2.02 DETERMINATION OF THE FORMULA OF A COMPLEX BY SPECTROPHOTOMETRY (4 points)

Outline

Spectrometry is widely used to monitor the progress of reactions and the position of equilibrium. Spectrophotometric measurements are often straightforward to make, and the technique is sensitive and precise, provided that relevant limitations (such as the regions over which Beer's law is valid) are recognised. Spectroscopic techniques are useful for determining the formulae of inorganic complexes, for which a number of different approaches may be used. In this experiment we study the complex formed by salicylic acid and ferric ions, using Job's method, and also determine the stability constant using two independent methods.

Background Information

Relevant lecture course: Introduction to thermodynamics (1st year), valence and electronic spectroscopy (2nd year). The URL for this experiment is http://ptcl.chem.ox.ac.uk/~hmc/tlab/experiments/202.html

Safety / COSHH

Wear safety glasses when handling acids. Do not pipette by mouth. You can access more detailed safety information about the chemicals you will be using through the web site for the experiment.

Theory

Job's method of continuous variation [1] is a simple method for finding the formula of a complex [2, 3]. It is most effective when only a single complex is formed.

The success of a Job's method experiment depends upon the extent to which Beer's law is followed. Beer's law is one of the most widely-applied relationships in chemistry, and is usually cast in terms of the absorbance A of a solution, defined by

$$A = \log_{10} I_o/I \qquad (1)$$

in which I_o is the intensity of light incident upon a sample and I the intensity of the transmitted light. The absorbance is related to concentration of the solution, c, through Beer's law, which is

$$A = \varepsilon c l \qquad (2)$$

In this equation ε is the molar extinction coefficient for a species and l is the optical path length.

ⓘ Comment: Equation (2) shows that concentration and absorbance are linearly-related. However, this relationship holds only over a limited range of concentration, being most accurate for dilute solutions, and factors such as the quality of the spectrometer used for measurement, the value of the extinction coefficient and the concentration of the absorbing species may cause experimental Beer's law plots to depart from linearity.

Job's method can be used to find the formula of the compound formed by two reacting species. The spectra of solutions of the two species are recorded over a range of concentrations, each solution containing the same *total* reagent concentration. In this experiment the reagents are Fe^{3+} and salicylic acid, so

$$[\text{ salicylic acid }] + [\ Fe^{3+}\ ] = \text{constant}$$

A wavelength at which the complex absorbs strongly is selected and the absorbance of each solution at this wavelength is determined.

As the concentration of one of the reactants, say the Fe^{3+}, increases from zero, so does the amount of complex, so that the absorbance rises. Absorbance reaches a maximum in the solution in which metal ion and ligand are in the same proportions as in the complex, since this solution will contain the highest concentration of complex. Further additions of metal ion give solutions that contain insufficient salicylic acid to complex with all the metal, so absorbance due to the complex then falls.

A plot of absorbance as a function of the amount of added ligand should give two straight lines, provided Beer's law is obeyed. Extrapolation of the two lines (in the direction away from zero concentration of each species) gives the formula of the

complex directly, since, where the two lines cross, ligand and metal are in the correct proportion to give maximum complex formation.

This method can, under favourable circumstances, be used to determine the stability constant for a complex, since the deviation of the experimentally-determined curve from the extrapolated lines arises from dissociation of the complex. However, a similar deviation can be caused by departures from Beer's law, so the method is only reliable for moderately-absorbing solutions in which Beer's law applies well.

Procedure

Prepare the following solutions, which are used throughout the experiment:

A solution of 0.0025M Fe^{3+} made by dissolving the appropriate amount of ferric ammonium sulfate in 500 cm^3 of 0.0025M sulfuric acid.

ⓘ Dissolution is quite slow, and can be encouraged by warming a conical flask under a gentle stream of hot water (but DO NOT heat a volumetric flask in this way - you may snap the neck off by swirling the contents too enthusiastically). Be sure to use the Fe(III) salt, not the Fe(II) salt, which is also available in the laboratory!

A solution of 0.0025M salicylic acid made by dissolving the appropriate amount of salicylic acid in 500 cm^3 0.0025M sulfuric acid.

This experiment can be performed using any of the UV/visible spectrometers in the laboratory. However, the UV2s are heavily used by 1st year students during Michaelmas and Hilary terms, and these students have priority over the machines. You are strongly advised to keep all your solutions until you have a complete set of spectra!

1. Obtain the spectra of separate solutions of Fe^{3+} and salicylic acid between 400 nm and 650 nm. Since your measurements are in the visible region, plastic cells can be used. Also record a reference spectrum of 0.0025M sulfuric acid.

? Question: What do you expect this reference spectrum will look like in the region between 400 nm and 650 nm?

2. Obtain the spectra of 1:9, 2:8, 3:7 .... 9:1 mixtures of Fe^{3+} and salicylic acid, recorded over the same range as before. If you are using the lambda 5 spectrometer overlay the spectra.

ⓘ Overlaid spectra should reveal the presence of an isosbestic point, which is a particular wavelength at which the extinction coefficients of the complex and ferric ion are equal. Since the spectra of all solutions containing excess ferric ion should pass through this point precise convergence of spectra at the isosbestic point is evidence that your experimental technique is good - and *vice versa*!

3. Record the wavelength of the maximum of the new band due to the complex.

4. Record the spectra of five solutions prepared by successive dilution from a starting 5:5 mixture of the two reagents. After recording the first spectrum, dilute the sample by a factor of two using 0.0025M sulfuric acid and record the spectrum of the diluted sample. Repeat, to give spectra of solutions which are nominally M/800, M/1600, M/3200, M/6400, M/12800 and M/25600 in complex.

   At the end of the experiment flush the solutions down a sink with plenty of water; wash the cell with demineralised water and return to the technician.

Calculations

At the wavelength of maximum absorption by the complex determine the total absorption for each sample.

Plot absorption vs composition of solution.

From your plot, which should show two almost linear portions, determine the stoichiometry of the complex. Determine also its molar absorbtivity at the absorption maximum from equation 2.

$$K = \frac{[\text{ complex }]}{[Fe^{3+}]^a\,[\text{Sal }]^b} \qquad (3)$$

The stability constant K can be calculated from the measured concentrations and absorbance A, provided that we know the extinction coefficient and formula of the complex (the formula, of course, determines the coefficients a and b in equation 3. The following discussion assumes that a = b = 1, but, if necessary, you should adjust your calculations if you find a and b are different).

There are a number of ways in which the extinction coefficient may be found; use your data to compare the following two methods:

a) Draw tangents to the lower part of the limbs of the Job plot; these cross at the apex, H.

Draw a smooth curve through all the data points; let the height of this curve at the composition corresponding to maximum absorption be M. The height of the apex H at this composition gives the absorbance of a solution with 100 percent complex formation, while the height of the Job maximum M is the absorbance of the solution containing the actual amount of equilibrated complex. Thus

$$M = \varepsilon l\,[\text{ complex }]$$
$$H - M = \varepsilon l\,[\text{ Fe}^{3+}\,]_{free} = \varepsilon l\,[\text{ salicylic acid }]_{free}$$

The total iron concentration, [complex] + $[Fe^{3+}]_{free}$ is known (equal to 0.00125M in a 5:5 sample). Hence

$$M + [H - M] = H = \varepsilon l\ [\text{total iron}]$$
$$\varepsilon l = H / [\text{total iron}] \qquad (4)$$

From equation 4 calculate ε, given that l, the length of the cell, is 1cm, and hence find K.

$$K = \frac{[complex]}{[Fe^{3+}]_{free}[Sal]_{free}} = \frac{M / \varepsilon l}{[(H - M) / \varepsilon l]^2} = \frac{MH}{[H - M]^2} \times \frac{1}{total\_iron}$$

b) Alternatively, you can use data from the third part of the experiment.

$$[Fe^{3+}]_{free} = [\text{salicylic acid}]_{free} = \text{total iron} - [\text{complex}]$$

Substitution in (2) and (3) gives

$$\frac{A / \varepsilon l}{([Fe]_{total} - A / \varepsilon l)^2} = K \quad \text{or} \quad \frac{[Fe]_{total}}{\sqrt{A}} = \frac{1}{\sqrt{(\varepsilon l \,.\, K)}} + \frac{\sqrt{A}}{\varepsilon l}$$

Prepare a suitable plot from which to find ε; include error bars.

Calculate K at each dilution and determine an average value.

Comment fully on your results, indicating the probable error in your values for ε and K.

References

1. Job, *Ann. Chim.* **10**, 9:113 (1928)
2. M.M.Krunz and L.B.Pfendt, *Microchem. J.* **28**, 162, (1983)
3. H.M.Cartwright, *Microchem. J.* **34**, 313, (1986)