Experiment 23

THE DETERMINATION OF THE FORMULA OF A COMPLEX ION OF SILVER[1]

MATERIALS:

50 mL and 25 mL graduated cylinders, 10 mL pipet, 50 mL beaker, 100 mL beaker, four 250 mL Erlenmeyer flasks, 50 mL buret, standard 0.010 M KBr, 0.010 M $AgNO_3$, 2.0 M NH_3 solutions.

DISCUSSION:

A complex ion is a cation or anion formed when neutral molecules or anions, or a combination of molecules and anions, attach to a certain metal cation. The species attached to the central cation are called <u>ligands</u>. The number of coordinate covalent bonds in a complex ion is the <u>coordination number</u> of the central metal ion. The formation of a complex ion can be represented by the chemical equation:

$$M^{m+} + n\,L^{-l} \rightleftharpoons (ML_n)^{m-nl} \qquad (1)$$

In general, chemists are usually concerned with the "stability" of a complex ion, and by convention, the chemical reaction represented by equation (1) is written as a dissociation reaction

$$(ML_n)^{m-nl} \rightleftharpoons M^{m} + n\,L^{-l} \qquad (2)$$

where the dissociation K_{diss} is defined as

$$K_{diss} = \frac{\left[M^{m+}\right]\left[L^{-1}\right]^n}{\left[ML_n^{(m-nl)+}\right]} \qquad (3)$$

The degree of dissociation depends on the strength of the metal cation - ligand bonds, and in general the percent dissociation is quite small.

If solutions containing silver ions and ammonia molecules are combined, complex ions are formed. The complex ions dissociate according to the chemical equation

$$Ag(NH_3)_n^{+} \rightleftharpoons Ag^{+} + n(NH_3) \qquad (4)$$

for which the dissociation constant, K_{diss}, is defined as

$$K_{diss} = \frac{\left[Ag^{+}\right]\left[NH_3\right]^n}{\left[Ag(NH_3)_n^{+}\right]} \qquad (5)$$

where n is the number of ligands attached to the silver cation, or its coordination number.

---

[1] See: Wolfenden, J.H., *Journal of Chemical Education*, **36**, 490 (1959).

According to equation (4) there will always be a small amount of silver ion in equilibrium with the complex silver ion. This silver ion must also obey any other equilibrium constraints imposed by the system of interest. For example, if bromide ions are added to a solution containing silver ions and ammonia molecules, the concentration of silver ions in solution must be low enough so that the ion product of silver bromide does not exceed the solubility product of silver bromide. That is

$$[Ag^+][Br^-] \# K_{sp} \tag{6}$$

If the ion product in equation (6) exceeds the K_{sp} value of silver bromide, silver bromide will precipitate. Now if enough bromide ions are added to cause the precipitate just to appear, the concentration of silver ions in solution must be

$$\left[Ag^+\right] = \frac{K_{sp}}{\left[Br^-\right]} \tag{7}$$

If we substitute equation (7) into equation (5),

$$K_{diss} = \frac{K_{sp}\left[NH_3\right]^n}{\left[Br^-\right]\left[Ag\left(NH_3\right)_n^+\right]} \tag{8}$$

or

$$\left[Br^-\right] = \frac{K_{sp}\left[NH_3\right]^n}{K_{diss}\left[Ag\left(NH_3\right)_n^+\right]} \tag{9}$$

and

$$\log\left[Br^-\right] = n\log\left[NH_3\right] + \log\frac{K_{sp}}{K_{diss}\left[Ag\left(NH_3\right)_n^+\right]} \tag{10}$$

Equations (7) - (10) are only true when the ion product of silver bromide equals or exceeds the K_{sp} of silver bromide. Under these conditions if the log $[Br^-]$ vs log $[NH_3]$ is plotted, a straight line should result, *the slope of which will be equal to the coordination number, n.*

PROCEDURE: (work individually)

1. Using the information in the table below, set up a series of four flasks, each containing the silver nitrate solution, ammonia solution and water. Use the 10 mL pipet to measure out the silver nitrate solution. Use a graduated cylinder to measure out the ammonia and water. Putting the correct amount of ammonia in all four flasks before adding water will minimize the number of rinses (of the graduated cylinder) required.

Flask #	0.010 M $AgNO_3$	2.0 M NH_3	H_2O
1	20.0	10.0	70.0
2	20.0	15.0	65.0
3	20.0	20.0	60.0
4	20.0	30.0	50.0

2. By titration, find the volume of the 0.010 M potassium bromide solution necessary to <u>just</u> produce a permanent cloud of silver bromide in each flask.

DATA AND CALCULATIONS:

Record your data in the table on the next page.

Calculate the concentration of ammonia and bromide ion in each flask, assuming that the amount of silver bromide formed is negligible. For each flask, plot log $[Br^-]$ against the log $[NH_3]$. From your results, deduce the formula for the complex ion formed between silver ion and ammonia in solution.

Data manipulation, graphing, and regression analysis (including linear regression) can be easily accomplished using a computer spreadsheet such as QUATTRO.

If the value of $K_{sp}(AgBr) = 4.1 \times 10^{-13}$, determine the value of K_{diss}, the dissociation constant for the silver amine complex, and then compare your value to that reported in the literature.

Name _____ Section _____

Partner _____ Date _____

DATA SECTION
Experiment 23

Conc. of standard solutions: $AgNO_3$ _____ NH_3 _____ Br^- _____

	Flask 1	**Flask 2**	**Flask 3**	**Flask 4**
vol of Br^- soln. added				
total volume				
moles NH_3 added				
$[NH_3]$ *				
moles Br^- added				
$[Br^-]$				
ln $[NH_3]$				
ln $[Br^-]$				

*** Assume <u>none</u> of the NH_3 is complexed. In practice the NH_3 is present in large excess, so only a small fraction of the total NH_3 is complexed.**

slope of graph, (ln $[Br^-]$ vs ln $[NH_3]$) = _____

value of n in $Ag(NH_3)_n^+$ = _____

	Flask 1	**Flask 2**	**Flask 3**	**Flask 4**
# moles Ag^+				
$[Ag^+]$ (= Ksp/$[Br^-]$)				
# moles $Ag(NH_3)_n^+$				
$[Ag(NH_3)_n^+]$				
# moles "free" NH_3 **				

****** # moles "free" NH_3 = [# moles NH_3 added - # moles NH_3 complexed]
= [# moles NH_3 added -n $Ag(NH_3)_n^+$]

	Flask 1	**Flask 2**	**Flask 3**	**Flask 4**
"free" [NH_3], to be used in calculating Kdiss				
K_{diss} (calculated)				

Average K_{diss} = _____

Literature value of K_{diss} = _____. Literature reference _____.

Percent "error" = _____