

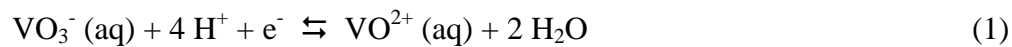
## Experiment 3

### Separation of the Beautiful Oxidation States of Vanadium

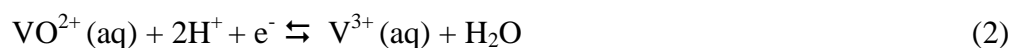
This lab has been adapted from "Microscale Inorganic Chemistry: A Comprehensive Laboratory Experience," 1991, John Wiley and Sons, New York, NY, p 246

#### Introduction

The transition element vanadium has four common oxidation states:  $V^{5+}$ ,  $V^{4+}$ ,  $V^{3+}$ , and  $V^{2+}$ . The stabilities and colors of these are investigated using ion exchange chromatography in this experiment. Starting with  $V^{5+}$  in the form of the ionic compound, ammonium metavanadate ( $NH_4VO_3$ ), a series of reductions is carried out to generate the lower oxidation states of vanadium. The first reduction is carried out in an acidic solution (HCl) to yield vanadium(IV) in the form of the vanadyl ion,  $VO^{2+}$ , according to the reaction scheme below.



A second reduction with zinc amalgam yields  $[V(H_2O)_6]^{3+}$  and  $[V(H_2O)_6]^{2+}$ .



Each oxidation state of vanadium exists as an aquo complex, where  $H_2O$  or  $OH^-$  ligands fill the coordination shell of vanadium in a tetrahedral or octahedral complex. Under our experimental conditions, the species in solution are as follows:

oxidation state	short-hand notation	complex
$V^{5+}$	$VO_3^-$	$[V(OH)O_3]^{2-}$
$V^{4+}$	$VO^{2+}$	$[V(H_2O)_5O]^{2+}$
$V^{3+}$	$V^{3+}$	$[V(H_2O)_6]^{3+}$
$V^{2+}$	$V^{2+}$	$[V(H_2O)_6]^{2+}$

These oxidation states are readily distinguishable by their different colors, as the  $VO^{2+}$  ion gives blue aqueous solutions, while the  $[V(H_2O)_6]^{3+}$  and  $[V(H_2O)_6]^{2+}$  ions give green and violet colored solutions, respectively.

**Ion exchange:** Ion exchange chromatography uses a charged resin that binds ions oppositely charged ions. In the present lab, you will use a cation-exchange resin that is composed of an inert polymer functionalized with sulfonate ( $-SO_3^-$ ) functional groups. By equilibrating the resin with HCl, you ensure that no ions other than  $H^+$  are initially present on the column. The cations we hope to separate, such as  $VO^{2+}$  (which is really  $[V(H_2O)_5O]^{2+}$ ) compete with  $H^+$  for the negatively charged sulfonate, and the most highly charged ions take the longest time to pass through the column. The concentration of  $H^+$  will affect the rate of travel through the column, as high  $[H^+]$  will tend to displace other cations from the sulfonate binding sites. *Please remember that the charge of the molecular species (the coordination complex) is NOT the same as the oxidation state of vanadium.*

## Experimental Procedure

**Preparation of the Chromatographic Column and Solutions** Use a glass rod to push a small wad of glass wool down to the stopcock of a 25-mL buret. With the stopcock of the buret closed, fill the buret with an aqueous slurry of AG50W-X2 cation exchange resin (100-200 mesh, H<sup>+</sup> form). Allow the resin to settle. Open the stopcock and continue adding the slurry of resin until the amount of the settled resin is ~4-5 in. high. Make sure the resin settles to form a tightly packed column. Close the stopcock as necessary to *keep the level of liquid above the top of the resin*.

**NOTE:** During the course of this experiment, do not allow the level of the liquid to fall below the top of the settled resin, or it will start to channel, short-circuiting the separation and destroying the effectiveness of the column.

After preparing the slurry and allowing it to settle, equilibrate the resin with 3 M HCl (~15mL), elute the acid, and then rinse the column with two volumes of distilled water (~20mL). Wash the resin with distilled water until the eluate is clear. This regenerates your resin, so that H<sup>+</sup> is the only cation bound to the column, and washing with water removes excess acid.

While settling, equilibrating, etc. are being completed, get ready for the next portion of your experiment by doing the following: Obtain ~25-30 test tubes and a rack for collecting fractions before you apply the solution to the column. In separate flasks, make up 50 mL each of 3M, 1M and 0.4 M HCl by diluting a stock 6M HCl solution. It is OK to use the approximate (~10% accuracy) gradations of your glassware for measuring your water and HCl, as the acid concentrations do not need to be known to a high degree of precision.

**Separation of VO<sub>3</sub><sup>-</sup> and VO<sup>2+</sup>** ***In the hood***, add 2.0 mL of concentrated HCl to 200 mg (1.71 mmol) of NH<sub>4</sub>VO<sub>3</sub> in a 150-mm test tube. Heat the mixture to boiling over a microburner for 2-3 min. ***Keep test tube pointed away from persons near you!*** To prevent bumping, do not heat the test tube at the bottom, but rather heat along the edges while gently moving the tube. Once the mixture boils, dilute it with 10 mL of distilled water, mixing well. The solution should change from its original color to a bright green color. VO<sub>3</sub><sup>-</sup> is yellow, whereas VO<sup>2+</sup> is electric-blue – this solution is green, as it is a mixture of these two vanadium oxidation states.

Pour the bright green solution onto the cation exchange column. After applying the solution to the column, begin collecting 3 mL fractions immediately, as a yellow fraction comes off of the column quite quickly. Allow the level of liquid to fall to just above the top of the resin, and then add 0.4 M HCl as necessary to keep the buret full during elution. The upper band is readily detected by its green color (it is actually blue, but the orange color of the resin makes it appear green).

Once all the yellow fractions have eluted, or when the eluate begins to turn green or blue, change the solution on the top of the column to 1.0 M HCl. Continue collecting fractions of 3 mL until the blue band has eluted. You will elute ~9 mL of yellow and ~24 mL of 'electric-blue' solution from this preparation, with a few mL of a blue-green mixture in between. Combine the blue fractions into one container and the darkest yellow fractions into another container, but do not combine any fractions that are yellow-green or blue-green. Make sure the column is still wet and sealed, as you will use it again.

**Separation of  $V(H_2O)_6^{3+}$  and  $V(H_2O)_6^{2+}$**  Place two thirds of the blue solution (~15-20 mL) in a 25-mL Erlenmeyer flask and add 2 g of zinc-mercury amalgam. The amalgam is easy to measure: tare the flask, and use your scoopula to weigh out the material. Stopper the flask and shake vigorously. After a little bit of shaking the solution will turn dark green ( $V^{3+}$ ), and then violet ( $V^{2+}$ ) a short while later. Stop the shaking at the first appearance of violet color (*do not allow it to become all violet!*), so that a mixture of  $V^{3+}$  and  $V^{2+}$  is present. Decant this solution onto the chromatographic column. Once the level of the liquid falls to the top of the resin (at which point all of your compound is in the column), add aliquots of 1.0 M HCl as necessary to keep the column wet and your compound moving through the column. Distinct green and violet bands should form. Collect the violet band in the 3-mL fractions as it elutes. After the violet band has eluted from the column, use 3.0 M HCl to elute the green species. Collect this in the same way. Combine the individual fractions in the same manner as in the first separation. To regenerate the column, wash with 3.0 M HCl until the eluate is clear, then pass 20-30 mL of water over the column. Remove the resin from the buret and collect the resin through gravity filtration.

**Characterization of the Different Oxidation States.**  $KMnO_4$  is a strong oxidizing agent, which will oxidize vanadium to its maximum oxidation state. Titrate a fraction from each vanadium complex with  $KMnO_4$  to determine the concentration of vanadium. Place precisely 1.0 mL of each of the four eluted solutions in a series of test tubes, and add 0.0010 M  $KMnO_4$  dropwise (via a Pasteur pipette) to each tube. Record the exact number of drops needed to give the first trace of the permanganate color (pale pink), and *use these values to calculate the concentration of the different vanadium complexes using dimensional analysis*. You will need to do a separate experiment to determine the volume of each drop.

### Questions

1. Explain why titration with  $KMnO_4$  can only be used to determine the concentration of three of the four complexes studied. Suggest a method for determining the concentration of the fourth complex.
2. Will the positively charged vanadium cations move fastest through the column at high or low pH's? Explain how the concentration of  $H^+$  ions affects the rate of travel through the column.
3. For each reaction that you carried out in this experiment, give a balanced equation indicating the oxidation state of the vanadium species and its color. Include in this list the various reactions with the oxidant  $KMnO_4$ , which re-oxidizes vanadium to  $V^{5+}$ . A list of half-reactions is given below to facilitate your responses.
4. This cation exchange chromatography used resins with negative charges, so that positively charged ions will bind to the resins. Draw Lewis structures for vanadium in each oxidation state (as 4 or 6-coordinate complexes with  $H_2O$ ). Draw a Lewis structure for the negatively charged functional group on AG50W-X2.

**Table 1.** Reduction Potentials relevant to this lab.

Reaction	$E^0$ (V)
1. $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4 \text{H}_2\text{O}$	1.52
2. $\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	1.36
3. $\text{VO}_3^- + 4\text{H}^+ + \text{e}^- \rightleftharpoons \text{VO}^{2+} + 2\text{H}_2\text{O}$	1.00
4. $\text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}$	0.34
5. $2\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightleftharpoons \text{SO}_3^{2-} + \text{H}_2\text{O}$	0.17
6. $\text{V}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{V}^{2+}(\text{aq})$	-0.26
7. $\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{Hg})$	-0.76