

Complexometric Titrations: Competition of Complexing Agents in the Determination of Water Hardness with EDTA

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The formation of colored complex ions is one of the key chemical steps used in the qualitative analysis of cations in aqueous solutions. In addition, the absorption of UV-vis radiation by these colored complexes is often used for the quantitative analysis of metal ions by spectrophotometry. Relevant to this demonstration, and widely used in the quantification of metal ions in undergraduate chemistry laboratories, are complexometric titrations in which the end point of the titration can be detected visually.

A well-known and interesting application of complexometric titrations is the determination of water hardness. Hard water contains multiply charged ions such as calcium, magnesium, and heavy metal ions, which replace sodium and potassium ions in soaps and detergents to form precipitates. These precipitates interfere with cleansing action and leave unsightly bathtub rings and scum. In addition, when water containing Ca^{2+} and HCO_3^- ions is heated or boiled, CaCO_3 is formed (1). This is the main component of the scales seen in tea kettles and can cause the clogging of pipes and boilers in industrial settings. Concentrations of Ca^{2+} and Mg^{2+} are usually much greater than concentrations of other ions causing hardness and thus hardness of water is equated to $[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$. Water hardness is usually expressed as the milligrams of CaCO_3 equivalent to the total amount of Ca^{2+} and Mg^{2+} present in one liter of water.

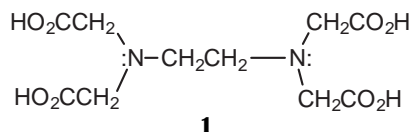
In the determination of water hardness, ethylenediaminetetraacetic acid (EDTA) is used as the titrant that complexes Ca^{2+} and Mg^{2+} ions. Although neither the EDTA titrant nor its calcium and magnesium complexes are colored, the end point of the titration can be visually detected by adding a metallochromic indicator to the water sample. A color change occurs when the indicator goes from its metal ion-bound form to the unbound form. This color change signals the end point, as it takes place when the EDTA, after complexing all of the unbound Ca^{2+} and Mg^{2+} ions, removes the Mg^{2+} ion bound to the indicator. This removal is only possible because the EDTA complexes Mg^{2+} more strongly than the indicator.

This demonstration can be used when discussing complex ion formation to emphasize the correlation between success in the competition of different complexing agents for the same metal ion with the values of their respective complex formation constants, K_f . In addition, the analytical relevance of complexation reactions can be demonstrated by measuring the hardness of water.

Concepts Involved in This Complexometric Titration

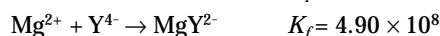
EDTA (1) is widely used in analytical chemistry, as it forms strong one-to-one complexes with most metal ions.

The neutral acid is tetraprotic and is often denoted as H_4Y .

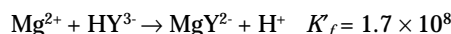
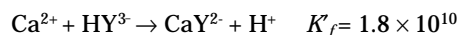


1
 H_4Y : ethylenediaminetetraacetic acid (EDTA)

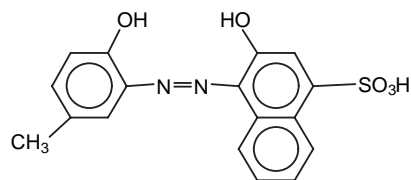
For Ca^{2+} and Mg^{2+} , the complexation reactions with Y^{4-} and corresponding formation constants K_f are (3, 4):



The large magnitude of these formation constants indicates that the above reactions will go to completion if the EDTA is present in its completely deprotonated form Y^{4-} . Furthermore, the great stability of the complexes would lead to sharper end points. To ensure that the titrant is in its completely deprotonated Y^{4-} form, pH values greater than 12 are necessary. Unfortunately, the precipitation of Ca^{2+} as CaCO_3 and of Mg^{2+} as $\text{Mg}(\text{OH})_2$ precludes the titration at such high pH. Instead, the titration can be carried out at pH 10. At this pH, a portion of the EDTA is in the HY^{3-} form and the additional complexation reactions and conditional formation constants at this pH are:



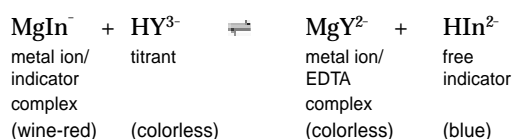
As EDTA and its metal ion complexes are colorless, a metal ion indicator that undergoes a color change when transformed from the metal ion-bound to the unbound form is needed. Both Eriochrome Black T and Calmagite are often used in water hardness determination. Calmagite, 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid, shown in structure 2 in its free acid form and denoted H_3In , was chosen for this demonstration because it provides a sharper end point and has a longer shelf life than Eriochrome Black T (4, 5).



2
Calmagite (H_3In)

As the EDTA titrant is added to a hard water sample, free Mg^{2+} and Ca^{2+} ions are captured first. After complexation of all the free ions, EDTA reacts with the small amount of bound metal ion-indicator complex. The metal ions are effectively removed from the indicator as EDTA binds more tightly to these ions. This victory in the competition for the metal ion is only possible because the value of the formation constant for the Mg^{2+} /Calmagite complex, MgIn^- , is smaller than that for the Mg^{2+} /EDTA complex, MgY^{2-} . Indeed, the effective formation constant for the MgIn^- complex has been reported (5) to be 4.9×10^5 and is almost three orders of magnitude smaller than that mentioned above for MgY^{2-} . Because the indicator binds too weakly to the Ca^{2+} ions ($K'_f = 4.4 \times 10^3$) to provide a sharp end point, a very small amount of Na_2MgY (disodium magnesium EDTA) reagent is added to the sample to ensure a distinct color transition.

The color change observed at the end point of the titration corresponds to the following reaction, with EDTA in the HY^{3-} form:



In the procedure below, a small amount of indicator is added to the hard water sample and the wine-red color of the MgIn^- complex is seen initially as a small amount of Mg^{2+} becomes complexed by the indicator. When the end point is reached, the blue color of unbound indicator HIn^{2-} signals the end point of the titration as all the ions, including those originally bound to the indicator, have been effectively complexed by the more powerful ligand EDTA.

Procedure

Place 25 mL of a hard water sample (see mock preparation below) in a 150-mL beaker on the overhead projector. Add 1 mL of pH 10 buffer solution. Then add 10 drops of the Na_2MgY reagent and 12 drops of the freshly made Calmagite indicator solution, and stir. The solution should be a wine rose color at this point. If the titration is to be used to demonstrate the relative values of formation equilibrium constants, add the first 20 mL of the EDTA solution with a graduated cylinder. The red wine color should persist. Approach the end point by slowly adding the last approximately 5 mL of EDTA solution with an eyedropper, while stirring. As discussed above, the color of the solution

will change to blue at the end point. Cycle about the end point by alternately adding more hard water and more EDTA titrant. A blank with distilled water in a second beaker could also be simultaneously titrated to contrast and accentuate the effect.

If the demonstration is used to highlight the applicability of complexometric titrations in quantitative analysis, the 25 mL of the "hard water" sample should be measured with a 25-mL transfer pipet and the EDTA solution should be added from a buret.

Preparation of Solutions

Hard water sample. A hard water sample that mimics very hard water with approximately 1,000 ppm Ca^{2+} ion may be prepared by creating a slurry of 0.25 g of anhydrous CaCO_3 with 3–4 mL of deionized water. Add 6 M HCl, a few drops at a time, until the CaCO_3 has dissolved. (Do not add more than 3 mL of HCl in this step.) Dilute to 250 mL with deionized water. The resulting concentration of the solution is about 1 mg CaCO_3/mL .

pH 10 buffer. Dissolve 64 g of NH_4Cl in 200 mL of distilled water. Add 570 mL of concentrated ammonia and dilute to 1.00 L with distilled water.

Calmagite indicator. Dissolve 0.5 g of Calmagite [1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid] in 1 L of distilled water. Stir the solution for one hour and let sit overnight. In spite of its long shelf life, the indicator should be prepared fresh every month.

EDTA titrant. A solution of approximately 0.010 M of EDTA may be prepared by weighing between 0.9 and 1.0 g of the disodium salt dihydrate of EDTA. Place this amount into a 500-mL flask and add 250 mL of deionized water to dissolve.

Na_2MgEDTA reagent. Weigh out 39.4 g of Na_2MgEDTA and add 750 mL deionized water. Add 15 mL of concentrated NH_4OH and 10 drops of Calmagite indicator. Add small portions of Na_2EDTA salt until the solution is almost blue. Dilute to 1000 mL with deionized water.

Literature Cited

1. Chang, R. *Chemistry*, 4th ed.; McGraw Hill: New York, 1991.
2. Harris, D. D. *Quantitative Chemical Analysis*, 3rd ed.; Freeman: New York, 1991.
3. Skoog, D. A.; West, D. M.; Holler, F. J. *Analytical Chemistry: an Introduction*, 6th ed.; Saunders College: Philadelphia, 1994.
4. Christian, G. C. *Analytical Chemistry*, 5th ed.; Wiley: New York, 1994.
5. Lindstrom, F.; Diehl, H. *Anal. Chem.* **1960**, *32*, 1123–1127.