

Effects of Concentration on Hexaaquacobalt(II)/Tetrachlorocobalt(II) Equilibrium. A Discovery-Oriented Experiment for Chemistry Students

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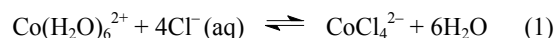
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Abstract: A solution of cobalt(II) chloride in HCl is commonly used to examine various effects, such as changes in temperature and concentration, on the $\text{Co}(\text{H}_2\text{O})_6^{2+}/\text{CoCl}_4^{2-}$ equilibrium (Le Châtelier's principle). In aqueous solution the cobalt(II) ion exists as a mixture of two complex ions at equilibrium, blue CoCl_4^{2-} and pink $\text{Co}(\text{H}_2\text{O})_6^{2+}$. As the ions have different colors, it is easy to determine the position of the equilibrium. A series of experiments was designed to allow students to examine the concentration of chloride ion, the dehydration effect, and how dissociation affects the equilibrium. Different compounds were added to the aqueous solution of cobalt(II) ion, and the position of the equilibrium was determined either visually or, more quantitatively, by means of UV-vis spectroscopy. This exercise is suitable for general chemistry students and is designed to introduce them to the complexity of the actual chemical reaction rather than presenting them with a simplistic model.

Introduction

A solution of cobalt(II) chloride in aqueous HCl is a system commonly used to illustrate the effects of temperature and concentration on the $\text{Co}(\text{H}_2\text{O})_6^{2+}/\text{CoCl}_4^{2-}$ equilibrium (Le Châtelier's principle). Several demonstrations using similar systems appear in the literature [1–3] as well as laboratory textbooks [4, 5]. Modern general chemistry textbooks usually use this example to illustrate the effect of temperature on the equilibrium without mentioning the effect of the change in concentration of the chloride ion or water [6–9]. One may speculate that the authors may consider the effect of change in concentration to be too complex [1–3] for consideration by freshmen chemistry students. In this laboratory exercise, a solution of cobalt(II) chloride in 6 M aqueous HCl is used to demonstrate the effects of concentration. In aqueous solution, cobalt(II) ion exists as a mixture of two complex ions at equilibrium, that is,



Position of the equilibrium depends on the temperature, concentrations of the species involved, entropy [10, 11] and probability [11] effects. As the ions have different colors, CoCl_4^{2-} is blue and $\text{Co}(\text{H}_2\text{O})_6^{2+}$ is pink [12], it is easy to observe the position and shift in equilibrium. A short discussion with students should help them come to the conclusion that, because the ions have different colors, they also have different visible spectra, and the position of the equilibrium can be determined from the visible spectrum of the mixture.

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In this laboratory exercise, several salts were added to the solution and the position of the equilibrium was observed either by comparison with a standard solution or, more quantitatively, by means of UV-vis spectroscopy.

Experimental

Safety warning. Concentrated sulfuric and hydrochloric acids can cause skin burns. Students and instructors should wear eye protection and safety gloves at all times. If any acid spills on skin, wash the area thoroughly for at least 15 minutes under running cold water. Addition of a drying agent to an aqueous solution is an exothermic process. Drying agent should be added slowly and the solution should be cooled in a water (or ice-water) bath.

Stock solution 1 was prepared by dissolving $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (5.00 g) in 6 M HCl (1 L). Stock solution 2 was prepared by dissolving 0.050 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 6 M HCl (1 L). Stock solution 1 was used to prepare solutions for visual determination of the equilibrium position and stock solution 2 was used to prepare solutions for acquiring UV-vis spectra. For experiment 1, students prepared solutions of cobalt (II) ion in 6 M, 10 M, and 12 M aqueous HCl. For experiment 2, various salts (NH_4Cl , LiCl , NaCl , KCl , CaCl_2 , $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) were added to the stock solutions to make the concentration of Cl^- ions 10 M. For experiment 3, various drying agents (concentrated sulfuric acid, anhydrous MgSO_4 , anhydrous Na_2SO_4 , anhydrous CaCl_2 , and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) were added to the stock solutions. UV-vis spectra were acquired using an HP 1000 UV-vis spectrometer or an Ocean Optics CHEM 2000. The spectra were saved as Excel files. Experimental details are provided in the Supporting Materials.

Results and Discussion

Experiment 1 (Co^{2+} in various concentrations of aqueous HCl) was designed so that the students can investigate the effect of dehydration and the concentration of chloride ion. When the concentration of hydrochloric acid is increased, the shift in the equilibrium position may be due to an increase in the concentration of chloride ions or to the dehydrating effect

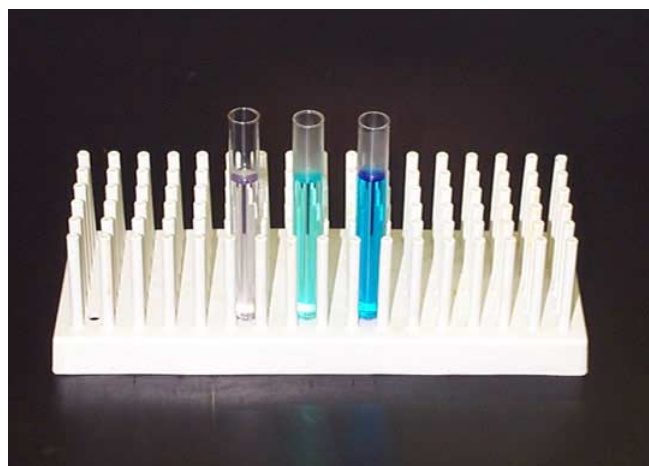


Figure 1. From left to right, solutions of Co^{2+} (21 mM) in 6, 10, and 12 M HCl.



Figure 3. Solutions of Co^{2+} (21 mM) in 6 M HCl with added (from left to right) LiCl, NH_4Cl , NaCl, and KCl.

of hydrochloric acid as was pointed out by Grant [3]. Grant added concentrated sulfuric acid to the solution to illustrate that the shift in equilibrium is due to a dehydrating effect; however, he did not report whether or not he controlled the temperature while adding sulfuric acid. The addition of sulfuric acid to an aqueous solution is a highly exothermic process and, depending on the experimental conditions, the increase in temperature may be the reason for the shift in the equilibrium towards the blue CoCl_4^{2-} [13]. As a strong acid, hydrochloric acid is completely ionized and, therefore, differences in the degree of ionization are not expected to affect the position of the equilibrium. Results of the experiment are shown in Figure 1.

In experiment 2 (addition of chloride salts to Co^{2+} in 6 M HCl) students investigate the effects of dehydration and the degree of ionization. Students are asked to investigate the effect of adding ammonium chloride and several alkali chlorides (LiCl, NaCl, KCl) on the position of the equilibrium. Results of the experiment are shown in Figures 3 and 4. Ionic salts are not completely dissociated in aqueous solution [14]. Thus, a simplified explanation is that different salts will

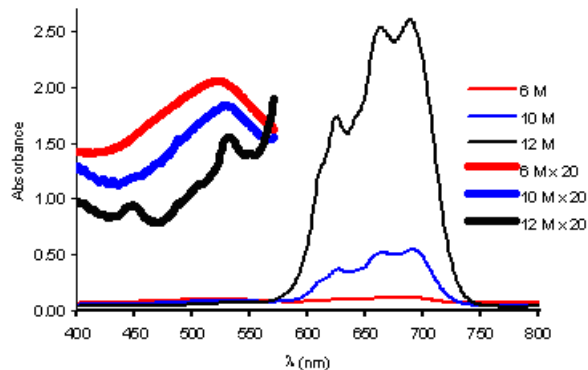


Figure 2. Spectra of Co^{2+} (2.1 mM) in 6, 10, and 12 M HCl. The baseline was adjusted. The region of 400–570 nm multiplied by a factor of 20 is shown at the left.

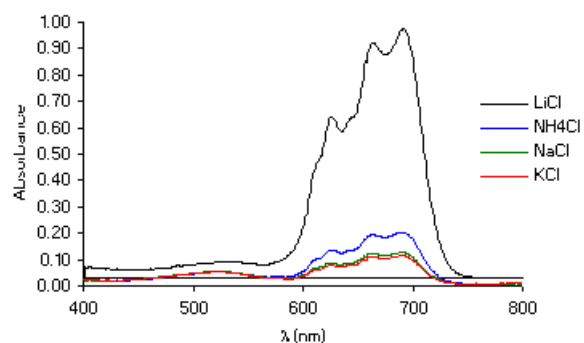


Figure 4. Solutions of Co^{2+} (21 mM) in 6 M HCl with added alkali chlorides.

provide different concentrations of chloride ions. In fact, each salt will be in the form of free ions, solvent separated ion pairs, and intimate ion pairs; therefore, there will be a complex equilibrium between the cobalt complexes and the other salts and ions. In addition, metal ions are solvated to a different extent [15]; thus, small highly charged ions will attract more solvent molecules (will have more hydration shells), and their dehydration effect will be stronger compared to larger ions of the same charge (K^+ , NH_4^+). As the concentrations of chloride ions are the same, the students should come to the conclusion that differences in equilibrium position are due to different degree of ionization of each salt and different solvation (degree of hydration) of metal cations. Instructors may wish to provide Table 2 from reference 14 to the students, or alternatively direct students to the original reference.

In experiment 3 (addition of drying agents to Co^{2+} in 6 M HCl) students study the dehydration effect. Because both addition of a reactant or removal of a product shift the equilibrium in the same direction, it is difficult to distinguish between the two. To examine the significance of the two effects, namely, increase in the concentration of chloride ions



Figure 5. Solutions of Co^{2+} (21 mM) in 6 M HCl with added (from left to right) H_2SO_4 , Na_2SO_4 , CaCl_2 , $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and MgSO_4 .

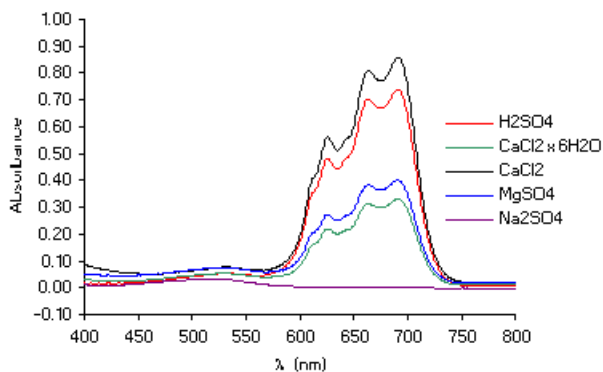


Figure 6. Solutions of Co^{2+} (21 mM) in 6 M HCl with added H_2SO_4 , Na_2SO_4 , CaCl_2 , $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and MgSO_4 .

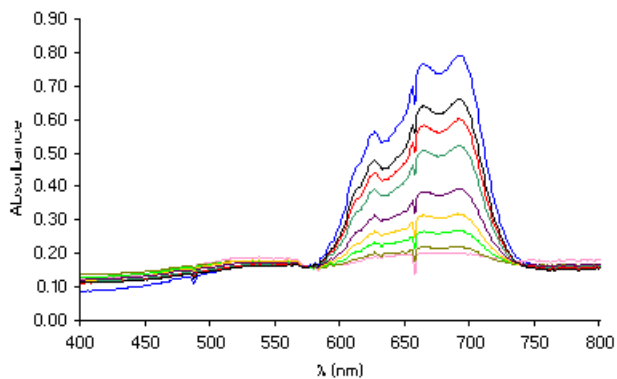


Figure 7. Changes in the spectrum of Co^{2+} (initial concentration 2.1 mM in 6 M HCl) as concentrated sulfuric acid was added to the stock solution 2. The pink line shows the spectrum at the beginning of the addition of concentrated sulfuric acid and the blue line at the end of the addition.

and removal of water by inorganic acids or salts (salting-out effect [16]), students are asked to add sulfuric acid and several salts, commonly used as drying agents, to the stock solutions. These salts were chosen for their high affinity for water. Some of the drying agents contain chloride ion while others do not.

As three of the drying agents do not contain chloride ion, their effect on the equilibrium is through dehydration effects only; therefore, students should use the results of this experiment to estimate the role of dehydration. As the addition of drying agents to water is exothermic and position of the equilibrium is temperature dependent, it is important to keep the temperature constant. In our experiments, the temperature was maintained at 25°C by immersing the test tubes in a water bath. Drying agents have a property called efficiency [17–19], intensity [20–23], or completeness [24]. This property is related to the amount of water left at equilibrium; thus, a reagent with higher intensity has a higher affinity for water and will leave a lesser amount of free water at equilibrium. The experiment described herein can be used to compare the intensity of a series of drying agents (however, one should keep in mind that the intensity of a drying agent also depends on the solvent being dried). A qualitative determination can be made by comparison of the colors of the solutions, while, for a more quantitative comparison, spectroscopic studies should be done. From the results of their study, students should conclude that, because in each case the concentration of chloride ions is the same, dehydrating and ionization effects play an important role in shifting the equilibrium. In the same experiment, students compare the effects of adding CaCl_2 and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Students can assume that $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is fully hydrated (of course that is not entirely true, Ca^{2+} ion will acquire additional layers of hydration in an aqueous solution) and that, upon its addition, the change in the position of the equilibrium is due to the change in concentration of chloride ion. Results of the experiment are shown in Figures 5 and 6. Figure 7 was recorded in the course of a slow addition of concentrated sulfuric acid to stock solution 2.

After considering the results of all three experiments, students should come to the conclusion that the dehydration effect appears to be most important in shifting the equilibrium towards CoCl_4^{2-} . The effect of added chloride ions is secondary, while the effect of differences in the degree of ionization does not appear to play a significant role. That is to be expected, as once chloride ions are complexed with Co^{2+} , those chloride ions are removed from the solution and degree of ionization of salt will increase (again Le Châtelier's principle).

Conclusion

In a general chemistry course, students are usually taught simplified systems and models and are conditioned to expect certainty. An experiment like this may help prepare students for more advanced study in chemistry by introducing them to more complex systems. Students who take general chemistry usually go on to take organic chemistry. Study of organic chemistry may be easier for these students because they have already encountered complex systems where a number of variables have to be considered and simplistic models are not sufficient.

This experiment is suitable as a discovery-based experiment for general chemistry students. It can be modified for chemistry students at different levels. In addition to illustrating Le Châtelier's principle, this experiment can be used to illustrate the salt effect in chemical reactions as well as concepts such as the hydration of ions and principles related to drying agents. An obvious variation is to include reactions that remove chloride ion from the equilibrium. Alternatively,

students can also acquire UV-vis spectra as either concentrated hydrochloric or sulfuric acid is being added, thus monitoring the changes as the addition progresses. Such an experiment can be used to introduce the isosbestic point to more advanced students.

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Supporting Materials. Instructor notes and spectra are available in the one compressed ZIP file (s00897020559b.zip) available at <http://dx.doi.org/10.1007/s00897020559b>.

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13. As a test, students can place a test tube with cobalt(II) solution (stock solution 1) in a beaker filled with water and slowly (and carefully) add concentrated sulfuric acid to it, with stirring. As the temperature in the beaker increases the color of the cobalt solution will change from pink to blue.
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