

Coloring a Superabsorbent Polymer with Metal Ions

An Undergraduate Chemistry Experiment

Jing-Fun Yang

Department of Food Science, National Kinmen Institute of Technology, Kinmen 893, Taiwan, ROC

Yueh-Huey Chen*

Department of Applied Science, National Dong Hwa University (Meilun Campus), Hualien 970, Taiwan, ROC;

*cyh@mail.nhlu.edu.tw

Undergraduate laboratories are usually designed to introduce fundamental theory to the students. However, the students frequently ask for laboratories that have some relevance to practical applications. A novel undergraduate experiment involving superabsorbent polymers commonly used in diapers and other personal care products (1, 2) is described. There are several activities involving superabsorbent polymers reported in this *Journal* (3–6). In this article we describe experiments designed to explore the ionic nature of these particular polymers. Metal(II) polyacrylates are generated by removal of some metal ions from aqueous solutions by the polymers. Unique colors are obtained with Cu^{2+} , Ni^{2+} , Co^{2+} , and Fe^{2+} . Changes in water absorbency and color were observed, and the ion-exchange capacity of the polymers was determined by colorimetry using Cu^{2+} .

This experiment is performed near the end of the second-semester general chemistry laboratory course. The fundamental concepts involved, such as ionic compounds, ionic-intermolecular interaction, ionic equilibrium in aqueous solution, concentration of solution, and functional groups of organic compounds, have been introduced in general chemistry lectures. The skills of quantitative analysis including the preparation of standard solutions and the construction of a calibration curve have been practiced in previous experiments. Prelab discussion covers the mechanism of swelling and the ionic nature of superabsorbent polyacrylates and a brief review of the Beer–Lambert law to acquaint the students with colorimetry analysis.

Overview of Superabsorbent Polymer

The superabsorbent polymers used in diapers are lightly cross-linked polymers of partially neutralized acrylic acid (7). This hydrophilic polymer absorbs large quantities of water without dissolving owing to the ionic nature and the interconnected

structure of the polymer (8). In addition to the extensive use in the commercial hygienic products, other applications for this water-absorbing polymer include water conserver for agriculture and horticulture (9), sealing-composite (10), water-blocking tape (11), humidity control (12), artificial snow (13), and gel actuator (14).

Metal Ion Uptake by Ion Exchange

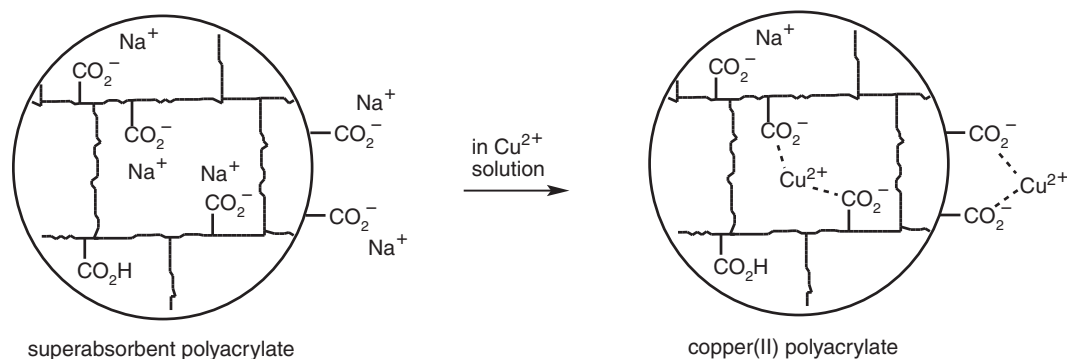
Superabsorbent polyacrylates are ionic polymer networks containing ionizable pendant groups, termed polyelectrolytes. When exposed to aqueous solution containing divalent metal ions, the carboxylate groups of the polymer take up the metal ions. The exchange between the divalent metal ions and the sodium ions on the polymer occurs irreversibly (Scheme I) (15). Consequently, the metal ions are withdrawn from the solution through the formation of metal(II) polyacrylates. The irreversible binding of divalent metal ions is reported to result in additional cross-links, causing a dramatic decrease in water absorbency (16).

Experimental Procedure

This experiment consists of two parts: the coloring of superabsorbent polymers^{1,2} and the ion exchange in the polymer with Cu^{2+} . The students work in pairs. More detailed experimental procedures are available in the online material.

Coloring of the Superabsorbent Polymer

The coloring procedures are performed with solutions of CoCl_2 , CaCl_2 , NiCl_2 , and FeCl_2 . Each pair of students test all the solutions to obtain various metal(II) polyacrylates. Approximately 0.8 g of superabsorbent polyacrylate³ is sealed in



Scheme I. The ion-exchange with Cu^{2+} and the additional cross-links formed in the polymer networks.

a tea bag⁴ ($5.5 \times 5.5 \text{ cm}^2$). The tea bag with polymer is soaked in 50 mL of 0.1 M metal halide solution with swirling. After soaking, the tea bag with the resulted metal(II) polyacrylate is washed thoroughly with water, dehydrated with ethanol, and oven dried at 110 °C.

Ion Exchange in the Polymer with Cu^{2+}

A SP-830plus spectrophotometer from Metertech Inc. Taiwan, ROC is used for absorbance measurement. A freshly prepared stock solution of 0.2 M CuCl_2 is provided. Students

Table 1. Color of the Metal(II) Polyacrylates

Metal Ion	Color
Na^+	white
Ca^{2+}	white
Cu^{2+}	greenish blue
Co^{2+}	dark purple
Ni^{2+}	bright green
Fe^{2+}	dark brown

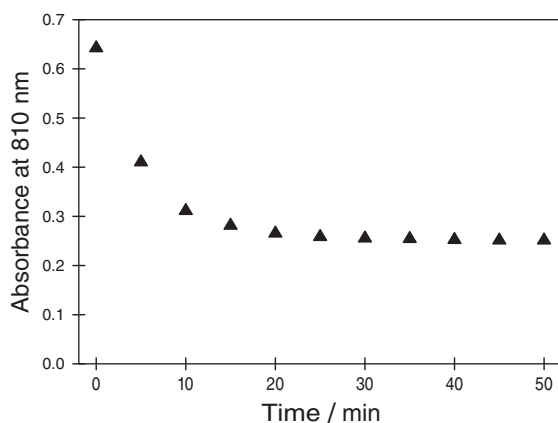


Figure 1. The absorbance of Cu^{2+} solution during the ion-exchange.

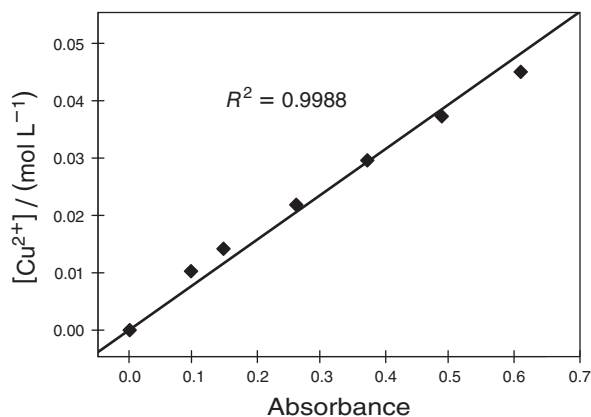


Figure 2. The calibration curve of $[\text{Cu}^{2+}]$ vs absorbance at 810 nm.

prepare five solutions of different concentrations in the range from 0.05 M to 0.005 M via the dilutions of the stock solution using standard volumetric procedures. The absorbance of each solution is measured at 810 nm. A calibration curve of $[\text{Cu}^{2+}]$ versus the absorbance is constructed.

Approximately 0.8 g of superabsorbent polyacrylate, weighed to three significant figures, is sealed in a tea bag. The tea bag is then placed in 100 mL of 0.05 M CuCl_2 solution with gentle stirring. The change in $[\text{Cu}^{2+}]$ is monitored by the absorbance of the solution. Each aliquot removed for the absorbance measurements is returned to the vessel. The absorbance measurements are stopped after the absorbance of the solution reaches a steady state. The solution containing residual Cu^{2+} is transferred into a volumetric flask. The tea bag and all the glassware involved are washed thoroughly with distilled water. The washing solutions are collected in the volumetric flask with the solution containing residual Cu^{2+} . The resulting solution is diluted with water to the mark, and the absorbance is measured. The quantity of the residual Cu^{2+} is calculated from the absorbance according to the least-squares equation derived from the calibration curve.

Hazards

The powder of superabsorbent polymer can irritate eyes, nose, and mouth. Contact with the polymers must be avoided. The metal halides may cause skin, eye, respiratory, and gastrointestinal tract irritation. They should be handled with care and not be ingested. Ethanol is highly flammable. There should be no open flames in the laboratory, and adequate ventilation must be used. Care must be taken while the hot plate is in use.

Student Results

Data have been collected for over fifty samples in the past three years. Example data and the calculations are available in the online material. The colors of the metal(II) polyacrylates are shown in Table 1. Typical graphs of the change in $[\text{Cu}^{2+}]$ with time and the calibration curve of $[\text{Cu}^{2+}]$ versus absorbance obtained by the students are shown in Figures 1 and 2. The concentration of Cu^{2+} decreased dramatically at the early stage of the ion exchange and gradually reached a steady state. The concentration of Cu^{2+} in the solution was calculated according to the least-squares equation derived from the calibration curve. The reported ion-exchange capacities of the superabsorbent polyacrylates were in the range of 3.5 to 4.2 mmol Cu^{2+} on the basis of one gram of the polymers.⁵

Summary

This experiment helps the students become familiar with the molecular structure of superabsorbent polymers and the chemistry involved in the ion-exchange of the polymer. The experiment contains several learning areas:

- Superabsorbent polymer structure and swelling
- Properties of metal polyacrylates
- Ion removal from aqueous solution by ion-exchange
- Quantitative analysis of solution preparation, calibration curve construction, colorimetry, Beer-Lambert law

The student feedback was positive. Most of the students enjoyed the real-world nature of this experiment. One student stated, "Doing experiments with real-world materials is exciting." Some students expressed that they are strongly motivated to take subsequent chemistry courses because they realized that chemistry knowledge is important. Although this experiment was originally designed for general chemistry laboratory, it is suitable for polymer chemistry laboratory. The chemistry of hydrophilic polymers, ionic polymers, polyelectrolyte hydrogels, and polymers for wastewater treatment can be included. This experiment can also be extended to an undergraduate research project. Factors such as various copper(II) salts,⁶ the concentration of Cu^{2+} solution, the pH of the solution, and various metal(II) ions on the ion-exchange capacity of the polymers can be studied. The dissolution of metal ions from the resulting metal(II) polyacrylates in aqueous solutions is also of interest.

Acknowledgments

The authors would like to express our gratitude to the reviewers for their constructive suggestions with regard to this manuscript. This work is supported by the National Science Council of Taiwan under grant NSC 97-2511-S-026-005.

Notes

1. The superabsorbent polymers used in this experiment were isolated from diapers. Three different types of diapers were used, Pampers Newborn Extra Soft size S for 3–8 kg infant from Procter & Gamble, Mamy Poko Extra Speed Dry size XL for 12–17 kg baby from Uni-Charm Corporation, and Pampers Easy Ups size 5 for 14–18 kg baby from Procter & Gamble. The experiment was also conducted with superabsorbent polymer purchased from Aldrich Chemical Co. Similar results were obtained.

2. The isolation of the superabsorbent polymers from diapers was carried out by the instructor or the student assistants prior to the lab. The procedures are stated in the Instructor's Notes available in the online material.

3. The superabsorbent polymers slightly swell at the beginning of the ion-exchange process. Overloading of the polymer may lead to the breakage of the tea bag owing to the expansion of the swollen polymer. The appropriate quantity of the polymer used is in the range of 0.7 g to 0.9 g.

4. The tea bags used in this experiment are pyramid-shaped from Lipton tea products purchased from market places in Taiwan. The bags are emptied, washed, and dried before the experiment.

5. The possible removal of Cu^{2+} by the tea bag is discounted, since the variation in the absorbance of the blank was negligible (Figure 2 in the online material).

6. We have conducted the experiment in CuSO_4 solution. Similar results were obtained except the quantity of Cu^{2+} removed is slightly less compared to that in CuCl_2 solution.

Literature Cited

1. *Superabsorbent Polymers*; Buchholz, F. L., Peppas, N. A., Eds.; ACS Symposium Series 573; American Chemical Society: Washington, DC, 1994.
2. *Absorbent Polymer Technology*; Brannon-Peppas, L., Harland, R. S., Eds.; Elsevier Science Publishing Company Inc.: New York, 1990.
3. Buchholz, F. L. *J. Chem. Educ.* **1996**, *73*, 512–515.
4. Garner, C. M.; Nething, M.; Nguyen, P. *J. Chem. Educ.* **1997**, *74*, 95–96.
5. Criswell, B. J. *J. Chem. Educ.* **2006**, *83*, 574–576.
6. Criswell, B. J. *J. Chem. Educ.* **2006**, *83*, 576A–576B.
7. Buchholz, F. L. Preparation Methods of Superabsorbent Polyacrylates. In *Superabsorbent Polymers*; Buchholz, F. L., Peppas, N. A., Eds.; ACS Symposium Series 573; American Chemical Society: Washington, DC, 1994; pp 27–38.
8. Lochhead, R. Y.; Davidson, J. A.; Thomas, G. M. Poly(acrylic acid) Thickeners. In *Polymers in Aqueous Media*; Glass, J. E., Ed.; Advances in Chemistry Series 223; American Chemical Society: Washington, DC, 1989; pp 113–147.
9. Shimomura, T.; Namba, T. Preparation and Application of High-Performance Superabsorbent Polymers. In *Superabsorbent Polymers*; Buchholz, F. L., Peppas, N. A., Eds.; ACS Symposium Series 573; American Chemical Society: Washington, DC, 1994; pp 112–127.
10. Tsubakimoto, T.; Shimomura, T.; Kobayashi, H. (Nippon Shokubai Kagaku Kogyo Co., Ltd., Japan). *Water Absorbents*. JP 62149335, 1987. Tsubakimoto, T.; Shimomura, T.; Kobayashi, H. (Nippon Shokubai Kagaku Kogyo Co., Ltd., Japan). *Water Absorbents*. JP 62149336, 1987.
11. Sheu, J. J. Cables such as Optical Fiber Cables Including Superabsorbent Polymeric Materials Which Are Temperature and Salt Tolerant. U.S. Patent 5,163,115, Nov 10, 1992.
12. Degouw, A. M.; Prins, J.; Dingerms, J. *Eur. Pat. Appl.* EP 68530, 1983.
13. Morioka, K.; Nakahigashi, S. *Refrigeration* **1992**, *67*, 28.
14. Kurauchi, N. *Kagaku to Kyoiku* **1991**, *39*, 618.
15. Mouginot, Y.; Morlay, C.; Cromer, M.; Vittori, O. *Anal. Chim. Acta* **2000**, *407*, 337–345.
16. Yin, Y. L.; Prud'homme, R. K.; Stanely, F. Relationship Between Poly(acrylic acid) Gel Structure and Synthesis. In *Polyelectrolyte Gels*; Harland, R. S., Prud'homme, R. K., Eds.; ACS Symposium Series 480; American Chemical Society: Washington, DC, 1992; pp 91–113.

Supporting JCE Online Material

<http://www.jce.divched.org/Journal/Issues/2009/Mar/abs347.html>

Abstract and keywords

Full text (PDF) with links to cited JCE articles

Supplement

Instructions for the students; Notes for the instructor