A frequent task in chemistry is to determine the formula of the product formed by the reaction of two reactants. In cases where the product is stable and isolable the task may be straightforward, e.g., through elemental analysis. However, there are cases in which the product is stable only in solution and cannot be isolated. Such may be the case in the formation of complex ions from transition metal ions and ligand species. In these reactions, the transition metal ion acts as a Lewis acid and accepts electron pairs from one or more Lewis base species which are called ligands. An example follows (equation 1):

\[
\text{Cr}^{3+} \text{(aq)} + 6 \text{NH}_3 \text{(aq)} \rightarrow [\text{Cr(NH}_3)_6]^3+ \text{(aq)}
\]

You may recall that the metal-ligand bonds formed in this way are called coordinate covalent bonds. Note that many stoichiometric possibilities exist for this seemingly simple reaction, keeping in mind that water, the solvent, is also a good ligand. Thus, one might envision products such as \([\text{Cr(NH}_3)_2(\text{H}_2\text{O})_5]^{3+}\), \([\text{Cr(NH}_3)_2(\text{H}_2\text{O})_4]^{3+}\), \([\text{Cr(NH}_3)_3(\text{H}_2\text{O})_3]^{3+}\), etc.

The system under investigation is that of \(\text{Ni}^{2+}\) with ethylenediamine (en), \(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2\). Note that this ligand contains two Lewis base sites (the two nitrogen atoms). The backbone of the molecule is flexible enough and of a proper size that both N atoms can conceivably bond to the same metal ion. Such a ligand is called a \textit{bidentate} (literally, two-toothed) ligand, and the resulting complex is called a \textit{chelate complex} (from the Greek word for claw). Section 8.5 of Shriver and Atkins describes these ligands and shows the mode of bonding. The general description of the reaction is as follows:

\[
\text{Ni}^{2+} \text{(aq)} + n \text{en(aq)} \rightarrow [\text{Ni(en)}_n]^{2+} \text{(aq)}
\]

with the goal being the determination of the values of \(n\) for complexes that actually exist in solution.

The method to be used is known as Job’s method, or the Method of Continuous Variation. Consider a general reaction as follows:

\[
a \text{A} + b \text{B} \rightarrow d \text{D}
\]

If we divide all of the stoichiometric coefficients by \(a\), we obtain

\[
\text{A} + k \text{B} \rightarrow m \text{D}
\]

where \(k = b/a\) and \(m = d/a\). Here, our goal is to determine \(k\), the mole ratio of B to A. In Job’s method a series of solutions is prepared in which the mole fraction of B is varied from 0 to 1 (hence, \textit{continuous} variation) but the total of the number of moles of A plus the number of moles of B is held constant. It can be \textit{shown} that the maximum amount of product is formed when the ratio of moles of B to moles of A is exactly \(k\). Then, a plot of amount of product \textit{versus} mole fraction of B will exhibit a maximum when the mole fraction corresponds to \(k\). The following table gives an illustration of this.

<table>
<thead>
<tr>
<th>Moles A</th>
<th>Moles B</th>
<th>Mole fraction B</th>
<th>Moles D</th>
<th>Moles A</th>
<th>Moles B</th>
<th>Mole Fraction B</th>
<th>Moles D</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1</td>
<td>0.1</td>
<td>1</td>
<td>4</td>
<td>6</td>
<td>0.6</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>0.2</td>
<td>2</td>
<td>3</td>
<td>7</td>
<td>0.7</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.3</td>
<td>3</td>
<td>2</td>
<td>8</td>
<td>0.8</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.4</td>
<td>4</td>
<td>1</td>
<td>9</td>
<td>0.9</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.5</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Now, if the number of moles of D is plotted against the mole fraction of B, two straight lines are observed. The lines intersect at the maximum amount of product formed, 5 moles of D. The corresponding mole fraction of B is 0.5. Thus the correct mole ratio is 0.5 mol B:0.5 mol A or 1:1.

Now the problem at hand is to find a method of measuring the amount of each product (remember that there may be several values of \( n \)). You will recall the Beer-Lambert Law, which deals with the amount of light absorbed by a species. If a beam of monochromatic light of initial intensity \( I_0 \) is directed upon a sample that absorbs some of the light, the emerging light has a lower intensity \( I \). The transmittance, \( T \), of the sample is then defined by \( T = I/I_0 \). The absorbance, \( A \), of the sample is defined as \( \log T \) or \( \log (I_0/I) \). Beer discovered that absorbance is directly proportional to the molar concentration of the absorbing species:

\[
A = \epsilon b c
\]  

(5)

where \( \epsilon \) is the molar absorptivity of the species (a constant), \( b \) is the path length of light through the sample, and \( c \) is the molarity of the absorbing species. Thus, the measured absorbance of a species can be used as a measure of its concentration. **Note:** Absorbance is the property being measured and it has a specific definition; do not refer to it as absorption or absorbency, which are not the same thing.

While there are several \([\text{Ni(en)}_n]^{2+}\) species formed, each has a different color and, hence absorbs a different wavelength. By constructing separate Job’s method plots for the absorbance data at each different wavelength, the different complex ions can be identified.

One last complication is the fact that \( \text{Ni}^{2+}(\text{aq}) \) also absorbs visible light (en is colorless and does not). Thus, the measured absorbances must be corrected for this fact. The corrected absorbance \( Y \) due only to the complex ion is calculated from the following expression:

\[
Y = A_{\text{meas}} - (1 - X) A_{\text{ni}}
\]  

(6)

where \( A_{\text{meas}} \) is the measured absorbance of a given solution, \( X \) is the mole fraction of en in the solution, and \( A_{\text{ni}} \) is the measured absorbance of the pure \( \text{Ni}^{2+}(\text{aq}) \) solution at the same wavelength.

**Prelab Assignment**

Look up or calculate the molar mass of \( \text{NiSO}_4\cdot6\text{H}_2\text{O} \). Look up the density and molar mass of ethylenediamine (you may have to use the IUPAC systematic name of the compound). Calculate the amounts of solid nickel sulfate hexahydrate and liquid ethylenediamine (volume) necessary to prepare 100 mL of a 0.400 \( M \) solution of each.

**EXPERIMENTAL**

Carefully prepare separate 0.400 \( M \) solutions of nickel(II) sulfate hexahydrate and ethylenediamine in 100-mL volumetric flasks. Transfer these solutions to clean, dry burettes. Make up solutions of 10-mL total volume in clean, dry, labeled test tubes with the following mole fractions of ethylenediamine: 0.20, 0.30, 0.40, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, and 0.90. Note the colors of the solutions.

Measure the absorbances of these eleven solutions and also of the 0.400 \( M \) nickel sulfate solution at the following wavelengths: 530, 545, 578, 622, and 640 nm. Place the solutions in 1-cm ABS plastic cuvettes and use deionized water as the reference solution in the rear beam of the spectrophotometer. Remember to zero the instrument properly before collecting data.
CALCULATIONS

Calculate Y values at each wavelength for each of the solutions, then make plots of Y vs X for each of the five wavelengths. On each graph, determine the position of the maximum and calculate the value of n for the complex (calculate the experimental value using significant figures properly, then round to the nearest whole number).

REPORT

Write a journal-style (formal) report. Include your spectra or spectral data, graphs, and copies of lab notebook pages. In your discussion, give the formulas of all complexes that you identified. Draw the structures of each of the complexes; the Ni$^{2+}$ ion prefers to have a coordination number of six. Discuss the colors of the solutions and how the wavelength absorbed relates to the color of the solution.

Post-lab Question

A reaction occurs between Co(ClO$_4$)$_3$ and LiNO$_3$ in t-butanol to form a complex of the type [Co(NO$_3$)$_n$]$^{(2-n)+}$. The following absorbance data at a specific wavelength were collected on solutions made up in the given concentrations of Co(ClO$_4$)$_3$ and LiNO$_3$:

<table>
<thead>
<tr>
<th>Co(ClO$_4$)$_3$, M</th>
<th>0.100</th>
<th>0.080</th>
<th>0.060</th>
<th>0.050</th>
<th>0.040</th>
<th>0.030</th>
<th>0.020</th>
<th>0.000</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$, M</td>
<td>0.000</td>
<td>0.020</td>
<td>0.040</td>
<td>0.050</td>
<td>0.060</td>
<td>0.070</td>
<td>0.080</td>
<td>0.100</td>
</tr>
<tr>
<td>Absorbance</td>
<td>0.250</td>
<td>0.302</td>
<td>0.354</td>
<td>0.385</td>
<td>0.433</td>
<td>0.408</td>
<td>0.329</td>
<td>0.000</td>
</tr>
</tbody>
</table>

The LiNO$_3$ does not absorb at this wavelength. Use the same methods as in your experiment to determine the formula of the likely complex and draw a reasonable structure for it. Carefully consider the structure of the nitrate ion before you draw the structure of the complex. Note that perchlorate ion (ClO$_4^-$) does not coordinate to the cobalt ion. Question: do you think that nitrate could be a bidentate ligand?

References


“Job’s Method for Determination of Stoichiometry,”
