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Vanadyl Complexes with Ethylenedithiodiacetic Acid

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The complex formation between vanadyl ions and ethylenedithiodiacetic acid (H_2L) has been studied at 25 °C in $0.5\,M$-$NaClO_4$ as inert medium, by measuring the hydrogen ion concentration with a glass electrode. In acidic medium and in the investigated concentration ranges ($2.07\,mM \leq C_M \leq 7.50\,mM$, C_L up to $12.5\,mM$)* the emf data can be explained assuming the equilibrium:

$$VO^{2+} + L^{2-} \rightleftharpoons VOL \qquad \log \beta_{101} = 2.68 \pm 0.03$$

(Keywords: Complexes, vanadyl ion; Ethylenedithiodiacetic acid)

Vanadyl-Komplexe mit Ethylendithiodiessigsäure

Die Komplexbildung zwischen Vanadyl-Ionen und Ethylendithiodiessigsäure (H_2L) wurde bei 25 °C in $0{,}5\,M$-$NaClO_4$ mittels Glaselektrode untersucht. In saurem Medium konnten die EMK-Daten im beobachteten Bereich ($2{,}07\,mM \leq C_M \leq 7{,}50\,mM$ und C_L bis zu $12{,}5\,mM$)* nach folgendem Gleichgewicht interpretiert werden:

$$VO^{2+} + L^{2-} \rightleftharpoons VOL \qquad \log \beta_{101} = 2{,}68 \pm 0{,}03$$

Introduction

Owing to the lack in the literature data on the metal complexes formed by ligands containing sulphur atoms in their molecule, thiodicarboxylic acids were extensively studied in our laboratory.

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* Symbols used in the text:
C_M analytical concentration of the vanadyl ions.
C_H analytical concentration of hydrogen ions.
C_L analytical concentration of the ethylenedithiodiacetic acid.
L^{2-} ethylenedithiodiacetate ion.
β_{pqr} formation constant of the $(VO)_pH_qL_r$ species.

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Vanadyl complexes with thiodiacetic acid were already investigated[1] and one mononuclear species was evidenced, in the 1:1 molar ratio, the stability constant of which was calculated in $0.5\,M$-$NaClO_4$ and at 25 °C.

In this paper the behaviour of vanadyl ions with ethylenedithiodiacetic acid is considered, in order to evidence the prevailing complexes that could be formed in aqueous solution and to calculate the corresponding stability constants.

Investigation was performed potentiometrically by measuring the hydrogen ion concentration with a glass electrode.

Experimental

Ethylenedithiodiacetic acid ("K & K") was used without purification and was standardized with NaOH. Solutions of the disodium salt, utilised in our titrations, were prepared by adding to the anhydrous acid the calculated quantities of sodium hydroxide and sodium perchlorate to obtain the right ionic strength.

A $0.05\,M$ vanadyl perchlorate solution was prepared from vanadyl sulphate ("Merck") according to *Rossotti* and *Rossotti*[2] and was standardized by *Ducret*'s method[3]. The analytical excess of hydrogen ions in this solution, kept $0.05\,M$ in order to prevent oxidation of V(IV) by air, was determined by the *Gran* plot[4].

A $5\,M$-$NaClO_4$ ("Merck") stock solution was prepared and standardized by drying a known volume of solution and weighing as $NaClO_4$.

Potentiometric measurements were carried out at 25.0 ± 0.1 °C in a constant ionic medium, $0.50\,M$-$NaClO_4$, with a Radiometer pHM4 potentiometer, giving a precision of 0.1 mV.

A cell similar to that utilised by *Forsling* et al.[5] was employed with a liquid bridge of $0.50\,M$-$NaClO_4$. The glass electrode ("Thalamid", Jenaglass) was calibrated in concentration units, so that, in this paper, the symbol $-\log[H^+]$ is used instead of *pH*.

In this conditions, the emf of the employed cell can be expressed, in mV units, as follows[6]:

$$E = E^\circ + 59.16 \log[H^+] + E_J$$

where E_J is the junction potential between test solution and the liquid bridge of $0.50\,M$ sodium perchlorate ($-100\,\text{mV}\,M^{-1}$ under our experimental conditions). Knowing E°, determined in the first part of each titration as later indicated, $[H^+]$ can be easily deduced from the above equation.

A stream of purified nitrogen, presaturated in $0.5\,M$-$NaClO_4$, was used to mix the solutions and to remove the carbon dioxide.

Results

The investigation was carried out using the procedure described by *Leden*[7], by measuring the hydrogen ion concentration in solutions in which both the analytical concentrations of the vanadyl ion, C_M, and of the hydrogen ion, C_H, were kept constant, while the ligand concentration, C_L, was progressively increased.

In the first part of the titration, the value of E° was calculated in the absence of the ligand, by adding to 20.0 ml of 0.50 M-$NaClO_4$ different amounts of a solution containing vanadyl perchlorate and perchloric acid (up to 20 ml). So, in this case, $[H^+]$ is known and equal to the concentration of the perchloric acid.

In the second part of the titration, equal volumes of the metal solution and of the ligand solution were added, and the formation function, $\bar{n} = \bar{n}(-\log[L^{2-}])$ was calculated by the following expressions:

$$[L^{2-}] = (C_H - [H^+])/\gamma$$
$$\bar{n} = (C_L - \alpha [L^{2-}])/C_M$$

where:

$$\alpha = 1 + \beta_{011}[H^+] + \beta_{021}[H^+]^2$$

and

$$\gamma = \beta_{011}[H^+] + 2\,\beta_{021}[H^+]^2$$

β_{011} and β_{021} are the protonation constants of the acid and are referred to the same experimental conditions of temperature and ionic medium[8].

In the above equations, polynuclear and mixed complexes with hydrogen or hydroxide ions are considered negligible as can be proved if the formation function is not depending on C_M and C_H. Also hydrolysis of the uncomplexed metal ion was not considered because it can be neglected for the values of -log$[H^+]$ used in the calculation[2].

An example of titration is reported in Table 1, while the formation function, $\bar{n}(\log[L^{2-}])$, is represented in Fig. 1. All the experimental

Table 1. *An example of titration.* V_1: $C_M = 8.30\,mM$, $C_H = 8.70\,mM$, $[ClO_4^-] = 0.50\,M$. V_2: $C_L = 49.7\,mM$, $[Na^+] = 0.50\,M$. *Initial volume = 20.0 ml of 0.50 M sodium perchlorate.* $E^\circ = 639.0\,mV$

V_1 (ml)	V_2 (ml)	E (mV)	E° (mV)	$-\log[L^{2-}]$	$\bar{n}$
4.0		806.8	639.0		
8.0		792.8	638.9		
12.0		785.9	639.1		
16.0		781.6	639.2		
20.0		778.1	638.8		
23.0	3.0	830.3		3.57	0.11
24.0	4.0	840.0		3.28	0.19
25.0	5.0	846.5		3.10	0.28
27.0	7.0	856.7		2.84	0.41
28.0	8.0	860.3		2.95	0.47
30.0	10.0	865.9		2.61	0.57

points fall on a single curve for different values of C_M (ranging from $2.07\,mM$ to $7.50\,mM$) and C_H (from $4.35\,mM$ to $10.20\,mM$), meaning that neither polynuclear nor mixed complexes are present in solution in a detectable amount.

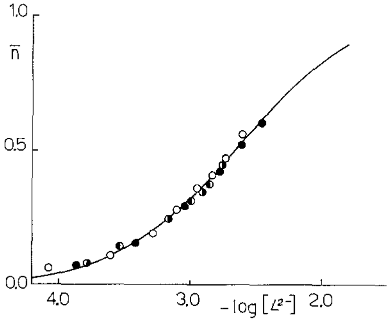

Fig. 1. Formation function of the vanadyl—ethylenedithiodiacetate system; the full curve is calculated using the stability constant obtained in this work. ○ $C_M = 4.15\,mM$, $C_H = 4.35\,mM$; ● $C_M = 4.15\,mM$, $C_H = 10.20\,mM$; ◑ $C_M = 2.07\,mM$, $C_H = 4.35\,mM$; ◐ $C_M = 7.50\,mM$, $C_H = 7.30\,mM$

A 1 : 1 complex was evidenced in our experimental conditions, as can be seen by computing the value $\bar{n}/(1-\bar{n})[L^{2-}]$, that is equal to β_{101} if only one species is prevailing in solution.

The logarithm of the mean value and the corresponding standard deviation are:

$$\log \beta_{101} = 2.68 \pm 0.03$$

The solid curve of Fig. 1 was calculated using the obtained value of the formation constant. The agreement between calculated curve and experimental points is good.

Discussion

The values of the stability constants of proton and vanadyl complexes with ethylenedithiodiacetic acid are collected in Table 2, together with the corresponding values of the complexes with thiodiacetic and glutaric acids, determined in the same experimental conditions.

The stability of the vanadyl complex with ethylenedithiodiacetic acid is less than that of the complex with thiodiacetic acid, according to the "hard" character of the metal ion.

On the other hand, besides carboxylic groups, also sulphur atoms are probably coordinated to the vanadyl ion, even if in a minor extent. In fact, a comparison of the stability of complex species must be referred to the basicity of the ligand, by computing the value $\log \beta_{101}/\log \beta_{021}$, as some authors propose[9,10].

Table 2. *Stability constants of proton and vanadyl complexes.* $T = 25\,^{\circ}\mathrm{C}$. $I = 0.50\,M\text{-NaClO}_4$.

	$\log \beta_{101}$	$\log \beta_{011}$	$\log \beta_{021}$	$\log \beta_{101}/\log \beta_{021}$
Thiodiacetic acid	3.14	4.03	7.13	0.44
Ethylene dithiodiacetic acid	2.68	3.90	7.13	0.38
Glutaric acid	3.18	5.10	9.10	0.35

The value for glutaric acid is markely less than that for thiodiacetic acid, and also the value for ethylenedithiodiacetic acid is greater. In the latter case, comparison could be made with suberic acid (octanedioic) complexes, but the stability decreases with increasing the chain in the α,ω-dicarboxylic acids. So, ethylenedithiodiacetate ion seems to act as tetradentate ligand with respect to the vanadyl ions.

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