:1 chelates.

TABLE -62

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl, 2.5×10^{-3}M IN 2,2'-DIPYRIDYL HYDROCHLORIDE AND 2.5×10^{-3}M IN TIRON WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH= = 0.1M(KCl). (Curve 4, Figure 26)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.30	10.0	3.30
1.0	2.36	10.5	3.41
2.0	2.42	11.0	3.54
2.5	2.46	11.5	3.70
3.0	2.50	12.0	4.00
3.5	2.54	12.5	4.66
4.0	2.58	13.0	5.58
4.5	2.61	13.5	6.10
5.0	2.64	14.0	6.40
5.5	2.69	14.5	6.68
6.0	2.74	15.0	6.96
6.5	2.80	15.5	7.28
7.0	2.86	16.0	7.62
7.5	2.92	16.5	8.10
8.0	2.98	17.0	8.64
8.5	3.05	17.5	9.22
9.0	3.12	18.0	9.94
9.5	3.21	19.0	10.60

TABLE = 63

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5x10^{-3}M IN VANADYL SULPHATE, 2.5x10^{-3}M IN HCl, 2.5x10^{-3}M IN 2,2'-DIPYRIDYL HYDROCHLORIDE AND 2.5x10^{-3}M IN CHROMOTROPIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH= 0.1M (KCl)

(Curve 4, Figure 27)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.30	10.0	3.33
1.0	2.36	10.5	3.45
2.0	2.44	11.0	3.59
2.5	2.48	11.5	3.78
3.0	2.52	12.0	4.10
3.5	2.56	12.5	4.78
4.0	2.60	13.0	5.90
4.5	2.63	13.5	6.40
5.0	2.66	14.0	6.82
5.5	2.71	14.5	7.22
6.0	2.77	15.0	7.78
6.5	2.82	15.5	8.22
7.0	2.88	16.0	8.56
7.5	2.94	16.5	8.90
8.0	3.01	17.0	9.26
8.5	3.09	17.5	9.66
9.0	3.15	18.0	10.06
9.5	3.23	19.0	10.50

TABLE -64

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl, 2.5×10^{-3}M IN 2,2'-DIPYRIDYL HYDROCHLORIDE AND 2.5×10^{-3}M IN SODIUM SALICYLATE WITH 0.1M POTASSIUM HYDROXIDE SOLUTION.

IONIC STRENGTH = 0.1M (KCl)

(Curve 4, Figure 28)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.41	9.5	3.94
1.0	2.48	9.8	4.12
2.0	2.56	10.0	4.28
2.5	2.59	10.2	4.50
3.0	2.62	10.5	4.93
3.5	2.68	11.0	5.61
4.0	2.74	11.5	5.92
4.5	2.79	12.0	6.30
5.0	2.86	12.5	6.98
5.5	2.92	13.0	7.42
6.0	2.99	13.5	7.80
6.5	3.07	14.0	8.12
7.0	3.13	14.5	8.48
7.5	3.22	15.0	8.88
8.0	3.34	15.5	9.36
8.5	3.50	16.0	9.88
9.0	3.68	17.0	10.44

TABLE -65

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML.SOLUTION OF $2.5x10^{-3}$M IN VANADYL SULPHATE, $2.5x10^{-3}$M IN HCl, $2.5x10^{-3}$M IN 2,2'-DIPYRIDYL HYDROCHLORIDE AND $2.5x10^{-3}$M IN SULPHOSALICYLIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION. IONIC STRENGTH = 0.1M(KCl)

(Curve 4,Figure 29)

ML.OF 0.1M KOH	pH	ML.OF 0.1M KOH	pH
0.0	2.14	13.5	3.40
1.0	2.18	14.0	3.70
2.0	2.23	14.5	4.15
3.0	2.28	14.8	4.50
4.0	2.32	15.0	4.75
5.0	2.38	15.2	5.20
6.0	2.44	15.5	5.40
7.0	2.49	16.0	5.95
7.5	2.52	16.5	6.45
8.0	2.56	17.0	6.85
8.5	2.61	17.5	7.16
9.0	2.66	18.0	7.54
9.5	2.72	18.5	7.86
10.0	2.78	19.0	8.16
10.5	2.83	19.5	8.60
11.0	2.90	20.0	8.95
11.5	2.97	20.5	9.25
12.0	3.03	21.0	9.70
12.5	3.13	22.0	10.34
13.0	3.24	23.0	10.60

TABLE -66

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl, 2.5×10^{-3}M IN 2,2'-DIPYRIDYL HYDROCHLORIDE AND 2.5×10^{-3}M IN LACTIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION, IONIC STRENGTH = 0.1M (KCl)

(Curve 4, Figure 30)

ML.OF 0.1M KOH	pH	ML.OF 0.1M KOH	pH
0.0	2.29	11.5	4.09
1.0	2.36	12.0	4.30
2.0	2.43	12.5	4.58
3.0	2.51	13.0	4.96
4.0	2.62	13.5	5.44
5.0	2.74	14.0	5.79
5.5	2.80	14.5	6.10
6.0	2.87	15.0	6.42
6.5	2.95	15.5	6.80
7.0	3.04	16.0	7.06
7.5	3.12	16.5	7.36
8.0	3.21	17.0	7.68
8.5	3.31	17.5	8.04
9.0	3.40	18.0	8.50
9.5	3.49	18.5	9.04
10.0	3.65	19.0	9.51
10.5	3.78	19.5	9.80
11.0	3.93	20.0	10.10

TABLE - 67

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl, 2.5×10^{-3}M IN 2,2'-DIPYRIDYL HYDROCHLORIDE AND 2.5×10^{-3}M IN MANDELIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 4, Figure 31)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.32	9.5	3.28
1.0	2.38	10.0	3.36
2.0	2.44	10.5	3.44
3.0	2.51	11.0	3.56
4.0	2.59	11.5	3.72
5.0	2.70	12.0	3.92
5.5	2.75	12.5	4.32
6.0	2.79	13.0	5.24
6.5	2.86	13.5	6.00
7.0	2.93	14.0	6.82
7.5	3.00	14.5	7.94
8.0	3.07	15.0	9.10
8.5	3.12	15.5	9.84
9.0	3.20	16.0	10.08

TABLE -68

TEMPERATURE = 30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION 2.5×10^{-3}M IN VANADYL SULPHATE, 2.5×10^{-3}M IN HCl, 2.5×10^{-3}M IN 2,2'-DIPYRIDYL HYDROCHLORIDE AND 2.5×10^{-3}M IN OXALIC ACID WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH = 0.1M (KCl)

(Curve 4, Figure 32)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.12	12.5	4.08
1.0	2.16	13.0	4.50
2.0	2.20	13.5	5.05
3.0	2.25	14.0	5.60
4.0	2.30	14.5	6.00
5.0	2.36	15.0	6.31
5.5	2.39	15.5	6.50
6.0	2.43	16.0	6.70
6.5	2.47	16.5	6.85
7.0	2.52	17.0	6.95
7.5	2.57	17.5	7.17
8.0	2.63	18.0	7.30
8.5	2.70	18.5	7.52
9.0	2.76	19.0	7.80
9.5	2.84	19.5	8.10
10.0	2.93	20.0	8.60
10.5	3.04	20.5	9.15
11.0	3.18	21.0	9.63
11.5	3.38	22.0	10.32
12.0	3.64	23.0	10.60

TABLE -69

TEMPERATURE=30±1°C

POTENTIOMETRIC TITRATION OF 100 ML. SOLUTION OF $2.5x10^{-3}$M IN VANADYL SULPHATE, $2.5x10^{-3}$M IN HCl, $2.5x10^{-3}$M IN 2,2'-DIPYRIDYL HYDROCHLORIDE AND $2.5x10^{-3}$M IN POTASSIUM HYDROGEN PHTHALATE WITH 0.1M POTASSIUM HYDROXIDE SOLUTION

IONIC STRENGTH=0.1M(KCl)

(Figure 33, Curve 4)

ML. OF 0.1M KOH	pH	ML. OF 0.1M KOH	pH
0.0	2.45	11.0	4.80
1.0	2.53	11.5	5.06
2.0	2.62	12.0	5.27
3.0	2.72	12.5	5.48
4.0	2.82	13.0	5.60
5.0	2.96	13.5	5.28
5.5	3.04	14.0	6.00
6.0	3.12	14.5	6.24
6.5	3.22	15.0	6.70
7.0	3.32	15.5	7.02
7.5	3.44	16.0	7.25
8.0	3.57	16.5	7.64
8.5	3.72	17.0	8.20
9.0	3.89	17.5	8.70
9.5	4.08	18.0	9.22
10.0	4.30	19.0	10.12
10.5	4.54	20.0	10.52

REFERENCES

1. L.G. Van Uitert and W.C. Fernelius, J.Am.Chem. Soc., 76, 375 (1954).

2. C.F. Timberlake, J. Chem. Soc., 4987 (1957).

3. R. Weinland and E. Walter, Z. anorg.Chem., 126, 145 (1923).

4. R. Weinland and E. Walter, Z.anorg.Chem., 126, 141 (1923).

5. R.Weinland and H. Sperl, Z.anorg. allgem.Chem., 150, 69 (1925).

6. G. Spacu and M.Kuras, J.prakt. Chem., 141, 201(1934).

7. R.Weinland and A. Dottinger, Z.anorg. allgem.Chem., 111, 167 (1920)

8. H. Reihlen, ibid., 123, 173 (1922)

9. A.Rosenheim and I. Baruttschisky, Ber., 58B,891(1925).

10. A. Rosenheim, I. Baruttschisky, W. Bulgrin, W.Plato and G.Ebert, Z. anorg. allgem. Chem., 200, 173(1931)

11. W.D. Treadwell, G. Szabados and E.Haimann, Helv. Chim. Acta, 15, 1049 (1932)

12. A.K. Babko, J. Gen. Chem. U.S.S.R., 16, 33(1946).

13. R.N. Kapoor and R.C. Mehrotra, Z. anorg. Chem., 293, 92(1957).

14. R.N. Kapoor and R.C. Mehrotra, ibid., 293, 104 (1957).

15. R.P. Agarwal and R.C. Mehrotra, J. Inorg. Nucl. Chem., 24, 821 (1962).

16. S.K. Verma and R.P. Agarwal, J. prakt. Chem., (in press)

17. A. Rosenheim and H. Mong, Z. anorg. Chem., <u>148</u>, 25, 34 (1925).

18. P.K. Bhattacharya and S.N. Banerji, Z. anorg. allgem. Chem., <u>315</u>, 118 (1962)

19. R.Trujillo and J. Cabrera, Anales real Soc. espan. fis. yquim., <u>52B</u>, 589 (1956).

20. S.Ya. Shnaiderman, Zh. Neorgan. Khim., <u>8</u>, 464 (1963).

21. R. Tobias, J. Chem. Educ.,<u>35</u>, 592 (1958).

22. F.J.C. Rossotti and H.S. Rossotti, Acta Chem.Scand., <u>9</u>, 1177 (1955).

23. G.A. Heureux and A.F. Martell, J. Inorg. Nucl.Chem., <u>28</u>, 481 (1966).

24. Ionic Equilibrium, Addison-Wesley Publishing Company, INC (1964) p.80 .

25. S.Chaberek, Jr., R.L. Gustafson, R.C. Courtney and A.E. Martell, J. Am. Chem. Soc., <u>81</u> , 515 (1959).

26. S.M. F. Rehman and A.U. Malik, J. prakt. Chem; <u>21</u> , 109 (1963).

27. G. Schwarzenbach, R.Gut and G. Anderegg, Helv.Chim. Acta, <u>37</u>, 937 (1954).

28. G.A. Barbieri, Atti Accad. Lincei, <u>23</u>(2), 47(1914).

29. G.A. Barbieri,Chem. Zentr., <u>2</u>, 1427 (1914).

30. B.C. Kar and S.K. Roy, J. Indian Chem. Soc., <u>25</u>, 397 (1948).

31. S.Ahrland, Acta Chem.Scand., <u>7</u> , 485 (1953).

32. C.H. Wirguim and D. Friedman, Bull. soc. chim. France, 970 (1958).

33. R.P. Bell and G.M. Waind, J. Chem. Soc., 2357 (1951).

34. R.K. Cannan and A. Kibrick, J. Am. Chem. Soc., 60, 2314 (1938).

35. P.K. Bhattacharya, M.C. Saxena and S.N. Banerji, J. Indian Chem. Soc., 39, 240 (1962).

36. J. B. Conn, U.S. Patent 3,076, 830 (Feb.5, 1963); Chem. Abstr., 58, 12375 (1963).

37. L.P. Ducret., Ann. Chim. (Paris), 6 , 705 (1951).

38. C.K. Jørgensen., Acta Chem. Scand., 11, 73 (1957).

39. B.C. Kar, J. Indian Chem. Soc., 25, 267 (1948).

40. B.C. Kar and S.K. Roy., J. Indian Chem. Soc., 25, 397 (1948).

41. A. Rosenheim and H. Mong., Z. anorg. Chem., 148, 25 (1925).

42. A. Rosenheim and H. Mong, ibid., 148, 34 (1925).

43. M. Ziegler, Naturwiss., 46, 492 (1959).

44. V.L. Zolotavin and N.I. Sintsov., J. Gen. Chem. USSR, 26, 33 (1956).

45. V.L. Zolotavin and T.A. Soboleva., Tr. Ural'sk. Politekhn. Inst., No.57, 50 (1956).

46. V.L. Zolotarin and T.A. Soboleva., Zh. Fiz. Khim., 28, 1950 (1954).

47. V.K. Zolotukhin., Zh. Prikl. Khim., 10, 1651 (1937)

48. I. Feldman, J.R. Hvill and W.F. Neuman, J. Am.Chem. Soc., 76, 4726 (1954).

49. J. Selbin., Chem. Rev. 65, 153 (1965).

50. J.C. Speakman, J. Chem. Soc, 855 (1940).

51. S. Chaberek and A.E. Martell, J.Am. Chem.Soc., 74, 5052 (1952).

52. R. Trujillo and F. Brito, Anales real soc. espan.fis. y quim., 53B, 249 (1957).

53. R. Riccardi and P. Franzosini, Boll. Sci. Fac.Chim. Ind., Bolgona, 15, 25 (1957).

54. A.E. Martell, S. Chaberek, JR., R.C. Courtney, S. Westerback and H. Hyytiainen, J. Am. Chem. Soc., 79, 3036 (1957).

55. J. Selbin and L.H. Holmes, J. Inorg. Nucl. Chem., 24, 1111 (1962).

56. G.E. Mont and A.E. Martell, J. Am. Chem. Soc., 88, 1387(1966).

57. Z.Fur, Anal. Chem., 189, 421 (1962).

58. G.L. Kelley and J.B. Conant, Ind. Eng. Chem., 8, 719(1916).

59. G.L. Kelley, J.A. Willey, R.T.Bohn and W.C. Wright, Ind. Eng. Chem., 11, 632 (1919).

60. N.H. Furman, J.Am. Chem. Soc., 50, 1675 (1928).

61. L.E. Stout and G.C. Whitaker, Ind.Eng.Chem., 20, 210 (1928).

62. O.E.A. Jackson, Thesis, London University, 1934.

63. H.T.S. Britton, J. Chem. Soc., 1842 (1934).

64. G. Jones and W.A. Ray, J. Am. Chem. Soc., 66, 1571 (1955).

65. G.A. Dean and J.F. Herringshaw, Talanta, 10 , 793 (1963).

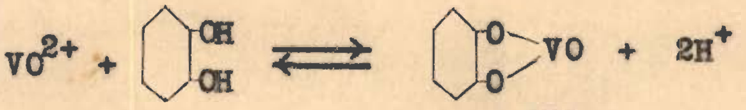
SUMMARY

A
Summary of the
CONCLUSIONS
from
the present investigations
NORMAL AND MIXED LIGAND CHELATES OF OXOVANADIUM (IV) WITH SOME OXYGEN AND NITROGEN DONOR LIGANDS

SIMPLE CHELATES OF OXOVANADIUM(IV)

Oxovanadium (IV) Chelates of Catechol.

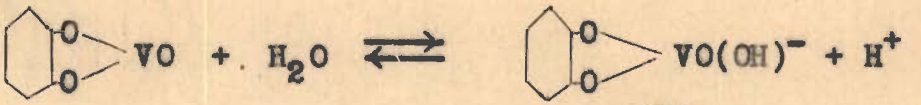
Potentiometric titration of vanadyl sulphate with KOH in the presence of an equimolar concentration of catechol showed a sharp inflexion at m = 3, where 'm' represents moles of KOH added per mole of the metal ion. For the reaction



... (i)

(I)

two moles of KOH per mole of the metal ion are required. Consumption of an extra one mole of KOH to the inflexion point and non-precipitation of metal hydroxide in the system indicated the occurrence of a reaction of the type:



...(ii)

(II)

The failure to obtain a titration break at m = 2 indicated that the reactions (i) and (ii) overlap.

By comparing the potentiometric curves obtained over a four-fold concentration range of the metal chelate, it has been concluded that the chelate species do not polymerize under the experimental conditions employed.

In order to verify the above conclusions, a mathematical analysis of the potentiometric data was carried out. Calculation of the equilibrium constant of reaction (i) ($K_1 = [VOA][H^+]^{?} / [VO^{2+}][H_2A]$) gave constant values up to pH of about four, above which a gradual fall in the values of pK_1 was observed indicating the commencement of the hydrolytic reaction (ii) in the system. The values of pK_1 were found to be independent of concentration of the metal chelate.

After determining the equilibrium constant of reaction (i), formation constant of the chelate ($K_{MA} = [VOA] / [VO^{2+}][A^{2-}]$) was determined with the help of the expression

$$K_{MA} = \frac{K_1}{K_{a_1} K_{a_2}}$$

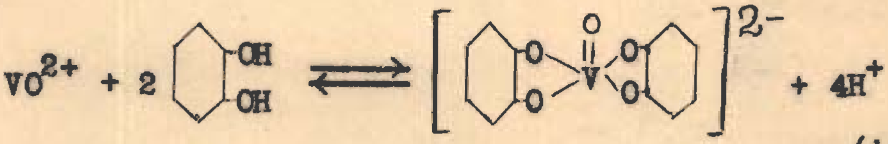
where K_{a_1} and K_{a_2} represent the first and the second dissociation constants of the ligand.

In view of a gradual fall in the values of pK_1 observed above pH values of about four, attempts were made to analyse the data by taking into account the reaction (ii). The hydrolysis constant of the chelate ($K_h = [VO(OH)A^-][H^+] / [VOA]$)and equilibrium constant ($K_H = [VO(OH)A^-][H^+]^3 / [VO^{2+}][H_2A]$) were calculated with the help of the material balance equations. Constant values of these constants obtained from various points of the curves showed that the species (I) and (II) are the only chelate species formed in the system. The concentration independence of the hydrolysis constant showed that the monohydroxo chelate species(II)also do not polymerize under the experimental conditions.

By the use of the equilibrium constants of the reactions and equations for the material balance, distribution of the chelate species (I) and (II) as a function of pH of the reaction mixture could be determined.

Interaction of one mole of vanadyl sulphate with two moles of catechol.

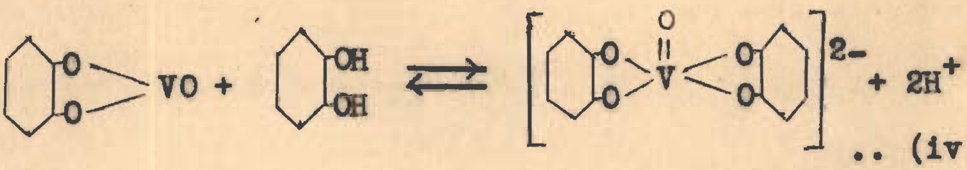
Potentiometric titration of vanadyl sulphate with KOH in the presence of two moles of catechol showed a sharp inflexion at m = 4. This is in accord with the reaction



... (iii)

In the initial stages (pH < 4), however, the titration data were in accord with the liberation of two hydrogen ions per mole of vanadyl ion indicating the formation of the normal 1:1 chelate (I) in the system.

A gradual fall in the values of pK_1, calculated above pH values of four, has been explained on the basis of the interaction of the 1:1 chelate with another mole of the ligand:



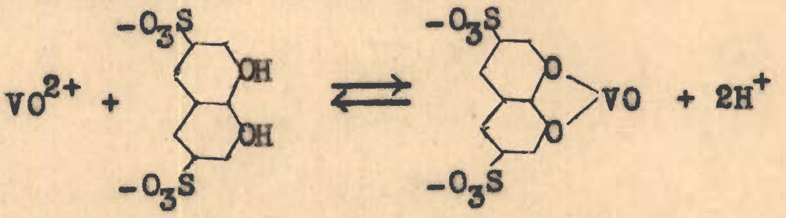
.. (iv)

Equilibrium constant of the above reaction was determined by taking into account the hydrolytic reaction (iii), since hydrolysis of the 1:1 complex occurred in the same pH range in which the formation of 1:2 complex took place.

Having determined the equilibrium constants for the reactions , distribution of the various chelate species as a function of pH of the solution could be determined.

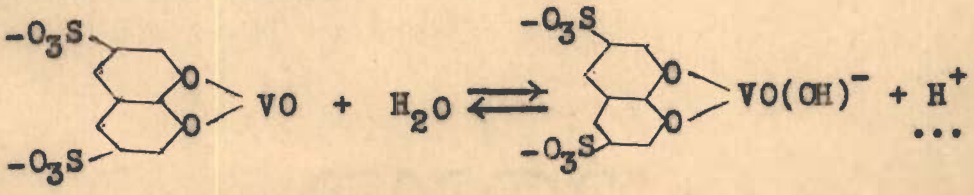
Oxovanadium (IV) Chelates of Chromotropic Acid

Potentiometric curve for the titration of an equimolar mixture of vanadyl sulphate and chromotropic acid (1, 8-dihydroxynaphthalene 3, 6-disulphonate, DNS) exhibited inflexions at m = 2 and 3. The first inflexion point is in accord with the reaction



... (i)

The second inflexion point has been explained on the basis of the reaction



... (ii)

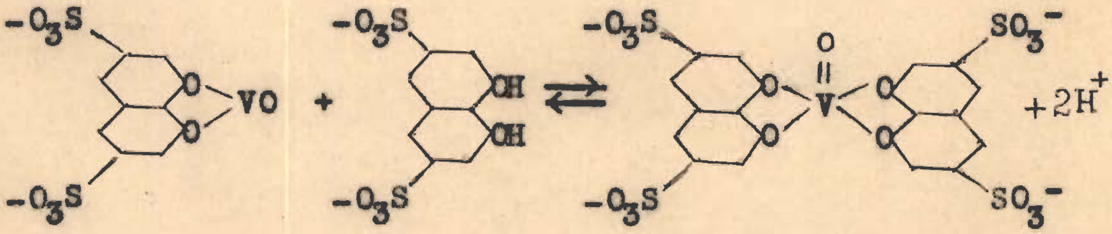
Constant values of the equilibrium constant K_1 of reaction (i), calculated in the range $0 < m < 2$ and the hydrolysis constant K_h of the chelate (i.e. equilibrium constant of reaction (ii), calculated from various points on the upper buffer region of the curve, supported the above conclusions.

After calculating the equilibrium constant of reaction (i) formation constant of the chelate was determined.

Interaction of 1:1 VO-DNS Chelate with another Mole of DNS.

The curve obtained by the titration of a 1:2 mixture of vanadyl sulphate and DNS showed inflexion points at m = 2 and 4. The first inflexion point corresponded to the formation of 1:1 chelate (reaction i).

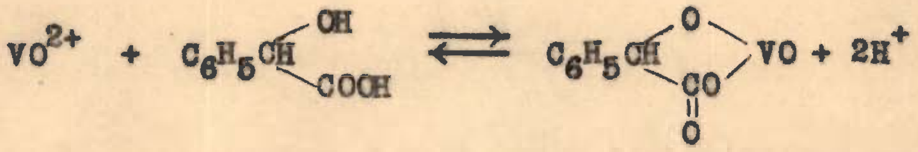
By a mathematical treatment of the data of the upper buffer region of the curve (i.e. m = 2-4), interaction of the 1:1 complex with another mole of the ligand has been shown to occur. The reaction may be represented as



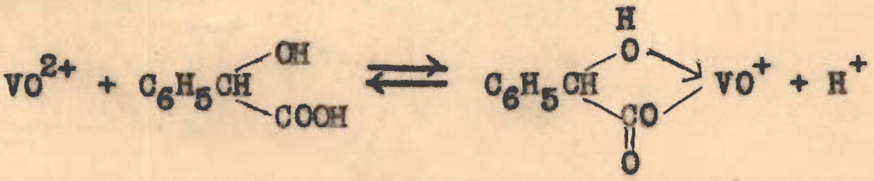
Formation constant of the 1:2 complex has been determined.

Oxovanadium (IV) Chelates of Mandelic and Lactic Acids.

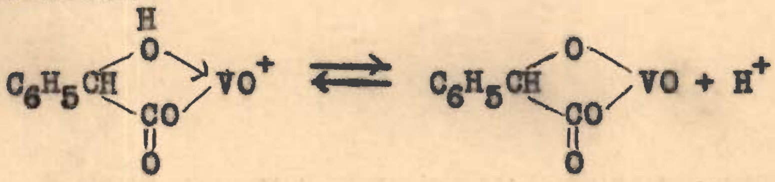
Potentiometric titration of a 1:1 mixture of vanadyl sulphate and mandelic acid (or lactic acid) yielded a curve with a slight inflexion at m = 2 followed by a sharp inflexion at about m = 3. The first inflexion point is in accord with the reaction :



In the initial stages of the titration, however, the reaction has been shown to proceed as



Calculation of formation constant (K_{MHA}) of the protonated complex $VOHA^+$ (i.e. equilibrium constant of reaction $VO^{2+} + HA^- \rightleftarrows VOHA^+$) gave constant values of log K_{MHA} up to about m = 0.2, above which a gradual rise in the values of log K_{MHA} was observed indicating the occurrence of the reaction

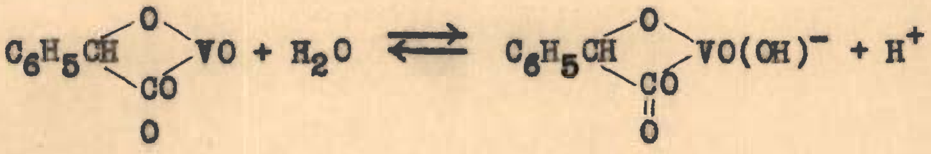


Above 'm' values of 0.2, therefore, attempts were made to analyse the data by taking into account the acid dissociation of the complex.

The success achieved in obtaining constant values of equilibrium constant of the reaction ($K = [VOA][H^+] / [VOHA^+]$) supported the above conclusions, i.e., formation of the chelate VOA takes place through an intermediate formation of a protonated complex. The concentration independence of the reaction constants showed that the chelate species do not polymerize under the experimental conditions employed.

Potentiometric curve obtained by the titration of a 1:2 mixture of vanadyl sulphate and mandelic acid (or lactic acid) was similar to the calculated curve obtained by the addition of abscissae of separate curves for mandelic acid and the 1:1 vanadyl sulphate-mandelic acid system, indicating that the interaction of 1:1 metal chelate with another mole of the ligand does not occur in the system.

The buffer region in the titration curves between m = 2 and m =3 has been explained on the basis of the reaction :



Oxovanadium (IV) Chelates of Tartaric and Malic Acids.

Titration of an equimolar mixture of vanadyl sulphate and tartaric acid (H_4A) showed inflexion points at m = 3 and m = 4. The first inflexion point has been interpreted on the basis of the reaction

$$VO^{2+} + H_4A \rightleftharpoons VOHA^{-} + 3H^{+}$$

The liberation of three hydrogen ions per mole of vanadyl ion in the system has been verified by a mathematical analysis of the potentiometric data.

The occurrence of a buffer region between m = 3 and m = 4 in the titration curves indicated that either hydrogen atom of the second hydroxy group of the ligand dissociates and the tartrate ion acts as a quadridentate ligand or a water molecule of the vanadyl ion undergoes dissociation to give one (or possibly a mixture) of the following species :

$$VOA^{2-} \quad , \quad VO(OH)HA^{2-}$$

Formation of the VOA^{2-} type of chelate species obtained support from the work of Jorgensen and Selbin. [Acta Chem. Scand., <u>11</u>, 73(1957); Chem. Rev. <u>65</u>, 153(1965)]. In the range m = 3-4, therefore, the reaction has been represented as

$$VOHA^{-} \rightleftharpoons VOA^{2-} + H^{+}$$

Determination of equilibrium constants of the reactions showed that the values of the constants were independent of concentration indicating that the chelate species do not polymerize under the experimental conditions.

The potentiometric titration for a solution containing 1:2 molar ratio of vanadyl sulphate to tartaric acid corresponded to a curve which would be predicted for a mixture of the 1:1 chelate and the free ligand (one mole). Formation of a 1:2 complex, therefore, did not appear to take place.

Vanadyl-Malate Chelate

Like the vanadyl-tartrate system, in this case also, the titration of an equimolar mixture of vanadyl sulphate and malic acid (H_3A) yielded a curve with inflexions at m = 3 and 4. The first inflexion point indicated the reaction :

$$VO^{2+} + H_3A \rightleftharpoons VOA^- + 3H^+ \qquad \text{... (i)}$$

However, calculations based on the above reaction did not give constant values of the equilibrium constant ($K = [VOA^-][H^+]^3 / [VO^{2+}][H_3A]$). A gradual rise in the values of pK was observed indicating that the concentratimn of hydrogen ions in the system was less than that would be on the basis of reaction (i). Attempts were, therefore, made to treat the titration data on the basis of the formation of VOA^- in two overlapping steps:

$$VO^{2+} + H_3A \rightleftharpoons VOHA + 2H^+ \qquad \text{... (ii)}$$

and

$$VOHA \rightleftharpoons VOA^- + H^+ \qquad \text{... (iii)}$$

In the initial stages of the titration ($m < 1.1$), the potentiometric data were in accord with the reaction (ii). A gradual fall in the values of pK_1 ($K_1 = [VOHA][H^+]^2 / [VO^{2+}][H_3A]$), calculated above 'm' values of about 1.1, indicated the occurrence of reaction (iii) in the system. This fact and the success achieved in obtaining constant values of the equilibrium constant of reaction (iii) showed that the chelate VOA^- is formed through the formation of the protonated complex VOHA.

The buffer region between m = 3 and m = 4 in the titration curves has been explained on the basis of the reaction :

$$VOA^- + H_2O \rightleftharpoons VO(OH)A^- + H^+$$

The potentiometric curve obtained by the titration of vanadyl sulphate in the presence of two moles of malic acid and did not give any indication for the combination of the 1:1 complex with another mole of the ligand.

Oxovanadium (IV) Chelates of Iminodiacetic Acid (IMDA)

Analysis of the potentiometric curves obtained by the titration of vanadyl sulphate in the presence of an increasing molar concentration of IMDA showed that in the pH range 2.5 - 4.5, a normal 1:1 complex is formed in accordance with the reaction

$$VO^{2+} + H_2A \rightleftharpoons VOA + 2H^+$$

and a monohydroxo derivative resulted in the pH range

4.5 - 5.5.

$$VOA + H_2O \rightleftharpoons VO(OH)A^- + H^+$$

In this case also the data did not give any indication for the combination of the 1:1 complex with another mole of the ligand.

In general, the data obtained in the study of simple vanadyl chelates indicated that they prefer combination with hydroxyl ions to a second mole of ligand. The only exceptions to this behaviour are the very basic anions of catechol and chromotropic acid which can compete with the hydroxyl ion to form stable 1:2 chelates.

Interaction of Vanadyl Sulphate with o-Phenanthroline and 2,2'-dipyridyl.

In both cases, in the initial stages (pH < 3) of the titration of vanadyl sulphate in the presence of an equimolar concentration of the ligand, the reaction

$$VO^{2+} + HL^+ \rightleftharpoons VOL^{2+} + H^+$$

(where HL^+ represents protonated form of the ligand) has been shown to occur. As pH of the solution is raised above a value of about three, appreciable hydrolysis of the chelate sets in making the solution more acidic than it would be in the absence of hydrolytic effects in the system. In the pH range 3-3.6, the hydrolysis occurs as:

$$VOL^{2+} + H_2O \rightleftharpoons VO(OH)L^+ + H^+$$

Above pH values of about 3.6, a gradual fall in the values of the hydrolysis constant was observed indicating further hydrolysis of the chelate. Since the object of this study was to determine equilibrium constants of the reactions which could be used in the determination of formation constants of the mixed ligand chelates containing o-phenanthroline and 2,2'-dipyridyl as primary ligands, analysis of the data of higher pH values was not considered necessary.

The equilibrium constants for the simple chelate systems studied in the present research are listed in table I.

<u>Table I</u>

Ligand	Reaction	-log K
Catechol (H_2A)	$VO^{2+} + H_2A \rightleftarrows VOA + 2H^+$	5.85
	$VO^{2+} + A^{2-} \rightleftarrows VOA$	15.28*
	$VOA + H_2O \rightleftarrows VO(OH)A^- + H^+$	5.10
	$VO^{2+} + H_2A + H_2O \rightleftarrows VO(OH)A^- + 3H^+$	10.97
	$VOA + H_2A \rightleftarrows VOA_2^{2-} + 2H^+$	8.11
	$VOA + A^{2-} \rightleftarrows VOA_2^{2-}$	13.02*
	$VO^{2+} + 2A^{2-} \rightleftarrows VOA_2^{2-}$	28.30*
Chromotropic acid (H_2A^{2-})	$VO^{2+} + H_2A^{2-} \rightleftarrows VOA^{2-} + 2H^+$	4.05
	$VO^{2+} + A^{4-} \rightleftarrows VOA^{2-}$	16.89*
	$VOA^{2-} + H_2O \rightleftarrows VO(OH)A^{3-} + H^+$	5.64
	$VOA^{2-} + H_2A^{2-} \rightleftarrows VOA_2^{6-} + 2H^+$	7.85
	$VOA^{2-} + A^{4-} \rightleftarrows VOA_2^{6-}$	13.09*

Ligand	Reaction	-log K
Mandelic acid (H_2A)	$VO^{2+} + HA^- \rightleftarrows VOHA^+$	3.45*
	$VOHA^+ \rightleftarrows VOA + H^+$	3.64
Lactic acid (H_2A)	$VO^{2+} + HA^- \rightleftarrows VOHA^+$	3.18*
	$VOHA^+ \rightleftarrows VOA + H^+$	3.78
Tartaric acid (H_4A)	$VO^{2+} + H_4A \rightleftarrows VOHA^- + 3H^+$	5.56
	$VOHA^- \rightleftarrows VOA^{2-} + H^+$	6.57
Malic acid (H_3A)	$VO^{2+} + H_3A \rightleftarrows VOHA + 2H^+$	3.34
	$VO^{2+} + HA^{2-} \rightleftarrows VOHA$	4.92*
	$VOHA \rightleftarrows VOA^- + H^+$	7.57
	$VOA^- + H_2O \rightleftarrows VO(OH)A^{2-} + H^+$	6.55
Iminodiacetic acid (H_2A)	$VO^{2+} + H_2A \rightleftarrows VOA + 2H^+$	2.99
	$VO^{2+} + A^{2-} \rightleftarrows VOA$	8.80*
	$VOA + H_2O \rightleftarrows VO(OH)A^- + H^+$	4.98
o-phenantholine (HL^+)	$VO^{2+} + L \rightleftarrows VOL^{2+}$	5.88*
	$VO^{2+} + HL^+ + H_2O \rightleftarrows VO(OH)L^+ + 2H^+$	3.04
2,2'-dipyridyl (HL^+)	$VO^{2+} + L \rightleftarrows VOL^{2+}$	5.08*
	$VO^{2+} + HL^+ + H_2O \rightleftarrows VO(OH)L^+ + 2H^+$	3.39

* log K values.

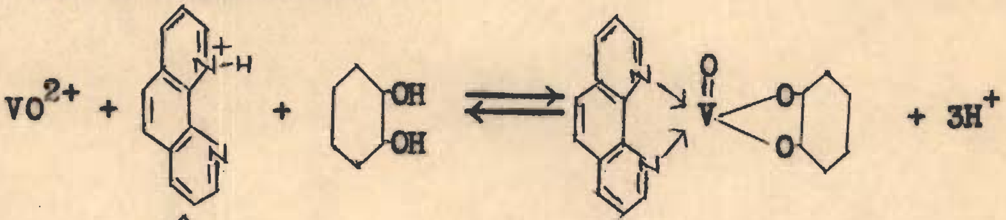
MIXED LIGAND CHELATES OF OXOVANADIUM (IV)

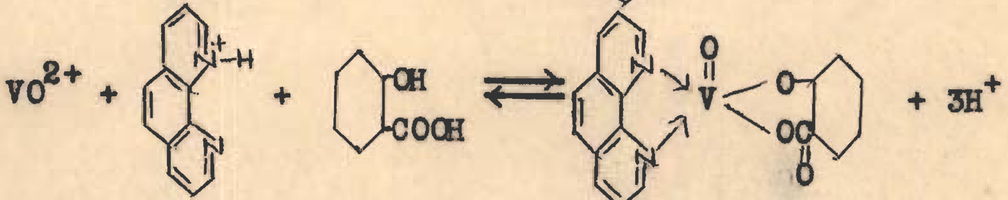
Potentiometric titration of vanadyl sulphate in the presence of an equimolar concentration of o-phenanthroline hydrochloride and a secondary ligand (catechol, tiron, chromotropic acid, salicylic acid, mandelic acid, lactic acid and oxalic acid) showed a sharp inflexion at m = 3. By a mathematical analysis of the titration data, formation of mixed ligand chelates has been shown to occur in two overlapping steps

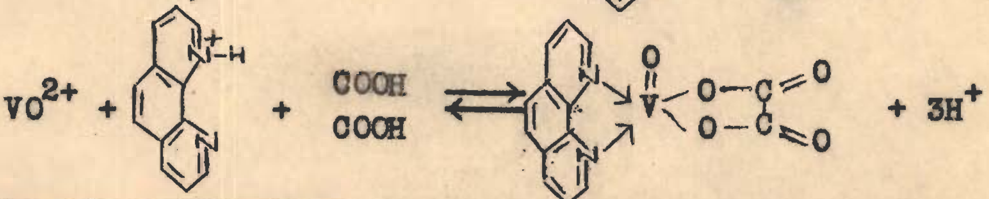
$$VO^{2+} + HL^{+} \rightleftharpoons VOL^{2+} + H^{+}$$

$$VOL^{2+} + H_2A \rightleftharpoons VOLA + 2H^{+}$$

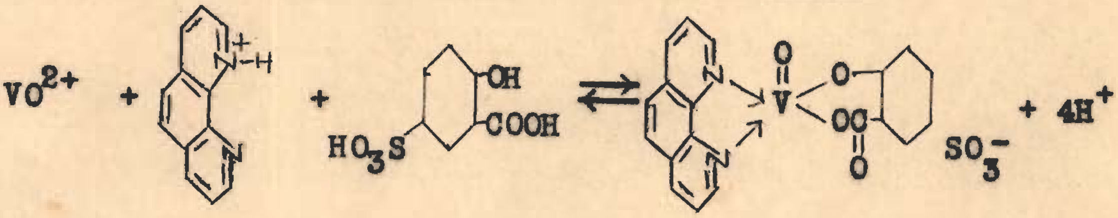
In the systems involving catechol, salicylic acid, oxalic acid as secondary ligands, for example, the overall reactions may be represented as:







In the mixed ligand system containing 5-sulphosalicylic acid, the titration curve exhibited an inflexion point at m = 4. This is in accord with the reaction



The potentiometric curve for the titration of the 1:1:1 VO-phen-phthalic acid system showed a poorly defined sloping inflexion. In this case, the titration data indicated the formation of a weak chelate.

Titrations of mixed ligand systems containing 2,2'-dipyridyl as a primary ligand corresponded to curves similar to those obtained for the analogous VO-phen-secd. ligand systems. On account of the presence of two moles of hydrochloric acid in solution of 2,2'-dipyridyl, the titration curves for the 1:1:1 VO-dipy-secd.ligand systems exhibited an inflexion point at m = 4. In these systems also, formation of mixed ligand chelates takes place in two overlapping steps.

The equilibrium constants of the reactions for the formation of mixed ligand chelates are listed in table II.

Table II

Primary Ligand : o- Phenanthroline

Secondary ligand	Reaction	-log K
Catechol (H_2A)	$VOL^{2+} + H_2A \rightleftharpoons VOLA + 2H^+$	4.44
	$VO^{2+} + HL^+ + H_2A \rightleftharpoons VOLA + 3H^+$	3.56

Secondary ligand	Reaction	-log K
	$VOL^{2+} + A^{2-} \rightleftarrows VOLA$	16.69*
	$VO^{2+} + L + A^{2-} \rightleftarrows VOLA$	22.57*
Tiron (H_2A^{2-})	$VOL^{2+} + H_2A^{2-} \rightleftarrows VOLA^{2-} + 2H^+$	2.85
	$VO^{2+} + HL^+ + H_2A^{2} \rightleftarrows VOLA^{2-} + 3H^+$	1.97
	$VOL^{2+} + A^{4-} \rightleftarrows VOLA^{2-}$	17.19*
	$VO^{2+} + L + A^{4-} \rightleftarrows VOLA^{2-}$	23.07*
Chromotropic Acid(H_2A^{2-})	$VOL^{2+} + H_2A^{2-} \rightleftarrows VOLA^{2-} + 2H^+$	2.85
	$VO^{2+} + HL^+ + H_2A^{2} \rightleftarrows VOLA^{2-} + 3H^+$	1.97
	$VOL^{2+} + A^{4-} \rightleftarrows VOLA^{2-}$	18.09*
	$VO^{2+} + L + A^{4-} \rightleftarrows VOLA^{2-}$	23.97*
Salicylic acid (H_2A)	$VOL^{2+} + A^{2-} \rightleftarrows VOLA$	13.34*
	$VO^{2+} + L + A^{2-} \rightleftarrows VOLA$	19.22*
Sulphosalicylic acid (H_3A)	$VOL^{2+} + A^{3-} \rightleftarrows VOLA^-$	11.75*
	$VO^{2+} + L + A^{3-} \rightleftarrows VOLA^-$	17.63*
Mandelic acid (H_2A)	$VOL^{2+} + H_2A \rightleftarrows VOLA + 2H^+$	precipitate almost in the begining.
Lactic acid (H_2A)	$VOL^{2+} + H_2A \rightleftarrows VOLA + 2H^+$	3.99
	$VO^{2+} + HL^+ + H_2A \rightleftarrows VOLA + 3H^+$	3.11
Oxalic acid (H_2A)	$VOL^{2+} + A^{2-} \rightleftarrows VOLA$	5.34*
	$VO^{2+} + L + A^{2-} \rightleftarrows VOLA$	11.22*

LIST OF PUBLICATIONS

1. Mixed-ligand chelates of oxovanadium (IV) with o-phenanthroline and some dihydric phenolic compounds. J. Less-Common Metals, 12, 269 (1967)

2. Equilibrium studies of the interaction of Vanadyl ion with catechol. Bull. Chem. Soc. Japan, (In press).

3. Equilibrium studies of the interaction of vanadyl ion with tartaric and malic acids. J. prakt. Chem. (communicated).

4. Mixed ligand chelates of Oxovanadium (IV) with o-phenanthroline and some carboxylic acids. Z.anorg. Chem.(Communicated).

5. Mixed ligand chelates of oxovanadium (IV) with 2,2'-dipyridyl and some oxygen donor ligand. Bull. Chem. Soc. Japan. (communicated).

6. Equilibrium studies of the interaction of vanadyl ion with mandelic and lactic acids. J. Indian Chem. Soc. (communicated)

7. Interaction of oxovanadium (IV) with iminodiacetic acid. Z. anorg. Chem. (communicated).

8. Composition and stability of chromotropic acid chelates of oxovanadium (IV). Z. anorg. Chem. (communicated).

9. Stability of Chromium chelates of 8-quinolinol - 5- sulphonate, J. Indian Chem. Soc. 43, No.3, 1966.