METHODS FOR DETERMINING THE COMPOSITION OF COMPLEXES IN SOLUTION

Schedule

This experiment takes two lab periods, one for the method of continuous variations and the other for the mole ratio and slope ratio experiments. Since the iron readily oxidizes, *no Fe^{2+} solution can be made up before the scheduled lab-period.*

Basis of the Experiment

Three general approaches to studying the composition of complexes using visible absorption spectrometry are described and compared.[1,2] Basic differences in the methods demonstrate that one must carefully evaluate the properties of a particular chemical system in order to select the best method for determining the composition of a complex.

Theory

Method of Continuous Variations. The method of continuous variations is both simple and widely used for the Spectrophotometric determination of formulas of metal complexes. The method is not limited to spectrophotometry, but is probably most frequently used with this measurement technique. The method assumes only a single complex is present in the solution, a situation which is often not the case. Consider a reaction:

$$aM^{n+} + bL \rightarrow M_a L_b^{n+} \qquad (1)$$

If we vary the concentration of M^{n+} and L, but keep the total combined analytical concentration constant, we can write:

$$C_M{}^{n+} + C_L = C$$

Assuming the initial stock solutions of metal and ligand have the same concentration, the following derivation applies.

The concentration of metal ion equals a fraction of the total concentration minus the amount which reacts to form the complex. If f is the fraction of the total volume of the ligand solution used, 1-f is the fraction of the total volume of the metal-ion solution and:

$$[M^{n+}] = C(1 - f) - a[M_aL_b{}^{n+}] \qquad (2)$$

$$[L] = C(f) - b[M_aL_b{}^{n+}] \qquad (3)$$

$$[M_aL_b{}^{n+}] = K[M^{n+}]^a\,[L]^b \qquad (4)$$

Obviously the concentration of the complex will change as f is varied: it will be zero when f is either zero or unity, and will have a maximum value at some intermediate point. If the absorbance is measured at a wavelength where the complex absorbs but M and L do not, the value of f at the point of maximum absorbance will naturally also be the value of f which corresponds to the maximum concentration of M_aL_b. This, in turn, will be the value of f at the, point where $[dM_aL_b{}^{n+}]/df$ is zero. Differentiating Eq. (4) with respect to f gives

$$\frac{d[M_aL_b{}^{n+}]}{df} = K\frac{d[M^{n+}]}{df}[L]^b\,a[M^{n+}]^{a-1} + \frac{d[L]}{df}[M^{n+}]^a\,b[L]^{b-1} \qquad (5)$$

The condition for maximum complex formation is $d[M_aL_b{}^{n+}]/df = 0$, so,

$$K\frac{d[M^{n+}]}{df}[L]^b\,a[M^{n+}]^{a-1} + \frac{d[L]}{df}[M^{n+}]^a\,b[L]^{b-1} = 0 \qquad (6)$$

From Eqs.(2) and (3) we find that when $d[M_aL_b{}^{n+}]/df=0$, $d[M^{n+}]/df = -C$ and $d[L]/df = C$ Substituting into Eq. (6) we obtain:

$$-C[L]^b a[M^{n+}]^{a-1} + C[M^{n+}]^a b[L]^{b-1} = 0 \qquad (7)$$

or

$$a[L] = b[M^{n+}] \qquad (8)$$

Substituting Eqs. (2) and (3) into Eq. (8) gives

$$a[Cf - b[M_aL_b^{n+}]] = b[C(1 - f) - a[M_aL_b^{n+}]] \qquad (9)$$

or finally

$$\frac{b}{a} = \frac{f}{1-f} \qquad (10)$$

Experimental determination of the value of f for which $[M_aL_b^{n+}]$ is maximum allows us to establish the ratio b/a. When the complex is the only absorbing species, the solution absorbance can be used to indicate the point of maximum absorbance. Accordingly, we plot the absorbances of our solutions against f, the mole fraction of the ligand in the mixture. For a 1:1 complex MX, the absorbance will pass through a maximum at f = 0.5; if the complex has the formula MX_2 the maximum will occur at f = 0.67; if its formula is M_2X, the maximum will be found at f = 0.33; and so on.

When a single, very stable complex is formed, a plot like that shown in Curve A of Figure 1 is obtained.

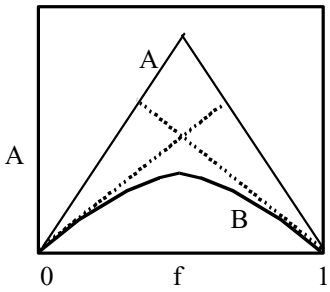

Figure 1. Typical data for a method of continuous variations experiment.

For complexes of lesser stability, the maximum may be broadened appreciably, like that of Curve B in Figure 1. The value of f at maximum concentration of complex (f_{Max}) can be obtained by measuring any one of a number of physical properties that can be directly related to concentration. For a moderately dissociated complex there will be considerable curvature resulting from the incompleteness of the reaction around the stoichiometric point. Provided that the complex is neither too weak nor too strong, this curvature can be used to estimate its dissociation constant by a procedure very similar to that employed in dealing with molar ratio data.

Some trouble, however, may be encountered in dealing with an extremely weak complex, for then the curve will be quite flat in the vicinity of the maximum. Of course, one may draw one straight line through the Points at low values of f, where the dissociation is largely repressed by the excess metal ion present, and another through the points at high values of f, where the dissociation is again largely repressed by the excess ligand. The point of intersection of these two lines then gives the stoichiometric value of f. Even with this technique, one might expect difficulty in distinguishing between a 1:3 and a 1:4 complex, whose maxima would occur at f = 0.75 and f = 0.80 respectively, but fortunately, this problem is very rare. The continuous variations method is one of the best available for the study of even very weak complexes.

It is necessary that only a single complex be formed if accurate results are to be obtained. The data will offer no direct proof that a single complex is being formed, but if other absorbing complexes are being formed, measurements taken at different wavelengths will usually produce different values for f_{max}, thereby indicating the probability of more than one complex being present.

As can be seen from the derivation, the data are most easily handled when equal concentrations of the reagents are mixed in various proportions, but giving a constant total volume.

Mole-Ratio Method. Perhaps the simplest of the spectrophotometric techniques that have been used for the study of complex-formation equilibria is the molar ratio method. A series of solutions are prepared which contain equal formal concentrations of a metal ion but different formal concentrations of the complexing agent. The ratio of these concentrations should usually vary from about 0.1 to 10 or 20. The absorbance of each solution is then measured. If only the complex absorbs at the wavelength where measurements are taken then these absorbances are proportional to the equilibrium concentrations of the complex ion in the solutions, and a plot of the absorbance against the ratio of the number of moles of ligand to the number of moles of metal ion (which is the same as the ratio of the corresponding total or formal concentrations) will resemble Figure 2.

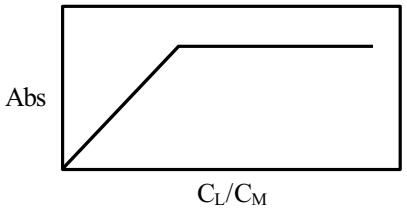

Figure 2. Typical data for a mole-ratio experiment.

The method is analogous to a spectrophotometric titration if one plots the absorbance, corrected for dilution, against the ratio of the number of moles of the ligand to metal ion. Note that, as in a spectrophotometric titration, this method yields results if the ligand or metal ion absorbs at the wavelength used for measurements but the shape of the curve is different from that shown in Figure 2.

The extent of the curvature in the vicinity of the end point depends on the degree of dissociation of the complex. However, the stoichiometric formula of the complex can be found by extrapolating the straight-line portions of the graph, which is to say that the point at which these lines intersect corresponds directly to the ratio of ligand to metal ion in the complex. This procedure works very well for weakly dissociated (i.e. mostly associated) complexes. But if the dissociation constant of the complex is too large, the molar ratio plot will become a smooth continuous curve and it will be impossible to locate the stoichiometric point. In such cases, better results can often be secured by the slope-ratio or continuous-variations methods. Within a certain rather restricted range, however, the curvature around the "end point" of a molar ratio plot can be turned to good advantage and used for the calculation of the dissociation constant of the complex. Another advantage of the mole ratio method over the method of continuous variations is its increased accuracy in differentiating ML_5 vs. ML_6 type complexes.

Slope-Ratio Method. This method is especially valuable since it can be applied to systems in which the complexes have large dissociation constants and are, therefore, not readily suited to the continuous variations or mole-ratio method. The method is based upon absorbance measurements of solutions in which dissociation of the complex is repressed by a large excess of one of the reactants; no long uncertain extrapolations are involved. The slope-ratio method, however, can be applied in relatively few cases. To be applicable, the system under investigation must not give rise to more than one complex, the complex must exhibit characteristic absorption, different from its progenitors, and Beer's law should be followed. If the complex formed in the reaction is of the form:

$$aM^{n+} + bL \leftrightarrow M_aL_b^{n+} \qquad (1)$$

and if the concentration of L is essentially constant and in sufficient excess to make dissociation negligible, the equilibrium concentration of the complex $M_aL_b^{n+}$ will be essentially proportional to the analytical concentration of M^{n+} added; so:

$$M_aL_b^{n+} = \frac{1}{a}C_{M^{n+}} \qquad (11)$$

At a wavelength where only the complex absorbs and Beer's law is obeyed,

$$A = \frac{\varepsilon b}{a}C_{M^{n+}} \qquad (12)$$

where b is the cell path length. By varying the amount of M^{n+} added over a limited range such that the change in concentration of the large excess of L is negligible, a plot of A vs. $C_M{}^{n+}$ can be prepared and will have a slope of εb/a. If the experiment is repeated using a large "constant" excess of M^{n+} , the plot of A vs. C has a slope of εb/b. The ratio of a to b may be found by taking the ratio of the two slopes. Further details are given in the original paper of Harvey and Manning (Ref. 5).

Apparatus

UV / Vis Spectrometer
Disposable Cuvetts
Volumetric flasks: 25 ml (12)
Pipets: 10 ml, 5 ml, 4 ml, 3 ml, 2 ml. 1 ml, 5 ml graduated
Graduated Cylinders: 10 ml

Reagents and Solutions

1,10-phenanthroline, 7.0×10^{-4} M and 2.1×10^{-3} M
Acetic acid-sodium acetate buffer, pH 4.0, total acetate 0.01 M
Hydroxylamine hydrochloride, 5% (wt/vol)
Ferrous ammonium sulfate hexahydrate

Waste: Inorganic

Procedure

If any of the stock solutions are colored see your lab instructor. You will need to prepare a fresh stock solution of ferrous ammonium sulfate each week for this experiment (0.0274 g/100 mL = 7.0×10^{-4} M). You might wish to add about 1.00 mL of the hydroxylamine hydrochloride solution to your flask to stop the oxidation.

WEEK 1 - METHOD OF CONTINUOUS VARIATIONS.

Transfer 0, 1.00, 2.00, 3.00, 4.00, 5.00, 6.00, 7.00, 8.00, 9.00, and 10.00 ml of the freshly prepared Fe(II) solution to separate 25 ml volumetric flasks. Add 5 ml of the acetate buffer followed by 1 ml of the Hydroxylamine hydrochloride solution. To each flask, respectively, add 10.00, 9.00, 8.00, 7.00, 6.00, 5.00, 4.00, 3.00, 2.00, 1.00, and 0 ml of the 7×10^{-4} M 1,10-phenanthroline solution. Dilute to the mark with distilled water and mix. After ten minutes, measure the absorbances of each solution vs. distilled water at each of the following wavelengths: 450, 490, and 510 nm.

WEEK 2 - MOLE-RATIO AND SLOPE-RATIO METHODS.

Since these methods are sensitive to the oxidation of Fe(II) to Fe(III), remember to make up your own 7.0×10^{-4} M ferrous ammonium sulfate solution again in distilled water (0.0274 g in 100 mL).

Slope-ratio method. Transfer exactly 5.000 ml of the 7×10^{-4} M Fe(II) solution to six separate 25 ml volumetric flasks. Add 5 ml of the acetate buffer followed by 1 ml of the hydroxylamine hydrochloride solution. Add 0, 1.00, 2.00, 3.00, 4.00, and 5.00 ml of the 7×10^{-4} M 1,10-phenanthroline solution to the flasks, dilute to volume with distilled water, and mix. After ten minutes, measure the absorbance of each solution at 508 nm vs. a distilled water reference. Repeat the operation, except use 10.000 ml of 2.1×10^{-3} M 1,10-phenanthroline reagent and 0, 0.500, 1.00, 1.50, 2.00, and 2.50 ml of the 7.0×10^{-4} M iron (II) solution.

Mole-ratio method. Transfer exactly 2.000 ml of the 7.0×10^{-4} M Fe(II) solution to ten separate 25 ml volumetric flasks. Add 5 ml of the acetate buffer followed by 1 ml of the hydroxylamine hydrochloride solution. Add 0, 2.00, 3.00, 4.00, 5.00, 6.00, 8.00, 10.00, 12.00, and 14.00 ml of 7×10^{-4}M 1,10-phenanthroline solution to the various flasks. Dilute to the mark with distilled water and mix. After 10 minutes, measure the absorbance of each solution at 508 nm vs. a distilled water reference.

Report

Tables. Describe any solutions you prepared in a table format in your "Experiment and Instrument" section. Record the data you obtained by each of the three methods in tables, which are to be numbered consecutively with a title at the top of the table.

Figures. Prepare figures for each of the three methods and perform the indicated calculations.

1. For the method of continuous variations, plot absorbance vs. mole fraction of 1,10-phenanthroline at each of the three wavelengths that you used. Extrapolate the linear portions of the curve and locate the intersection. From the intersection, mathematically demonstrate how you determined the ratio of iron (II) and 1,10-phenanthroline.

2. For the mole-ratio method, plot absorbance vs. moles of reagent/mole of iron. Extrapolate the linear portions of the graph and mathematically locate the intersection. Determine the formula of the complex.

3. For the slope-ratio method, plot absorbance vs. concentration of iron (II) and 1,10-phenanthroline.
   a. Calculate the slopes for each plot and take their ratio. What is the significance of this ratio?
   b. Evaluate the molar absorptivity for the complex.

4. Postulate the formula of the complex. Explain your reasoning.

Questions for your Write-Up (Discussion)

1. Explain how, for the method of continuous variations, measurement at several different wavelengths might give different values for f_{max} if more than one absorbing complex was being formed.

2. Suppose in the method of continuous variations that the metal absorbs slightly at the measurement wavelength. Is it necessary to correct for this background absorption? How would this best be accomplished? Would it also be necessary in the mole-ratio method?

3. Which of the several methods is useful for studying the composition of weak complexes and why?

4. Which, if any, of the methods is useful if more than one complex is formed and why?

5. You should include the structure of the ligand in your discussion. Is your proposed formula reasonable for a complex of iron(II)

References

***PLEASE**, do not remove references from the library.

1. Meites and Thomas, "Advanced Analytical Chemistry", McGraw Hill, New York, 1958, Chap. 8, 293-8. (QD75 .M4) - All Methods.
2. "Treatise on Analytical Chemistry", Wiley and Sons, New York, 1964 Part I, Volume 5, Chapter 54, 2980-2. (QD75 .K6) - All Methods.
3. W.C. Vosburgh and R.K. Gould, J. Am. Chem. Soc., **64:**1630 (1942) - Continuous Variation.
4. A.S. Meyer and G.H. Ayres, J. Am. Chem. Soc., **79**:49 (1957) - Mole Ratio.
5. A.E. Harvey and D.L. Manning, J. Am. Chem. Soc., **72**:4488 (1950) - Slope Ratio.
6. D. Skoog and J. Leary, "Principles of Instrument Analysis", Harcourt, Brace, and Jovanovich, 1992, pages 123-173.

HP Diode Array Spectrometer

The HP 8453 diode array spectrometer operates on a Windows 95 platform. Many of the commands are intuitive, but here are a few pointers to get you going on the spectrometer.

1. Turn on the instrument (lower left) and computer if necessary.
2. Log onto computer (if necessary) and start the spectrometer program by clicking on "UV-Vis Instrument". Click cancel on the UV-Vis Chem Station password screen.
3. Click on Instrument in the menu and set the following:
   Lamps – set both to on.
   Set up Sampling System – 1 cm path length
   Select Sampling System – Manual
   Set up Sectrometer – Enter wavelength range (400-700 nm), Integration time =0.5 s, interval = 1 nm.
4. Click Method, Set up analysis and do the following.
   Enter wavelength values to report absorbance at.
   Select data type – Absorbance
   Display Spectrum from 400 to 700 nm.
5. Place the blank in the spectrometer and record its spectrum by clicking on Measure, Blank.
6. Place a sample in the spectrometer and record its spectrum by clicking on Measure, Sample. Repeat this step for each sample which uses the previous blank.
7. You may have the spectrometer print out the absorption of spectral peaks by clicking on Tasks Spectrum Peaks
8. To turn off the spectrometer, click on Instrument, Lamps and turn off. Close the program by double clicking on the X in the upper right hand corner.