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A Potentiometric Study on Complex Formation of Oxovanadium(IV) with Malonic Acid

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In the previous work we found a protonated oxovanadium(IV)-glycine complex MHGly (where M and Gly denote VO^{2+} and glycinate ions, respectively) along with the MGly and $M(Gly)_2$ complexes (charges are omitted for simplicity) by spectrophotometric measurements.[1] In the present study we employed potentiometric titrations for studying reactions between oxovanadium(IV) ion and malonic acid as another topic of the complex formation of multidentate ligands with metal ions.

Experimental

Reagents. Oxovanadium(IV) perchlorate solution was prepared by the method described in the preceding papers.[1,2] Sodium perchlorate and sodium hydroxide solutions were prepared and purified by the usual methods. Reagent grade malonic acid (Wako Pure Chemicals, Co. Ltd.) was recrystallized twice from distilled water and dried under a reduced pressure in a desiccator over silica gel.

Apparatus. A six-neck titration vessel was used, which was set with a glass electrode and the "Wilhelm" type reference electrode,[3] burets and glass tubes for nitrogen gas inlet and outlet. Nitrogen gas free from carbon dioxide was preequilibrated with 3 M $NaClO_4$ aqueous solution. Glass electrodes of Beckman No. 40498 were used in combination with a Radiometer PHM-4d pH meter (Copenhagen).

Emf measurements were carried out at 25.00±0.01 °C in a paraffin oil thermostat in a room thermostated at 25±1 °C. 3 M sodium perchlorate was used as an ionic medium.

Method of Measurements. Potentiometric titrations were carried out in 3 M $NaClO_4$ aqueous solution at a constant total metal concentration during the course of the titrations. The hydrogen ion concentration at equilibrium [H] was determined by means of emf measurements by the use of the Nernst equation;

$$E = E^\circ + 59.15 \log [\mathrm{H}] + E_\mathrm{j} \quad (1)$$

under an assumption of a constant activity coefficient of hydrogen ion. The liquid junction potential E_j was calculated from the relation $E_\mathrm{j} = -16.5[\mathrm{H}]$ mV/M.[4] Since malonic acid dissociates to some extent even in an acid solution (pH ~2), E° was determined by means of a Gran plot[5] at each titration in a constant ionic solution which contained oxovanadium(IV) perchlorate but no malonic acid in the pH range where oxovanadium(IV) ions did not appreciably hydrolyze. After the determination of E° a suitable amount of malonic acid solution was added to prepare a test solution, the mole ratio of V(IV): malonic acid being controlled to be 1:10. The concentration of V(IV) covered the range of 0.0007562 to 0.007499 M.

Results and Discussion

Dissociation constants of malonic acid were determined as $pK_1 = 2.82 \pm 0.01$ and $pK_2 = 5.78 \pm 0.01$ in 3 M $NaClO_4$ at 25 °C. Hydrolysis of oxovanadium(IV) ion in 3 M $NaClO_4$ has been studied by Rossotti and Rossotti[6] who reported values $\log \beta_{11} = -6.0 \pm 0.1$ and $\log \beta_{22} = -6.88 \pm 0.04$. In the present work we used these values in preliminary calculations of stability constants of oxovanadium(IV) malonate complexes, although we will briefly discuss whether the values of β_{11} and β_{22} are reasonalbe or not at the final stage of refinement of the results by computer calculations.

Titration curves of mixtures of oxovanadium(IV) perchlorate and malonic acid are shown in Fig. 1.

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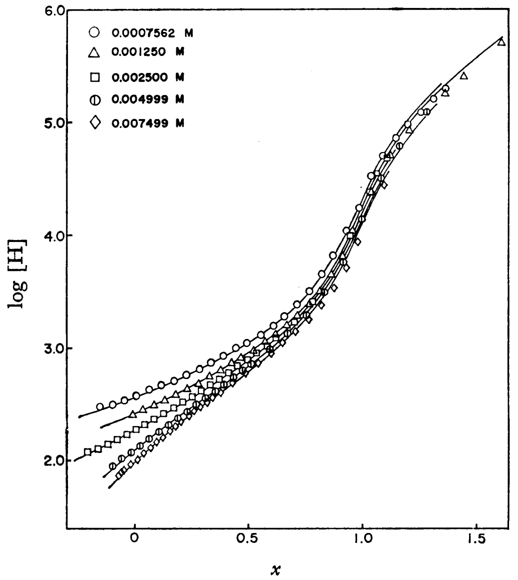


Fig. 1. Titration curves of mixtures of oxovanadium(IV) perchlorate and malonic acid in 3M $NaClO_4$. Curves are plotted against the degree of neutralization of malonic acid, x, at various total oxovanadium(IV) concentrations. Solid lines are calculated titration curves with $pK_1=2.82$, $pK_2=5.78$, $\log \beta_{11}=-6.0$, $\log \beta_{22}=-6.88$, and $\log \beta_{111}=7.41$.

Data obtained in an acid region where no hydrolysis of oxovanadium(IV) ion is expected were used for the first approach of stability constants. Since the concentration of malonate ion A^{2-} could be neglected in the pH range less than 3, the complex formation of oxovanadium(IV) ion with malonic acid may, in general, be described by the following equation:

$$p\mathrm{VO}^{2+} + r\mathrm{HA}^- + (q-r)\mathrm{H}^+ = (\mathrm{VO})_p\mathrm{H}_q\mathrm{A}_r^{(2p+q-2r)+} \quad (2)$$

The equilibrium constant of the reaction (2) is defined as

$$\kappa_{pqr} = \frac{[\mathrm{M}_p\mathrm{H}_q\mathrm{A}_r]}{[\mathrm{M}]^p[\mathrm{HA}]^r[\mathrm{H}]^{q-r}} \quad (3)$$

The total concentrations of malonic acid (C_A) and proton to be dissociated (C_H) are given as follows:

$$C_A = [\mathrm{H_2A}] + [\mathrm{HA}] + \sum_r r[\mathrm{M}_p\mathrm{H}_q\mathrm{A}_r] \quad (4)$$

$$C_H = C_A + H = [\mathrm{H}] + [\mathrm{H_2A}] + \sum_{q-r}(q-r)[\mathrm{M}_p\mathrm{H}_q\mathrm{A}_r] \quad (5)$$

where H represents the analytical excess of hydrogen ion in a test solution. Since C_A is about ten times larger than the total metal C_M in any solution, it is reasonably assumed that the term $\sum_r r[\mathrm{M}_p\mathrm{H}_q\mathrm{A}_r]$ is much smaller than the sum of C_A and H so that [HA] can be obtained, without introduction of any serious error, as follows:

$$[\mathrm{HA}] = \frac{(C_A+H-[\mathrm{H}])K_1}{[\mathrm{H}]} \quad (6)$$

The average number of HA combined with V(IV) in solution $\bar{n}_{\mathrm{M(HA)}}$ is given as

$$\bar{n}_{\mathrm{M(HA)}} = \frac{C_A-[\mathrm{H_2A}]-[\mathrm{HA}]}{C_M} = \frac{\sum_r r[\mathrm{M}_p\mathrm{H}_q\mathrm{A}_r]}{C_M}$$
$$= \frac{\sum_r r\kappa_{pqr}[\mathrm{M}]^{p-1}[\mathrm{HA}]^r[\mathrm{H}]^{q-r}}{1+\sum_p p\kappa_{pqr}[\mathrm{M}]^{p-1}[\mathrm{HA}]^r[\mathrm{H}]^{q-r}} \quad (7)$$

Almost all points of $\bar{n}_{\mathrm{M(HA)}}$ plotted against log [HA] fell on a single curve which was drawn by a normalized function $y=x/(1+x)=f(\log x)$ and no systematic scattering of data was observed with varying C_M and [H]. This result showed that Eq. (7) was not a function of [M] and [H] and thus, $p-1=0$ and $q-r=0$. Therefore, we concluded that the complex formed in this pH range was MHA. The equilibrium constant κ_{111} was determined as $10^{1.65}$ by means of curve fitting, or $\beta_{111}=[\mathrm{MHA}]/[\mathrm{M}][\mathrm{H}][\mathrm{A}]=10^{7.43}$.

In the range of pH larger than 3, hydrolysis of oxovanadium(IV) must be taken into account in evaluation of stability constants of complexes. If the formula of a complex present in solution is generally described as $\mathrm{M}_p\mathrm{H}_q\mathrm{A}_r$, the mole balances lead to following relations:

$$C_H = 2C_A + H = [\mathrm{H}] + [\mathrm{H}][\mathrm{A}]K_2^{-1}$$
$$+ 2[\mathrm{H}]^2[\mathrm{A}]K_1^{-1}K_2^{-1} - \beta_{11}[\mathrm{M}][\mathrm{H}]^{-1}$$
$$- 2\beta_{22}[\mathrm{M}]^2[\mathrm{H}]^{-2} + \sum_q q\beta_{pqr}[\mathrm{M}]^p[\mathrm{H}]^q[\mathrm{A}]^r \quad (8)$$

$$C_M = [\mathrm{M}] + \beta_{11}[\mathrm{M}][\mathrm{H}]^{-1} + 2\beta_{22}[\mathrm{M}]^2[\mathrm{H}]^{-2}$$
$$+ \sum_p p\beta_{pqr}[\mathrm{M}]^p[\mathrm{H}]^q[\mathrm{A}]^r \quad (9)$$

$$C_A = [\mathrm{A}] + [\mathrm{H}][\mathrm{A}]K_2^{-1} + [\mathrm{H}]^2[\mathrm{A}]K_1^{-1}K_2^{-1}$$
$$+ \sum_r r\beta_{pqr}[\mathrm{M}]^p[\mathrm{H}]^q[\mathrm{A}]^r \quad (10)$$

Since we found the MHA complex in the acid solution, we examined if we could explain whole data by assuming the formation of only the complex. Under the present assumption the following relations could readily be derived from Eqs. (9) and (10):

$$[\mathrm{A}] = \frac{C_A}{1+[\mathrm{H}]K_2^{-1}+[\mathrm{H}]^2K_1^{-1}K_2^{-1}+\beta_{111}[\mathrm{M}][\mathrm{H}]} \quad (11)$$

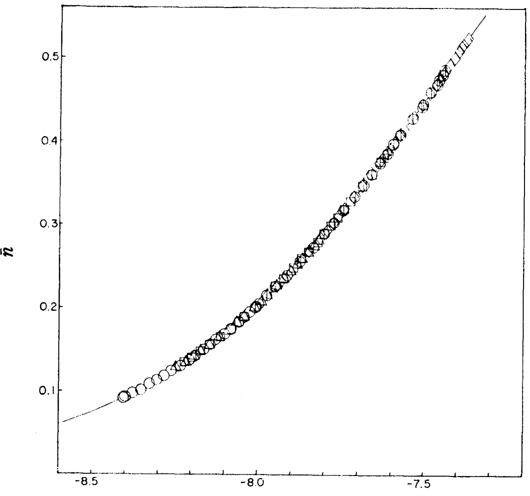
$$[\mathrm{M}] = [\{(1+\beta_{11}[\mathrm{H}]^{-1}+\beta_{111}[\mathrm{H}][\mathrm{A}])^2 + 8C_M\beta_{22}[\mathrm{H}]^{-2}\}^{1/2}$$
$$- (1+\beta_{11}[\mathrm{H}]^{-1}+\beta_{111}[\mathrm{H}][\mathrm{A}])]/4\beta_{22}[\mathrm{H}]^{-2} \quad (12)$$

Successive approximations were repeated until [A] and [M] converged to certain values with which Eqs. (11) and (12) were satisfied simultaneously, β_{111} being known. The average number of malonate ion per oxovanadium(IV) ion $\bar{n}$ is calculated by the following equation after the correction of hydrolysis of oxovanadium(IV) ions;

$$\bar{n} = \frac{C_A-([\mathrm{A}]+[\mathrm{H}][\mathrm{A}]K_2^{-1}+[\mathrm{H}]^2[\mathrm{A}]K_1^{-1}K_2^{-1})}{C_M-\beta_{11}[\mathrm{M}][\mathrm{H}]^{-1}-2\beta_{22}[\mathrm{M}]^2[\mathrm{H}]^{-2}} \quad (13)$$

and was plotted against log [H]+log [A] as seen in Fig. 2. All points fitted very well a normalized curve drawn by the function $y=x/(1+x)=f(\log x)$. This shows that experimental results are satisfactorily explained in terms of the formation of the MHA complex and no other ones, besides the hydrolyzed species MOH and $\mathrm{M_2(OH)_2}$, over the whole range of pH and the metal concentration studied.

The stability constants of complexes in solution were refined by means of a non-linear least squares method with the help of an electronic computer. If we set constant K_1, K_2, β_{11}, and β_{22} and variable β_{111}, the value of $\beta_{111}=10^{7.41}$ was obtained as the best one to interprete experimental data. When we set K_1 and K_2 as constants and β_{11}, β_{22}, and β_{111} as variable parameters, a slightly better agreement between calculated



log[H] + log[A]

Fig. 2. Relationship between $\bar{n}$ and log [H] + log [A]. A solid line is a curve drawn by a normalized function, $y=x/(1+x)=f(\log x)$ at the position of best fit. Symboles are the same as those used in Fig. 1.

and experimental titration curves was obtained with values of $\beta_{11}=10^{-5.0}$, $\beta_{22}=10^{-6.71}$, and $\beta_{111}=10^{7.50}$. However, the value $10^{-5.0}$ is far beyond the uncertainty of β_{11} estimated by Rossotti and Rossotti,[6] although diversed values of the stability constant of the VOOH$^+$ complex appear in literature.[7] Therefore, we finally adopted the value $\beta_{111}=10^{7.41\pm0.02}$, which is in good agreement with the value obtained in the acid region, instead of $10^{7.50}$. The results were not improved by the assumption of formation of two complexes HMA and MA together with MOH and $M_2(OH)_2$. Thus we concluded that only the MHA complex is formed in solutions we examined. Other complexes such as MA and MA_2 may be formed in more basic solution containing malonic acid of much higher concentration.

The complex MHA is so stable that the complex does not release a proton even at pH$\simeq$6. This fact shows that the dissociation constant of MHA to MA and H must be less than 10^{-6}, which is smaller than K_2. In many protonated complexes of highly charged metal ions, the dissociation of a proton in a complex is usually more enhanced than that of the corresponding free acid by electrostatic repulsion between a leaving proton and the central metal ion. However, the dissociation of a proton in the protonated oxovanadium(IV) malonate complex is not the case. This phenomenon may be interpreted in terms of formation of an intramolecular hydrogen bond between the oxygen atom in VO^{2+} ion and a proton in a malonic acid molecule coordinated as a monodentate ligand to the central metal ion.

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