ability of a localized pair of electrons on the oxygen atom. The kinetic data suggest that delocalization by π bonding occurs to a lesser extent in the pyrophosphite than in the pyrophosphate linkage, making it more receptive to attack by the hydrogen ion. This explanation is consistent with the conclusion reached by Grant and Payne[9] in explanation of the absence of chelation stabilization in pyrophosphite complexing.

The hydrolysis of pyrophosphite resembles closely that of trimetaphosphate which is both acid and base catalyzed.

Acknowledgment. The authors gratefully acknowledge the assistance of Dr. M. M. Crutchfield in the interpretation of the nmr spectra and A. W. Dickinson and A. G. Weisner for computer calculations made for this study.

Equilibria Involving the Formation, Hydrolysis, and Olation of Oxovanadium(IV) Chelates in Aqueous Solution[1,2]

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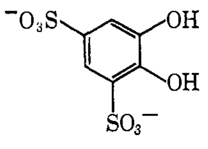
Abstract: The interaction of the oxovanadium ion with 3,5-disulfopyrocatechol, salicylic acid, 5-sulfosalicylic acid, 5-sulfo-8-hydroxyquinoline, and salicyl phosphate was studied by potentiometric measurement of hydrogen ion concentration. Data taken over a range of metal ion and ligand concentrations were used to determine formation constants of the metal chelates having a 1 : 1 molar ratio of ligand-to-metal ion, their hydrolysis constants, and the equilibrium constants for the formation of binuclear diolated chelates. Suggestions are made for the bonding and structures of these coordination compounds in aqueous solution.

The purpose of the investigation was to determine the complex species present in systems containing vanadyl salts, organic ligands, and salicyl phosphate by potentiometric measurements. Such information is required for a study of the kinetics of the vanadyl ion and vanadyl chelate catalyzed solvolysis of salicyl phosphate in aqueous solution, to be reported in a subsequent paper. As a result of this study, the species present in solution will be described in terms of the stability constants of the metal chelate compounds formed, the equilibrium constants for the formation of polynuclear complexes, and the acid dissociation constants of all other solution constituents.

A search of the literature revealed that only a few equilibrium formation constants of vanadyl chelates have been reported. Constants for the formation of the ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA) and cyclohexanediamine-N,N,N′,N′-tetraacetic acid (CDTA) chelates have been reported by Schwarzenbach, *et al.*[4] The formation constant for the interaction of the vanadyl ion and oxalic acid has been described.[4] Several constants also have been reported by Trujillo and co-workers with acetylacetone, pyrocatechol, 1,10-phenanthroline, and 8-hydroxyquinoline.[5-8]

The ligands employed in the investigation were 3,5-disulfopyrocatechol (I), salicylic acid (II), 5-sulfosalicylic acid (III), 5-sulfo-8-hydroxyquinoline (IV), and salicyl phosphate (V). The selection of I–IV was predicated on the fact that these were the only readily available ligands which formed partially co-



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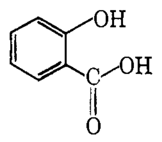

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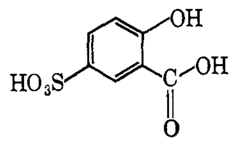

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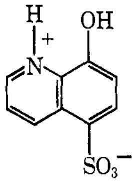

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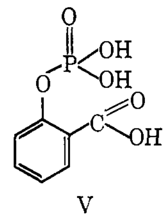

V

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[1] Abstracted in part from a dissertation submitted by G. E. Mont to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This work was supported by the National Science Foundation under Research Grants G-9998 and G-21055 to Clark University and Illinois Institute of Technology, respectively.

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ordinated aquooxovanadium(IV) ions with stability over a convenient pH range in solution. A previous survey of vanadyl–ligand interactions[9] showed that many ligands provide such little stability that solid hydrolysis products are formed, while, on the other hand, others are so stable that the vanadyl ion is completely coordinated, and the resulting chelates do not exhibit catalytic activity on salicyl phosphate hydrolysis.

Experimental Section

Reagents. Salicyl phosphate was obtained from the California Foundation for Biochemical Research and was used without further purification, since potentiometric titration of an aqueous solution showed no detectable impurities, and the melting point was in agreement with that reported (162.5–163.0°).[10]

Vanadyl sulfate was standardized by titration with standard potassium permanganate solution according to the method described by Scott.[11]

The bidentate ligands were the highest quality commercial samples available, obtained from sources described previously.[9,12] The purity of the ligands was further checked by potentiometric titration of the acid forms with base and calculation of equivalent weights from the inflections in the titration curves. In all cases the values obtained were very close to the theoretical values. Acid dissociation constants were also calculated.[9]

Potentiometric Titration. A Beckman Model GS pH meter was employed to determine the hydrogen ion concentration. The pH meter was fitted with extension glass and calomel electrodes, which were calibrated in terms of hydrogen ion concentration by titration with hydrochloric and acetic acids as described by Courtney, *et al.*[13] The use of KNO_3 to adjust the ionic strength to 0.10 M effectively establishes 0.10 M KNO_3 solution as the standard state for the equilibrium constants, enthalpies, and entropies of reaction reported in this paper.[14,15]

Titrations were carried out in a jacketed glass cell, through which constant temperature water was circulated. The circulating water was pumped from a constant temperature bath maintained at 9.5° ± 0.1 in the case of the lower temperature, and at 25.0° ± 0.1 and 34.9° ± 0.1 for the higher temperatures. Nitrogen was passed over ascarite, presaturated with water, and bubbled through the solution to keep the system free of carbon dioxide.

Results

Salicylic Acid (SA). Potentiometric titration of a 2:1 molar ratio of salicylic acid to OV(IV) shows the start of an inflection just prior to $m = 3$ (m = moles of base per gram ion of metal). By potentiometric titration, carried out in the usual way, it was not possible to reach the point where 3 moles of base had been added under equilibrium conditions. This effect was probably due to extensive hydrolysis of the chelate compound. An attempt to calculate a formation constant for the 2:1 complex, from data obtained for values of "m" (moles of base added per gram ion of metal) less than 3, proved unsuccessful. By addition of the abscissas of separate potentiometric titration curves for salicylic acid and the 1:1 vanadyl–salicylic acid chelate, a calculated curve was obtained for a system involving no interaction between the second mole of salicylic acid and the 1:1 chelate. The calculated curve was similar to the experimental curve, with an inflection at a value of $m = 3$, and thus indicated that a 2:1 chelate compound is not formed in significant amounts under the experimental conditions employed.

Potentiometric titration of a 1:1 molar ratio of salicylic acid and VO^{2+} gave generally unsatisfactory results. Beyond 2 moles of base per mole of ligand a very slow but irreversible hydrolysis began to take place, so that it was not possible under these conditions to calculate equilibrium constants for hydroxo complex formation and polymerization of mononuclear chelates.

Sulfosalicylic Acid. The results obtained from the titrations of a 2:1 molar ratio of sulfosalicylic acid and vanadyl ion were similar to those obtained with salicylic acid. The titration curve appeared to approach an inflection at about $m = 3$. That there was probably no interaction between the 1:1 chelate and the second mole of sulfosalicylic acid under the experimental conditions employed was also shown in this case by the calculation of the titration curve with the assumption that the 2:1 chelate is not formed. There was excellent agreement between the experimental 2:1 titration curve and the composite curve obtained by adding the abscissas of the 1:1 vanadyl–sulfosalicylic acid curve and the free ligand curve at appropriate concentrations.

When the titration of the 1:1 molar ratio of vanadyl salt and sulfosalicylic acid was carried out beyond the value of $m = 2$ as rapidly as possible, it was found that in contrast to the results obtained with salicylic acid, the data thus obtained could be employed in the calculation of dimerization and hydrolysis constants. The following reactions are assumed to take place in the region between $m = 2$ and $m = 3$

$$ML^- \rightleftharpoons M(OH)L^{2-} + H^+$$
$$2ML^- \rightleftharpoons (M(OH)L)_2^{4-} + 2H^+$$

where M^{2+} is the vanadyl ion and ML^- is the 1:1 vanadyl–sulfosalicylate chelate formed by the displacement of 2 equiv of hydrogen ion from the donor groups (*i.e.*, carboxyl and phenolic groups) of the ligand. $M(OH)L^{2-}$ is the monohydroxo chelate formed by the dissociation of an equivalent of hydrogen ions from water bound to the metal ion, and $(M(OH)L)_2^{4-}$ is the dimer formed by the combination of 2 moles of the monohydroxo chelate. The equilibrium constant expressions for these reactions are

$$K_{M(OH)L} = \frac{[M(OH)L^{2-}][H^+]}{[ML^-]} \tag{1}$$

and

$$K_D = \frac{[(M(OH)L)_2^{4-}][H^+]^2}{[ML^-]^2} \tag{2}$$

If these are the only metal complex species in solution, then the following expression is obtained

$$\frac{[H^+](aT_L + [H^+] - [OH^-])}{[ML^-]} = \frac{2[ML^-]}{[H^+]} K_D + K_{M(OH)L} \tag{3}$$

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[10] J. D. Chanley, E. M. Grindler, and H. Sabotka, *J. Am. Chem. Soc.*, 74, 4347 (1952).

[11] "Scott's Standard Methods of Chemical Analysis," N. H. Furman, Ed., 5th ed, D. Van Nostrand Co., Inc., New York, N. Y., 1939.

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[14] For a standard state of 0.10 M KNO_3 it follows that activities of solutes, s, are defined as $\lim(M \rightarrow 0)\, a_s/M_s = 1$. The very small slope of this extrapolation for most ionic species makes the equilibrium constants reported in this paper very close to the true thermodynamic constants for this standard state.

[15] The use of definite concentrations of supporting electrolyte as standard states for complex formation has been recommended recently by the Commission on Equilibrium Data, IUPAC. Copies of reports describing this recommendation are available from L. G. Sillén, Stockholm, and from A. E. Martell, Chicago.

Table I. Equilibrium Constants for the Interaction of Oxovanadium(IV) with Various Ligands (25°, $\mu = 0.10$ (KNO_3))

Ligand	pK_1	pK_2	Log K_{ML}	p$K_{M(OH)L}$	Log K_d[d]
Salicylic acid	2.70 ± 0.02	13.90 ± 0.10	13.38 ± 0.03	....	...
Sulfosalicylic acid	2.67 ± 0.04	11.67 ± 0.03	11.71 ± 0.07	7.22 ± 0.05	5.33 ± 0.05
Tiron[a]	7.60 ± 0.04	12.60 ± 0.06	16.74 ± 0.03	6.30 ± 0.20	4.30 ± 0.20
5-Sulfo-8-hydroxoquinoline	3.92 ± 0.03	8.48 ± 0.05	11.79 ± 0.03	6.45 ± 0.03	4.84 ± 0.04
Salicyl phosphate	3.69 ± 0.05[b]	6.61 ± 0.04[c]	5.81 ± 0.04	5.70 ± 0.20	2.30 ± 0.30

[a] Log $K(VOL^{2-} + L^{4-} \rightleftharpoons VOL_2^{6-}) = 14.20 \pm 0.04$. [b] p$K_2$. [c] p$K_3$. [d] $K_d = [(M(OH)L)_2]/[M(OH)L]^2$.

where T_M is the total concentration of metal species, T_L is the total concentration of ligand species, and a = moles of base added per mole of ligand present (thus aT_L = total moles of base added = T_{OH}). Thus, if a dimer is formed, a plot of $[H^+](aT_L + [H^+] - [OH^-])/[ML^-]$ against $2[ML^-]/[H^+]$ should give a straight line, the slope of which is equal to K_D and the intercept of which at $2[ML^-]/[H^+] = 0$ is equal to $K_{M(OH)L}$.

The equilibrium constant for possible trimer formation is

$$K_T = \frac{[(M(OH)L)_3{}^{6-}][H^+]^3}{[ML^-]^3} \tag{4}$$

and can be determined by employing the following equation.

$$\frac{[H^+](aT_L + [H^+] - [OH^-])}{[ML^-]} = \frac{3K_T[ML^-]^2}{[H^+]^2} + K_{M(OH)L} \tag{5}$$

A plot of the data corresponding to eq 3 is shown in Figure 1. The straight-line correlation, in addition to the fact that the corresponding plot of eq 5 does not give a straight line, indicates that a dimer is probably initially formed in the hydrolysis of the 1:1 chelate compound. If the solution is allowed to stand, then further polymerization takes place and a straight-line plot is no longer obtained. The values of the negative logs of the equilibrium constants obtained at 25 and 34.9° are listed in Tables I and II.

Table II. Equilibrium Constants for the Interaction of Oxovanadium(IV) with Various Ligands (34.9°, $\mu = 0.10$ (KNO_3))

Ligand	pK_1	pK_2	Log K_{ML}
Salicylic acid	2.45 ± 0.02	13.40 ± 0.10	12.89 ± 0.05
Sulfosalicylic acid	2.36 ± 0.02	11.59 ± 0.03	11.29 ± 0.08
Tiron	7.49 ± 0.02	12.08 ± 0.05	16.05 ± 0.05
5-Sulfo-8-hydroxy-quinoline	3.85 ± 0.04	8.41 ± 0.02	11.32 ± 0.04
Salicyl phosphate	3.60 ± 0.03[a]	6.45 ± 0.01[b]	5.68 ± 0.02

[a] pK_2. [b] pK_3.

The titration of a 1:1 molar ratio of sulfosalicylic acid and OV(IV) was also carried out at a temperature of 9.5°. The equilibrium constant at 9.5° for the following reaction was found to be 6.17×10^{-3}.

$$OV(IV) + H_2L \rightleftharpoons VOL^- + 2H^+$$

3,5-Disulfopyrocatechol (Tiron). If a 2:1 molar ratio of Tiron to OV(IV) is titrated, as is indicated in Figure 2, an inflection at $m = 2$ and a second inflection at about $m = 4$ are observed. In the region above m = 2, the following equation will apply

$$K_{ML_2} = \frac{[ML_2{}^{6-}]}{[ML^{2-}][L^{4-}]} \tag{6}$$

$$K_{ML_2} = \frac{T_L - X[L^{4-}] + K_{ML}[L^{4-}]T_M - X[L^{4-}]}{K_{ML}X[L^{4-}]^3} \tag{7}$$

where T_M, T_L, and a have the same meaning as before, and

$$[L^{4-}] = \frac{(2-a)T_L - [H^+] + [OH^-]}{2[H^+]^2/K_1 + [H^+]/K_2}$$

$$X = \frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1$$

$[L^{4-}]$ is the concentration of the completely ionized ligand; $[ML_2{}^{6-}]$ and $[ML^{2-}]$ are the concentrations of the 2:1 and 1:1 chelate, respectively; K_{ML} is the equilibrium formation constant of the 1:1 chelate, and K_1 and K_2 are the first and second dissociation constants of the ligand. The logs of the formation constants calculated from eq 7 are given in Tables I and II. Hydrolysis and dimerization constants of the 1:1 chelate, determined as described above, are listed in Table I.

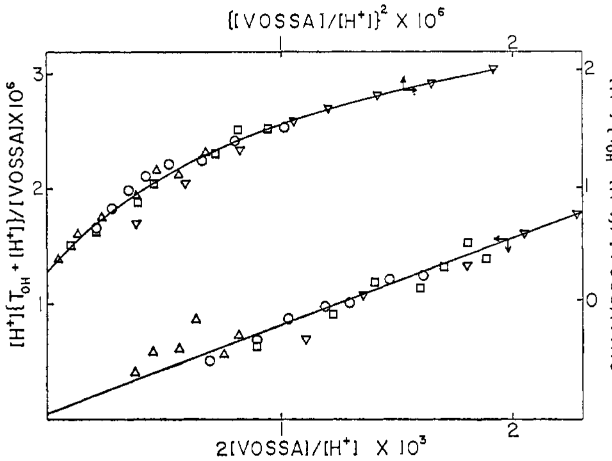


Figure 1. Plot of $[H^+](aT_L + [H^+])/[ML^-]$ against $2[ML^-]/[H^+]$ for the 1:1 OV(IV)–SSA chelate, illustrating the presence of a dimer at 25°; concentrations: ○—○ 3.13×10^{-3} M, □—□ 1.59×10^{-3} M, △—△ 7.74×10^{-4} M, ▽—▽ 4.74×10^{-4} M (top). Plot of $[H^+]\cdot(aT_L + [H^+]/[ML^-])$ against $3([ML^-]/[H^+])^2$ for the 1:1 OV(IV)–SSA chelate illustrating the absence of a trimer at 25°; concentrations: □—□ 2.78×10^{-3} M, ▽—▽ 4.14×10^{-3} M, △—△ 7.59×10^{-4} M, ○—○ 1.47×10^{-3} M (bottom); $aT_L = T_{OH}$.

An attempt was made to determine if a dimeric species persists in the 1:1 system over an extended period of time by use of the graphical method described above for the vanadyl–sulfosalicylic acid system. The solutions of the 1:1 chelate compound were

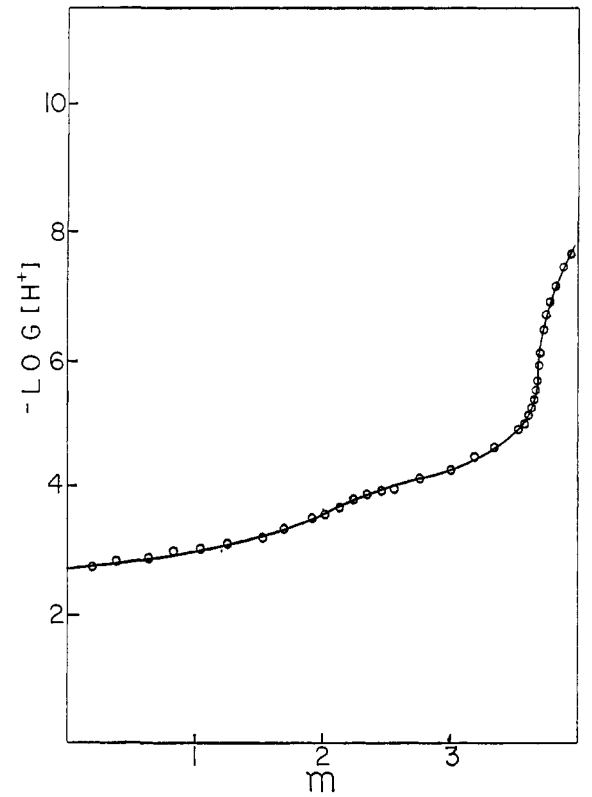


Figure 2. Potentiometric titration of 1:2 OV(IV)–Tiron chelate; $\mu = 0.10$ (KNO_3); $2T_A = T_M = 3.13 \times 10^{-3}$ *M* at 25°.

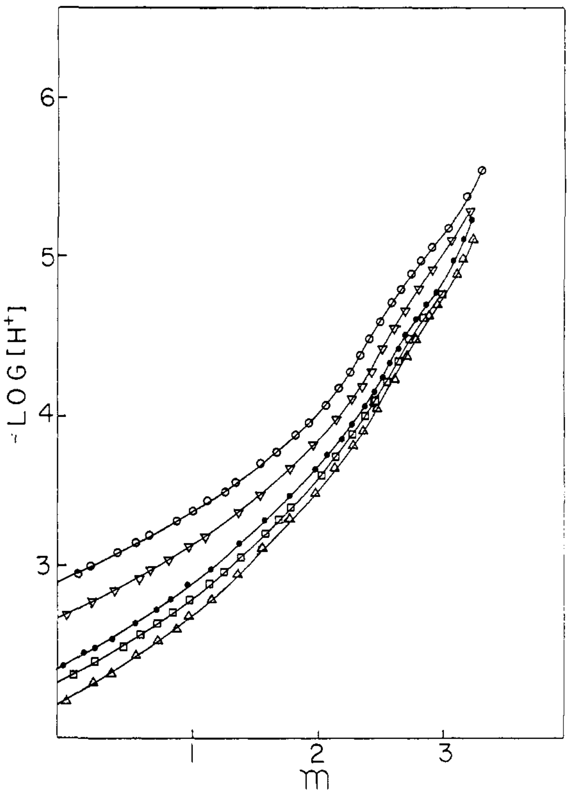


Figure 3. Potentiometric titration of 1:1 OV(IV)-salicyl phosphate chelate at 9.5° and $\mu = 0.10$ (KNO_3); concentrations: ○—○ 7.90 $\times 10^{-4}$ *M*, ▽—▽ 1.58 $\times 10^{-3}$ *M*, ●—● 3.13 $\times 10^{-3}$ *M*, □—□ 4.76 $\times 10^{-3}$ *M*, △—△ 6.36 $\times 10^{-3}$ *M*.

prepared at two different concentrations, and a sufficient amount of standard base was added in order to obtain *m* values of from 2.3 to 2.8. The samples were then thermostated at 25° and the pH measurements were taken at various time intervals. The pH values were found to be still decreasing over a 1-month period. In some cases a precipitate was formed. In addition, plots of eq 3 and 5 did not give a straight line.

5-Sulfo-8-hydroxyquinoline (HQS). Titration, at 25 and 34.9°, of a 1:1 molar ratio of vanadyl salt to 5-sulfo-8-hydroxyquinoline gave a titration curve with an inflection at $m = 2$. Calculations based on the titration curve in the region $m = 0.2$ to 1.0 gave constant values of the formation constant of the 1:1 chelate compound for each temperature and concentration at which the titration was carried out. The formation constant was calculated by means of an equation similar to (8), and the hydrolysis and olation reactions were calculated as described above (eq 3). The resulting equilibrium constants are given in Tables I and II.

Interaction of OV(IV) and Salicyl Phosphate. In order to determine the extent of interaction of vanadyl ion and the substrate, titrations of different concentrations and ratios of metal salt to salicyl phosphate were carried out at two different temperatures, 25 and 9.5°. The titrations were performed as rapidly as possible to minimize the error caused by hydrolysis of salicyl phosphate. Titration of a 1:1 molar ratio of OV(IV) salt to salicyl phosphate gives a very slight inflection at about $m = 3$, followed by a sloping buffer region, which continues on beyond $m = 4$. The 1:1 titration curves obtained at 9.5° for different concentrations are shown in Figure 3.

Calculations based on the part of the titration curve from $m = 1$ to $m = 1.7$ gave constant values for the formation constant of the 1:1 chelate compound for each temperature and concentration at which the titration was carried out. The formation constant was calculated by means of the following equations

$$K_{ML} = \frac{T_L - X[L^{3-}]}{X[L^{3-}]^2} \tag{8}$$

where

$$[L^{3-}] = \frac{(2 - a)T_L - [H^+]}{2[H^+]^2/K_2K_3 + [H^+]/K_3}$$

and

$$X = [H^+]^2/K_2K_3 + [H^+]/K_3 + 1$$

where K_2 and K_3 are the second and third dissociation constants of salicyl phosphate. The values obtained for log K_{ML} are listed in Tables I and II.

In the region between $m = 3$ and $m = 4$ an attempt was made to determine if a dimeric species was formed. The plot at 25°, based on eq 3, gave a scatter of points, from which rough values of pK_D (9.1) and of p$K_{M(OH)L}$ (5.7) were calculated. At 9.5° the dimer plot was not so satisfactory and the values obtained are 9.7 for pK_D and 6.9 for p$K_{M(OH)L}$. In spite of the scatter, the data in Figure 4 were fitted to a straight line by least squares. The resulting solution of eq 3 indicates that the formation of a dimeric species is probable. This conclusion is further supported by the fact that a trimer plot was not linear.

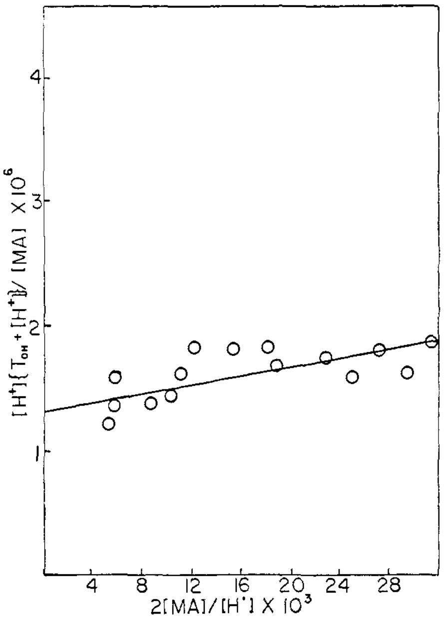


Figure 4. Plot of $[H^+](T_{OH} + [H^+])/[ML^-]$ against $2[ML^-]/[H^+]$ for the 1:1 OV(IV)-salicyl phosphate chelate at 9.5° illustrating the presence of a dimer; the data are taken from the potentiometric titration curves presented in Figure 3. The line represents a least-squares fit of the data; $aT_L = T_{OH}$.

The titration of a 2:1 molar ratio of vanadyl salt to substrate resulted in inflections at $m = 1.5$, $m = 2.5$, and $m = 3.5$, as is seen in Figure 5. The inflection at $m = 1.5$ indicates the possible formation of a species of the type M_2L. Formation of hydroxo complex species would possibly give inflections at $m = 2.5$ and also at 3.5. The following reaction would give an inflection at $m = 1.5$.

$$2M^{2+} + H_3L \rightleftharpoons M_2L^+ + 3H^+$$

A reaction such as

$$M_2L^+ \rightleftharpoons M_2L(OH)_2^- + 2H^+$$

would explain the inflection at $m = 2.5$. The equilibrium constant for the latter reaction was calculated by the following equations.

$$K_{M_2(OH)_2L} = \frac{[M_2L(OH)_2^-][H^+]^2}{[M_2L^+]} = \frac{(aT_L + [H^+] - [OH^-])[H^+]^2}{(2 - a)T_L - [H^+] + [OH^-]}$$

where T_L is the total ligand concentration and T_M is the total metal ion concentration. The value obtained for $-\log K_{M_2(OH)_2L}$ is 9.28 ± 0.07.

In order to explain the inflection at $m = 3.5$, the reaction proposed is

$$M_2L(OH)_2^- \rightleftharpoons M_2L(OH)_4^{3-} + 2H^+$$

Calculations based on this assumption were unsuccessful. It was then assumed that in competition with this reaction, the reaction to form the dimer was taking place. The equations were derived and were transformed to the slope–intercept form. The dimer plot, however, gave an unsatisfactory (negative) slope so that mathematical treatment of the type described did not support the proposed reactions.

Titration of a 1:2 molar ratio of vanadyl salt to salicyl phosphate (Figure 6) gave an inflection at $m =$

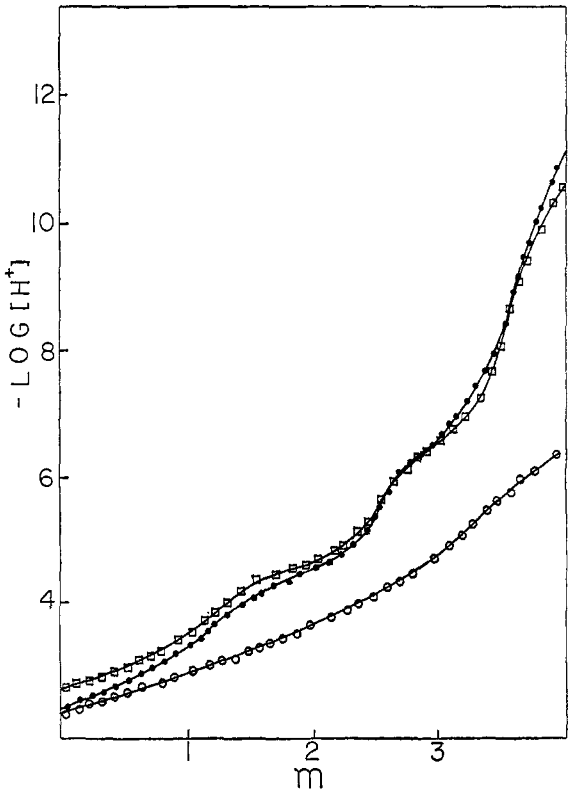


Figure 5. Potentiometric titration of 2:1 and 1:1 OV(IV)-salicyl phosphate at $\mu = 0.10$ (KNO_3) and 9.5°; concentrations: ●—● $T_M = 2T_A = 3.17 \times 10^{-3}$ M, ○—○ $T_M = T_A = 3.17 \times 10^{-3}$ M, □—□ $T_M = 2T_A = 1.58 \times 10^{-3}$ M, m = moles of base added per mole of metal ion.

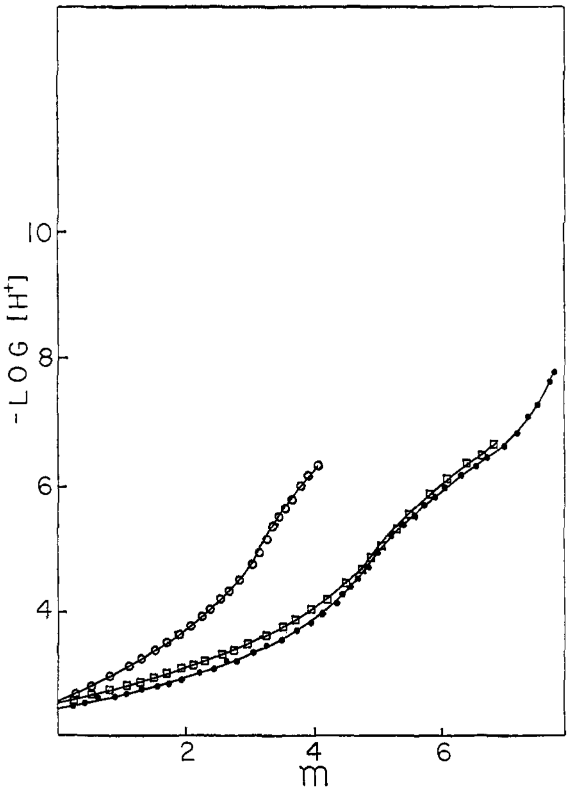


Figure 6. Potentiometric titrations of 1:1 and 1:2 OV(IV)–salicyl phosphate chelates and the 1:2 calculated titration curve at 25° and $\mu = 0.10$ (KNO_3); concentrations: ○—○ $T_A = T_M = 3.17 \times 10^{-3}$ M for 1:1 experimental titration curve, ●—● $T_A = 2T_M = 3.09 \times 10^{-3}$ M for 1:2 experimental titration curve, □—□ calculated titration curve, m = moles of base added per mole of metal ion.

5. The only possible way to explain this observation is to assume that there is no interaction between the 1:1 vanadyl–salicyl phosphate chelate and the second mole of salicyl phosphate. This assumption is verified by the addition of abscissas of the titration curves for the 1:1 chelate and for salicyl phosphate. The resulting calculated curve shows an inflection at $m = 5$ in agreement with the experimental results (Figure 6).

To gain some insight into the interaction between the substrate and the various chelate compounds which were used as catalysts, titrations of 1:1:1 molar ratios of metal to ligand to substrate were carried out. An inflection at $m = 4$ was observed in each case. If a stable mixed ligand chelate were formed, the inflection would be expected to occur at an m value of 5.

If it is assumed that there is no interaction between the metal chelate and the substrate, one can calculate a theoretical titration curve. The actual titration curve and the theoretical curve for VO–SSA–SP were compared. The agreement was good, and it seems reasonable to assume that no stable mixed chelate is formed and that there is no appreciable degree of mixed ligand complex formation between the 1:1 vanadyl–sulfosalicylic acid chelate and the -salicyl phosphate.

The equilibrium data obtained at two or more temperatures were used in calculating the heats and entropies of formation of the vanadyl complexes containing 1 mole of ligand per mole of oxovanadium ion. The results are given in Table III.

Table III. Thermodynamic Data for Formation of 1:1 OV(IV) Chelates of Various Ligands (25–35°, $\mu = 0.10$ (KNO_3))

Ligand	$-\Delta H°$, kcal/mole	$+\Delta S°$, eu
Salicylic acid	2.1 ± 0.5	54 ± 3
Sulfosalicylic acid	1.7 ± 0.5	45 ± 3
Tiron	2.5 ± 0.5	67 ± 3
5-Sulfo-8-hydroxyquinoline	1.7 ± 0.5	45 ± 3
Salicyl phosphate	0.5 ± 0.5	25 ± 3

Discussion

Salicylic Acid and Sulfosalicylic Acid. In the case of both salicylic acid and sulfosalicylic acid, a chelate compound having a 1:1 ratio of ligand to metal ion is formed, and 2 moles of acid is produced per mole of metal chelate formed. The salicylic acid chelate is about 100 times more stable than the corresponding sulfosalicylic acid chelate. Neither of these ligands forms chelate compounds containing 2 moles of ligand per gram ion of metal.

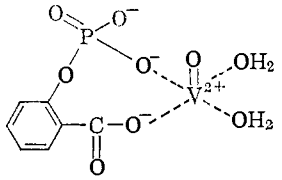
The fact that the 1:1 chelate of sulfosalicylic acid combines with hydroxyl ion was shown by the determination of the dimerization and hydrolysis constants calculated in the region beyond the point where 2 moles of base has been added. If the titrations are carried out rapidly, dimeric species are initially formed, as was demonstrated in Figure 1. When the solution was allowed to stand after the addition of each increment of base, it was not possible to detect a dimer, although the solutions remained homogeneous in most cases. It seems probable, therefore, that extensive polymerization takes place through the initial formation of a dimeric species, which condenses further to higher polynuclear complexes.

3,5-Disulfopyrocatechol (Tiron). Further evidence of polymerization of the vanadyl chelate through the formation of a dimer is given by the 1:1 vanadyl–Tiron system. When the titration was carried out rapidly, a reasonably good dimer plot was obtained. However, when the pH measurements were taken over a long period of time, no evidence of the dimeric species could be found. However, many of the solutions remained free of precipitation, while gradual drift of pH to lower values indicated that progressive hydrolysis was occurring. The system did not appear to be at equilibrium even after a period of a month.

The only ligand in this investigation which forms a 2:1 ligand–metal chelate compound with OV(IV) is Tiron. This complex seems to form in two steps: the formation of the 1:1 chelate, followed by the binding of the second mole of the ligand at higher pH.

5-Sulfo-8-hydroxyquinoline. A 1:1 chelate compound, which has a stability roughly equivalent to that of the sulfosalicylic acid chelate, is formed with 8-hydroxyquinoline-5-sulfonate. The observed inflection at $m = 2$ is indicative of the binding of the vanadyl ion to the aromatic nitrogen and phenolic oxygen to form a five-membered ring.

Salicyl Phosphate. The interaction of the substrate itself with the vanadyl ion is quite complex and interesting. The most acidic hydrogen of the phosphate group of the salicyl phosphate is completely ionized in aqueous solution at low pH in the absence of a metal ion. In the presence of OV(IV), the titration shows a slight inflection at $m = 3$, which indicates that a chelate compound having the arrangement of coordinate bonds shown in VI is probably formed.

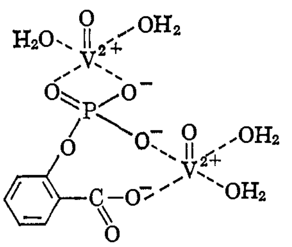


VI

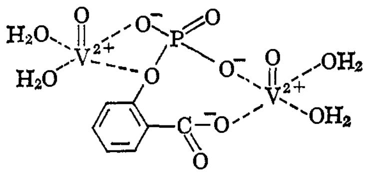
If the vanadyl ion was bound only to the phosphate, an inflection at $m = 2$ would be expected since the influence of coordination on the acidity of the remote carboxyl group would not be sufficient to increase its dissociation constant to the point where it would not be observed as a separate step in the titration curve. If the metal ion were bound only to the carboxylate group, the acidity of the acid phosphate group would not be greatly affected. It seems, therefore, that the vanadyl ion is probably bound to both the carboxylate and phosphate groups with the formation of a weak eight-membered chelate ring. This conclusion is supported by the rather low stability found for this metal chelate compound.

As the pH is raised, the OV(IV) chelate hydrolyzes and forms a binuclear diolated complex. The formation of the dimer is indicated by the success of the correlation shown in Figure 4 and the failure of other types of correlation attempted. It was not possible to measure the hydrogen ion concentration over a long period of time because of the slow solvolysis of the salicyl phosphate ligand to salicylate and phosphate ions. It is also quite likely that further polymerization takes place, but such a reaction is probably very complicated and cannot be determined by potentiometric techniques of the type used in this research.

It appears from the results obtained that a binuclear chelate compound of the type M_2L is formed between the vanadyl ion and salicyl phosphate. If a chelate compound with 2:1 molar ratio of metal ion per ligand is formed, the titration should show an inflection at $m = 1.5$. The complexes formed might have the arrangements of coordinate bonds as shown in VII or VIII. From potentiometric titration data it is impossible to determine which arrangement is the more probable but VII is favored because of the relative basicities and charges of the oxygen atoms bound to the metal ions.

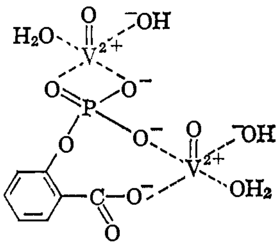


VII

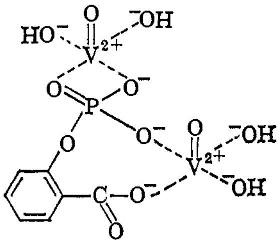


VIII

The inflections which occur at $m = 2.5$ and at $m = 3.5$ then seem reasonable if water molecules coordinated to the vanadyl ion are assumed to dissociate to give IX and X, respectively. The formation of the hydrolyzed species IX would then account for the inflection at $m = 2.5$, and the formation of X would account for the inflection at $m = 3.5$. Other arrangements of groups are, of course, possible.



IX



X

Thermodynamic Data. The heats and entropies of formation of the 1:1 vanadyl chelates listed in Table III are quite similar in magnitude, indicating the similarities of the reactions involved. The greatest difference is the less favorable entropy of formation of the 1:1 vanadyl–salicyl phosphate chelate, in accordance with the much larger chelate ring formed in this case. The heats of reaction show that the strengths of the metal–ligand bonds in these chelates are not much greater than the metal–oxygen bonds of the hydrated vanadyl ion, and that the driving force of these reactions comes mainly from the entropy of reaction, which is in turn due primarily to the change in hydration that occurs on charge neutralization as a result of complex formation.

Relative Stabilities. A comparison of the stabilities of the chelates studied shows that the most stable 1:1 chelate is formed by Tiron. The binding of the very basic catecholate group to the vanadyl ion results in a very stable chelate compound. In addition, only Tiron is able to form a chelate compound of the type ML_2. The salicylic acid chelate is about three orders of magnitude less stable than the Tiron chelate. The less basic carboxyl group apparently does not interact as strongly with OV(IV) as the phenolate group. The sulfonate group in sulfosalicylic acid has little effect on the acidity of the carboxyl group but increases the acidity of the phenolic group and results in the formation of a 1:1 chelate compound which is approximately one-hundredth as stable as the salicylic acid chelate. The 1:1 chelate compound of 5-sulfo-8-hydroxyquinoline is about equivalent in stability to the sulfosalicylic acid chelate. It appears that the presence of the basic phenolic group helps the formation of the 1:1 chelate since the diamines[8] previously studied do not form stable chelates with OV(IV). On this basis it is not surprising that the least stable of the 1:1 chelate compounds of OV(IV) is that formed with salicyl phosphate. The rather low stability might be the result of the formation of an eight-membered chelate ring as proposed, VI.

A comparison of the stabilities of the vanadyl chelate compounds, given in Table I, with other transition metal chelates and the same ligands shows that the oxovanadium chelates generally are more stable. The following order of stabilities is observed: OV(IV) > Cu(II) > Zn(II) > Co(II) > Ni(II) > Fe(II). In particular, it should be noted that in all cases the vanadyl chelate compounds are more stable than those formed with Cu(II). This might possibly be a result of the influence of the highly electronegative oxygen which is bound to the vanadium atom. The resulting higher electropositive character of the vanadium would thus make it a stronger Lewis acid and lead to more stable chelates.

The remarkable ease of hydrolysis of the vanadyl chelate compounds should also be emphasized. The vanadyl chelate compounds hydrolyze much more easily than any of the other metal chelates of the first transition series. The vanadyl chelates discussed above prefer combination with hydroxyl ions to a second mole of ligand. The only exception to this is the very basic catecholate dianion which can compete with the hydroxyl ion to form a stable 2:1 chelate compound.

Other Ligands. Titration of solutions having 1:1 and 2:1 ratios of ethylenediamine, hydroxyethylethylenediamine, diethylenetriamine, and triethylenetetramine to vanadyl salt all lead to precipitation of vanadyl hydrous oxide. It seems reasonable to assume that, since the precipitates formed in all cases at approximately the same pH value of 4.4 (the pH at which VO^{2+} salts precipitate), either no chelate is formed or that any chelate formed is extremely weak.