11. Practice: Studying simultaneous solution equilibria

11.1 Introduction

The basic aim of the study of solution equilibria is to determine the stoichiometry and formation (stability) constants of associates (molecular complexes) in solutions. Knowledge of the equilibrium concentrations of various species in solution is important for many applications. These equilibrium concentrations can be calculated from the total (analytical) concentrations (this is what we know from weigh in a certain molar amount of compound into a certain volume of solvent) and from the formation constants. The aim of the practice is to determine the formation constants of complexes in the Cu(II)-ammonia system in which the equilibrium processes overlap.

11.2 Experimental methods for studying solution equilibria

Recent experimental methods for the determination of equilibrium constants mainly involve pH-metry and spectrophotometry. Both methods requires due care and precise experimental work. In the present practice we will rely on spectrophotometric measurements. The connection between the measured absorbances of colored species and their concentrations is described by Lambert-Beer's law. Within its validity range the absorbance is an additive property, which is the sum of the absorbances (at the studied wavelength) of all of the light-absorbing species that are present simultaneously in the solution.

11.3. Practical methods for constructing solution series for determination of stability constants

- Job's method (continuous variation method)
  In a series of solutions, the sum of total concentrations of the metal ion and the ligand is constant, while the molar fraction of the ligand is varied between 0 and 1. As an example, one makes a 10-membered series of solutions containing Copper sulfate and EDTA (very common organic molecule that acts as ligand to coordinate to copper(II) ions), with a total solute concentration of 10 mM in all of the six solutions. In Job's method, the first solution then contains only 10 mM $CuSO_4$, the second contains 9 mM $CuSO_4$ and 1 mM EDTA, the third 8 mM $CuSO_4$ and 2 mM EDTA, etc...., while the last one only 10 mM EDTA. Note that this is just an example and for very colorful species the actual total concentration may be significantly less than 10 mM, and the useful set of concentration data may not be linear. The absorbances of the solutions are then measured and in simplest cases (when only one or two kinds of complexes are formed) as the absorbances are plotted against the molar fraction of the ligand, maximum functions are obtained. Knowing the molar fraction at the maximum absorbance (x_{max}), the stoichiometry of the complex (associated molecule) is obtained as:

  $mM + nL = M_mL_n$, $n/m = x_{max}/(1-x_{max})$

- Molar ratio method
  The method is similar to Job's method in a sense that a series of solutions with varying ligand-to-metal ratios are investigated. However, in this case, the concentration of one of the components is kept constant and the change of light absorption at increasing concentrations of the other component is monitored. Here, a sharp break point is observed in the absorbance-concentration function, when a stable complex compound is formed.
- Competition method at constant ligand and metal concentration
  This method applies constant concentrations for both the metal ion and the ligand, while adding various amounts of acids or bases. Since the majority of ligands are weak or moderately strong base, the complexation process can be considered as a competition between the metal ion and the hydrogen cation (H^+) for the ligand.

11.4. Spectrophotometric study of the copper(ii)-tetramine system

The students will make a series of solutions in which the total concentration of copper(II) ions is constant (**R**), and the ligand concentration (NH_3) is varied by changing the deprotonation degree of ammonium ions in the solutions.

The teacher informs the students about the following data:

- temperature of the measurements (typically ambient temperature)
- wavelength range (typically 400 to 900 nm)
- the fixed Cu(II) concentration (**R**) within the 6-13 mM range
- the ionic strength (**I**) between 0.6-1.0 M
- the degree of deprotonation of ammonium ions (**P**) between 18 and 42 %.

TASKS FOR WEEK 1:

The stock solutions to be prepared are as follows (in total volumes of 100 mL).

A: 0.5 M HNO_3 stock solution, the exact concentration of which must be determined by titration with a hydrogen carbonate ion containing salt, using methyl red as indicator. WARNING: obey precautions when diluting strong mineral acids!

B: 0.5 M KOH stock solution (1M if P>30%), the exact concentration of which must be determined by titration with the A solution in the presence of methyl red indicator. Here care must be exercised to avoid carbonation of the sample because carbonate ions interfere with the complexation equilibrium between ammonia and Cu(II). Thus, a double mass of KOH pastilles must be weighed into a beaker and roughly half of the amount of solid must be washed off. The remaining solid is then transferred to a volumetric flask and dissolved completely.

C: **R** M $CuSO_4$, 0.05 M HNO_3 and (**I-4R-0.05**) M NH_4NO_3

D: **R** M $CuSO_4$, and (**I-4R**) M NH_4NO_3

E: **R** M $CuSO_4$, (**I-4R**) M NH_4NO_3 and a calculated amount of **B** solution, by the addition of which **P%** of the ammonium ions will be deprotonated

TASKS FOR WEEK 2:

Register the spectra of the following solutions:

- solution **C**

- solution **D**

- solution **E**

- 40 mL of **D** + solution **E** in different amounts:

Sample no.	1	2	3	4	5	6	7	8	9
V_E (mL)	0.5	1.0	1.5	2.0	2.5	3.2	4.0	4.8	5.6

continued…

Sample no.	10	11	12	13	14	15	16	17	18
V_E (mL)	6.5	7.5	8.7	10.0	12.0	14.0	17.0	25.0	that's all!

The measurements are performed by titrating solution **D** with solution **E** from a 25 mL burette, and the spectra of samples with the above compositions are measured. One can proceed with the titration without considerable loss of solution by carefully pouring back the solution in the cell into the titration vessel (Erlenmeyer flask).

EVALUATION

1) The measured spectra are collected in ASCII files (data files), all spectra as a separate file. The file contains the wavelengths in the first and the respective absorbances in the second column.

2) Another file is to be prepared that contains the experimental conditions and the file names.

The structure of the file must be exactly as shown to the right.

- The first six rows contain the name of the students, the time, the initial volume of the titrated solution and the values of **R**, **I** and **P**.
- The 7th row gives the number of wavelengths considered for calculation. Lines 8th- … contain the chosen wavelengths.
- The forthcoming rows contain a file name and corresponding titration volume.
- The last two lines contain the file name of the spectrum of solution **E** (with the necessary 10000.0!) and the file name for **C** solution.

```
1: Pontos János
2: 1997.01.18.
3: 40.0
4: 0.008
5: 0.8
6: 25.0
7: 51
8: 400
9: 410
⋮   ⋮
58: 900
59: p002.csv      0.0
60: p003.csv      0.5
⋮   ⋮
81: p019.csv     25.0
82: p020.csv  10000.0
83: p001.csv
```

3

3) The above files give the basis for the computational evaluation of experimental data. The "ATFED.EXE" software is used to formulate data acceptable for the widely used software for evaluation of solution equilibrium data (PSEQUAD) and to obtain the complex formation constants. The evaluation is performed with the help of the teacher.

4) Using the stepwise formation constants and molar absorbance data obtained from PSEQUAD, two figures must be submitted. First gives the molar absorbance spectra of various Cu(II) species, and the second gives the distribution diagrams of the copper(II)-amine complexes. These diagrams show the relative abundance (α) of a certain complex species as the function of the ligand concentration. Since the latter covers a wide range, the logarithmic plot is favored ($-\lg[NH_3]$).

To make an informative distribution diagram, tabulate 50-100 different values for $[NH_3]$ in the 10^{-7} to 1 M range. You can freely choose the values but they should be more or less uniformly separated. The values of α are given as:

$$\alpha_i = \frac{[Cu(NH_3)_i]^{2+}}{T_{Cu^{2+}}} = \frac{\beta_i[Cu^{2+}][NH_3]^i}{[Cu^{2+}] + \sum\limits_{j=1}^{n}\beta_j[Cu^{2+}][NH_3]^j} = \frac{\beta_i[NH_3]^i}{1 + \sum\limits_{j=1}^{n}\beta_j[NH_3]^j}$$

, where β_j is the stability constant of the j-th complex.

Short test questions (some may not be explicitly found in the description – then consult textbooks or undisputed Wikipedia content)

WEEK 1

1) What is the definition of stability constants and the cumulative stability constant? Write the three corresponding expressions for the following system:

$$M + 2L \rightleftharpoons ML_2$$
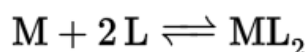
2) What is the definition of ionic strength?

3) What is the ionic product of water?

4) Note down the possible complex formation equilibrium equations for the formation of Copper(II) amine complexes from Cu(II) ions and NH_3 ligands! Consider the maximum coordination number to be 4.

5) What is the ionic strength in a 1M NH_4NO_3 solution that contains 100 mM $CuSO_4$?

WEEK 2

1) What is the Beer-Lambert law? Define the symbols used in the formula!

2) Describe Job's method in 2-3 sentences!

3) Describe the molar ratio method in 2-3 sentences!

4) Describe Job's method in 2-3 sentences!

5) Describe the competition method!

6) What is the distribution diagram?