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Microscale Demonstration of Charge Modification upon Complexation by Ion Exchange

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Abstract: A small plastic syringe (or a Pasteur pipet) is used as an ion-exchange microcolumn model to demonstrate the principles of ion exchange and charge modification upon complexation. In the first part of the experiment, the removal of cobalt ions (cations) from aqueous solution is visually demonstrated. Then, Co^{2+} is reacted with the negatively charged EDTA (ethylenediaminetetraacetate) ion to form a complex anion. When passed through a cation exchange column, the Co^{2+} ions are completely retained whereas the complexed cobalt ions are not removed at all. This experiment is appropriate for a first-year chemistry laboratory, and takes approximately one hour to complete.

Introduction

Commercially, ion exchange is used for the removal of unwanted ions from aqueous solutions or for the recovery of valuable species. It normally refers to the replacement of ions in an insoluble phase (typically, but not exclusively, a resin) by ions contained in a solution [1]. These resins possess functional groups capable of binding either cations or anions. Typical of the former are the $–SO_3H$ and $–COO^–$ groups and of the later are $–NR_4^+$ groups [2]. The replacement of an adsorbed, readily exchangeable ion by another is a surface phenomenon involving charged species in the outer, diffuse layer of the surface. The affinity of the exchanger for polyvalent metal ions is larger than that for monovalent ions (e.g., H^+, Na^+) [3]. The rate of the exchange reaction depends on the number of sites available in the resin [4, 5]. For these processes, it is important to use a regenerated resin (i.e., a resin containing large amounts of H^+ or Na^+) in order to ensure that all the metallic ions in the target solution are extracted [6].

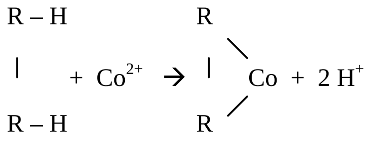
Basically, three different types of ion exchangers exist: (1) cationic exchangers, (2) anionic exchangers, and (3) mixed-bed exchangers (anionic and cationic).

Cationic exchangers are commonly used to soften waters that contain Ca^{2+} and Mg^{2+} ions. The anionic exchangers are typically used to remove chloride ($Cl^–$), sulfate ($SO_4^{2–}$), and carbonate ($CO_3^{2–}$) ions from water [7]. Mixed-bed exchangers are employed to deionize water used in laboratories.

The global reaction for a cationic exchange can be represented as follows.

$$\text{RH} + (\text{cation})(\text{anion}) \rightarrow \text{R-(cation)} + \text{H-(anion)} \quad (1)$$

Here, RH is the cation-exchange resin in its protonated form. In the following demonstration a cationic exchanger (e.g., an Amberlite resin) is used for the removal of Co^{2+} (in a $CoCl_2$ or $Co(NO_3)_2$ solution). Amberlite IR120 is a commercial synthetic resin composed of water (51%) and a divinylbenzene/styrene sulfonated copolymer (49%) [8]. It is available through several regular suppliers of chemical reagents (e.g., Aldrich, Sigma) and also from reference 8. Its cost is on the order of $60 (U.S.) per kilogram. When moistened with deionized water and put in contact with the Co^{2+} solution, it takes up these ions, liberating two H^+ ions:



(2)

On the other hand, Co^{2+} will form a complex with a common ligand, ethylenediaminetetraacetate (EDTA). A complex ion consists of a central metal cation with empty orbitals and a chemical moiety with at least one unshared pair of electrons (ligand). These are united by a coordinated covalent bond and the charge on the complex corresponds to the sum of the charges of the constituent parts. Some uses of EDTA include medicinal and personal care products, food, cleaning, photographic applications, and formation or dissolution of precipitates [9–11]. It is called a *multidentate* ligand (meaning several teeth), because it has six possible binding sites for a given metal ion.

In the following demonstration, both the Co^{2+} solution and the Co-EDTA complex solution will be separately passed through two identical exchange columns, loaded with the same resin, to observe and discuss the behavior of the cobalt species in each case. This experiment is appropriate for a first-year chemistry laboratory, and takes approximately one hour to complete.

Constructing the Experimental Setup

This experiment will be performed at the microscale level. Microscale chemistry decreases the amounts of substances used in laboratory work. In addition to cutting costs dramatically, this also decreases the need for treatment and disposal of hazardous substances, reduces accidents, permits the usage of otherwise inaccessible costly materials, and exposes students to environmental issues. The set-up used in this experiment is small, simple, and inexpensive, as is described below.

Place a small moistened piece of cotton in the lower part of the column (a small-diameter, 3-mL transparent syringe or a regular Pasteur pipet are recommended) in order to avoid resin beads from

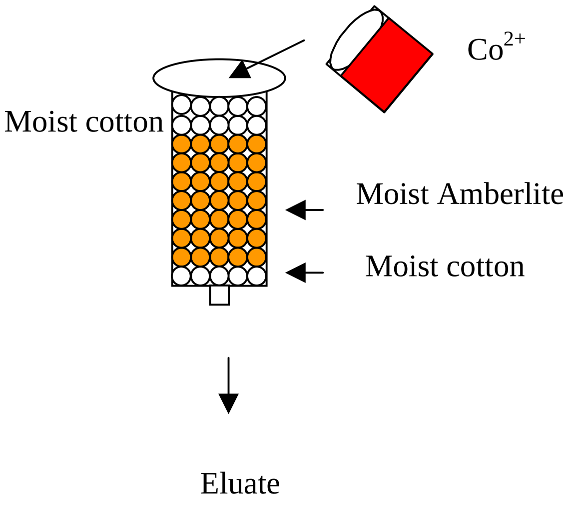


Figure 1. Experimental setup.

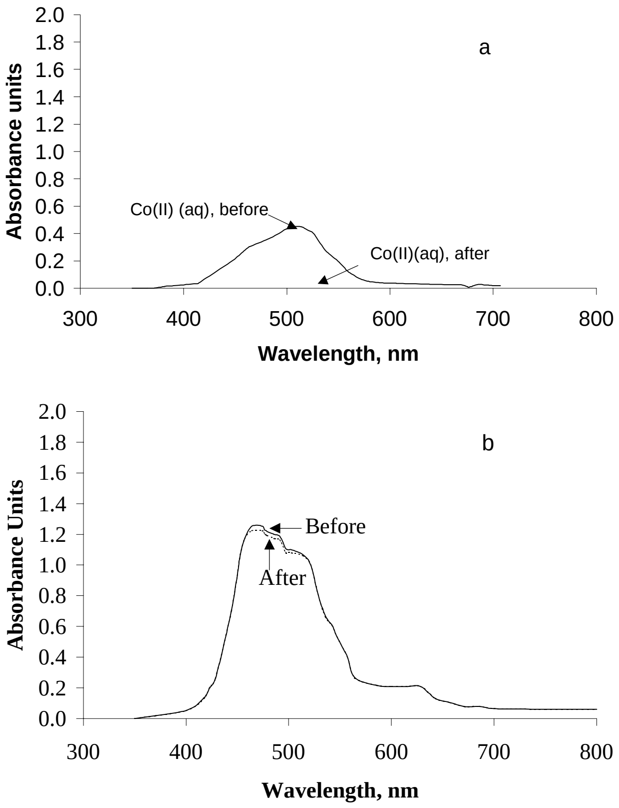


Figure 2. (a) Visible spectra of the Co^{2+} solution before and after passing it through the ion-exchange resin in column 1. (b) Visible spectra of the $[CoEDTA]^{n-}$ solution before and after passing it through the ion-exchange resin in column 2.

exiting, as shown in Figure 1. Pack three-fourths of the column with Amberlite and moisten it with a small amount of deionized water. It is important to keep the resin wet throughout the entire experimental procedure. This ensures an even distribution and avoids the problem of solution passing through without coming in contact with the resin. (This undesirable phenomenon is called *channeling*.) Place another piece of moist cotton in the upper part of the column. Use of deionized water throughout the experiment is recommended in order to avoid any possible contamination. Make two experimental setups so as to have two microcolumns. Use a clamp to secure each column on a stand in order to have both hands free. We will label these columns as column 1 and column 2.

The Demonstration

Prepare a small volume (for example, 5 mL) of a 0.1 M Co^{2+} solution by dissolving the appropriate amount of a Co(II) salt (for example, $CoCl_2$ or $Co(NO_3)_2$) in deionized water to the desired volume. This is labeled solution 1. Repeat the above procedure, but this time also dissolve enough Na_2EDTA salt (after dissolving the Co salt) as to give an excess of EDTA with respect to Co^{2+}. (Note: a 1.5:1 molar ratio works well. In other words, prepare a solution that is 0.1 M in Co^{2+} and 0.15 M in EDTA.) If the solution of $[CoEDTA]^{n-}$ does not dissolve completely, it could be due to a low pH, where the insoluble tetraprotonated form, H_4EDTA predominates. Increase the pH by adding dilute NaOH dropwise, until complete dissolution is observed. The resulting solution is labeled solution 2. Now, take 1 mL of solution 1 and pass it through column 1. Save the remaining Co^{2+} solution as a color control. Then, take 1 mL of solution 2 and pass it through column 2. Save the remaining Co-EDTA solution as a color control. Record your observations. If a UV–vis spectrophotometer is available, take the visible spectrum of each solution before and after this step.

Results and Discussion

Solution 1 becomes colorless after leaving column 1, and the column adopts a reddish color from top to bottom. This is due to the exchanged Co^{2+} ions. If enough solution were passed, the resin would run out of H^+ ions layer by layer until pink Co^{2+} ions could be observed in the effluent (saturation point). The general reaction is

$$\underset{\text{amber}}{RH_2} + \underset{\text{pink}}{Co^{2+}} \rightarrow \underset{\text{pink}}{RCo} + \underset{\text{colorless}}{2H^+} \qquad (3)$$

Solution 2 maintains its pink color after being passed through the column 2. When the complex ion is formed, the cobalt is “encapsulated” and forms part of the anion; therefore, the cationic resin does not adsorb it. (A nice three-dimensional rotating model for this complex can be seen in reference [12]). This is so because the EDTA is an anion with a –3 or –4 charge at any pH value above approximately 6, and as a result the Co(II) complex is negatively charged.

$$\underset{\text{amber}}{RH_2} + \underset{\text{pink}}{[CoEDTA]^{n-}} \rightarrow \text{NO REACTION} \qquad (4)$$

After completing the experiment, UV–vis spectroscopy or atomic absorption spectrometry can be used to verify the observations made with the naked eye. In Figure 2a, the visible spectra of the Co^{2+} solutions before and after the experiment are shown. It can be seen that virtually all of the initial Co^{2+} has been retained by column 1. In Figure 2b, the visible spectra of [CoEDTA] show that essentially the entire initial complex passed through the resin in column 2.

If a more analytically oriented experiment is desired, advanced students can calculate the distribution of species for each system, make a graph [13], and interpret the graph in terms of the above discussion.

At the end of the demonstration, the resin in column 1 is ready for regeneration for reuse in future experiments. (Column 2 does not require regeneration.) This can be accomplished by passing a few milliliters of a 3–6 M solution of HNO_3 or HCl through it dropwise. *Warning: Use appropriate safety goggles.* This regenerates the resin by donating H^+ ions and “redissolving” the Co^{2+} ions.

$$\underset{\text{pink}}{\mathrm{RCo}} + \underset{\text{colorless}}{2\mathrm{HNO_3}} \rightarrow \underset{\text{amber}}{\mathrm{RH_2}} + \underset{\text{pink}}{\mathrm{Co(NO_3)_2}} \qquad (5)$$

Finally, the excess acid can be washed away with deionized water and the resin set aside for storage.

Conclusion

A microscale experiment using a plastic syringe or a Pasteur pipet and a cation-exchange resin can be used to demonstrate the principle of cation ion exchange and the possibility of altering the charge of a given metal ion upon complexation with a ligand under the appropriate conditions.

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References and Notes

1. *Wastewater Engineering: Treatment, Disposal and Reuse,* 3rd. ed. Metcalf and Eddy, Inc. McGraw-Hill: New York, 1991, Chapter 11.
2. Stumm, W.; Morgan, J. J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters;* Wiley Interscience: New York, 1996. Chapter 9.
3. Manahan, S. E. *Environmental Chemistry*, 6th. ed.; Lewis Publishers: Boca Raton, FL, 1994, Chapter 8.
4. Remco Engineering Environmental Water Systems And Controls, Inc. http://www.remco.com/di.htm (accessed Feb 2000), 410 Bryant Circle, Ojai, CA 93023, email: remcobob@remco.com.
5. Hiroyuki, Y.; Takeshi, K.; Seiichi, F. *Chem. Eng. Sci.* **1986,** *41*, 2517–2524.
6. Samuelson, O. *Ion Exchange Separations in Analytical Chemistry;* John Wiley & Sons: New York, 1963; pp 98–100.
7. Bayer Corporation. http://www.ion-exchange.com/ (accessed Feb 2000), 100 Bayer Road, Pittsburgh, PA 15205-9741, email: tony.decola.b@bayer.com.
8. Rohm and Haas Company. http://www.rohmhaas.com/ionexchange/fr_resins.htm (accessed Feb 2000), Home Office, 100 Independence Mall West, Philadelphia, PA 19106-2399, email: UStatesW1@rohmhaas.com.
9. Hart, J. R. *J. Chem. Educ.* **1984,** *61,* 1060–1061.
10. Hart, J. R . *J. Chem. Educ.* **1985,** *62,* 75–76.
11. Swaddle, T. W. *Applied Inorganic Chemistry;* University of Calgary Press: Calgary, 1990; Chapter 11.
12. University of the West Indies. http://wwwchem.uwimona.edu.jm:1104/courses/comligs.html (accessed Mar 2000), Dr. Robert J. Lancashire, The Department of Chemistry, University of the West Indies, Mona Campus, Kingston 7, Jamaica; email: rjlanc@uwimona.edu.jm.
13. Rojas-Hernandez, A.; Ramirez, M. T.; Gonzalez, I.; Ibanez, J. G. *J. Chem. Educ.* **1995,** *72,* 1099–1105.