

pH-Metric Studies on the Binary and Ternary Complexes of Oxovanadium(IV)

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With 4 Figures

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The interaction of oxovanadium(IV) with some hydroxy acids, salicylic (*SA*), 5-sulphosalicylic (*SSA*) and 8-hydroxyquinoline-5-sulphonic (*HQSA*) acids, has been studied potentiometrically. Further, pH-metric studies of the ternary systems, VO^{2+} —*HQSA*-dicarboxylic or hydroxy acids (where dicarboxylic acids = phthalic and maleic acids and hydroxy acids = *SA* and *SSA*) have been carried out and the formation of 1 : 1 : 1 mixed complexes inferred from the potentiometric curves. The equilibrium, chelate formation and hydrolysis constants have been calculated in the case of binary systems. The ternary complexes have been found to be more stable as indicated by their formation constants.

The study of mixed-ligand complexes is now receiving considerable attention¹⁻⁴. Solution stabilities of mixed-ligand systems, where both the ligands simultaneously combine with metal ion, have been studied by different methods. During the course of the present investigations, pH-metric studies on the interaction of oxovanadium(IV) with *SA*, *SSA* and *HQSA* and with *HQSA* in presence of *SA*, *SSA*, phthalic and maleic acids have been carried out. The formation of 1 : 1 : 1 mixed-ligand complexes has been shown in the ternary systems studied.

For calculating the equilibrium constants of 1 : 1 : 1 mixed-ligand complexes, the values of the constants of the reactions associated with the formation of 1 : 1 binary chelates were required. Although, *Mont* and *Martell*⁵ have studied the binary systems with *SA*, *SSA* and *HQSA* potentiometrically and calculated the formation constants of the 1 : 1 chelates formed, they have reported that the potentiometric titration of a 1 : 1 molar ratio mixture of *SA* and VO^{2+} gave generally unsatisfactory results. In the 1 : 1, VO^{2+} —*HQSA* system also constant values of the formation constants have been obtained in the region

of $m = 0.2$ to 1.0 only. They have not, however, accounted for the formation of hydroxo complexes while calculating the stability constants of the resulting complexes. These systems, therefore, were reinvestigated and the results are presented in this paper.

Experimental

A stock solution of vanadyl sulphate (BDH) was prepared in doubly distilled water and standardized as described in an earlier communication⁶. Phthalic (BDH), maleic (Burgoyne) and salicylic (AnalaR BDH) solutions were prepared by direct weighing and standardized potentiometrically against a standard KOH solution. 5-Sulphosalicylic acid (AnalaR Riedel) was dissolved as monopotassium salt. 8-Hydroxy-quinoline-5-sulphonic acid (Kodak) was first recrystallized with doubly distilled water and then weighed out directly for each investigation on account of its low solubility. All the ligands were used in the diprotonated form. The pH-titrations were carried out at 30 ± 0.5 °C with a Cambridge pH-meter standardized against a 0.05M-solution of potassium hydrogen phthalate (AnalaR BDH).

The following pH-metric titrations were carried out:

1. 10 ml (0.025M) ligand.
2. 10 ml (0.025M) ligand in presence of 10 ml (0.025M) vanadyl sulphate [VO^{2+} : Ligand, 1 : 1].
3. 10 ml (0.025M) each of primary and secondary ligands in presence of 10 ml (0.025M) vanadyl sulphate [VO^{2+} : Primary ligand : Secondary ligand, 1 : 1 : 1].

The ionic strength of all the solutions was kept constant ($\mu = 0.1 \text{KNO}_3$) by adding 5 ml of 1M- KNO_3 to each solution and using low concentrations of the ligand and the metal ion. The final volume was raised to 50 ml by mixing with a requisite volume of doubly distilled water before each titration.

Results and Discussion

Curve 1, Fig. 1 and curve 3, Figs. 1, 2, 3, and 4 represent the potentiometric titrations of 8-hydroxyquinoline-5-sulphonic, phthalic, maleic, salicylic and 5-sulphosalicylic acids respectively with 0.1M-KOH. The acid dissociation constants (k_1 and k_2) of phthalic acid were calculated using *Noyes* method⁷ and those of maleic, salicylic, 5-sulphosalicylic and 8-hydroxyquinoline-5-sulphonic acid by the method of *Chaberek* and *Martell*⁸. The values are presented in Table 1.

Curve 2, Fig. 1, and curve 4, Figs. 1, 2, 3, and 4 represent the potentiometric titrations of solutions containing equimolar quantities of vanadyl sulphate and 8-hydroxyquinoline-5-sulphonic, phthalic, maleic, salicylic or 5-sulphosalicylic acids resp. The calculation of equilibrium, chelate formation and hydrolysis constants for the systems, VO^{2+} —phthalic acid and VO^{2+} —maleic acid have been reported in an earlier communication⁹. In the case of 1:1 VO^{2+} —*HQSA* and VO^{2+} —*SSA*

systems, two inflections at $m = 2$ and 3 (where m represents the moles of base added per mole of metal ion) are indicated. However, in the case of $1 : 1 \text{ VO}^{2+} - \text{SA}$ system only one inflection at $m \approx 3$ occurs. The poor inflections at $m = 2$ in the case of $\text{VO}^{2+} - \text{HQSA}$ and

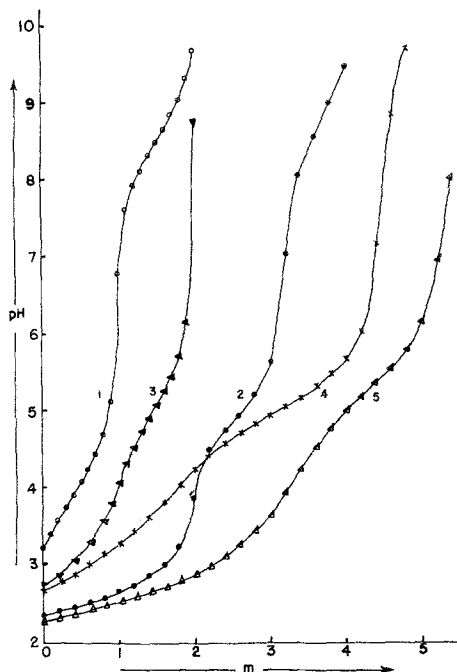


Fig. 1. Potentiometric titration curves of the normal and mixed-ligand chelate systems of oxovanadium(IV) having 8-hydroxyquinoline-5-sulphonic (*HQSA*) and phthalic acids as ligands: Curve I, *HQSA*; 2, 1 : 1 $\text{VO(IV)} - \text{HQSA}$; 3, phthalic acid; 4, 1 : 1 $\text{VO(IV)} - \text{phthalic acid}$; 5, 1 : 1 : 1 $\text{VO(IV)} - \text{HQSA} - \text{phthalic acid}$. m = moles of base added per mole of metal ion

Table 1. *Dissociation Constants of the Ligands*

Ligand	pK_1	pK_2
Phthalic acid	2.89 ± 0.02	5.04 ± 0.01
Maleic acid	2.23 ± 0.02	5.97 ± 0.04
<i>SA</i>	2.99 ± 0.02	13.60^{12}
<i>SSA</i>	2.68 ± 0.06	11.42 ± 0.03
<i>HQSA</i>	4.06 ± 0.04	8.49 ± 0.04

VO^{2+} — SSA systems and no inflection at this stage in the VO^{2+} — SA system probably indicate that the formation of the 1:1 chelate and its hydrolysis overlap. In the initial stages, the reaction may be represented as:

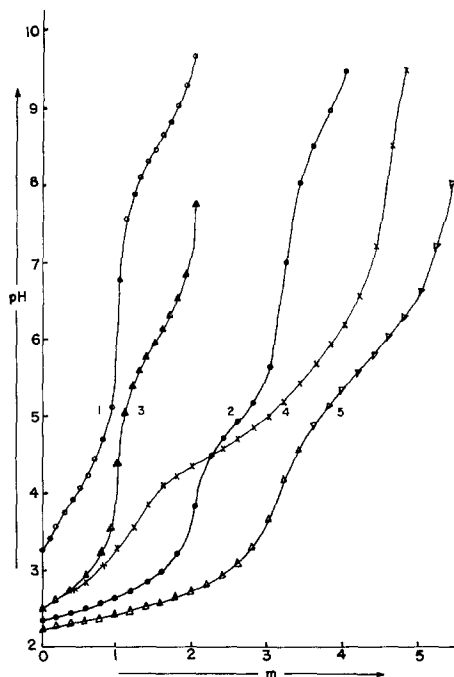
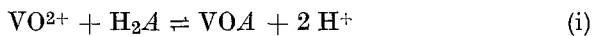


Fig. 2. Potentiometric titration curves of the normal and mixed-ligand chelate systems of oxovanadium(IV) having 8-hydroxyquinoline-5-sulphonic (HQSA) and maleic acids as ligands: Curve I, HQSA ; 2, 1:1 $\text{VO(IV)}-\text{HQSA}$; 3, maleic acid; 4, 1:1 VO(IV) -maleic acid; 5, 1:1:1 $\text{VO(IV)}-\text{HQSA}$ maleic acid. m = moles of base added per mole of metal ion

where H_2A represents the hydroxy acids used. The equilibrium constant, K_1 of the reaction may be defined as:

$$K_1 = \frac{[\text{VOA}][\text{H}^+]^2}{[\text{VO}^{2+}][\text{H}_2\text{A}]} \quad (1)$$

The formation constant, K_{MA} of the chelate may be given by:

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

If T_M and T_A represent the total concentrations of all the metal and ligand species respectively and T_{OH} be the concentration of the base added to the reaction mixture during the titration, the following

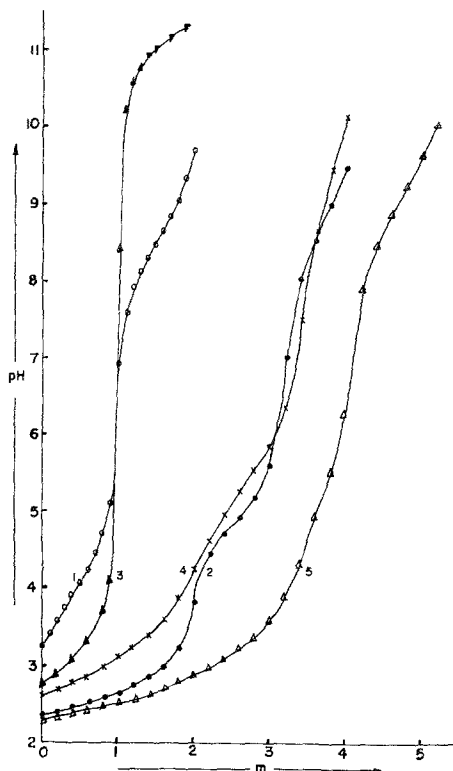


Fig. 3. Potentiometric titration curves of the normal and mixed-ligand chelate systems of oxovanadium(IV) having 8-hydroxyquinoline-5-sulphonic (*HQSA*) and salicylic (*SA*) acids as ligands: Curve I, *HQSA*; 2, 1:1 $VO(IV)$ -*HQSA*; 3, *SA*; 4, $VO(IV)$ -*SA*; 5, 1:1:1 $VO(IV)$ -*HQSA*-*SA*. m = moles of base added per mole of metal ion

equations for maintaining the material balance, are obtained:

$$T_M = [VO^{2+}] + [VOA] \quad (3)$$

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

$$T_A = [H_2A] + [HA^-] + [VOA] \quad (5)$$

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

other species present in the reaction mixture. From the above relations, it may be shown that:

$$[\text{H}_2\text{A}] = \frac{(2T_M - T_{\text{OH}} - [\text{H}^+])}{\left(2 + \frac{k_1}{[\text{H}^+]}\right)} \quad (6)$$

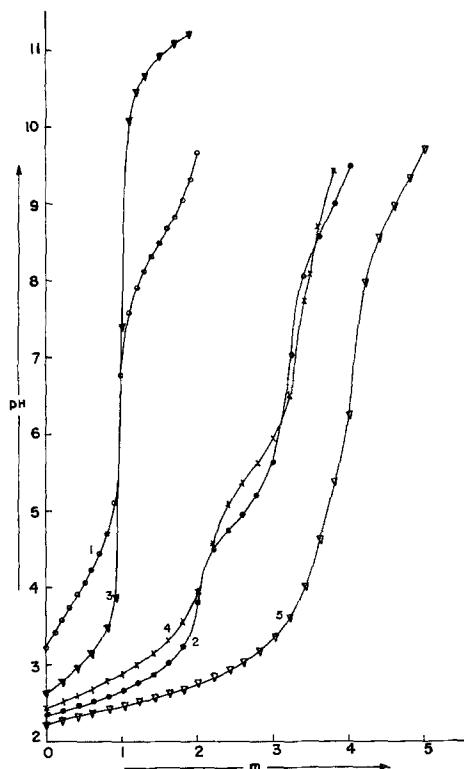


Fig. 4. Potentiometric titration curves of the normal and mixed-ligand chelate systems of oxovanadium(IV) having 8-hydroxyquinoline-5-sulphonic (*HQA*) and 5-sulphosalicylic (*SSA*) acids as ligands: Curve 1, *HQA*; 2, 1:1 $\text{VO(IV)}-\text{HQA}$; 3, *SSA*; 4, $\text{VO(IV)}-\text{SSA}$; 5, 1:1:1 $\text{VO(IV)}-\text{HQA}-\text{SSA}$. m = moles of base added per mole of metal ion

and

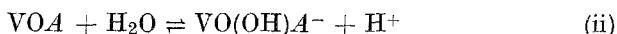
$$[\text{VO}^{2+}] = \frac{(2T_M - T_{\text{OH}} - [\text{H}^+]) \left(1 + \frac{k_1}{[\text{H}^+]}\right)}{\left(2 + \frac{k_1}{[\text{H}^+]}\right)} \quad (7)$$

The concentration of other species present in the solution may be

determined algebraically from equations (3)–(5) and also the values of K_1 and K_{MA} .

Hydrolysis of 1:1 Chelates

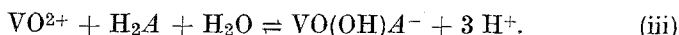
A gradual increase in the values of $\log K_{MA}$ at $m > 0.9, 1.1$ and 1.4 in the case of $\text{VO}^{2+}\text{—HQA}$, $\text{VO}^{2+}\text{—SSA}$ and $\text{VO}^{2+}\text{—SA}$ systems resp., probably indicates that the normal 1:1 chelate undergoes hydrolysis with the formation of a hydroxo complex and the solution becomes more acidic than it would be in the absence of hydrolyzed species. The hydrolytic reaction may be represented as:



The hydrolysis constant K_h may be defined as:

$$K_h = \frac{[\text{VO(OH)A}^-][\text{H}^+]}{[\text{VOA}]} \tag{8}$$

The overall reaction in the system may be written as:



The equilibrium constant for the above reaction may then be given by:

$$K = \frac{[\text{VO(OH)A}^-][\text{H}^+]^3}{[\text{VO}^{2+}][\text{H}_2\text{A}]} \tag{9}$$

The following equations are obtained from the material balance:

$$T_M = [\text{VO}^{2+}] + [\text{VO(OH)}^+] + 2[\{\text{VO(OH)}\}_2^{2+}] + [\text{VOA}] + [\text{VO(OH)A}^-] \tag{10}$$

$$T_{\text{OH}} + [\text{H}^+] = [\text{VO(OH)}^+] + 2[\{\text{VO(OH)}\}_2^{2+}] + 2[\text{VOA}] + 3[\text{VO(OH)A}^-] + [\text{HA}^-] \tag{11}$$

$$T_A = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{VOA}] + [\text{VO(OH)A}^-]. \tag{12}$$

In the pH range studied, the concentrations of OH^- and A^{2-} were negligible in comparison with those of other species present in the equilibrium mixture. However, the concentrations of the hydrolyzed species of the free vanadyl ions were taken into account, since the chelation also occurs at $\text{pH} > 3.5$. For this purpose, the values of hydrolysis constants, viz.

$$K_{h_1} = \frac{[\text{VO(OH)}^+][\text{H}^+]}{[\text{VO}^{2+}]} = 10^{-6.0} \tag{13}$$

and

$$K_{h_2} = \frac{[\{\text{VO(OH)}\}_2^{2+}][\text{H}^+]^2}{[\text{VO}^{2+}]^2} = 10^{-6.88} \tag{14}$$

as reported by *Rossotti* and *Rossotti*¹⁰ have been used.

Combination of equations (1), (10)–(14) and using the expressions for the dissociation constants (k_1 and k_2) of the ligands and rearrangement of the terms in the form of a polynomial, yield:

$$a [\text{VO}^{2+}]^3 + b [\text{VO}^{2+}]^2 + c [\text{VO}^{2+}] - d = 0 \quad (15)$$

where

$$a = \frac{2 K_1 \times 10^{-6.88}}{[\text{H}^+]^4}, \quad b = \frac{4 \times 10^{-6.88}}{[\text{H}^+]^2} + \frac{K_1}{[\text{H}^+]^2} + \frac{2 k_1 \times 10^{-6.88}}{[\text{H}^+]^3} + \frac{K_1 \times 10^{-6.0}}{[\text{H}^+]^3}.$$

$$c = 3 + \frac{2 \times 10^{-6.0}}{[\text{H}^+]} + \frac{2 \times k_1}{[\text{H}^+]} + \frac{k_1 \times 10^{-6.0}}{[\text{H}^+]^2}$$

$$\text{and } d = (3 T_M - T_{\text{OH}} - [\text{H}^+]) \left(1 + \frac{k_1}{[\text{H}^+]} \right).$$

Table 2. *Equilibrium, Chelate Formation and Hydrolysis Constants of 1:1 VO²⁺—Hydroxy Acid Chelates*

Ligand	— log K_1	log K_{MA}	— log K_h	— log K_H
SA	3.41 ± 0.08	13.18 ± 0.08	4.63 ± 0.05	8.04 ± 0.05
SSA	2.73 ± 0.03	11.37 ± 0.03	4.34 ± 0.11	7.07 ± 0.11
HQSA	2.07 ± 0.10	10.48 ± 0.10	3.72 ± 0.13	5.79 ± 0.13

The equilibrium concentration of the free vanadyl ions present in the solution may be obtained by solving equation (15) with the help of *Newton—Raphson's* method¹¹. The concentrations of other species can then be calculated from the above equations and also the values of K_h and K_H . The values of the equilibrium, chelate formation and hydrolysis constants are listed in Table 2.

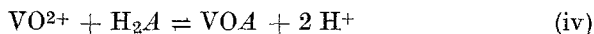
Mixed Ligands Chelates

Curve 5, Figs. 1–5 represents the potentiometric titration of vanadyl sulphate in presence of equimolar concentrations of 8-hydroxyquinoline-5-sulphonic acid (H_2A) and one of the secondary ligands (H_2L). Comparison of this curve with composite curve representing the titrations of the free ligand and the binary system, indicates that the formation of a mixed-ligand chelate, MAL is the only possibility in the ternary systems studied during the course of the present investigations. From the analysis of the potentiometric curves and the stability constants, it may be inferred that in the initial stages of the titration of the ternary systems, the concentration of the mixed ligand chelate, VOAL^{2-} ,

is much lower than that of the binary chelate of *HQSA* and the formation of the ternary complex takes place through 1:1 VO^{2+} —*HQSA* chelate.

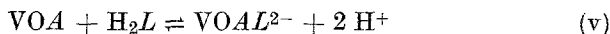
(a) *Calculation of Equilibrium Constants for the Systems,*
 VO^{2+} —*HQSA*—*Dicarboxylic Acids*

As shown previously, the formation of 1:1 VO^{2+} —*HQSA* chelate may be represented as:

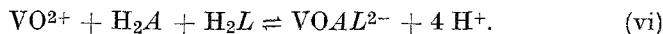


where H_2A represents the *HQSA*.

The formation of the mixed ligand chelate may be shown as:



and the overall reaction for the formation of the mixed ligand chelate may be represented as:



If K' and K'' be the equilibrium constants of the reactions (v) and (vi) respectively, then:

$$K' = \frac{[\text{VOAL}^{2-}][\text{H}^+]^2}{[\text{VOA}][\text{H}_2\text{L}]} \tag{16}$$

and

$$K'' = \frac{[\text{VOAL}^{2-}][\text{H}^+]^4}{[\text{VO}^{2+}][\text{H}_2\text{A}][\text{H}_2\text{L}]} \tag{17}$$

Other pertinent equations are:

$$T_M = [\text{VO}^{2+}] + [\text{VOA}] + [\text{VO(OH)A}^-] + [\text{VOAL}^{2-}] \tag{18}$$

$$T_{\text{OH}} + [\text{H}^+] = 2[\text{VOA}] + 3[\text{VO(OH)A}^-] + 4[\text{VOAL}^{2-}] + [\text{HA}^-] + [\text{HL}^-] + 2[\text{L}^{2-}] \tag{19}$$

$$T_A = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{VOA}] + [\text{VO(OH)A}^-] + [\text{VOAL}^{2-}] \tag{20}$$

$$T_L = [\text{H}_2\text{L}] + [\text{HL}^-] + [\text{L}^{2-}] + [\text{VOAL}^{2-}] \tag{21}$$

where T_L represents the total concentration of the secondary ligand. In the pH range studied, concentrations of OH^- , A^{2-} and the hydrolyzed species of the vanadyl ions were negligible as compared to those of other species present in the reaction mixture. Since $T_M = T_A = T_L$, using the above equations and the expressions for the first dissociation constant (k_1) of *HQSA* and for the first and second dissociation constants (k_1' and k_2') of the secondary ligand, it may be shown that:

$$a[\text{VO}^{2+}]^2 + b[\text{VO}^{2+}] - c = 0 \tag{22}$$

where

$$a = \left(2 + \frac{k_1'}{[\text{H}^+]}\right) \frac{K_1}{[\text{H}^+]^2} + \left(1 - \frac{k_1' k_2'}{[\text{H}^+]^2}\right) \frac{K_H}{[\text{H}^+]^3}, \quad b = 2XY + Y + \left(1 - \frac{k_1' k_2'}{[\text{H}^+]^2}\right) X,$$

$$c = (4T_M - T_{\text{OH}} - [\text{H}^+]) XY, \quad X = 1 + \frac{k_1}{[\text{H}^+]}, \quad \text{and } Y = 1 + \frac{k_1'}{[\text{H}^+]} + \frac{k_1' k_2'}{[\text{H}^+]^2}.$$

(b) *Calculation of the Equilibrium Constants for the Systems,
VO²⁺—HQSA—Hydroxy Acids*

Calculations for these systems are similar as in the case (1) except that the concentration of L²⁻ can also be neglected in comparison to other species present in the reaction mixture. Neglecting [L²⁻], equations (19) and (21) take the form:

$$T_{\text{OH}} + [\text{H}^+] = 2[\text{VOA}] + 3[\text{VO(OH)A}^-] + 4[\text{VOAL}^{2-}] + [\text{HA}^-] + [\text{HL}^-] \quad (19a)$$

$$T_L = [\text{H}_2L] + [\text{HL}^-] + [\text{VOAL}^{2-}] \quad (21a)$$

Using above relations, it may be shown that:

$$a[\text{VO}^{2+}]^2 + b[\text{VO}^{2+}] - c = 0 \quad (22a)$$

where

$$a = \left(2 + \frac{k_1'}{[\text{H}^+]}\right) \frac{K_1}{[\text{H}^+]^2} + \frac{K_H}{[\text{H}^+]^3}, \quad b = 2XY' + Y' + X$$

$$c = (4T_M - T_{\text{OH}} - [\text{H}^+]) XY' \quad \text{and } Y' = 1 + \frac{k_1'}{[\text{H}^+]}$$

The equilibrium concentration of the free vanadyl ions present in the reaction mixture can be determined by solving equations (22) and (22a). Concentrations of other species can then be calculated and also the values of K' and K''.

Stability of 1 : 1 : 1 Mixed-Ligand Chelates

The stability constants of the ternary complexes may be defined as:

$$K_{MAL} = \frac{[\text{VOAL}^{2-}]}{[\text{VOA}][L^{2-}]}$$

and may be determined by the expression:

$$K_{MAL} = \frac{K'}{k_1' k_2'}$$

Where K' is the equilibrium constant of the reaction (v).

The overall stability constant of the mixed ligand chelate:

$$K'_{MAL} = \frac{[\text{VOAL}^{2-}]}{[\text{VO}^{2+}][\text{A}^{2-}][\text{L}^{2-}]}$$

may be calculated from the expression:

$$K'_{MAL} = \frac{K''}{k_1 k_2 k'_1 k'_2}$$

Where K'' represents the equilibrium constant of the overall reaction (vi). The values of equilibrium and chelate formation constants of the ternary chelates are presented in Table 3.

Table 3. *Equilibrium and Chelate Formation Constants of Mixed-Ligand Chelates*

Secondary ligand	$-\log K'$	$-\log K''$	$\log K_{MAL}$	$\log K'_{MAL}$
Phthalic acid	4.53 ± 0.16	6.60 ± 0.16	3.40 ± 0.16	13.88 ± 0.16
Maleic acid	2.72 ± 0.13	4.79 ± 0.13	5.48 ± 0.13	15.96 ± 0.13
SA	3.86 ± 0.21	5.93 ± 0.21	12.73 ± 0.21	23.21 ± 0.21
SSA	3.36 ± 0.18	5.43 ± 0.18	10.74 ± 0.18	21.22 ± 0.18

In all the ternary systems (Curve 5, Figs. 1-4), poor or no inflection at $m = 4$ indicates the decomposition of the mixed ligand chelate into other species, which is supported by a gradual decrease in the values of the stability constants of the ternary chelates at $m > 1.9$ in the case of systems with phthalic and maleic acids and at $m > 2.1$ with salicylic and 5-sulphosalicylic acids as the secondary ligands.

A comparative study of the binary and ternary complexes implies that the formation constants of the mixed complexes studied during the present investigations are greater than those of the binary complexes. The reason for this is that the mixed complex has more formation energy than the average energies of the parent complexes. The electrostatic ligand effect also promotes the formation of the mixed complex. A comparison of the data given in Tables 2 and 3 indicates that the order of stability of the binary as well as the ternary complexes is:

(i) Maleic acid $>$ phthalic acid.

(ii) SA $>$ SSA $>$ HQSA.

Thus the relative stabilities of the mixed-ligand chelates of maleic and phthalic acids follow the order of the basicities of these ligands. In the case of complexes of SA, SSA and HQSA, the relative order may be explained on the basis of the presence of sulphonate group in SSA and HQSA and the steric factors. The sulphonate group increases

the acidity of the phenolic group and results in the formation of less stable complexes. The steric inference increases with increasing size of the ligand and invariably decreases the stability of the chelate.

Further, a comparison of the stability constants of the binary chelates of oxovanadium(IV) with the corresponding chelates of other transition elements reveals that the former are generally more stable than the latter. This might be due to the presence of a highly electronegative oxygen atom in the vanadyl ion since the chelate stability increases with an increase in the electronegativity of the metal ions.

Acknowledgement

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