

The Ethylenediaminetetraacetate Complexes of Vanadium(V)

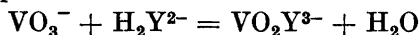
ANDERS RINGBOM, SOINI SIITONEN and BENGT SKRIFVARIS

Institutet för analytisk och oorganisk kemi, Åbo Akademi, Åbo, Finland

Pentavalent vanadium forms with ethylenediaminetetraacetic acid (H_4Y) a complex compound VO_2Y^{3-} with a stability constant $\log K = 18.05$. At pH values below about 3.5 the complex VO_2HY^{2-} is formed; the acidic dissociation constant of this compound is $pK = 3.60$. In alkaline solutions vanadates are formed.

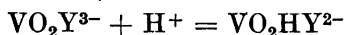
The complexes of divalent, trivalent and tetravalent vanadium with ethylenediaminetetraacetic acid (EDTA) have been investigated by Schwarzenbach¹, but about the complexes of pentavalent vanadium little is known. Polarographic investigations of Pecsok and Juvet² and of Micka and Tockstein³ point to the formation of some complexes. However, there seems to be no information in the literature about the composition and the stability of these compounds. In the following the results of some investigations made in order to clear up these questions will be reported.

It seems likely that in a weak acid solution a compound VO_2Y^{3-} is formed. This assumption is made on the basis of the fact that when a solution of ammonium metavanadate is titrated with the disodium salt of EDTA the acidity remains constant (pH \sim 6.5) until the equivalence point is reached, which points to the reaction



A compound of this formula is also in accordance with the results recently obtained by Rossotti and Rossotti⁴ in an investigation on the hydrolysis products of pentavalent vanadium.

When the solution is made more acid — at pH values below 3 — another complex is formed. Equilibrium measurements showed that this reaction involves the addition of one hydrogen ion. In other words, Y^{4-} is replaced by HY^{3-} according to



A change of the shade of the greenish yellow colour is connected with this reaction.

It is possible to determine photometrically the stability constants of the complexes on the basis of the colours of the various compounds. The stability ranges of these complexes will be clear from Fig. 1 giving the absorbance index of vanadium as a function of pH.

Tables 1 and 2 illustrate the way of calculating the equilibrium constants.

Table 1. Determination of the stability constant $K_{VO_2HY^{2-}} = \frac{[VO_2HY^{2-}]}{[VO_2^+][HY^{2-}]}$

$C_V = C_{EDTA}$ M	pH	$\log \beta_{HY}$	$A_{VO_2HY}^{340}$	$A_{VO_2}^{340}$	A^{340}	$\alpha = \frac{A_{VO_2HY} - A}{A_{VO_2HY} - A_{VO_2}}$	$\log K_{VO_2HY^{2-}} = \frac{\log \frac{[VO_2HY^{2-}]}{(1-\alpha)}}{\log \frac{\alpha^2 \beta_{HY} C}{}}$
1×10^{-3}	0.85	-8.38	0.400	0.190	0.272	0.610	11.40
1×10^{-3}	1.25	-7.22	0.400	0.190	0.357	0.204	11.50
1×10^{-3}	1.45	-6.66	0.400	0.190	0.367	0.157	11.20
1×10^{-3}	1.75	-5.86	0.400	0.190	0.388	0.057	11.32
			$A_{VO_2HY}^{320}$	$A_{VO_2}^{320}$	A^{320}		
2×10^{-4}	1.40	-6.80	0.148	0.062	0.122	0.302	11.38
2×10^{-4}	1.65	-6.12	0.148	0.062	0.137	0.127	11.55
1×10^{-4}	1.20	-7.37	0.074	0.031	0.051	0.535	11.58
1×10^{-4}	1.40	-6.80	0.074	0.031	0.056	0.419	11.32
1×10^{-4}	1.60	-6.26	0.074	0.031	0.063	0.256	11.31
1×10^{-4}	1.95	-5.36	0.074	0.031	0.070	0.093	11.38

Average: 11.39

Table 2. Determination of the dissociation constant $k_{VO_2HY^{2-}} = \frac{[H^+][VO_2Y^{3-}]}{[VO_2HY^{2-}]}$

C_V	C_{EDTA}	pH	$A_{VO_2Y}^{360}$	$A_{VO_2HY}^{360}$	A^{360}	$\alpha = \frac{A_{VO_2Y} - A}{A_{VO_2Y} - A_{VO_2HY}}$	$\frac{-\log k_{VO_2HY^{2-}}}{-\log \frac{[H^+](1-\alpha)}}{\alpha}$
1×10^{-4}	5×10^{-3}	2.75	0.210	0.148	0.156	0.872	3.58
1×10^{-4}	5×10^{-3}	2.90	0.210	0.148	0.158	0.839	3.62
1×10^{-4}	5×10^{-3}	3.10	0.210	0.148	0.165	0.726	3.52
1×10^{-4}	5×10^{-3}	3.60	0.210	0.148	0.183	0.435	3.49
1×10^{-4}	5×10^{-3}	3.95	0.210	0.148	0.190	0.322	3.63
1×10^{-4}	5×10^{-3}	4.25	0.210	0.148	0.197	0.210	3.67
1×10^{-4}	5×10^{-3}	4.40	0.210	0.148	0.201	0.145	3.63
			$A_{VO_2Y}^{360}$	$A_{VO_2HY}^{360}$	A^{360}		
5×10^{-3}	4×10^{-2}	3.00	0.740	0.625	0.656	0.730	3.43
5×10^{-3}	4×10^{-2}	3.40	0.740	0.625	0.663	0.670	3.71
5×10^{-3}	4×10^{-2}	3.60	0.740	0.625	0.674	0.574	3.73
5×10^{-3}	4×10^{-2}	4.05	0.740	0.625	0.708	0.278	3.64
5×10^{-3}	4×10^{-2}	4.35	0.740	0.625	0.723	0.148	3.59

Average: 3.60

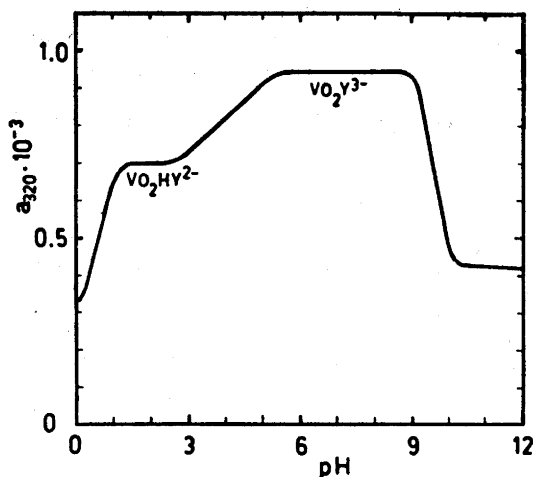


Fig. 1. Absorbance index of vanadium at an excess of EDTA as a function of pH. $C_V = 10^{-3}$, $C_{EDTA} = 5 \times 10^{-3}$.

The absorbances are designed by A . β_{HY} is the fraction of EDTA not bound to vanadium that appears as HY^{-3} ions. Usually β_{HY} is calculated from the equation

$$\beta_{HY} = \frac{[H^+]\beta_Y}{k_4}$$

β_Y can be determined graphically⁵ or from the equation

$$\beta_Y = \frac{[H^+]^4}{k_1 k_2 k_3 k_4} + \frac{[H^+]^3}{k_2 k_3 k_4} + \frac{[H^+]^2}{k_3 k_4} + \frac{[H^+]}{k_4} + 1$$

The following values of the dissociation constants of EDTA were used: $pk_1 = 2.0$; $pk_2 = 2.76$; $pk_3 = 6.16$; $pk_4 = 10.26$. α is the fraction of vanadium present in the less coloured form (VO_2^+ in Table 1, VO_2HY^{2-} in Table 2).

Perchloric acid was used for the regulation of the acidity. The ionic strength was kept at approximately 0.1 by the addition of sodium perchlorate. The temperature was *ca.* 20°.

By combining the constants obtained above it is possible to calculate in addition the following constant

$$K_{VO_2Y} = \frac{[VO_2Y^{3-}]}{[VO_2^+][Y^{4-}]} = \frac{K_{VO_2HY} k_{VO_2HY}}{k_4} = 10^{18.05}$$

The vanadium(V)-EDTA complex is thus almost as strong as the corresponding copper complex.

Fig. 1 points to the formation of vanadates in alkaline solution. It is likely that the compound stable at the pH range 10—12 is a pyrovanadate ⁶ and that in a still more alkaline solution orthovanadate VO_4^{3-} is formed.

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