

1. Under certain conditions silver is extremely toxic to microorganisms and marine invertebrates. In fact, several researchers have hypothesized that elevated concentrations of silver in the sediments of San Francisco Bay were responsible reduced species diversity among aquatic organisms and metal-induced stress observed in benthic-dwelling organisms in the South Bay during the 1908s, when Kodak ran a large silver processing facility near Palo Alto. In response to concerns related to silver, the silver processing plant was closed and several Bay Area communities have implemented aggressive programs designed to minimize silver use and disposal.
  - a. It has been established that  $\text{Ag}^+$  is the form of silver that is toxic to aquatic organisms. Using the data provided below, calculate the percentage of dissolved silver that consists of  $\text{Ag}^+$  in water from the freshwater region of San Francisco Bay (Water A) and water closer to the open ocean (Water B). Show all of your work and specify any assumptions that you have made. Remember to include activity coefficients in your calculations and to include bicarbonate in you estimate of ionic strength. Data on stability constants for silver can be found in Tables 8.2 and 8.3 of your textbook.
  - b. Aside from  $\text{Ag}^+$ , what other species of silver is present in significant quantities in these two waters?
  - c. Discuss differences in the predicted toxicity and behavior of silver in these two waters.

Species	Concentration (mM)	
	Water A	Water B
$\text{Na}^+$	0.25	230
$\text{Ca}^{2+}$	0.20	5.0
$\text{Mg}^{2+}$	0.10	27
$\text{K}^+$	0.03	5.0
$\text{Cl}^-$	0.32	270
$\text{SO}_4^{2-}$	0.20	14
Ag(I)	$5 \times 10^{-11} \text{ M}$	$5 \times 10^{-12} \text{ M}$
pH	8.0	8.0

- d. Use MINEQL+, to predict the speciation of Ag(I) as a function of chloride as chloride varies from 0.32 mM to 270 mM. Use a total Ag(I) of  $5 \times 10^{-11} \text{ M}$  and pH 8.0. Allow the program to correct for the effects of ionic strength. Plot your results.
- e. Regulatory agencies often use empirical simplifications to set regulations to protect aquatic organisms from pollutants for which toxicity varies with water chemistry (e.g., regulations for unionized ammonia in assignment 1). Try writing an empirical formula to set standards for silver as a function of chloride concentrations. You may not come up with a perfect formula, but this exercise should give you an idea of how these kind of calculations could be used in the regulatory process.

(over)

2. A researcher is interested in the photochemistry of Fe(III) complexes with organic ligands. To study these reactions, she must choose solution conditions that meet the following requirements:

- Highest possible concentration of the Me-organic ligand complex;
- Less than 1% of the total Fe(III) present as  $\text{FeOH}^{2+}$  (this is the only photoreactive inorganic Fe(III) species. If it were present it would be difficult to study the photochemistry of the organic complex).

She would like to study the photochemistry of Fe(III)-citrate complexes under the following conditions:

$$[\text{Fe(III)}] = [\text{citrate}]_{\text{tot}} = 1 \mu\text{M}.$$

Ionic strength = 1 mM

- a. Use the solids mover to deactivate the solids that might precipitate. Plot the speciation of dissolved Fe(III) as a function of pH. What is the optimal pH for these experiments? Are her criteria met?
- b. Evaluate the possibility that ferrihydrite (*i.e.*, the most soluble solid phase in your database) will precipitate by turning this solid phase on in the solids mover. Indicate on your plot the pH range (if any) where the solution is oversaturated with respect to Fe(III). (It is only necessary to consider the precipitation of ferrihydrite under these conditions because it is the only precipitate that is likely to form over the short time interval between preparing the solutions and conducting the experiments.)