**Mom’s Saline Solution**

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It's that time of the year when it seems like everyone around you is getting sick with something. You are worried that you too may have caught something because your throat has been slightly sore. You have a couple of big exams coming up and some important assignments that are due soon. You cannot afford to miss any classes or study time so you call your mom to see if she has any suggestions for how you can keep from getting sicker.

Mom suggests that you prepare a saline solution and gargle with it twice a day. This has the added benefit that you can use a few drops of the same solution to help relieve nasal congestion if your nose becomes stuffy. The directions she gives you for preparing the solution are simple; keep adding table salt to hot water while stirring until no more salt will dissolve.

Since you don't want to take time to prepare more solution each day, you decide to prepare enough to fill an empty water bottle you have in your room. At first, you add a small amount of salt at a time which dissolves rapidly so you start adding a larger amount each time. It seems to take a lot of salt but eventually you end up with about a dime size pile of salt crystals in the bottom of the container. The solution is still too hot to safely gargle with so you go do something else while it cools. When you come back, you notice that the amount of solid seems to have increased to about the size of a quarter. This seems strange to you since salt is soluble in water.

You remember from your chemistry class that table salt is sodium chloride which dissociates into Na+ and Cl− when it dissolves in water. In fact, you remember doing an experiment where you determined whether the dissolution reaction was endothermic or exothermoic and you can even write the equation for the reaction:

NaCl(s) Na+(aq) + Cl−(aq)

You wonder once again if there is anything in terms of chemistry that can explain why the salt stops dissolving even though there is way more water than salt present and why more solid is present after the solution cools down.

**Background**

We've spent some time investigating what controls the rate of a reaction and how we can make reactions go faster. Equally important is how far a reaction goes. Sometimes, no matter how fast a reaction goes or how long you wait, there is still some measurable amount of the limiting reagent left. Why? It turns out that chemical reactions go in both forward and reverse directions all at the same time (equation 1).

*a*A + *b*B *c*C + *d*D (1)

When the rate of reaction is the same in both directions, we say that the system is at equilibrium. This doesn't mean that the amount of products and reactants are equal, just that the amounts don't change because the rates of the forward and reverse reactions are the same. In fact, we can characterize the relative amounts of products and reactants as a ratio. This ratio stays constant as long as the temperature remains the same. Since the ratio is constant, we can express it mathematically (equation 2) where *K* is the equilibrium constant for the specific reaction and the exponents are the stoichiometric coefficients of the balanced equation for the reaction.

$K =\frac{\left[C\right]^{c}\left[D\right]^{d}}{\left[A\right]^{a}\left[B\right]^{b}}$ (2)

From this we can see that if *K* is much larger than one, we will have significantly more products than reactants. Conversely, if *K* is much smaller than one, we will have significantly more reactants than products. In both cases, if the reaction is run multiple times using different amounts of reactants, we should still end up with a ratio of products to reactants and therefore an equilibrium constant that is the same each time.

In order to experimentally determine the constant at equilibrium, *K*, there are two things you need to know:

1. the concentration of all reactants and products before the reaction begins.
2. how to measure the final concentration of at least one product or reactant once the reaction comes to equilibrium.

The specific reaction that we are going to try to determine the equilibrium constant for is the reaction of iron (III) ions with thiocyanate ions to form iron (III) thiocyanate complex ions (equation 3). Fe(SCN)2+  forms a strongly colored complex that can be analyzed by visible absorption spectroscopy.

Fe3+(aq)  + SCN−(aq) FeSCN2+(aq) (3)

Some of you may recall that spectroscopy makes use of the fact that chemical species absorb energy from light with specific wavelengths based on transitions between energy levels corresponding to ground and excited states. All the light that is not absorbed is reflected back or transmitted through a solution which produces the color that we see. Inside a spectrophotometer, a grating or prism is used to separate white light into individual wavelengths. A slit is then positioned so that only one wavelength at a time shines through a solution of the molecule or ion of interest. In addition to the wavelength, the intensity of the light shining on the sample is measured. Since the solution is in a clear and colorless cuvette, the light passes through the sample and the intensity of light that comes out the other side is measured by a detector. The instrument then compares the initial intensity to the final intensity and calculates of amount of light absorbed at each wavelength.

Because the amount of light absorbed is related to the excitation of electrons in the dissolved molecules or ions, it is also related to the concentration of these species. This relationship is known as the Beer-Lambert Law which states that the absorbance is directly proportional to the molar absorptivity or molar extinction coefficient (L/(mol cm)), ε, the cell path length (cm), l, and the concentration (mol/L), c (equation 4).

A = ε × l × c (4)

The cell path length is the distance the light must travel through the cell containing the solution. Since this is determined by the size of the cell and the cell is usually a 1 cm square cuvette, this term becomes 1 and can be dropped from the equation.

If we prepare a series of solutions with known concentrations of the solute and measure the absorbance of each, we can create a Beer’s Law plot (Figure 1). When absorbance is on the y axis and concentration is on the x axis, the slope of the equation of the line is then the molar absorptivity (ε). Once a standard curve is created the equation of the line can then be used to determine the concentration of the solute in solutions where the concentration is unknown.

**Procedure**

You will be designing your own procedure to determine the equilibrium constant for the formation of FeSCN2+ according to equation 3. *This will be a two week lab and the bulk of the first week will be spent creating a procedure that will be used by the entire class.* The following materials and equipment will be available to you:

0.200 M Fe(NO3)3 in 0.10 M HNO3

2.00 × 10-3 M Fe(NO3)3 in 0.10 M HNO3

2.00 × 10-3 M KSCN in 0.10 M HNO3

0.10 M HNO3

burets

pipets

small beakers and flasks

4 mL cuvettes

genesys spec 20 spectrophotometers

To help you get started, answer the following questions before coming to lab:

1. What is the equilibrium expression for our reaction?
2. When a large excess of one reagent is used, what happens to the concentration of the other reagent at equilibrium? How might this information be used to drive a reaction to completion?
3. You will need solutions with a known concentration of product to create a standard curve. How can solutions with a known concentration of the product be made?
4. What’s different about reaction solutions for determining the equilibrium constant from those used to create the standard curve?
5. How can you calculate the equilibrium concentrations of the reactants from the concentration of the product?
6. The plot of the absorbance from spectrophotometer versus the concentration of solute is linear when the absorbance is between 0.1 and 1.0. What will you need to do to your solutions if the absorbance is greater than 1.0? What if it is <0.1?
7. What is a “blank” used for in spectrophotometry. How might you create one?
8. List five things that you will need to include in your procedure.
9. Create a table which relates color with the approximate wavelength of light that is absorbed for the following colors: red, orange, yellow, green, blue, indigo and violet. Also indicate the complementary colors for each color.