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Hydrolytic Behavior of Oxovanadium(IV) Ions

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The hydrolysis of VO^{2+} was investigated in 0.1 M $LiClO_4$ by potentiometric, conductometric and turbidimetric measurements. The following values of the equilibrium constants were obtained: $\beta_{11}=[VOOH^+][H^+]/[VO^{2+}]=9.0\times10^{-6}$ M (M=mol dm^{-3}); $\beta_{22}=[(VO)_2(OH)_2{}^{2+}][H^+]^2/[VO^{2+}]^2=1.9\times10^{-7}$ M. The solubility product of $VO(OH)_2$ given by $K_{sp1}=[VO^{2+}][OH^-]^2$ was found to be 6.6×10^{-23} M^3 from the pH values at which precipitation occurs. Only one species with a stoichiometric ratio VO/OH=2.5 is present in basic solutions in the pH range 9—12. The solubility product of $VO(OH)_2$ given by $K_{sp2}=[H^+][(VO)_2(OH)_5{}^-]$ is $\log K_{sp2}=-11.1$. A less soluble salt $Na(VO)_2(OH)_5$ or $NaHV_2O_5$ was isolated from strongly basic solutions. Measurements of Na^+ concentration at which the solid phase first appears give $\log K_{sp3}=-3.74$ as its solubility product, $K_{sp3}=[Na^+][(VO)_2(OH)_5{}^-]$.

The species with metal-oxygen multiple bonds are of particular interest in connection with their reactivities and structures.[1,2] The oxovanadium(IV) ion seems to be the most stable diatomic ion known, forming a wide variety of stable complexes and persisting in VO^{2+} entity.[3] The susceptibility of the VO^{2+} ion to hydrolysis, however, may greatly complicate the coordinative behavior of vanadium(IV) in aqueous solution. Investigations[4–6] on the hydrolysis of VO^{2+} in acidic solutions have provided strong evidence for the existence of a simple monohydroxo species accompanied by the formation of a dinuclear species. On the other hand, only a few quantitative studies have been made on the nature of vanadium(IV) in neutral or basic solutions. Titration curves obtained by Britton and Welford[7] showed the presence of the $V_4O_9{}^{2-}$ species in basic solutions. The polarographic data by Lingane and Meites[8] were interpreted in terms of the formation of two ions $V_2O_5{}^{2-}$ and $V_4O_9{}^{2-}$. A recent ESR study[9] showed that the vanadium(IV) species in basic solutions was monomeric $VO(OH)_3{}^-$. Various vanadate(IV) compounds, often called either vanadites or hypovanadates, were isolated from strongly basic solutions of vanadium(IV).[10,11] The present authors have examined the hydrolysis of VO^{2+} over a wide range of pH, using potentiometric, conductometric and turbidimetric techniques, in order to identify the hydrolysis species of vanadium(IV) and clarify their formation equilibria.

Experimental

Materials. Chemicals of guaranteed quality were used without further purification. Stock solutions of oxovanadium perchlorate in dilute perchloric acid (*ca.* 0.1 M) were prepared by dissolving vanadium(IV) hydroxide in a perchloric acid solution, and standardized by permanganate titration. The free acid in the oxovanadium perchlorate solution was determined by passing an aliquot portion of the stock solution through a cation-exchange resin, and titrating the effluent with a standard base. Lithium perchlorate was prepared from perchloric acid and lithium carbonate, and recrystallized twice from water. A standard carbonate-free sodium hydroxide solution was prepared by the usual procedure from a saturated NaOH solution, and stored in a polyethylene bottle under a CO_2-free atmosphere. Perchloric acid solutions were prepared by dilution of concentrated perchloric acid (Wako Super Special Grade).

Apparatus and Procedures. Potentiometric titration was carried out by means of a Horiba F-7SS pH meter with a Horiba glass electrode and an asbestos fiber-junction calomel electrode in a gas-tight cell under a stream of purified nitrogen. All the pH measurements were made in $LiClO_4$ solutions at a constant ionic strength (I=0.1 M) and at 25±0.05 °C. The electrode system was calibrated in terms of free hydrogen ion concentration, h, with standard $HClO_4$ and NaOH solutions. The liquid junction potential of the cell was independent of h within the limit of experimental error (0.5 mV) in the range $h\leq0.001$ M. The value of h in the vanadium solutions was determined by comparing the cell potential of the solutions with that of a standard solution of 0.001 M $HClO_4$ in 0.1 M $LiClO_4$. In order to remove the oxygen dissolved, nitrogen was bubbled through sample solutions for 1 h before titration. Small increments of a standardized NaOH or $HClO_4$ solution were added to the titration cell with a microburet and the pH was read every 2—3 min after each addition of the titrant. The decrease in concentration of ions due to dilution in the course of titration was below 2% of initial concentration over the pH range studied. The concentrations of ions were corrected for the dilution effect on the basis of the added amount of titrant.

Conductometric titration was carried out under purified nitrogen at 25±0.01 °C with the use of a Yokogawa conductance bridge (1000 Hz) and a conductometric cell with platinized platinum black electrodes. Precipitation boundaries were determined by measuring the concentration of H^+ or Na^+ at which a solid phase first appeared in vanadium(IV) solutions. The experimental procedure was similar to that for the potentiometric titration, except that titrants were added very slowly to the cell. The turbidity of the vanadium solutions was observed either visually under irradiation with a beam of light or by means of a Hitachi 124 spectrophotometer. The formation of a solid phase was detected as a sudden development of turbidity. Electronic spectra of solutions were recorded on a Hitachi 124 spectrophotometer with the use of matched 10 mm quartz cells fitted with ground-glass stoppers. All solutions for spectral measurements were prepared under anaerobic conditions. In basic solutions, extreme care was required to prevent oxidation of vanadium(IV).

Results and Discussion

Hydrolysis in Acidic Solution. The average number of hydroxide ions bound per vanadium, $\bar{n}$, is calculated at any point of titration from the following relationship:

$$\bar{n}=\frac{h-C_H}{C_m}, \tag{1}$$

where C_H and C_m are the total analytical concentrations of H^+ and vanadium(IV). The hydrolysis of VO^{2+}

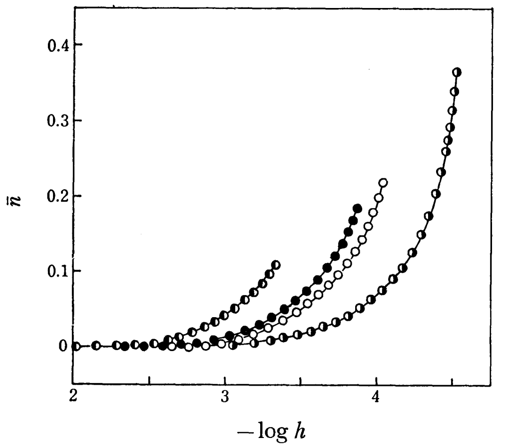

Fig. 1. Average number, $\bar{n}$, of hydroxide ions bound per vanadium as a function of log h.
The total concentrations of vanadium: ◐, 5×10^{-2} M; ●, 10^{-2} M; ○, 5×10^{-3} M; ◑, 10^{-3} M.

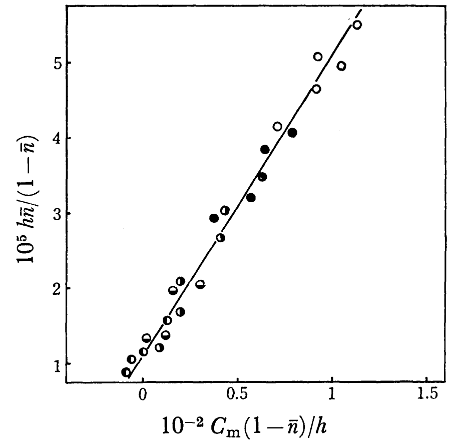

Fig. 2. A plot of $h\bar{n}/(1-\bar{n})$ as a function of $C_m(1-\bar{n})/h$.
The total concentrations of vanadium: ○, 5×10^{-2} M; ●, 10^{-2} M; ◑, 10^{-3} M; ◒, 5×10^{-4} M; ◐, 10^{-4} M.

can be expressed by

$$p\mathrm{VO}^{2+} + q\mathrm{H_2O} \rightleftharpoons (\mathrm{VO})_p(\mathrm{OH})_q{}^{2p-q} + q\mathrm{H}^+, \tag{2}$$

where p and q are positive integral numbers. Equilibrium constants β_{pq} and $\bar{n}$ are defined as follows:

$$\beta_{pq} = [(\mathrm{VO})_p(\mathrm{OH})_q{}^{2p-q}][\mathrm{VO}^{2+}]^{-p}h^q, \tag{3}$$

$$\bar{n} = \frac{\Sigma\, q[(\mathrm{VO})_p(\mathrm{OH})_q{}^{2p-q}]}{C_\mathrm{m}}. \tag{4}$$

The total concentration of vanadium is given by

$$C_\mathrm{m} = [\mathrm{VO}^{2+}] + \Sigma p[(\mathrm{VO}]_p(\mathrm{OH})_q{}^{2p-q}]. \tag{5}$$

Precipitation of vanadium hydroxide at a low value of $\bar{n}$ restricts the region of measurements accessible to the study of solution equilibrium. As shown in Fig. 1, $\bar{n}$ *vs.* log h curves in the region without precipitation are parallel to each other over the range $C_\mathrm{m}=0.001$—0.05 M. The treatment for the general 'core-links' complexes[12] was applied. Analysis of the data in the range $C_\mathrm{m}=0.001$—0.05 M strongly indicates the species with $p=2$ and $q=2$ to be the predominant hydrolysis product of VO^{2+}, in agreement with Rossotti and Rossotti.[4] A value of β_{22} of 1.9×10^{-7} M was obtained on the assumption that only the $(\mathrm{VO})_2(\mathrm{OH})_2{}^{2+}$ species was formed. The assumption could not, however, explain satisfactorily the experimental data for C_m below 0.001 M. The possible presence of hydrolysis species other than $(\mathrm{VO})_2(\mathrm{OH})_2{}^{2+}$ was tested by a curve-fitting procedure. The potentiometric data over a wide range of C_m could best be interpreted in terms of the additional formation of the mononuclear VOOH^+ species at lower C_m values. The β values evaluated by the procedure were $\beta_{11}=(9\pm1)\times10^{-6}$ M and $\beta_{22}=(1.9\pm0.5)\times10^{-7}$ M. If the species $(\mathrm{VO})_2(\mathrm{OH})_2{}^{2+}$ and VOOH^+ are the only two complexes formed, the following relation can also be derived from Eqs. 3, 4, and 5.

$$h\bar{n}(1-\bar{n})^{-1} = \beta_{11} + 2\beta_{22}C_\mathrm{m}h^{-1}(1-\bar{n}). \tag{6}$$

A plot of $h\bar{n}(1-\bar{n})^{-1}$ *vs.* $C_\mathrm{m}\, h^{-1}(1-\bar{n})$ should give a straight line with a slope equal to $2\beta_{22}$ and an intercept equal to β_{11} (Fig. 2). The straight line gives the same values of β as those obtained above. The β_{22} value we obtained is in good agreement with that of $10^{-6.88}$ M in 3 M $\mathrm{NaClO_4}$ reported by Rossotti and Rossotti,[4] whereas our β_{11} value is 8—9 times as large as that[4] in 3 M $\mathrm{NaClO_4}$. A noticeable difference is also observed between the β_{11} values in literature.[4,13-15]

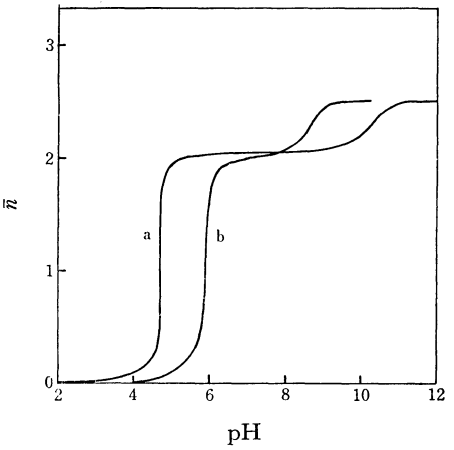

Fig. 3. The $\bar{n}$ *vs.* pH curves over a wide range of $\bar{n}$.
The total concentrations of vanadium: a, 10^{-3} M; b, 5×10^{-5} M.

Figure 3 shows $\bar{n}$ *vs.* pH curves over a wide range of $\bar{n}$. The curves exhibit a plateau at $\bar{n}=2$ corresponding to the precipitation of vanadium(IV) hydroxide. The IR spectrum of the hydroxide isolated (found: V, 50.2%) has a strong band at *ca.* 970 cm^{-1} assigned to the V=O stretching vibration. According to Selbin[3], a very strong band at 985 ± 50 cm^{-1} indicates the presence of the V=O bond. Thus the vanadium hydroxide appears to have the formula $\mathrm{VO(OH)_2}$ or $\mathrm{VO_2\cdot H_2O}$ (calcd: V, 50.5%). The solubility product, K_sp1, of $\mathrm{VO(OH)_2}$ given by Eq. 8 was determined as follows:

$$\mathrm{VO}^{2+} + 2\mathrm{OH}^- \rightleftharpoons \mathrm{VO(OH)_2(s)} \tag{7}$$

$$K_\mathrm{sp1} = [\mathrm{VO}^{2+}][\mathrm{OH}^-]^2 \tag{8}$$

In the pH range where no precipitation of $\mathrm{VO(OH)_2}$ occurs, the concentration of unhydrolyzed oxovanadium(IV) ions is given by

$$[\mathrm{VO}^{2+}] = (1-\bar{n})C_\mathrm{m}. \tag{9}$$

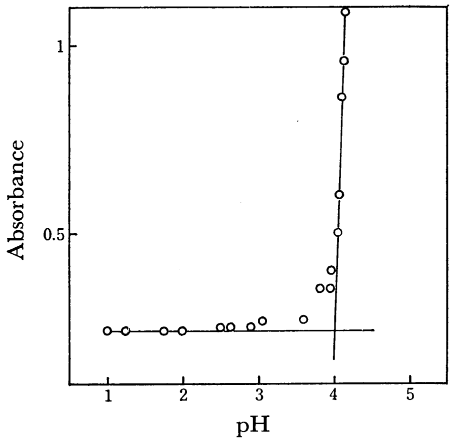

Fig. 4. The absorbance of vanadium(IV) solution as a function of pH.
The concentration of vanadium is 10^{-3} M. Wavelength, 240 nm.

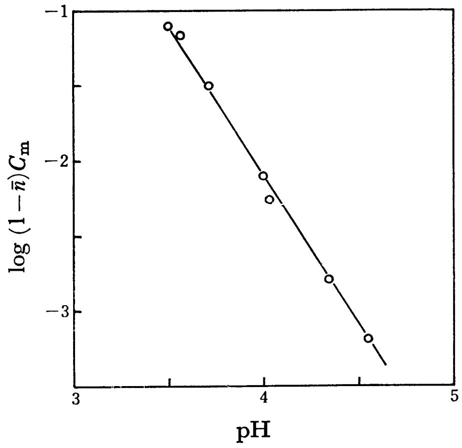

Fig. 5. The relation between the total concentration of vanadium and the pH at which vanadium hydroxide first appeared in acidic solutions.

Equation 9 can be derived from Eqs. 4 and 5, since only the $VOOH^+$ and $(VO)_2(OH)_2{}^{2+}$ species are the hydrolysis products of VO^{2+}. If Eq. 9 holds at the pH at which precipitation first takes place, the following relation can be derived from Eqs. 8 and 9:

$$\log K_{sp1} = \log (1-\bar{n})C_m + 2\log K_w + 2\text{pH}, \tag{10}$$

where K_w is the ionic product of water. The pH at which precipitation first takes place was determined by measuring the absorbance of vanadium(IV) solutions at a given C_m as a function of pH. Figure 4 shows the plot at $C_m=0.001$ M. Extrapolation of the linear portion in the plot gave the critical pH at which solid phase first appeared at the given C_m. Figure 5 shows a plot of the critical pH *vs.* $\log (1-\bar{n})C_m$, giving a straight line with a slope −2 which corresponds to the value given by Eq. 10. If we use $\log K_w = -13.78$ in 0.1 M $NaClO_4$,[16] the K_{sp1} value of 6.6×10^{-23} M^3 is obtained from the intercept.

Table 1. Electronic spectra (λ_{max}/nm) of vanadium(IV)[a]

0.1 M $HClO_4$	0.5 M NaOH
764 (17.4)	790 (14)
620sh (7.50)	525 (15)
240 (242)	418 (25)

a) Molar absorption coefficients ($M^{-1}\,cm^{-1}$) are given in parentheses.

Species of Vanadium(IV) in Basic Solution. The $VO(OH)_2$ precipitate dissolves in alkali to give a golden brown solution indicative of the formation of a new species. The electronic spectra of vanadium(IV) in basic solutions are given in Table 1, together with those of VO^{2+} for comparison. The spectrum of the vanadium species in basic solutions differs from that of VO^{2+} in the appearance of the third d-d band which is hidden under the strong charge-transfer band at 240 nm in the spectrum of VO^{2+}. The same spectrum of vanadium(IV) in a basic solution has also been obtained by Iannuzzi and Rieger.[9] They indicated that the Raman spectrum of vanadium(IV) in 1 M NaOH has a strong band at 987 cm^{-1} indicating the presence of the V=O group in the vanadium species. Basic solutions of vanadium(IV) may contain any species of the general formula $(VO)_p(OH)_q{}^{2p-q}$. The vanadium species in a basic solution were formulated in the following way. A solution of NaOH in 0.1 M $LiClO_4$ was titrated with a vanadium-containing solution of $HClO_4$ and a vanadium-free solution of $HClO_4$, respectively. The values of $\bar{n}$ are then given by

$$\bar{n} = \frac{C_{OH}-C_{OH}'}{C_m}, \tag{11}$$

where C_{OH} and C_{OH}' are the total analytical concentrations of OH^- added to reach the same pH in the presence and in the absence, respectively, of vanadium. Addition of VO^{2+} to NaOH solutions gave the soluble species in the basic pH region followed by precipitation of a vanadium compound in the region of nearly neutral pH. Table 2 gives the $\bar{n}$ values obtained in the pH region where no precipitation occurs. The potentiometric data indicate that $\bar{n}$ is 2.5 over the range of C_m and pH studied. A constant value of $\bar{n}=2.5$ suggests that only one species with a stoichiometric ratio $q/p=2.5$ is present in basic solutions in the pH range 9—12. The formation of this species is also seen as the second plateau of the potentiometric titration curves (Fig. 3), for which low C_m values were used in order to cause rapid redissolution of the oxovanadium hydroxide precipitated. Further evidence of the above stoichiometry was obtained by means of conductometric titration, in which an acid solution of $VO(ClO_4)_2$ was added incrementally to a NaOH solution. The titration was carried out at low C_m value so as to effect no precipitation up to neutral pH. From the electroneutrality condition on the titration system, we have

$$C_b + [H^+] = C_a + [OH^-] + \Sigma q[(VO)_p(OH)_q{}^{2p-q}], \tag{12}$$

where C_a and C_b are the analytical concentrations of $HClO_4$ and NaOH, respectively, in the system. At $[H^+]=[OH^-]$, $\bar{n}$ is given as follows from Eqs. 4 and 12:

$$\bar{n} = \frac{C_b-C_a}{C_m}. \tag{13}$$

The point of minimum conductivity in titration curves

TABLE 2. THE $\bar{n}$ VALUES EVALUATED POTENTIOMETRICALLY IN BASIC SOLUTIONS OF VANADIUM(IV)

pH	a) (10^4 C/M)				pH	b) (10^3 C/M)			
	C_{OH}'	C_{OH}	C_m	$\bar{n}$		C_{OH}'	C_{OH}	C_m	$\bar{n}$
11.8	25.9	36.0	3.98	2.54	12.0	5.80	8.81	1.23	2.45
11.4	16.4	33.2	6.70	2.51	11.6	3.08	8.02	2.01	2.46
11.0	11.1	31.7	8.20	2.52	11.2	1.90	7.69	2.31	2.51
10.6	8.41	31.0	9.01	2.51	10.8	1.37	7.55	2.45	2.52
10.0	6.21	30.4	9.59	2.52	10.4	1.10	7.47	2.53	2.52
9.60	5.12	30.1	9.89	2.53	9.80	0.88	7.39	2.61	2.49
9.00	4.05	29.7	10.4	2.47	9.40	0.79	7.36	2.64	2.49
8.60	3.45	29.4	10.6	2.45	9.00	0.69	7.32	2.68	2.47

a) A solution of 0.004 M NaOH in 0.1 M $LiClO_4$ was titrated with a solution 0.1 M in $VO(ClO_4)_2$ and 0.1 M in $HClO_4$, and a 0.1 M $HClO_4$ solution, respectively. b) A solution of 0.01 M NaOH in 0.1 M $LiClO_4$ was titrated with a solution 0.2 M in $VO(ClO_4)_2$ and 0.2 M in $HClO_4$, and a 0.2 M $HClO_4$ solution, respectively.

TABLE 3. THE $\bar{n}$ VALUES OF BASIC VANADIUM SPECIES DETERMINED BY CONDUCTOMETRIC TITRATIONS^a)

C_b	C_a	C_m	$\bar{n}$
7.84	3.08	1.87	2.55
7.56	1.35	2.48	2.50
3.87	0.650	1.28	2.52
1.94	0.316	0.639	2.54

a) Each C (10^{-3} M) is the concentration at $[H^+]=[OH^-]$.

was taken as that corresponding to the relation $[H^+]=[OH^-]$. The conductometric data (Table 3) indicate that the $\bar{n}$ values obtained are practically 2.5, regardless of C_m. This is in line with the potentiometric measurements. At low C_m, the occurrence of precipitation in the neutral pH region, if any, probably leads to no significant error in the estimation of $\bar{n}$. Attempts were made to determine ionic charge (z) of the vanadium species in basic solutions by use of an anion-exchange resin. However, the results are not decisive, although the ion-exchange behavior of the species suggests that $|z|$ is not greater than 2. The experiments were accompanied with a great difficulty due to the fact that the species is highly sensitive to oxygen. If the smallest integers giving the above stoichiometric ratio are taken as the values of p and q, the dinuclear, probably monohydroxo-bridged ion $(VO)_2(OH)_5^-$ or $HV_2O_5^-$ should be presented as the vanadium species in basic solutions. In the range of pH below 12, no evidence was found for the monomeric $VO(OH)_3^-$ species proposed by Iannuzzi and Rieger9) corresponding to the stoichiometric ratio $q/p=3$. They obtained an indication of the $VO(OH)_3^-$ ion from experiments in more basic solutions, in which potentiometric measurements seemed impracticable.

A dark brown precipitate of vanadium is obtained on addition of acid to its basic solution, and a gray precipitate on neutralization of its acidic solution. Britton and Welford7) state that oxovanadium hydroxide, on first precipitation, is grayish-white, turning dark brown as precipitation proceeds. The color change results from the formation of a sparingly soluble sodium vanadite. Stoichiometry of the formation of the dark brown precipitate might be expressed as follows;

$$(VO)_2(OH)_5^- + mH^+ + yM^+ \rightleftharpoons M_y(VO)_2(OH)_{2n}(s) + mH_2O, \qquad (14)$$

where M^+ is a +1 charged ion, $n=(5-m)/2$, and $y=1-m$. The solubility product, K_{sp2}, of the solid is defined by

$$K_{sp2} = [(VO)_2(OH)_5^-][H^+]^m[M^+]^y. \qquad (15)$$

If the concentration of $(VO)_2(OH)_5^-$ is still equal to $C_m/2$ at the pH where precipitation first occurs, the following relation is obtained:

$$\log K_{sp2} = \log C_m/2 - m\text{pH} + y \log [M^+]. \qquad (16)$$

The pH at which the solid phase first appears was determined at a given ionic strength (0.1 M). Figure 6 represents a plot of the critical pH *vs.* log $C_m/2$ giving a straight line. The slope $m=1$ of the line indicates that $n=2$ and $y=0$. Thus the dark brown precipitate also has the formula $VO(OH)_2$. The dark brown color of the precipitate might be due to co-precipitation of the $(VO)_2(OH)_5^-$ ion, as presumed from its formation reaction,

$$(VO)_2(OH)_5^- + H^+ \rightleftharpoons 2VO(OH)_2(s) + H_2O. \qquad (17)$$

The solubility product of $VO(OH)_2$ in basic solutions is found to be $\log K_{sp2}=-11.1$ from the intercept of the line in Fig. 6. From the values of K_{sp1} and K_{sp2}, we can estimate the equilibrium constant, β_{25}^{b}, for the reaction,

$$2VO^{2+} + 5OH^- \rightleftharpoons (VO)_2(OH)_5^-, \qquad (18)$$

$$\beta_{25}^{b} = \frac{[(VO)_2(OH)_5^-]}{[VO^{2+}]^2[OH^-]^5} = \frac{K_{sp2}}{K_w K_{sp1}{}^2} = 1.8\times10^{47}\ M^{-6}. \qquad (19)$$

Vanadium(IV) is less soluble even in strongly basic solutions, as noticed by Iannuzzi and Rieger.9) Various vanadates(IV) compounds have been isolated from basic solutions of vanadium, *e.g.*, $M_2^IV_4O_9\cdot xH_2O$,10,11) $M_2^IV_2O_5\cdot xH_2O$10) and $K_2V_3O_7\cdot 2H_2O$.9) When a large excess of Na^+ is added to a basic solution containing $(VO)_2(OH)_5^-$ ion, a solid is precipitated owing to the common ion effect. The formula of the compound was determined on the basis of stoichiometry of its precipitation. Figure 7 shows the concentration of Na^+ at which the solid phase first appears at given C_m and basicity. A plot of $\log[Na^+]$ *vs.* log $C_m/2$ gives a straight line with

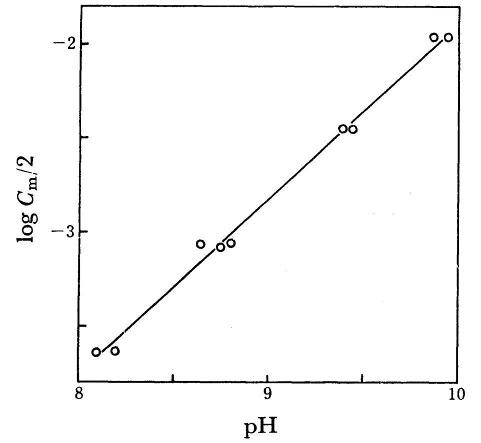

Fig. 6. The relation between the total concentration of vanadium and the pH at which the vanadium hydroxide first appeared in basic solutions.

a slope of -1. Thus the value of y in Eq. 16 is 1, and the values of m and n in reaction 14 are 0 and 2.5, respectively. The results of the measurements indicate that the less soluble compound may have the stoichiometric formula $Na(VO)_2(OH)_5$ or $NaHV_2O_5$ apart from the hydration water. The formula corresponds to sodium vanadate(IV) $Na_2V_4O_9 \cdot xH_2O$ which has occasionally appeared in literature.[7,10,11] The intercept of the straight line gives $\log K_{sp3} = -3.74$ as the solubility product of the compounds defined by Eq. 21.

$$Na^+ + (VO)_2(OH)_5^- \rightleftharpoons Na(VO)_2(OH)_5\ (s), \tag{20}$$

$$K_{sp3} = [Na^+][(VO)_2(OH)_5^-]. \tag{21}$$

Under the experimental conditions, the present work gave no indication of such salts as $M_2^IV_2O_5$ and $K_2V_3O_7$ formulated by Crow[10] and by Iannuzzi and Rieger,[9] respectively.

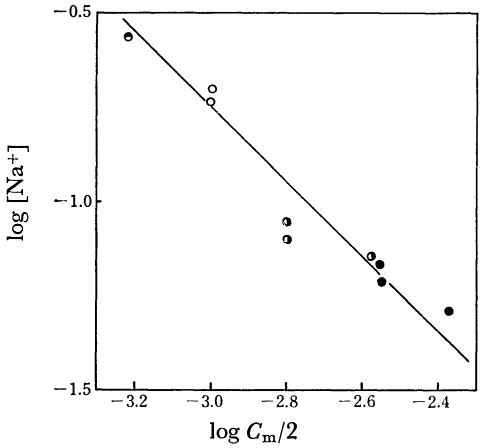

Fig. 7. The concentrations of sodium ion at which less soluble vanadium salt first appeared in NaOH solutions. The concentrations of NaOH: ◓, 0.01 M; ○, 0.015 M; ●, 0.03 M, ◑, 0.05 M.

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