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Complexation Equilibria of Vanadium(V) with 8-Quinolinolate in Aqueous Solutions

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The complexation equilibria of vanadium(V) with 8-quinolinolate ion(ox$^-$) were investigated spectrophotometrically. Depending upon the acidity of the solution various 1 : 1 and 1 : 2 complexes are formed: VO_3ox^{2-}, VO_3Hox^-, VO_2ox, and $VO_2ox_2^-$. The formation and protonation constants of these complexes are discussed in terms of their structures.

Vanadium(V) reacts with 8-quinolinol(Hox) to give a black precipitate in weakly acidic solution. This complex has been identified to be $V_2O_3ox_4$ or VO(OH)-ox_2 from the vanadium content.[1–5] This complex, reacting with alcohols (ROH), gives rise to a red complex, of which the structure has been established as VO(OR)ox_2 by X-ray study.[6] Furthermore, a yellow precipitate has also been isolated from nearly neutral solution, for which the composition $NaVO_2ox_2$ has been given according to the elemental analysis.[1,4,7] It seems interesting to make it clear why the protonation of $NaVO_2ox_2$ causes such a pronounced color change.

The solvent extraction of vanadium(V) with 8-quinolinol has also revealed the metal to ligand ratio of 1 : 2, from which the composition of VO(OH)ox_2 has been given to the black extracted species.[8,9] This extraction system has been utilized to determine the hydrolysis constants of dioxovanadium(V).[9,10] In these studies no complexed species being assumed in the aqueous phase, it is sometimes indispensable to take into account the formation of lower complexes especially in the extraction of multivalent metals.[11,12] Vanadium(V) itself tends to be hydrolyzed and is correspondingly expected to form various 1 : 1 and 1 : 2 complexes with 8-quinolinolate of various degree of hydrolysis. The complexation reactions of Mo(VI) and W(VI) with 8-quinolinolate were studied under limited conditions.[13] However, the stepwise complex formation of multivalent ions has been little studied.

In order to understand the complexation reaction and the extraction behavior of vanadium(V) with 8-quinolinol, we first study the complexation reaction of vanadium(V) with 8-quinolinolate under conditions where no black precipitate appears in the aqueous solution.

Experimental

Reagent. *Dioxovanadium(V) Perchlorate*: Ammonium metavanadate, recrystallized from isothermally distilled ammonia, was dissolved in sodium hydroxide solution. Then the solution was heated with nitrogen gas bubbling to expell ammonia. After cooling, perchloric acid was added to obtain dioxovanadium(V) perchlorate solution, which was standardized titrimetrically against a standard potassium permanganate solution.

8-Quinolinol: Reagent grade 8-quinolinol was recrystallized twice from aqueous acetone.

The method of preparation of sodium perchlorate and sodium hydroxide has been described previously.[11]

Measurement. All the experiments were carried out in a room thermostated at 25±0.5 °C. All the measurements were performed in a thermoelectric circulating bath thermostated at 25±0.1 °C. The ionic strength was maintained at 1.00 mol dm^{-3} with sodium perchlorate. Spectrophotometric measurements were performed on a UNION High Sens Spectrophotometer SM-401 with a thermostated cell compartment. Hydrogen ion concentration was determined by a Radiometer pH meter (PHM 22 type) with a Radiometer glass electrode (G 202 C type) and a calomel electrode filled with a saturated sodium chloride as an internal solution. A 1.00×10^{-2} mol dm^{-3} perchloric acid solution of ionic strength 1 mol dm^{-3} was used as a standard of hydrogen ion concentration: $-\log[H^+]=2.00$. The change of a liquid-junction potential was taken into account.[14]

In order to avoid the polymerization of vanadium(V),[15] it is indispensable to control the total concentration of vanadium(V), to observe the order of mixing various solutions, and to stir the solution vigorously. All the experiments have been carried out under conditions where no polymerized species occurs. The formation of polymers was always monitored by the near ultraviolet and visible spectra.

Results

Protonation Equilibria of 8-Quinolinolate Ion. The protonation equilibria of 8-quinolinolate are expressed by Eqs. 1 and 2:

$$ox^- + H^+ \xrightleftharpoons{K_{Hox}} Hox \qquad (1)$$

$$Hox + H^+ \xrightleftharpoons{K_{H_2ox}} H_2ox^+ \qquad (2)$$

The absorbance at 350 nm of the solution containing 3.91×10^{-4} mol dm^{-3} 8-quinolinol was plotted against $-\log[H^+]$. According to the plot we have two equilibria, which are separated enough to treat them as two independent steps. The plot was compared with a set of normalized curves; $X=\log x$, $Y=a/(1+x)$. The values of the protonation constants and the molar extinction coefficients obtained are as follows:

$$\log K_{H_2ox} = 5.36 \pm 0.02;\ \varepsilon_{H_2ox} = 1560;$$
$$\log K_{Hox} = 9.43 \pm 0.02;\ \varepsilon_{Hox} = 260;$$
$$\varepsilon_{ox} = 2710$$

at 25±0.1 °C and at an ionic strength of 1.0($NaClO_4$).

Protonation Equilibrium of Hydrogen Orthovanadate Ion. The protonation of hydrogen orthovanadate ion is expressed by Eq. 3:[16]

$$HVO_4^{2-} + H^+ \xrightleftharpoons{K_{VO_3}} VO_3^- \qquad (3)$$

The ultraviolet spectra of the solutions containing about

5×10^{-4} mol dm^{-3} vanadium(V) were measured at various hydrogen ion concentrations. A distinct isosbestic point is observed at 290 nm over the range of $-\log[\mathrm{H^+}]=7.6$—10. The deviation of the isosbestic point at $-\log[\mathrm{H^+}]$ value lower than 7.6 was thought to be due to the formation of polymers. The absorbance change at 265 nm was plotted against $-\log[\mathrm{H^+}]$ over the range of $-\log[\mathrm{H^+}]=7.6$—10. The plot was compared with a normalized curve; $X=\log x$, $Y=a/(1+x)$ and we obtained $\log K_{\mathrm{VO_4}}=8.07\pm0.06$. The value obtained by Schwarzenbach and Geier ($\log K_{\mathrm{VO_4}}=8.04$ at 20 °C and 1 mol dm^{-3} KCl)[17] agrees with ours.

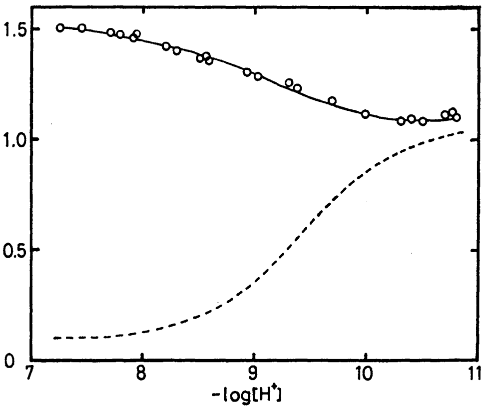

Fig. 1. Absorbance change at 350 nm as a function of $-\log[\mathrm{H^+}]$. $C_\mathrm{V}=1.39\times10^{-3}$ mol dm^{-3}, $C_\mathrm{Hox}=3.93\times10^{-4}$ mol dm^{-3}. The solid line: the calculated curve with the constants obtained; the dotted line: data in the absence of vanadium(V).

Complexation Equilibria. The absorbance at 350 nm of the solution containing 1.39×10^{-3} mol dm^{-3} vanadium(V) and 3.93×10^{-4} mol dm^{-3} 8-quinolinol was plotted against $-\log[\mathrm{H^+}]$ (Fig. 1). The absorbance change under the same conditions without vanadium(V) is also shown by the dotted line. Thus the difference between these two lines can be ascribed to the complex formation.

In the presence of an excess amount of vanadium(V), the formation of only 1 : 1 complex is anticipated and the equilibrium is generally expressed by Eq. 4:

$$\mathrm{HVO_4}^{2-} + m\mathrm{H}^+ + \mathrm{ox}^- \overset{\beta_{1m1}}{\rightleftharpoons} \mathrm{VO_4H}_{m+1}\mathrm{ox}^{(3-m)-} \tag{4}$$

where m is the number of protons involved in the complexation reaction and β_{1m1} is the overall formation constant of the species formed. We have Eqs. 5 and 6:

$$\frac{A-A'}{\varepsilon_{1m1}C_\mathrm{Hox}-A} = \beta_{1m1}\frac{[\mathrm{HVO_4}^{2-}][\mathrm{H^+}]^m}{\alpha_\mathrm{ox}} \tag{5}$$

$$[\mathrm{HVO_4}^{2-}] = \frac{1}{\alpha_{\mathrm{HVO_4}}}\left(C_\mathrm{V} - \frac{A-A'}{\varepsilon_{1m1}C_\mathrm{Hox}-A'}\times C_\mathrm{Hox}\right) \tag{6}$$

where A and A' are observed absorbances in the presence and in the absence of vanadium(V), respectively, C_Hox and C_V are the total concentration of 8-quinolinol and vanadium(V), respectively, and α_ox and $\alpha_{\mathrm{HVO_4}}$ are the side reaction coefficients taking into account the protonation reaction of 8-quinolinolate ion and hydrogenorthovanadate ion, respectively. At 350 nm the molar extinction coefficients of the uncomplexed vanadium(V) species are negligibly small as compared with those of the complexes and the ligand. ($\log((A-A')/(\varepsilon_{1m1}C_\mathrm{Hox}-A))-\log[\mathrm{HVO_4}^{2-}]+\log\alpha_\mathrm{ox}$) being plotted against $-\log[\mathrm{H^+}]$, a straight line with a slope of m and an intercept of $\log\beta_{1m1}$ will be obtained, provided only one complex is involved in reaction given by Eq. 4.

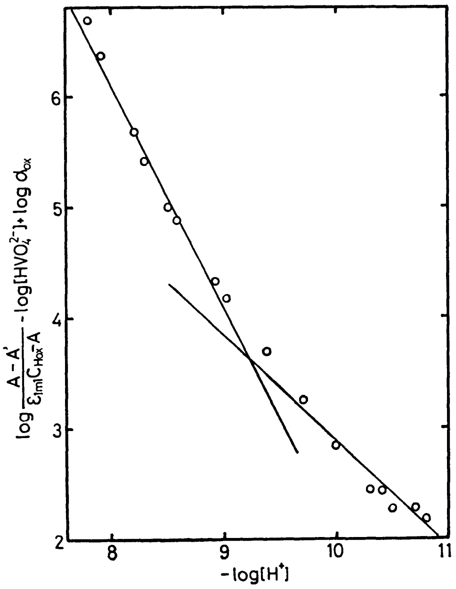

Fig. 2. Determination of the formation constants of vanadium(V)-8-quinolinolate complexes. Plot of $\log((A-A')/(\varepsilon_{1m1}C_\mathrm{Hox}-A))-\log[\mathrm{HVO_4}^{2-}]+\log\alpha_\mathrm{ox}$ *vs.* $-\log[\mathrm{H^+}]$.

The slope of the plot is close to 2 at lower value of $-\log[\mathrm{H^+}]$, while at higher value of $-\log[\mathrm{H^+}]$ it tends to be unity (Fig. 2). This points to the formation of two types of 1 : 1 complex, namely $\mathrm{VO_3Hox^-}$ and $\mathrm{VO_3ox^{2-}}$. The complex is now described not to have more than 1 proton by the repeated elimination of two protons with one oxo group as one water (see Discussion). The overall formation constants and the molar extinction coefficients obtained by the graphical plot were refined with an electronic computer to have the following values:

$$\log\beta_{121} = 22.1\pm0.1;\ \varepsilon_{121} = \varepsilon_{\mathrm{VO_3Hox}} = 3830\pm50;$$

$$\log\beta_{111} = 12.8\pm0.1;\ \varepsilon_{111} = \varepsilon_{\mathrm{VO_3ox}} = 3650\pm100.$$

The data for the solution containing 1.48×10^{-4} mol dm^{-3} vanadium(V) and 7.82×10^{-5} mol dm^{-3} 8-quinolinol are also well interpreted with the above constants. This confirms the absence of polymerization under the present experimental conditions: the above results are regarded as reliable.

Equilibria in more acidic media were studied by decreasing the total concentrations of vanadium(V) and 8-quinolinol to 5.92×10^{-5} and 3.13×10^{-5} mol dm^{-3}, respectively, the polymerization of vanadium(V) being avoided. The absorbance of the solution at 400 nm was measured at various hydrogen ion concentration and plotted against $-\log[\mathrm{H^+}]$ (Fig. 3). Under these conditions protonation equilibria of vanadium(V), Eqs. 7 and 8, must also be considered:[18]

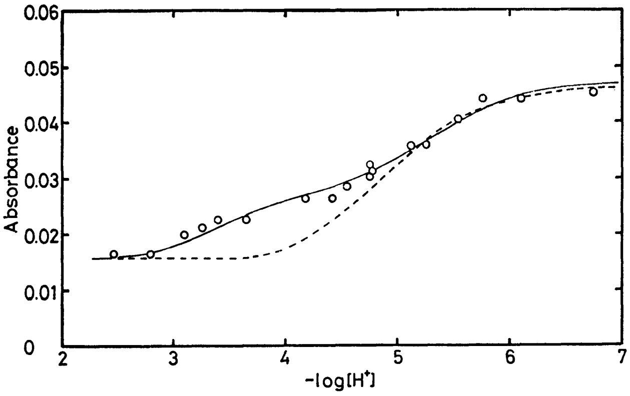

Fig. 3. Absorbance change at 400 nm as a function of $-\log[H^+]$. $C_V=5.92\times10^{-5}$ mol dm^{-3}, $C_{Hox}=3.13\times10^{-5}$ mol dm^{-3}. The solid line: the calculated curve with the constants obtained; the dotted line; the calculated curve without taking into account the formation of VO_2ox.

$$VO_3^- + H^+ \overset{K_{HVO_3}}{\rightleftharpoons} HVO_3 \qquad (7)$$

$$HVO_3 + H^+ \overset{K_{VO_2}}{\rightleftharpoons} VO_2^+ \qquad (8)$$

The assumption of VO_3Hox^- as a sole species leads to the deviation at lower value of $-\log[H^+]$ as shown by the dotted line in Fig. 3. This deviation points to the formation of a further protonated species, for example VO_2ox. The combination of the formation constants and the molar extinction coefficients of the above two protonated species, VO_3Hox^- and VO_2ox, leads to the best fit curve indicated by the full line in Fig. 3 with the following:

$$\log\beta_{131} = 27.5\pm0.1;\ \varepsilon_{131} = \varepsilon_{VO_2ox} = 1100\pm50.$$

The absorbance at 350 nm of the solution containing 7.00×10^{-5} mol dm^{-3} vanadium(V) and 3.91×10^{-4} mol dm^{-3} 8-quinolinol was plotted against $-\log[H^+]$ (Fig. 4). In the presence of excess amounts of 8-quinolinol the formation of 1 : 2 complex is also anticipated:

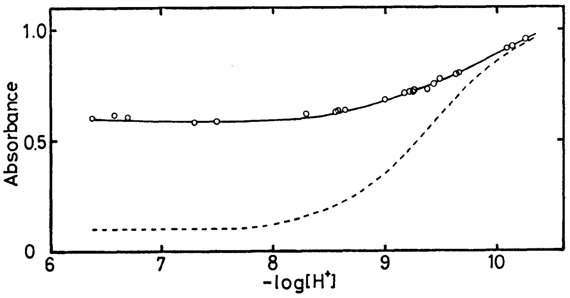

Fig. 4. Absorbance change at 350 nm as a function of $-\log[H^+]$. $C_V=7.00\times10^{-5}$ mol dm^{-3}, $C_{Hox}=2.91\times10^{-4}$ mol dm^{-3}. The solid line: the calculated curve with the constants obtained; the dotted line: data in the absence of vanadium(V).

$$HVO_4^{2-} + mH^+ + 2ox^- \overset{\beta_{1m2}}{\rightleftharpoons} VO_4H_{m+1}ox_2^{(4-m)-} \qquad (9)$$

It was revealed that in addition to 1 : 1 complexes only $VO_2ox_2^-$ with $m=3$ forms. The combination of the overall formation constant and the molar extinction coefficient giving a minimum error square sum is as follows:

$$\log\beta_{132} = 36.0\pm0.1;\ \varepsilon_{132} = \varepsilon_{VO_2ox_2} = 7660\pm100.$$

Discussion

Species identified in this study are represented in Scheme 1 together with pK_a and logarithmic formation constants.[18,19]

In Scheme 1 the changes from left to right correspond to hydrolytic reactions and the changes from upper to lower complexation reactions. It can be seen that the complexation ability decreases with increasing degree of hydrolysis of vanadium(V): the formation constant of VO_3ox^{2-} is $10^{5.6}$ times as low as that of VO_3Hox^-. The same trend has been observed in the complexation of tungsten(VI) with 8-quinolinolate,[13] where the formation constant of WO_4Hox^{2-} is $10^{5.6}$ times as low as that of WO_3ox^-, as evident from the following scheme:

$$\begin{tikzcd}
H_2WO_4 \arrow[r, "3.5", shift left] \arrow[r, leftarrow, shift right] \arrow[d, "14.2", shift left] \arrow[d, leftarrow, shift right] & HWO_4^- \arrow[r, "2.3", shift left] \arrow[r, leftarrow, shift right] \arrow[d, "8.6", shift left] \arrow[d, leftarrow, shift right] & WO_4^{2-} \\
WO_3ox^- \arrow[r, "9.1", shift left] \arrow[r, leftarrow, shift right] & WO_4Hox^{2-} &
\end{tikzcd}$$

This difference is mainly attributable to the effect of charge and the number of oxo groups.

The formation constants of the dioxovanadium complexes with various ligands are summarized in Table 1, in which $\sum$ pK_a, the summation of the loga-

Table 1. Formation constants of dioxovanadium complexes with various ligands at 25 °C

Number	Ligand	Ionic strength mol dm^{-3}	log β	$\sum$ pK_a	Reference
1	edda^{2-}	1.0($NaClO_4$)	14.5	20.5	14
2	nta^{3-}	1.0($NaClO_4$)	13.8	14.5	14
3	mida^{2-}	1.0($NaClO_4$)	10.2	13.4	14
4	pda^{2-}	1.0($NaClO_4$)	8.7	7.3	20
5	edta^{4-}	3.0($NaClO_4$)	15.5	20.3	21
6	nta^{3-}	3.0($NaClO_4$)	13.8	15.1	21
7	2ox$^-$	1.0($NaClO_4$)	21.0	29.6	this work

edda^{2-}, nta^{3-}, mida^{2-}, pda^{2-} and edta^{4-} denote ethylenediamine-*N*,*N*′-diacetate, nitrilotriacetate, *N*-methyliminodiacetate, 2,6-pyridinedicarboxylate and ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate, respectively.

$$\begin{tikzcd}
 & VO_2^+ \arrow[r, "3.2", shift left] \arrow[r, leftarrow, shift right] \arrow[d, "12.4", shift left] \arrow[d, leftarrow, shift right] & HVO_3 \arrow[r, "3.8", shift left] \arrow[r, leftarrow, shift right] \arrow[d, "10.3", shift left] \arrow[d, leftarrow, shift right] & VO_3^- \arrow[r, "8.1", shift left] \arrow[r, leftarrow, shift right] \arrow[d, "4.7", shift left] \arrow[d, leftarrow, shift right] & HVO_4^{2-} \arrow[r, "13", shift left] \arrow[r, leftarrow, shift right] & VO_4^{3-} \\
 & VO_2ox \arrow[r, "5.3", shift left] \arrow[r, leftarrow, shift right] \arrow[d, "8.6", shift left] \arrow[d, leftarrow, shift right] & VO_3Hox^- \arrow[r, "9.3", shift left] \arrow[r, leftarrow, shift right] & VO_3ox^{2-} & & \\
\text{black ppt.} \arrow[r, shift left] \arrow[r, leftarrow, shift right] & VO_2ox_2^- & & & &
\end{tikzcd}$$

Scheme 1.

$$\begin{tikzcd}
\mathrm{VO(OH)_3(OH_2)_2} \arrow[r, shift left, "3.8"] \arrow[d, shift left, "1.8"] & \mathrm{VO_2(OH)_2(OH_2)_2^-} \arrow[l, shift left] \arrow[r, shift left, "8.1"] \arrow[d, shift left, "0.3"] & \mathrm{VO_3(OH)(OH_2)_2^{2-}} \arrow[l, shift left] \arrow[r, shift left, "13"] \arrow[d, shift left, "-1.0"] & \mathrm{VO_4^{3-}} \arrow[l, shift left] \\
\mathrm{VO(OH)_2ox(OH_2)} \arrow[u, shift left] \arrow[r, shift left, "5.3"] & \mathrm{VO_2(OH)ox(OH_2)^-} \arrow[u, shift left] \arrow[l, shift left] \arrow[r, shift left, "9.3"] \arrow[dd, shift left, "0.1"] & \mathrm{VO_3ox(OH_2)^{2-}} \arrow[u, shift left] \arrow[l, shift left] & \\
\mathrm{[not\ VO_2ox(OH_2)_2]} & & \mathrm{[not\ VO_2(OH)_2ox^{2-}]} & \\
& \mathrm{VO_2ox_2^-} \arrow[uu, shift left] & &
\end{tikzcd}$$

Scheme 2.

rithmic stepwise protonation constants for the donor atoms which actually coordinate to the central metal, is also listed. When the overall formation constant is plotted against $\sum \mathrm{p}K_\mathrm{a}$, a fairly good linear relationship is observed (Fig. 5).[22]

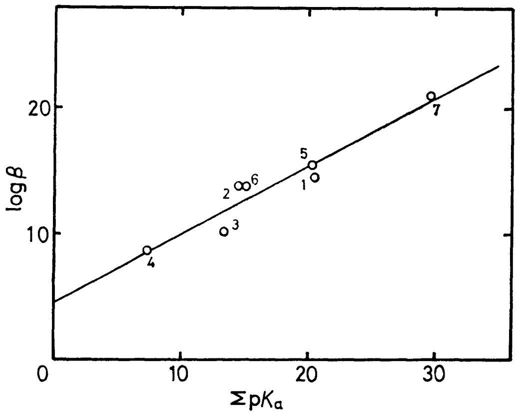

Fig. 5. Correlation of the overall formation constant of vanadium(V) complex with $\sum \mathrm{p}K_\mathrm{a}$ of the ligand. For the number Table 1 should be referred to.

In order to compare $\mathrm{p}K_\mathrm{a}$ values Scheme 1 is rewritten as Scheme 2 with probable structures[23] and logarithmic constants. In Scheme 2 the species are arranged to have a same charge in a row. So the change from upper to lower is the substitution reaction of hydroxo group by 8-quinolinolate. $\mathrm{VO_2ox}$ and $\mathrm{VO_3ox^{2-}}$ have more than one possible structures.

The $\mathrm{p}K_\mathrm{a}$ of a neutral acid of the formula $\mathrm{H_aXO_{a+1}}$, which have one oxo group, lies in the range of 2—3 and increases by 4—5 for each successive proton dissociation with increase of oxo groups.[25,26] Vanadic acid belongs to this category and can be described as $\mathrm{VO(OH)_3(OH_2)_2}$, which gives rise to $\mathrm{VO_2(OH)_2(OH_2)_2^-}$ and $\mathrm{VO_3(OH)(OH_2)_2^{2-}}$ upon proton dissociation. The formulation $\mathrm{VO(OH)_4(OH_2)^-}$ for metavanadate ion[10] seems unlikely.

When $\mathrm{p}K_\mathrm{a}$ values of complexes are compared with those of the corresponding vanadic acid, nearly the same difference is observed: 3.8 as compared to 5.3 for the first proton dissociation (difference of 1.5) and 8.1 as compared to 9.3 for the second proton dissociation (difference of 1.2). These differences may be ascribed to the difference in electron donating ability between hydroxide and 8-quinolinolate. Thus we may conclude that the change in the number of oxo groups during the hydrolysis of the complex is the same as in the proton dissociation of vanadic acid and that the skeleton of vanadium(V) species is retained during the complexation. Thus $\mathrm{VO_2ox}$ is $\mathrm{VO(OH)_2ox(OH_2)}$ and not $\mathrm{VO_2ox(OH_2)_2}$, and $\mathrm{VO_3ox^{2-}}$ is $\mathrm{VO_3ox(OH_2)^{2-}}$ and not $\mathrm{VO_2(OH)_2ox^{2-}}$.

Furthermore, this Scheme suggests that the constant of the substitution reaction of one hydroxide by 8-quinolinolate is largely affected by the number of coordinated oxo groups: 1.8 for $\mathrm{VO(OH)_2ox}$, 0.3 for $\mathrm{VO_2(OH)ox^-}$, and -1.0 for $\mathrm{VO_3ox^{2-}}$. On the other hand, the coordinated 8-quinolinolate does not affect much the subsequent coordination of the same ligand: 0.3 for $\mathrm{VO_2(OH)ox^-}$ as compared to 0.1 for $\mathrm{VO_2ox_2^-}$ in Scheme 2.

The $\mathrm{p}K_\mathrm{a}$ values are also available for *N*-methylimino-diacetato and 2,6-pyridinedicarboxylato complexes:[14,20]

$$\mathrm{VO_2(mida)(OH_2)^-} \rightleftharpoons \mathrm{VO_2(mida)(OH)^{2-}} + \mathrm{H^+}$$

$$\mathrm{p}K_\mathrm{a} = 6.13 \pm 0.05$$

$$\mathrm{VO_2(pda)(OH_2)^-} \rightleftharpoons \mathrm{VO_2(pda)(OH)^{2-}} + \mathrm{H^+}$$

$$\mathrm{p}K_\mathrm{a} = 5.87 \pm 0.02$$

However these reactions involving no increase of oxo groups, they can not be discussed on the same ground as in the present case.

Among the species which have been identified, $\mathrm{VO_3ox^{2-}}$, $\mathrm{VO_3Hox^-}$, and $\mathrm{VO_2ox_2^-}$ have the absorption maximum at 363 nm. On the survey of ultraviolet and visible spectra of various metal 8-quinolinolate complexes, it is noticed that the absorption maximum depends upon the oxidation number of metal ions, *e.g.* 410—460 nm for $\mathrm{Mox_2}$, 380—420 nm for $\mathrm{Mox_3}$, 380 nm for $\mathrm{Mox_4}$, and 360—370 nm for $\mathrm{MO_2ox_2}$ (hexavalent).[27] Vanadium(V) complexes mentioned above are well lined up in this series, whereas the black complex has absorption maximum at 550 nm. On the other hand complexes with the dimeric $\mathrm{Mo_2O_3^{4+}}$ unit have a fairly strong absorption maximum near 510 nm and monomeric species containing the same ligand do not.[28] This absorption maximum is attributable to the oxo bridged structure of molybdenum and the absorption maximum at 550 nm for the black vanadium(V) complexes also seems to be ascribed to the oxo bridged dimeric structure. The dimeric structure of black vanadium(V) 8-quinolinolate has recently been established by the solvent extraction in our laboratory. Details on this point will be shortly published elsewhere.

References

1) R. Montequi and M. Gallego, *Anales. Soc. Espan. Fis. Quim.*, **32**, 134 (1934).
2) S. Ishimaru, *J. Chem. Soc. Jpn.*, **56**, 72 (1935).
3) M. Borrel and R. Paris, *Anal. Chim. Acta*, **4**, 267 (1950).

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

5) A. J. Blair and D. A. Pantony, *Anal. Chim. Acta*, **13**, 1 (1955); A. J. Blair, D. A. Pantony, and G. J. Minkoff, *J. Inorg. Nucl. Chem.*, **5**, 316 (1958).

6) W. R. Scheidt, *Inorg. Chem.*, **12**, 1758 (1973).

7) H. Nakamura, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **34**, 1143 (1961).

8) N. Kurmaiah, D. Satyanarayana, and V. P. R. Rao, *Talanta*, **14**, 495 (1967).

9) M. Tanaka and I. Kojima, *J. Inorg. Nucl. Chem.*, **29**, 1769 (1967).

10) S. Yamada, S. Funahashi, and M. Tanaka, *J. Inorg. Nucl. Chem.*, **37**, 835 (1975).

11) J. Rydberg, *Acta Chem. Scand.*, **4**, 1503 (1950).

12) D. Dyrssen, *Sv. Kem. Tidskr.*, **65**, 43 (1953).

13) P. F. Knowles and H. Diebler, *Trans. Faraday Soc.*, **64**, 977 (1968); H. Diebler and R. E. Timms, *J. Chem. Soc. A*, **1971**, 273.

14) S. Yamada, J. Nagase, S. Funahashi, and M. Tanaka, *J. Inorg. Nucl. Chem.*, **38**, 617 (1976).

15) F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, **10**, 957 (1956).

16) The formulation of species involved in Eq. 3 does not strictly correspond to the actual structure in solution (see Discussion).

17) G. Schwarzenbach and G. Geier, *Helv. Chim. Acta*, **46**, 906 (1963).

18) D. Dyrssen and T. Sekine, *J. Inorg. Nucl. Chem.*, **26**, 981 (1964).

19) L. Newman, W. J. La Fleur, F. J. Brousaides, and A. M. Ross, *J. Am. Chem. Soc.*, **80**, 4491 (1958).

20) S. Funahashi, K. Haraguchi, and M. Tanaka, *Inorg. Chem.* **16**, 1349 (1977).

21) J. Lagrange, P. Lagrange, and K. Zare, *Bull. Soc. Chim. Fr. I*, **1978**, 7.

22) This type of linear free energy relationship generally holds in the complexation of multivalent metal ions; *e.g.* Ti(IV), Zr(IV), Hf(IV), and Mo(VI) and W(VI). A. Yuchi, unpublished results.

23) Some vanadium(V) complexes are characterized structurally by X-ray studies,[6,24] which indicated the octahedral configuration with a comparably long weak bond *trans* to oxo ligand and when more than one oxo ligands are involved they are *cis* to each other.

24) W. R. Scheidt, C. Tsai, and J. L. Hoard, *J. Am. Chem. Soc.* **93**, 3867 (1971); W. R. Scheidt, D. M. Collins, and J. L. Hoard, *ibid*, **93**, 3873 (1971); W. R. Scheidt, R. Countryman, and J. L. Hoard, *ibid*, **93**, 3878 (1971).

25) L. Pauling, "General Chemistry," W. H. Freeman and Co., San Francisco (1947).

26) J. E. Ricci, *J. Am. Chem. Soc.*, **70**, 109 (1948).

27) I. U. P. A. C., "Tables of Spectrophotometric Absorption Data of Compounds Used for the Colorimetric Determination of Elements," Butterworths, London (1963).

28) E. I. Stiefel, "Progress in Inorganic Chemistry," John Wiley and Sons, Inc. (1977), Vol. 22.