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MATHEMATICS OF THE VARIATION AND MOLE RATIO METHODS OF COMPLEX DETERMINATION

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INTRODUCTION

Two well known methods for complex determination have been used for some time to obtain the ratio of the atoms, molecules, or ions in the species. These are the Job variation method (1) as modified by Vosburgh and Cooper (2) and the mole ratio method (3).

The variation method works for most complexes where the complex has a measurable property such as optical absorption that is different from the reactants. The ratio of units in the complex is determined by a maximum or minimum in a plot of $\Delta A$ (difference in expected and observed magnitude of a property) versus mole fraction of one of the complexing agents. This maximum or minimum is the intersection of two straight lines for a strong complex. For a weaker complex there is an intersection of a line from the points near mole fraction 1.0.

In the mole ratio method, the ratio of the units in the complex species is determined by the inflection point in a plot of a property such as optical absorption versus the mole ratio of the reactants. This method only works for a strong complex.

Since both of the methods involve the intersection of two straight lines in the limit of very strong complexes, one should be able to develop equations for these lines. These equations would explain why the method works and allow for further information to be obtained from slopes and intercepts. This development is the object of this discussion.

VARIATION METHOD

For the discussion of the variation method, only the maximum in $A$ will be considered remembering that maximum can be replaced by minimum in all cases. $A$ will be considered as the difference between observed optical absorption and expected optical absorption at a given wavelength if no complexing occurs.

Vosburg and Cooper (2) used the following equations:

\[ \Delta A = A_{\text{obs}} - A_{\text{calc}} = b(a_Ac_A + a_Bc_B + a_cc_c) - b[a_A^M(l-x) + a_B^Mx]. \] (1)

\[ c_c = M(l-x) - c_A \] (2)
\[ c_B = Mx - c_C \]  

(3)

for the reaction

\[ A + nB \rightarrow AB_n \]  

(4)

Where \( b \) is the sample path length; \( a_i \) is the absorptivity; \( c_A, c_B, \) and \( c_C \) are concentrations in the moles/liter of \( A, B, \) and \( AB_n \), respectively; \( M \) is the sum of the moles/liter of \( A \) and \( B \) initially; and \( x \) is the mole fraction of \( B \).

Initially for a strong complex, \( B \) is the limiting reagent and the following equations are obtained:

\[ c_B = 0 = Mx - nc_C \]

\[ c_C = \frac{Mx}{n} \]

\[ c_A = M(1-x) - \frac{Mx}{n} \]

\[ \Delta A_I = \frac{(a_C^{-n_a} - a_B^{-n_B})bMx}{n} \]  

(5)

Where \( \Delta A_I \) denotes \( \Delta A \) before the maximum.

After the maximum \( A \) is limiting and will be essentially all complexed, the following equations are obtained:

\[ c_A = 0 \quad c_B = Mx - nM(1-x) \quad c_C = M(1-x) \]

\[ \Delta A_{II} = \frac{(a_C^{-n_a} - a_B^{-n_B})bM(1-x)}{n} \]  

(6)

where \( \Delta A_{II} \) denotes \( \Delta A \) after the maximum.

At the intersection of Equations (5) and (6):

\[ \Delta A_I = \Delta A_{II} \]

and

\[ n = \frac{x}{1-x} \]

which is the result of Vosburgh and Cooper for \( n \).

Using Equations (5) and (6), \( (a_C^{-n_a} - a_B^{-n_B}) \) can be determined in three ways — the slope of \( \Delta A_I \) versus \( x \), the slope of \( \Delta A_{II} \) versus \( x \), and the intercept of \( \Delta A_{II} \) at \( x = 0 \). Since \( b, M, \) and \( n \) are known and \( a_A \) and \( a_B \) can be determined independently, \( a_C \) can be calculated. The average of the three values for \( a_C \) should give a dependable value.

If \( n < 1 \), the procedure works the same but the final equations are slightly different:

\[ \Delta A_I = \frac{(a_C^{-n_a} - a_B^{-n_B})bMx}{n} \]

\[ \Delta A_{II} = \frac{(a_C^{-n_a} - a_B^{-n_B})bM(1-x)}{n} \]
MOLE RATIO METHOD

Yoe and Jones (3) introduced the mole ratio method which is applicable to strong complexes without any theory. In the following, the mathematics of the mole ratio method will be developed and it will be shown how absorptivities can be obtained.

Assuming that the complex formation is represented by the following equation:

\[ A + nB \xrightarrow{\text{z}} AB_n \]  

(4)

where \( A, B, \) and \( AB_n \) can be atoms, molecules, or ions, the following can be written for some additive property such as optical absorption:

\[ A = b (a_A c_A^0 + a_B c_B^0 + a_C c_C^0) \]  

(7)

In Equation (7), \( b \) is the sample path length, \( a_I \) is the absorptivity, \( c_I \) is the concentration in moles 1 liter and \( C \) represents the complex \( AB_n \).

For a strong complex where \( B \) is limiting:

\[ c_A = c_A^0 - c_C \]  

(8)

\[ c_B = c_B^0 - n c_C = 0 \]  

(9)

were the superscript represents the concentration assuming no complex is formed. The added amount of \( A \) is held constant while \( B \) is varied so \( c_A \) is a constant but \( c_B \) is varying with each addition of \( B \). Substituting Equations (8) and (9) in Equation (7) yields:

\[ A = (a_C - a_A) bc_C + a_A bc_A^0 \]  

(10)

Now

\[ c_C = c_B^0 / n = \left( \frac{c_B^0}{c_A^0} \right) \frac{c_A^0}{n} \]  

(11)

When Equation (11) is substituted for \( c_C \) in Equation (10) one obtains:

\[ A_I = (a_C - a_A) \frac{b c_A^0}{n} \left( \frac{c_B^0}{c_A^0} \right) + a_B b c_A^0 \]  

(12)

When enough \( B \) is added that \( A \) becomes limiting:

\[ c_A = 0 \]  

(13)

\[ c_C = c_A^0 \]  

(14)

\[ c_B = c_B^0 - n c_C \]  

(15)

Now if Equations (13 - (15) are substituted into Equation (7), one obtains the following equation:
By multiplying the last term on the right hand side of Equation (16) by \( \left( \frac{c_A^o}{c_A} \right) \) one obtains:

\[
A_{II} = \left( a_c - na_B \right) bc_A^o + a_B bc_B^o
\]

(18)

Equations (12) and (18) will intersect at the point where

\[
c_C = \frac{c_B^o}{n} + c_A^o
\]

so that

\[
n = \frac{c_B^o}{c_A^o}
\]

A plot of \( \Delta A \) versus \( c_B^o / c_A^o \) will give a straight line up to the point where \( A \) becomes limiting, and then a change in slope will occur. If a second complex is formed, the slope will depend on it. When no further complexing occurs the plot will level off at a constant value unless \( B \) absorbs at the wavelength.

From Equations (12 and 18) the \( a_A^o \) and \( a_C^o - na_B \) can be determined from intercepts at a mole fraction of 0. Then \( a_C^o - a_A^o \) and \( a_B^o \) can be determined from the slopes. Combining these findings or using previous knowledge of \( a_A^o \) and \( a_B^o \) two independent values of \( a_C^o \) can be obtained.

APPLICATIONS

These methods have been used to determine absorptivities of complexes of \( \text{NpO}^{2+} \) with phenolphthalein and complexes of \( \text{NpO}_2 \) with oxalate (4). The absorptivities were determined for two complexes each with a precision of better than 1%. Using the absorptivities, concentrations of all species were determined and then equilibrium constants were calculated.

SUMMARY

From the slopes of the lines before and after the maximum (or minimum) in the standard plots of optical absorption versus mole fraction of complexing agent used in the variation method of complex determination, the absorptivity of the complex can be determined.

The mathematics of the mole ratio method have been developed, and with this development, equations for the determination of absorptivities evolved. The slopes of the lines in the standard absorption versus mole ratio plots are used for the determination of absorptivities.
Mathematics of Complex Determination

REFERENCES


