CHEM 334 Quantitative Analysis Laboratory

Determination of Calcium by EDTA Titration

Introduction

Complexometric titration is a form of volumetric analysis in which the formation of a colored complex is used to indicate the equivalence point of a titration. This type of titration is particularly useful for the determination of a mixture of different metal ions in solution. An indicator capable of producing an unambiguous color change is required to detect the equivalence point of the titration.

In principle, a complexation reaction can be used as a volumetric technique provided (1) the reaction reaches equilibrium rapidly after each portion of titrant is added, (2) interfering reactions do not occur and (3) a suitable indicator is available. Eriochrome Blue-Black R is a suitable indicator for calcium ions. It exhibits a blue and pink color in aqueous solution in the absence and presence of Ca^{2+}, respectively.

Ethylenediaminetetraacetic acid (EDTA) has four carboxyl groups and two amine groups that can act as electron pair donors or Lewis bases. The ability of EDTA to potentially donate its six lone pairs of electrons for the formation of coordinate covalent bonds to cations makes EDTA a **hexadentate** ligand. However, in practice EDTA is usually only partially ionized, and thus forms fewer than six coordinate covalent bonds with cations.

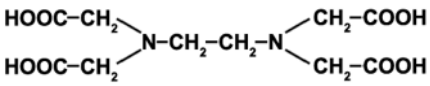

Figure 1. The structure of ethylenediaminetetraacetic acid.

EDTA, in its disodium form, is commonly used as a titrant of multivalent cations. EDTA forms an octahedral complex with most +2 cations, M^{2+}, in aqueous solution. The main reason that EDTA is used so extensively in the standardization of cation solutions is that the association constants for most cation-EDTA complexes is very high, meaning that the equilibrium for the reactions

$$M^{2+} + H_2Y^{2-} \rightarrow MH_2Y \quad (1)$$

$$M^{2+} + Y^{4-} \rightarrow MY^{2-} \quad (2)$$

lie far to the right. Depending upon the pH of the solution either reaction (1) or (2) will hold true. For most purposes, it can be considered that the formation of the EDTA-cation complex goes to completion.

To carry out cation titrations using EDTA, it is necessary to use an indicator to determine when the equivalence point has been reached. Common indicators are organic dyes that bind to cations in solution and form colored complexes. Since EDTA binds to cations much more strongly than does the dye used as an indicator, the EDTA will scavenge the cations from the dye as EDTA is added to the solution of analyte. A color change in the solution being titrated indicates that all of the cations have transferred from the dye to the EDTA and that the equivalence point has been reached. Thus, the presence of free (versus complexed) indicator serves as the equivalence point indicator.

Procedures

Preparation of Unknown Sample: Obtain one antacid tablet (you will need a second one of the same type later so take two now) and record the manufacturer's identification (photograph the bottle? both sides?) and tablet's characteristics, that is, weigh it in a 150-mL beaker. Calculate the volume of 6 M hydrochloric acid required to completely react with the manufacturer's specified mass of calcium carbonate in the tablet. (You will need a balanced equation to perform this.) Slowly add 110 % of this volume of acid to the beaker. Foaming will occur from the carbon dioxide evolution. After the

tablet has completely dissolved add approximately 20 mL of water to the beaker and place it on a hot plate set to 150 °C (outside of a hood is fine). Heat for roughly five minutes to remove any remaining traces of carbon dioxide. Cool the beaker to room temperature. Quantitatively transfer the beaker's contents to a 100 mL volumetric flask and make up the volume with water. Let the sediment settle and when you need to take an aliquot of this solution use the clear (not necessarily colorless) supernatant. A small amount of cloudiness in the aliquot will not interfere with the titration.

Preparation of Standard EDTA Titrant Solution: Prepare 250 mL of a solution of tetrasodium EDTA (Na_4EDTA) approximately 50 mM but known accurately.

It is possible that tetrasodium EDTA is not available in the laboratory but disodium EDTA (Na_2H_2EDTA) is. In this case an additional step in the preparation of the titrant solution is required. Place the salt in a volumetric flask, add 20 mL of 1.0 M sodium hydroxide, then bring the volume to no more than one-half the volumetric flask's volume with water. Swirl until the salt is dissolved (this will take an annoyingly long time) and make up to the mark with water.

Unknown Sample Determination: Add 5.0 mL aliquot of unknown analyte solution (this volume may require adjustment depending upon the amount of calcium carbonate in the tablet being analyzed) and approximately 40 mL of water to a suitable titration flask (Erlenmeyer or beaker, your choice) then add sufficient 1.0 M sodium hydroxide to bring the pH to 11-12 using a single strip of pH indicator paper. The indicator strip is left in the titration vessel during the entire titration. Add five drops of eriochrome indicator (5 g L^{-1} Eriochrome Blue-Black R in 50 vol% methanol). Use additional indicator if the tablet color interferes. Titrate using the standard EDTA solution to a barely purple endpoint. Titrate two more aliquots of the unknown solution in a similar fashion.

Prepare a second unknown solution from a second antacid tablet from the same bottle using the above procedure and titrate three aliquots from this solution as described above.

Results

Report the set of titration measurements in tabular form including the averaged values together with their uncertainty where appropriate. Report the mass of calcium carbonate contained in each antacid tablet with a standard uncertainty analysis. How does the tablet-to-tablet consistency appear?

Discussion

In addition to the standard discussion of the results presented in the Report, discuss the following: (1) the (quantitative!) quality of your measurements as evidenced by their precision; (2) the veracity of the manufacturer's claim of antacid dosage and (3) the precision of the manufacturer’s claim of antacid dosage – in the context of your measurement precision.

References

- Harris, D.C., "Quantitative Chemical Analysis" (2007) seventh edition, Freeman & Co., NY, Chapter 11, pp 235-245.