A Spectrophotometric Study of the Complex Formation between Vanadium (V) and Hydroxylamine in Strongly Acidic Perchlorate Solutions

GÖSTA BENGTSSON

Division of Inorganic Chemistry 1, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden

The complex formation between vanadium(V) and hydroxylamine has been studied within the hydrogen ion concentration range $[H^+] = 0.010 - 0.900$ M by two spectrophotometric methods, the so-called M-method and the L-method. The former method gives $\beta_1 = 19 \pm 11$ M^{-1} and the latter $\beta_1 = 12.5 \pm 0.4$ M^{-1}. The results agree within the experimental errors and it seems probable that only one complex is present in appreciable concentrations. The value of $\beta_1 = [ML]/[M][L]$ is independent of $[H^+]$ within the hydrogen ion concentration range studied. Thus the complex formed seems to be $VO_2NH_3OH^{2+}$.

In a previous paper[1] the kinetics of the reaction between vanadium(V) and hydroxylamine within the hydrogen ion concentration range $[H^+] = 0.2 - 1.0$ M was studied. The reaction was found to follow a two term rate law,

$$- \frac{d[V(V)]}{dt} = k[V(V)][NH_2OH] + k'[V(V)]^2[NH_2OH] \tag{1}$$

where $[V(V)]$ and $[NH_2OH]$ represent the over-all concentrations of vanadium(V) $(= [VO_2^+])$ and hydroxylamine $(= [NH_3OH^+])$, respectively. At sufficiently low $[V(V)]$ $([V(V)] \leq 5 \times 10^{-4}$ M) the third order term becomes negligible. The first step in the reaction seems to be the rapid formation of a complex between the two reactants. This complex formation manifests itself in an immediate increase of the absorbance as compared with a vanadium(V) solution of the same concentration at wave lengths below about 250 nm when the reactant solutions are mixed. The present paper describes a spectrophotometric study of the complex formation equilibria within the hydrogen ion concentration range 0.010 − 0.900 M. However, optical methods are not the most general for the determination of stability constants of complex ions in solution. But in the present case there was not, however, any more reliable method available.

SYMBOLS AND NOTATIONS

C_M over-all concentration of the central ion M ($= VO_2^+$) (mol/l).
C_L over-all concentration of the ligand L ($= NH_3OH^+$) (mol/l).
ε_X molar absorption coefficient of the species X (M^{-1} cm^{-1}).
A absorbance ($A = \sum \varepsilon_X c_X l$; c_X = concentration; l = path length).
a absorption coefficient ($a = A/l$) (cm^{-1}).
ε formal molar absorption coefficient ($\varepsilon = a/C_M$) (M^{-1} cm^{-1}).
λ wave length (nm).

EXPERIMENTAL

The chemicals used were of the same kind as those described in Ref. 1, and so were the procedures used for the preparation of the solutions and determination of their concentrations. The temperature was $25.00 \pm 0.05°C$, the ionic strength 1.00 M. Sodium perchlorate and perchloric acid were used to keep the ionic strength constant.

The measurements were carried out spectrophotometrically within the ultraviolet region of the spectrum ($\lambda = 225 - 235$ nm). The narrow wave length range used was due to two factors: (1) The absorption of the ligand should be as small as possible. (2) The effect of the complex formation on ε should not be too small. At each series of measurements performed the slit width was kept constant and the wave length knob was not touched until the whole series was completed. Thereby the effects of small differences in the wave length (which can give large errors, if the wave length is on the slope of an absorption curve) were eliminated as far as possible.

THEORY

The most reliable spectrophotometric method for the study of complex formation is the method of corresponding solutions.[3,4] This method requires, however, optimal conditions which were not met with in the present study. Thus two less reliable methods, the M-method and the L-method (*cf.* Ref. 5) had to be applied. In both these methods it is assumed that only one mononuclear complex is formed.

In the M-method [6] $C_M \gg C_L$. C_L is kept constant while the difference $(\varepsilon - \varepsilon_M)$ is determined as a function of C_M. ε is the formal molar absorption coefficient of a solution containing both M and L. If the absorbance of the ligand can be neglected, the following relations can be derived:

$$\frac{1}{\varepsilon - \varepsilon_M} = \frac{1 + \beta_1 C_L}{(\varepsilon_{ML} - \varepsilon_M)\beta_1 C_L} + \frac{[M]}{(\varepsilon_{ML} - \varepsilon_M)C_L} \tag{2}$$

$$[M] \approx \frac{C_M}{1 + \beta_1 C_L} \tag{3}$$

As a first approximation we put $[M] \approx C_M$ and β_1 is evaluated from the straight line representing $1/(\varepsilon - \varepsilon_M)$ *versus* C_M. If necessary, the calculations can be repeated using the approximate value of β_1 for the calculation of [M]. If polynuclear complexes can be neclected, the assumption of only one complex formed seems justified. A disadvantage of this method is, however, that $(\varepsilon - \varepsilon_M)$ often represents a small difference between two large numbers. It is therefore very sensitive even to small experimental errors.

In the L-method $C_L \gg C_M$ and $(\varepsilon - \varepsilon_M)$ is determined as a function of C_L, while C_M is kept constant. If the concentrations of higher complexes than ML can be neglected, the following relation can be derived:

$$\frac{C_L}{\varepsilon - \varepsilon_M} = \frac{1 + \beta_1[M]}{(\varepsilon_{ML} - \varepsilon_M)\beta_1} + \frac{C_L}{(\varepsilon_{ML} - \varepsilon_M)} \qquad (4)$$

Since $\beta_1[M] \ll 1$ the stability constant is obtained from $C_L/(\varepsilon - \varepsilon_M)$ *versus* C_L. The validity of the assumption that the higher complexes can be neglected is often less certain in this method. It yields often too low values of β_1 due to this neglect (*cf.* Refs. 3 and 5). Since it has been misused on several occasions it has obtained a bad reputation and should be used with great care. It yields, however, sometimes a better precision to the obtained stability constants, and if the result agrees with the result obtained by the M-method, it seems reasonable to accept the former value. Furthermore, the formation of poly-nuclear complexes may be eliminated, since it is possible to perform the measurements at very low central ion concentrations.

MEASUREMENTS AND RESULTS

The complex formation between vanadium(V) and hydroxylamine is rapid ("momentaneous") and is succeeded by a slow oxidation of hydroxylamine.[1] The absorbances considered in this paper are therefore absorbances extrapolated to the time $t = 0$ after mixing the reactant solutions. Since the redox reaction is slow at $[H^+] > 0.050$ M this does not affect the precision noticeably, except at low hydrogen ion concentrations ($[H^+] < 0.050$ M) where the kinetics of the succeeding reactions becomes more complicated with a rather rapid change of the absorbance with time.[7]

The M-method was applied at $[H^+] = 0.200$ M and $\lambda = 228$ nm. The results are shown in Fig. 1. During these measurements special care was taken to ascertain that the corresponding values of ε and ε_M were measured at equal conditions. The path lengths were chosen such that the absorbances would not change too much when C_M was changed. The validity of Lambert-Beer's
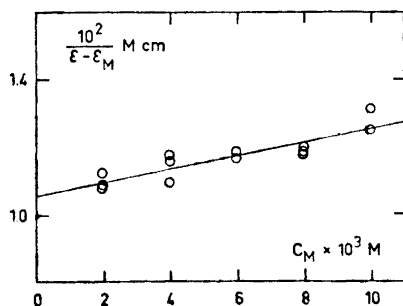

Fig. 1. $1/(\varepsilon - \varepsilon_M)$ *versus* C_M. $\lambda = 228$ nm; $C_L = 2.00$ mM; $C_{HClO_4} = 0.200$ M.
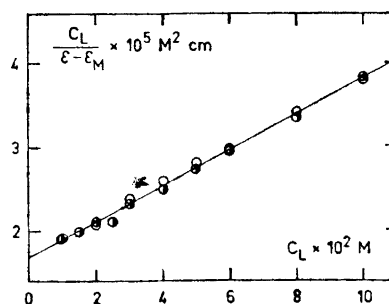
Fig. 2. $C_L/(\varepsilon - \varepsilon_M)$ *versus* C_L. $\lambda = 225$ nm; O $C_M = 1.00$ mM, $C_{HClO_4} = 0.200$ M; ◑ $C_M = 0.050$ mM, $C_{HClO_4} = 0.900$ M.

law was established as concerns the central ion. The slope and the intercept of the straight line $1/(\varepsilon - \varepsilon_M)$ *versus* C_M was calculated by a least squares program on a desk-top computer. $\beta_1 = 19 \pm 11$ M^{-1} and $(\varepsilon_{ML} - \varepsilon_M) = (2.5 \pm 1.3) \times 10^3$ M^{-1} cm^{-1}. The error limits throughout this paper represent three standard deviations.

The results of the L-method, applied at two hydrogen ion concentrations (0.200 and 0.900 M) and two wave lengths (225 and 235 nm) are shown in Table 1 and Fig. 2. The values of β_1 and $(\varepsilon_{ML} - \varepsilon_M)$ were calculated from

Table 1. The L-method. Experimental conditions and stability constants obtained.

$C_M \times 10^3$ M	λ nm	C_{HClO_4} M	β_1 M^{-1}	$(\varepsilon_{ML} - \varepsilon_M) \times 10^{-3}$ M^{-1} cm^{-1}
1.00	225	0.200	12.7 $\pm$ 1.6	4.68 $\pm$ 0.31
0.150	225	0.200	12.2 $\pm$ 1.4	4.66 $\pm$ 0.33
0.150	235	0.200	12.4 $\pm$ 3.1	1.66 $\pm$ 0.25
0.150	225	0.900	12.9 $\pm$ 2.5	4.72 $\pm$ 0.55
0.050	225	0.900	12.4 $\pm$ 1.6	4.78 $\pm$ 0.37
		Mean value	12.5 $\pm$ 0.4	

$C_L/(\varepsilon - \varepsilon_M)$ *versus* C_L by the least squares program. The differences between the formal molar absorption coefficients $(\varepsilon - \varepsilon_M)$ from some of the series of measurements, including those at [H$^+$] = 0.010 and 0.020 M, are shown in Fig. 3. The full drawn line has been calculated using the mean values of β_1 and $(\varepsilon_{ML} - \varepsilon_M)$ from Table 1.

DISCUSSION

The values of the stability constant β_1 obtained by the two methods used agree within the experimental error. The fact that the value obtained by the M-method is larger than that obtained by the L-method might indicate an influence on the absorbances from higher complexes (*cf.* Refs. 3 and 5). Both the reactants are, however, positively charged (VO$_2$$^+$ and NH$_3$OH$^+$, *cf.* below) and it seems reasonable to believe that the higher complexes are very weak. Since the L-method yields the most precise values, the mean value $\beta_1 = 12.5 \pm 0.4$ M^{-1} is accepted.

As can be seen from Table 1, β_1 is independent of [H$^+$] within the hydrogen ion concentration range 0.2 $-$ 0.9 M, and Fig. 3 shows that $(\varepsilon - \varepsilon_M)$ as a function of C_L at [H$^+$] = 0.010 M and 0.020 M can be accomodated to the same line as the values for higher [H$^+$] (within the large experimental errors at these [H$^+$]). At 25°C and the ionic strength 1 M the hydroxylammonium ion NH$_3$OH$^+$ has a pK_a-value of about 6,[8] so at the hydrogen ion concentrations used in this study hydroxylamine is present almost entirely as NH$_3$OH$^+$. The complex formation therefore occurs without any loss of the proton from NH$_3$OH$^+$. It does not seem very likely that VO$_2$$^+$ should be able to accept a proton
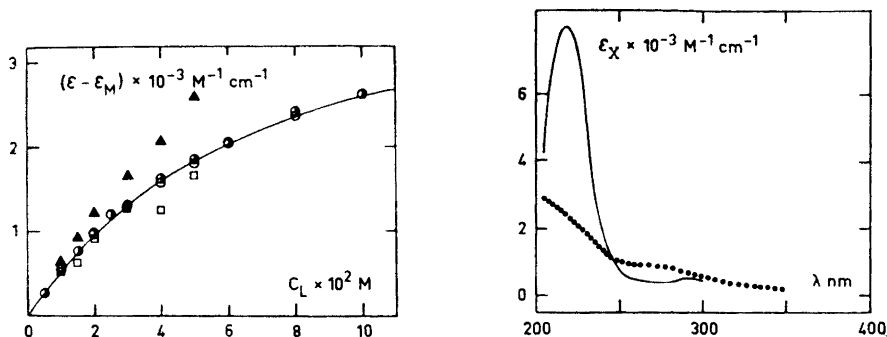
Fig. 3. $(\varepsilon - \varepsilon_M)$ versus C_L. $\lambda = 225$ nm;
   ○ $C_M = 1.00$ mM, $C_{HClO_4} = 0.200$;
   ◑ $C_M = 0.050$ mM, $C_{HClO_4} = 0.900$;
   □ $C_M = 0.100$ mM, $C_{HClO_4} = 0.020$ M;
   ▲ $C_M = 0.100$ mM, $C_{HClO_4} = 0.010$ M.

Fig. 4. Absorption curves of VO_2^+ ··· and $VO_2NH_3OH^{2+}$ ——.

within this hydrogen ion concentration range. It might therefore be concluded that the oxygen atom of the hydroxylammonium ion is the ligand atom (as might be guessed from other considerations).

    Fig. 4 shows the absorption curves of VO_2^+ and $VO_2NH_3OH^{2+}$ within the wave length range $200-350$ nm. The curve of the complex has been calculated using extrapolated absorbance values for a solution with $C_M = 1.00 \times 10^{-4}$ M, $C_L = 0.020$ M in 1.000 M $HClO_4$, known values of ε_M, and the β_1-value given above. The curve has been interrupted at 300 nm since at larger wave lengths the experimental errors have too strong an influence for the results to be meaningful.

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