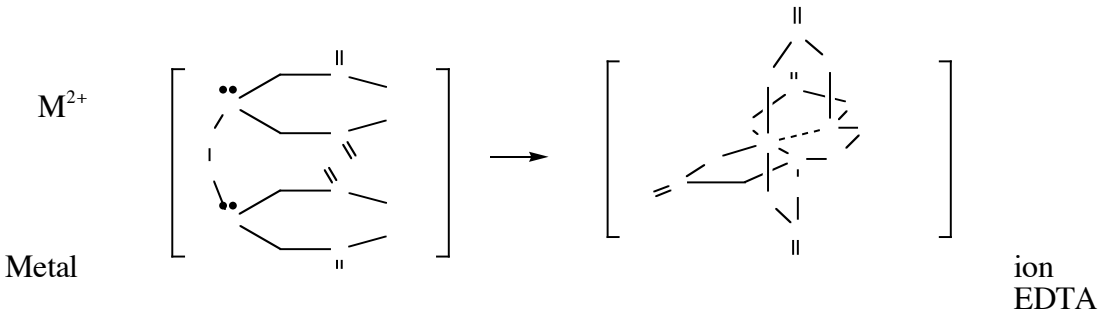
Chemistry 201 Laboratory Summer, 2006

EXPERIMENT 1: HARDNESS OF WATER BY EDTA TITRATION

INTRODUCTION

Water 'hardness' is a measure of the amount of hard water cations in water. These hard water cations include calcium, magnesium, iron, zinc and the other polyvalent metal ions. In most water samples, calcium and magnesium are the chief contributors to water hardness.
Calcium and magnesium are easily measured by titration with the complexing agent ethylene-diaminetetraacetate (EDTA). The EDTA complexes the Ca^{2+} or Mg^{2+} metal ion as shown in the equation below.



EDTA-Metal Complex

$$M^{2+} + Y^{4-} \longrightarrow MY^{2-}$$

The Y^{4-} ion that forms a 1:1 complex with the metal ion is the completely deprotonated anion of ethylenediaminetetraacetic acid ("H_4Y"). At pH=10, the EDTA is present in solution primarily as its monoprotonated form, HY^{3-}. The endpoint of an EDTA titration is determined with a *metallochromic* indicator. These indicators are themselves complexing agents that change color as they combine with a metal ion. Two popular indicators for titrating Ca^{2+} or Mg^{2+} are *eriochrome black* T and *calmagite*. These indicators (shown as In^{3-} in the equations below) change from blue to red color when they combine with a metal ion to form a complex ion:

$$M^{2+} + HIn^{2-} + H_2O \text{ <--> } MIn^{-} + H_3O^{+}$$
blue red

In a titration, EDTA, a stronger complexing agent than the indicator, displaces the indicator form the metal ion allowing the indicator to return (through shades of violet) to a pure blue color, indicating the end of the reaction.

$$MIn^{-} + HY^{3-} \text{ <--> } MY^{2-} + HIn^{2-}$$
red blue

Since Ca^{2+} does not form a stable red complex with the indicator, some Mg^{2+} (and an equivalent amount of EDTA) is added to the titration solution to assure a good color change in samples that do not have Mg^{2+} in them naturally.

Comments

The sharpness of the titration endpoint increases with increasing pH, since more of the EDTA is in the free Y^{4-} form at higher pH. However, the pH cannot be increased indefinitely because $CaCO_3$ or $Mg(OH)_2$ will precipitate at very high pH. The pH can also change the color of the indicator, since only the HIn^{2-} form is blue (H_2In^{-} is red and In^{3-} is

orange).Some metal ions (commonly Fe^{3+} and Cu^{2+}) interfere with the endpoint by causing fading or indistinct endpoints. This interference can be eliminated by adding appropriate inhibitors, one of which is the hydroxylamine hydrochloride added to the indicator solution in this procedure. The titrations are best done at room temperature. The chemical reactions causing the color changes become slow at low temperatures and the indicators may decompose at high temperature.

EXPERIMENTAL PROCEDURE

Standard Solution

Accurately weigh 0.5 g of dried (i.e. to constant weight), pure $CaCO_3$ into a 250 mL beaker. Add approximately 25 mL of distilled H_2O, then 1 mL of conc. HCl carefully, cover with watchglass spaced with glass hooks until dissolved. **Note**: If $CaCO_3$ does not dissolve completely, add another 0.5 mL of conc. HCl. Next, evaporate volume to about 2 mL maintaining watchglass on beaker to expel carbon dioxide. Rinse watchglass, transfer quantitatively and make up volumetrically to 500 mL.

EDTA Solution

Prepare a 0.01 M EDTA solution by weighing out approximately 4 g of reagent grade disodium EDTA into a 250 mL beaker. Add 0.1 g magnesium chloride hexahydrate, five pellets of NaOH and add about 200 mL of distilled water to dissolve. The EDTA will dissolve slowly over a period of a half an hour. Magnesium chloride is added to enhance the sharpness of the endpoint (It forms a more stable complex with the indicator). Filter the EDTA solution into a 1 L bottle, then add approximately 750 mL of water.

Titration Procedure

Pipet three 25 mL aliquots of standard calcium solution into 250 mL Erlenmeyer flasks, add 4 mL ammonium chloride buffer (pH 10) and 3-8 drops of Eriochrome Black T indicator solution. Titrate with EDTA from violet through wine-red to blue. It is recommended to experiment with a 5 mL aliquot to get an idea of the color and titre. The indicator color changes slowly, thus, the titrant must be added slowly near the endpoint with thorough stirring. Calculate the molarity of the EDTA.

Titrate with standard EDTA, 50 mL of unknown solution after addition of 4 mL pH 10 buffer and 2-5 drops of indicator solution following the procedure above. Repeat this in triplicate. Express the concentration of calcium carbonate in the unknown sample in ppm.

Additional notes: It is highly recommended that you also do some preliminary steps for the nickel experiment (refer to nickel experiment for more details), especially if it is your next experiment. Ask for your nickel ore unknown the lab period prior to your scheduled start and dry it to constant weight. As a second priority, clean the glass crucibles and dry them to constant weight.

Informal report

Experiment: Hardness of Water by EDTA Titration

Name_____

Locker #_____

Date submitted_____

Time submitted_____

Values Obtained:

(1)_____ppm $CaCO_3$

(2)_____ppm $CaCO_3$

(3)_____ppm $CaCO_3$

Average value_____

Std Deviation_____

Weight of calcium carbonate (weighed by difference)_____ (g)

Standardization Titration

	I	II	III
Buret reading at start of titration (mL)			
Buret reading at end of titration (mL)			
Volume of EDTA solution used (mL), V_e			
Molarity of EDTA (M)			
Average molarity of EDTA			

Titration of Unknown Sample

Buret reading at start of titration (mL)			
Buret reading at end of titration (mL)			
Volume of EDTA solution used (mL), V_e			
Concentration of calcium carbonate in unknown			

Sample calculations: (FW of $CaCO_3$ = 100.09)
Let's say you titrate 50.0 mL of unknown:

$$\text{ppm } CaCO_3 = \frac{(M_{EDTA})(V_e \text{ in mL})\left(\frac{100.09\ mg}{mmol}\right)}{(mL\ of\ ukn)\left(\frac{1\ L}{10^3\ mL}\right)}$$