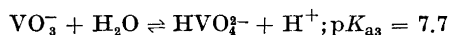


The Mononuclear Hydrolysis of Vanadium(V)

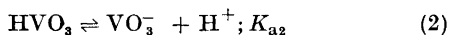
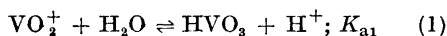
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The hydrolysis of vanadium(V) has been studied by emf titrations at this laboratory ^{1,2}. Because of the unusual stability of the decavanadates, it was not possible to detect the mononuclear hydrolytic species in acid solutions ¹. However, in 0.5 M Na(OH,Cl) solutions Ingri and Brito ² could calculate the equilibrium constants for the mononuclear reactions.



The purpose of the present work was to study the mononuclear hydrolysis of vanadium(V) in the lower pH range and to determine the acidity constants of the following equilibria at 25°C:



(From X-ray work on solid vanadium compounds, there is reason to believe that the vanadium(V) is five-coordinated with oxygen except in some VO_4^{3-} compounds, but we have chosen here to write the formula with as few H_2O as possible.)

To avoid polymerization of the hydrolytic species it was desirable to work with solutions of very low vanadium concentrations. (Spectrophotometric work ³ has shown that the decavanadates probably exist even at 10^{-4} M.) For this purpose, carrier-free ⁴⁸V was prepared by deuteron irradiation of pure titanium metal in the Swedish cyclotron at the Nobel Institute of Physics.

Methods such as emf titrations, which are based on the measurement of the amount of protons released from the vanadyl ion, cannot be used for very low metal concentrations. We, therefore, tried to find a suitable solvent extraction system. Instead of introducing a hydrophobic chelating re-

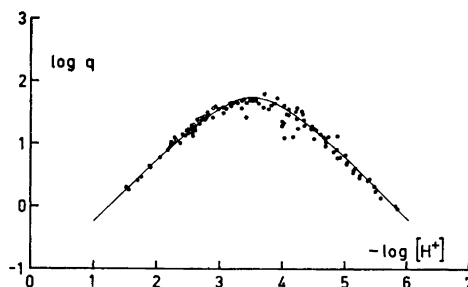


Fig. 1. The distribution of ⁴⁸V between hexol and 0.5 M (H,Na)ClO₄.

agent that would form an uncharged extractable VO_2^+ complex, we wished to use an organic solvent which would extract uncharged HVO_3 . The alcohol, methyl-*isobutyl*carbinol (hexol), was found to give a measurable distribution ratio (*cf.* Fig. 1) and was chosen for the investigation. The aqueous phase was 0.5 M (H,Na)ClO₄ which was buffered with small amounts of sodium acetate.

The results for carrier-free ⁴⁸V are given in Fig. 1 as $\log q$ ($q = \gamma$ -activity of ⁴⁸V in the hexol phase/ γ -activity of ⁴⁸V in the aqueous phase) as a function of $-\log[\text{H}^+]$. In some experiments (open circles) a solution of ⁴⁸V in 0.5 M HClO₄ was added to the aqueous layer. In other experiments (closed circles) a solution of ⁴⁸V in hexol was added to the organic layer. The results of these two procedures agreed quite well.

The following conclusions may be drawn from Fig. 1 even though there is considerable scattering of the points. The slope +1 shows the existence of an uncharged vanadium species in the hexol phase with one proton less than $\text{VO}_2(\text{H}_2\text{O})_n^+$. The slope -1 shows that there exists a monovalent negative vanadium ion in the aqueous phase with one proton less than the uncharged complex in the organic phase. The rather sharp bending of the curve shows that the stability range of the uncharged complex is not very large. In each run, about the same amount of ⁴⁸V was added to the system and, therefore, the total vanadium concentration in each phase varies with the distribution ratio. Still the limiting slopes in Fig. 1 are exactly +1 and -1. This indicates that no polynuclear species

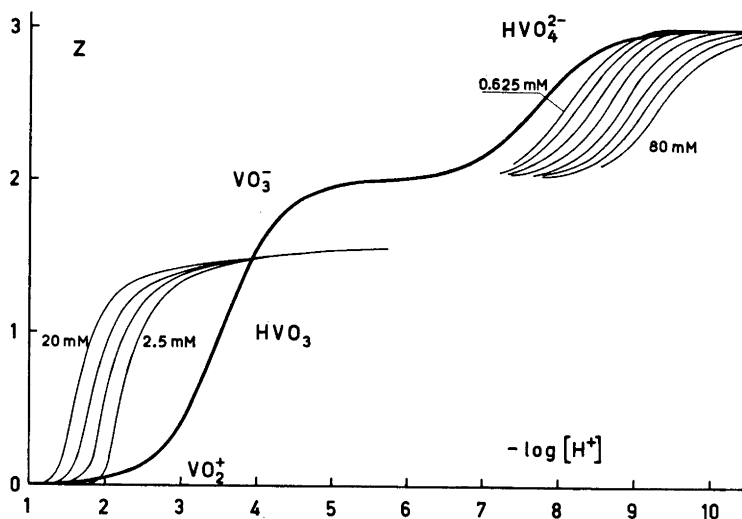


Fig. 2. The number of OH^- added to VO_2^+ , as a function of $-\log [\text{H}^+]$. The thick curve represents the mononuclear hydrolysis. The thin curves are based on emf titrations^{1,2} at various concentrations of V, and show the effect of the formation of polynuclear species.

are formed. This was further confirmed by the addition of inactive vanadium(V). A shift of the extraction curve was obtained by the addition of 10^{-5} M vanadium or more.

The expression for the distribution ratio q that is compatible with these observations is

$$q = \frac{[\text{HVO}_3]_{\text{org}}}{[\text{VO}_2^+] + [\text{HVO}_3] + [\text{VO}_3^-]}$$

Using the equilibrium constants of reactions (1) and (2) and the partition coefficient of HVO_3 , λ , one obtains

$$q = \frac{\lambda}{K_{a1}^{-1}[\text{H}^+] + 1 + K_{a2}[\text{H}^+]^{-1}}$$

By curve-fitting^{4,5}, the following approximate values of λ , K_{a1} , and K_{a2} were determined:

$\log \lambda = 2.10$; $\text{p}K_{a1} = 3.30$; $\text{p}K_{a2} = 3.70$

With these acidity constants and the data of Ingri and Brito², it is possible to calculate the average number of hydroxyl groups attached to VO_2^+ as a function of pH (Fig. 2) for the mononuclear hydrolysis of vanadium(V). The constants will be refined by high-speed computing using the LETAGROP program^{6,7}. Details will be given in the full paper.

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1. Rossotti, F. J. C. and Rossotti, H. *Acta Chem. Scand.* **10** (1956) 957.
2. Ingri, N. and Brito, F. *Acta Chem. Scand.* **13** (1959) 1971; *Anales fis. y quim. (Madrid)* **56 B** (1960) 165.
3. Newman, L. and Quinlan, K. P. *J. Am. Chem. Soc.* **81** (1959) 547.
4. Dyrssen, D. and Sillén, L. G. *Acta Chem. Scand.* **7** (1953) 663.
5. Sillén, L. G. *Acta Chem. Scand.* **10** (1956) 186.
6. Dyrssen, D., Ingri, N. and Sillén, L. G. *Acta Chem. Scand.* **15** (1961) 694.
7. Ingri, N. and Sillén, L. G. *Acta Chem. Scand.* *In print.*

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