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Equilibrium Studies of the Interaction of Vanadyl Ions with Catechol

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A quantitative study of the interaction of vanadyl ions with catechol (H_2A) has been carried out by means of potentiometric titrations of vanadyl sulphate with potassium hydroxide in the presence of varying concentrations of catechol. The formation of 1 : 1 and 1 : 2 complexes has been indicated. The equilibrium constants for the $VO^{2+}+H_2A \rightleftarrows VOA+2H^+$ and $VOA+H_2A \rightleftarrows VOA_2^{2-}+2H^+$ reactions have been found to be 1.41×10^{-6} and 7.76×10^{-9} respectively, giving the values of 1.90×10^{15} and 1.05×10^{13} for the formation constants of 1 : 1 and 1 : 2 chelates respectively. Above pH 4, the 1 : 1 complex has been shown to hydrolyze, and the equilibrium constant for the $VOA+H_2O \rightleftarrows VO(OH)A^-+H^+$ reaction has been found to be 7.94×10^{-6}.

Although catechol derivatives of vanadyl ions have been studied earlier,[1-4] a survey of the literature revealed that a quantitative study of the equilibria involved in the interaction of vanadyl ions with catechol has not yet been carried out. The present investigation was, therefore, undertaken in order to determine the equilibrium and stability constants of the formation of vanadyl chelates catechol. For the detection of the polymerization of the chelates, the equilibrium constants were determined over a four-fold concentration range of the metal chelate.

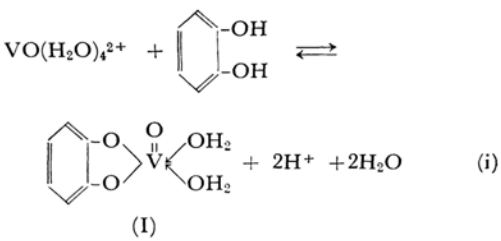
Experimental

A stock solution of vanadyl sulphate was standardized by titrating it with sodium hydroxide in the presence of an excess of the disodium salt of EDTA according to the method of Schwarzenbach.[5] The strength of the solution was also checked by titrating it with a standard potassium permanganate solution, using phosphoric acid as a catalyst and ferroin as an indicator.[6] In order to prevent the oxidation[7] of the vanadyl ions, a known amount of a standard solution of hydrochloric acid was added to the vanadyl sulphate solution. The catechol (E. Merck, G. R.) solution was made by direct weighing. Potassium chloride (B. D. H., Analar) was used for keeping the ionic strength constant. All the solutions were prepared in freshly-distilled conductivity water.

pH measurements were made at room temperature (30 ± 1°C) with a Gambridge pH-meter standardized against a 0.05 M solution of potassium hydrogen phthalate. For pH titrations, known amounts of vanadyl sulphate, catechol, and potassium chloride solutions were pipetted into a titration cell. Conductivity water was added to obtain the desired volume and ionic strength (0.1 M). This reaction mixture was then titrated with a potassium hydroxide solution (0.1 N) in a nitrogen atmosphere, and the pH readings were recorded after the system had reached equilibrium. All the titrations were repeated twice to ensure the reproducibility of the results.

Results and Discussion

Curves 1, 2 and 3 (Fig. 1) for the potentiometric titrations of 1 : 1 mixtures of vanadyl sulphate and catechol at initial concentrations of 5×10^{-3}, 2.5×10^{-3} and 1.25×10^{-3} M respectively exhibit a sharp inflexion at $m=3$, where "m" represents the number of moles of potassium hydroxide added per mole of the metal ion. For the formation of the normal diaquo 1 : 1 chelate (I) in accordance with the reaction:



two moles of potassium hydroxide are required. The extra consumption of one mol of alkali indicated that one of the water molecules of the diaquo chelate undergoes dissociation. The reaction may be represented as:

1) A. Rosenheim and Hsin Yu Mong, *Z. anorg. u. allgem. Chem.*, **148**, 25, 34 (1925).
2) R. Trujillo, F. Brito and J. Cabrera, *Anales. real soc. espan, fix. Yquim.*, **52B**, 589 (1956).
3) S. Ya, Shnaiderman (Polytech, Inst., Kiev), *Zh. Norgan. Khim.*, **8**, 464 (1963).
4) P. K. Bhatacharya & S. N. Banerji, *Z. anorg. u. allgem. Chem.*, **315**, 118 (1962).
5) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 331 (1948).
6) *Z. Analyt. Chem.*, **189**, 421 (1962).
7) G. Jones and W. A. Ray, *J. Am. Chem. Soc.*, **66**, 1571 (1955).

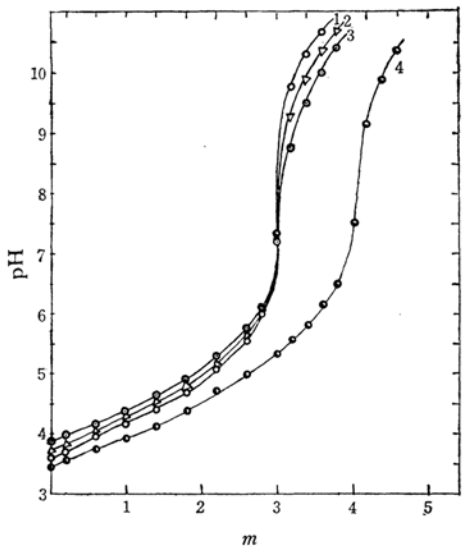
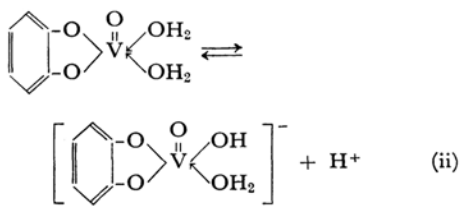


Fig. 1. Potentiometric titrations of 1 : 1 vanadyl catechol chelate systems with KOH (0.1 N). Concentrations: curve 1, 5×10^{-3} M; curve 2, 2.5×10^{-3} M; curve 3, 1.25×10^{-3} M. Curve 4, represents similar titrations of 1 : 2 vanadyl-catechol chelate system. $T_M=5\times10^{-3}$ M. Ionic strength=0.1 M (KCl). m=moles of base added per mole of the metal ion. Portion of the curve for neutralization of HCl present in VO-(IV) soln. has been eliminated in the lower buffer regions



(II) (ii)

The formation of the 1 : 1 vanadyl-catechol chelate is supported by the spectrophotometric study of Shnaiderman.[3]

The effect of the concentration on the potentiometric titration data, illustrated by curves 1, 2 and 3 (Fig. 1), is so slight that no polymerization of the metal chelate seems to occur. The spread of the low buffer regions seen in these curves can be accounted for entirely on the basis of the variation in the concentration of hydrogen ions as a function of the 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 in the buffer region may be accounted for on the basis of the free hydroxide ion present (*i. e.*, the spread is due to the fact that different quantities of the potassium hydroxide solution are required to produce the same "m" value since the total concentration of the chelate differed considerably).

In view of the above interesting results concerning the interaction of one mole of catechol with one mole of the vanadyl ion, it was considered worthwhile to carry out a mathematical analysis of the potentiometric titration data. The method for the determination of the equilibrium constant is outlined below:

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

$$VO^{2+} + H_2A \rightleftarrows VOA + 2H^+ \qquad (i)$$

The equilibrium constant, K_1, may be expressed as:

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

For the sake of clarity, water molecules of hydration and charges on the chelate species have been eliminated in writing their formulae in the mathematical treatment of the data. In order to account for the initial hydrolysis of vanadyl ions, the following equilibria, reported by Rossotti and Rossotti,[8] were considered:

$$VO^{2+} + H_2O \rightleftarrows VO(OH)^+ + H^+$$

$$K_{h_1} = \frac{[VO[OH]^+][H^+]}{[VO^{2+}]} = 10^{-6.00} \qquad (2)$$

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

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

If T_M represents the total concentration of all the metal species and T_A, that of the various ligand species, and if T_{OH} be the amount of alkali added to the reaction mixture during titration, we have:

$$T_M = [VO^{2+}] + [VO[OH]^+] + 2[(VO[OH])_2^{2+}] + [VOA] \qquad (4)$$

$$T_{OH} + [H^+] = [VO[OH]^+] + 2[(VO[OH])_2^{2+}] + 2[VOA] \qquad (5)$$

$$T_A = [H_2A] + [VOA] \qquad (6)$$

In the pH range studied, the concentrations of HA^-, A^{2-} and OH^- were negligible as compared with those of the other ionic species present in the reaction mixture. The combination of Eq (1)—(6) gives:

$$[VO^{2+}] = \frac{-b\pm\sqrt{b^2+4ac}}{2a} \qquad (7)$$

where

$$a = \frac{2\times10^{-6.88}}{[H^+]^2}, \qquad b = 2 + \frac{10^{-6.00}}{[H^+]}$$

and $$c = 2T_M - T_{OH} - [H^+]$$

8) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

After the computation of the equilibrium concentration of the free metal ions, the concentrations of the other species present in the solution could be determined from Eqs. (4)—(6). The calculation of K_1 at various points of the titration curves (Fig. 1) gave relatively constant values up to a pH value of about 4 only for solutions containing either 1 : 1 or 2 : 1 ratios of the ligand to the metal ions. This indicated that up to a pH of about 4 the diaquo 1 : 1 chelate (I) is the only chelate species present in both the systems. The mean values of these constants, as determined from the titration data of curves 1—4 (Fig. 1), are listed in Table 1.

TABLE 1

T_A/T_M	T_M, M	pK_1
1	5×10^{-3}	5.86
1	2.5×10^{-3}	5.88
1	1.25×10^{-3}	5.85
2	5×10^{-3}	5.81

Average value of $pK_1 = 5.85$

It is evident from Table 1 that the value of pK_1 is almost independent of the concentration of the metal chelate, indicating that the chelate does not undergo polymerization under the present experimental conditions.

Stability of the 1 : 1 Chelate. If k_1 represents the formation constant of the 1 : 1 chelate, and if k_{a_1} and k_{a_2} be the dissociation constants of catechol, it may be shown that:

$$k_1 = \frac{K_1}{k_{a_1} \cdot k_{a_2}}$$

The value of $-\log K_1 = 5.85$ (from Table 1) and the values of $-\log k_{a_1}$ and $-\log k_{a_2}$ equal to 9.20 and 11.93 respectively reported by Heureux and Martell[9] correspond to a $\log k_1$ value equal to 15.28.

Hydrolysis of the 1 : 1 Chelate. A gradual fall in the pK_1 values above a pH value of about 4 in the 1 : 1 vanadyl sulphate-catechol system (curves 1—3 (Fig. 1)) together with the single inflexion at $m=3$, indicate that the diaquo chelate(I) undergoes hydrolysis with the formation of a hydroxo complex and that there is overlapping between the two successive reactions. The hydrolytic reaction may be represented as:

$$VO^{2+} + H_2A + H_2O \rightleftarrows VO(OH)A^- + 3H^+ \qquad \text{(ii)}$$

The equilibrium constant, K_H, may be expressed as:

$$K_H = \frac{[VO(OH)A][H^+]^3}{[VO^{2+}][H_2A]} \qquad (8)$$

or

$$VOA + H_2O \rightleftarrows VO(OH)A^- + H^+$$

$$k_h = \frac{[VO(OH)A][H^+]}{[VOA]} \qquad (9)$$

Other pertinent equations are;

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

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

$$T_A = [H_2A] + [VOA] + [VO(OH)A] \qquad (12)$$

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

The combination of Eqs. (1)—(3), (8), and (10)—(12) gives:

$$a[VO]^3 + b[VO]^2 + c[VO] - d = 0 \qquad (13)$$

where:

$$a = \frac{2K_1 \times 10^{-6.88}}{[H^+]^4}$$

$$b = \frac{4 \times 10^{-6.88}}{[H^+]^2} + \frac{K_1 \times 10^{-6.00}}{[H^+]^3} + \frac{K_1}{[H^+]^2}$$

$$c = 3 + \frac{2 \times 10^{-6.00}}{[H^+]}$$

and $$d = 3T_M - \langle T_{OH} + [H^+] \rangle$$

Knowing the value of K_1 (from Table 1), the equilibrium concentration of the free metal ions could be determined from Eq (13) by using an I. B. M. 1620 computer. The concentrations of the other species present in the equilibrium mixture could then be calculated, and thus the values of K_H and K_h could be determined. Here also, in order to detect the polymerization of the hydroxo chelate, these constants were determined over the fourfold concentration range of the metal chelate. The mean values obtained from the titration data of curves 1, 2, and 3 (Fig. 1) are presented in Table 2.

TABLE 2

T_A/T_M	T_M, M	pK_H	pK_h
1	5×10^{-3}	10.93	5.09
1	2.5×10^{-3}	11.03	5.15
1	1.25×10^{-3}	10.94	5.06

Average values $pK_H = 10.97$, $pK_h = 5.10$

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

9) G. A. Heureux and A. F. Martell, *J. Inorg. Nucl. Chem.*, **28**, 481 (1966).

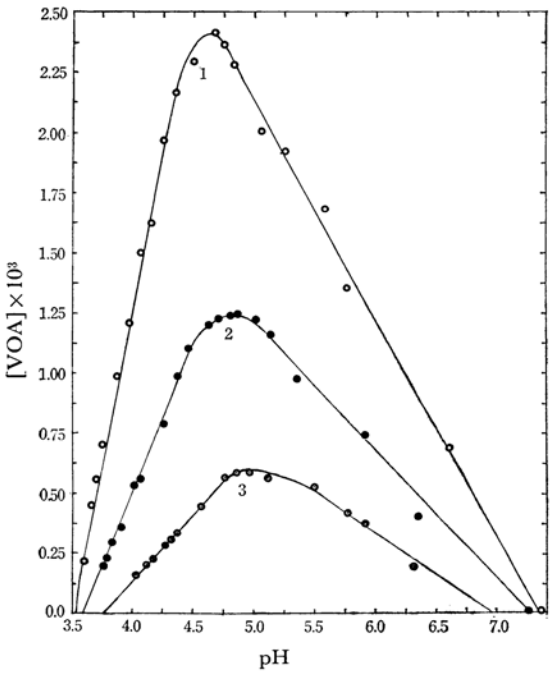


Fig. 2. Distribution of chelate, VOA, as a function of pH in 1 : 1 vanadyl-catechol system (curves 1, 2 & 3, Fig. 1).
Curve 1, $T_M = 5\times10^{-3}$ M
Curve 2, $T_M = 2.5\times10^{-3}$ M
Curve 3, $T_M = 1.25\times10^{-3}$ M

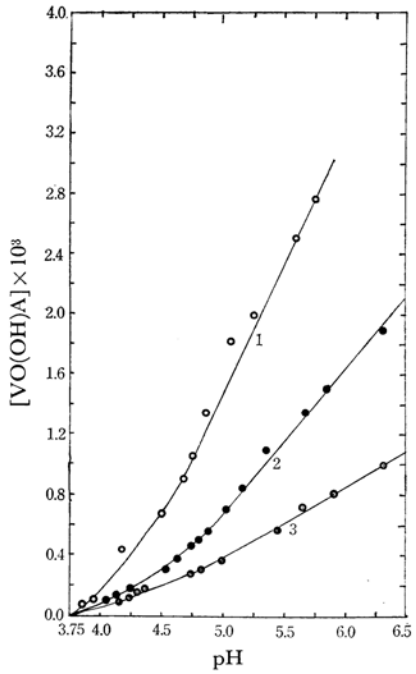
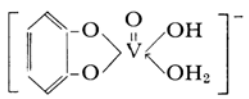


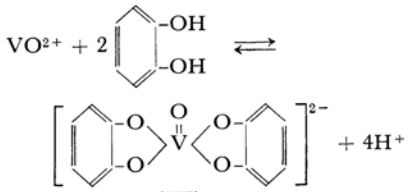
Fig. 3. Distribution of chelate VO(OH)A, as a function of pH in 1 : 1 vanadyl-catechol system (curves 1, 2 & 3, Fig. 1).
Curve 1, $T_M = 5\times10^{-3}$ M
Curve 2, $T_M = 2.5\times10^{-3}$ M
Curve 3, $T_M = 1.25\times10^{-3}$ M

that the monohydroxo complex is present in a solution mainly as a monomer under the present experimental conditions. The hydroxo chelate may thus be formulated as:



By the use of the equilibrium constants presented in Tables 1 and 2 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 functions of the pH and of the total metal chelate concentration present in the equilibrium mixture. These plots, shown in Figs. 2 and 3, indicate a gradual replacement of the diaquo chelate I by the monohydroxo chelate II in the solution.

Equilibrium Constant for the Formation of the 1 : 2 Chelate. 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 potentiometric titration of vanadyl sulphate in the presence of one mole of catechol. The lowering, however, increases above a pH of about 4, and the sharp inflexion at $m=4$ may be explained on the basis of the formation of the 1 : 2 complex in accordance with this equation:



(III)

The above conclusion is supported by the spectrophotometric study reported by Bhattacharya and Banerji.[4] The mathematical analysis of the potentiometric titration, data (Table 1) showed that, below a pH of 4, the diaquo 1 : 1 chelate (I) is the predominant chelate species present in the system. Above a pH of about 4, the [VOA], [VO(OH)A], and [VOA_2] chelate species have been found to exist. The equilibrium constant, K_2, for the reaction:

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

may be expressed as:

$$K_2 = \frac{[VOA_2][H^+]^4}{[VO^{2+}][H_2A]^2} \qquad (14)$$

or K_2', the equilibrium constant of the reaction:

$$VOA + H_2A \rightleftarrows VOA_2 + 2H^+$$

may be given by:

TABLE 3

KOH (ml)	6.00	6.40	6.80	7.20	7.60	8.00	8.40	8.80	9.20
pH	4.17	4.25	4.34	4.43	4.53	4.66	4.79	4.89	5.05
pK_2	13.86	13.91	14.07	14.03	13.95	14.01	14.00	13.88	13.97
pK_2'	8.01	8.06	8.22	8.17	8.09	8.15	8.15	8.02	8.11

Average values: $pK_2=13.96$, $pK_2'=8.11$

$$K_2' = \frac{[VOA_2][H^+]^2}{[VOA][H_2A]} \qquad (15)$$

Other pertinent equations are:

$$T_M = [VO^{2+}] + [VO(OH)^+] + 2[(VO(OH))_2^{2+}] + [VOA] + [VO(OH)A] + [VOA_2] \qquad (16)$$

$$T_{OH} + [H^+] = [VO(OH)^+] + 2[(VO[OH])_2^{2+}] + 2[VOA] + 3[VO(OH)A] + 4[VOA_2] \qquad (17)$$

$$T_A = [H_2A] + [VOA] + [VO(OH)A] + 2[VOA_2] \qquad (18)$$

The combination of Eqs. (1)—(3), (8), and (14)—(18) gives:

$$a[VO]^3 + b[VO]^2 + c[VO] + d = 0 \qquad (19)$$

where:

$$a = \frac{2\times10^{-6.88}}{[H^+]^4}\left(\frac{K_H}{[H^+]} - K_1\right)$$

$$b = \frac{10^{-6.00}}{[H^+]^3}\left(\frac{K_H}{[H^+]} - K_1\right) + \frac{2}{[H^+]^2}\left(\frac{K_H}{[H^+]} - 3\times10^{-6.88}\right)$$

$$c = \frac{1}{[H^+]^2}\left(\frac{K_H}{[H^+]} + K_1\right)(T_{OH} + [H^+] - 4T_M) - \frac{3\times10^{-6.00}}{[H^+]} - 4$$

and

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

Since the values of K_1 and K_H are known from Tables 1 and 2 respectively, the equilibrium concentration of the free vanadyl ions present in the solution could be computed by solving Eq. (19). The concentrations of the other species present in the equilibrium mixture could then be calculated, and the values of pK_2 and pK_2' could thus be determined at various points of the titration curve. These values are listed in Table 3, while the distribution of the various chelate species present in the equilibrium mixture as a function of the pH of the solution is presented in Fig. 4. These plots (Fig. 4) indicate the successive replacement of the diaquo 1 : 1 chelate, VOA, by the VO(OH)A and VOA_2^{2-} chelate species. In this connection it may be pointed out that, since the hydrogen ion concentration appears as the fourth power in the expression for K_2 (Eq. 14), an experimental error of only ±0.02 pH unit would give an appreciable deviation in the pK_2 values. These values are, therefore, approximate.

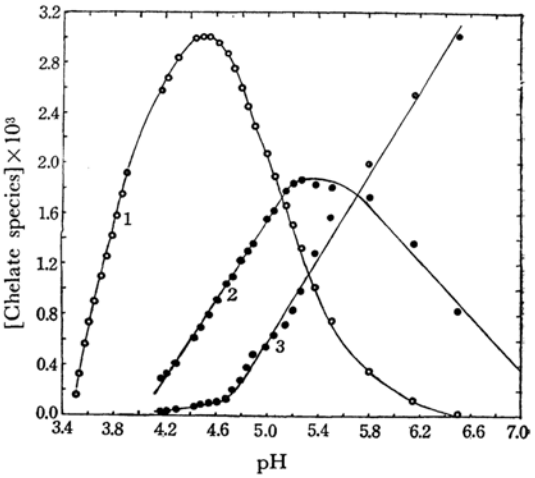


Fig. 4. Distribution of chelate species VOA, $VO(OH)A^-$ and VOA_2^{2-} (curves 1, 2 & 3 respectively) as a function of pH in a 1 : 2 vanadyl-catechol chelate system (curve 4, Fig. 1).

Stability of the 1 : 2 Chelate. After determining the equilibrium quotient $[VOA_2][H^+]^2/[VOA][H_2A]$, (*i. e.*, K_2' in Table 3), the stability constant, k_2, which may be defined as:

$$k_2 = \frac{[VOA_2]}{[VOA][A^{2-}]}$$

may be determined by the expression:

$$k_2 = \frac{K_2'}{k_{a_1}\cdot k_{a_2}}$$

where k_{a_1} and k_{a_2} represent first and second dissociation constants of catechol. The substitution of the values of K_2' (from Table 3) and k_{a_1} and k_{a_2} reported by Heureux and Martell[9] gave a $\log k_2$ value equal to 13.02.

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