Exercise 27

DETERMINATION OF THE COORDINATION NUMBER OF A COORDINATION COMPOUND

Key concepts: Coordination compounds. Chemical bonds: single and multiple covalent bonds, coordinate covalent bond, ionic bond. Electron transition in coordination complexes. Charge transfer transitions. Coordination number. Stability constant of a coordination compound.

Iron ions in aqueous solutions form three types of complexes with salicylate ions. Below pH = 4 in solution there is mainly an iron(III) monosalicylate cation $[FeSal]^{+}$, above pH = 9 there is almost exclusively an iron(III) trisalicylate anion $[Fe(Sal)_3]^{-3}$, and in the intermediate pH region the iron(III) bisalicylate anion $[Fe(Sal)_2]^{-}$ predominates.

The determination of the coordination number (n), *i.e.* the number of ligands (L) bonded to the central atom (M), usually comes down to the determination of the mol fraction of the reacting components, such as the method of continuous variation, also known as Job's method. This method involves measuring any, but necessarily additive, property of the series of solutions in which the sum of the concentrations of the metal forming the complex and the ligand is a constant quantity. The condition for the application of Job's method is that the concentration of the complex or any physical quantity proportional to it can be measured. Determination of the coordination number of a complex compound is possible by applying spectrophotometric measurement only if the Lambert-Beer law is fulfilled in the studied range of concentration.

A series of solutions are then prepared with a gradually changing ratio of concentrations of the reactants forming the complex compound, while keeping the sum of the concentrations of the two components in all solutions constant. Absorbance is then measured as a quantity proportional to the concentration of the complex formed. The maximum concentration of the complex is for a solution in which the ratio of the ligand concentration to the metal ion concentration is equal to the coordination number. If the results are presented in the form of a graph of the dependence of the concentration of the complex (or of a quantity proportional to it) on the composition of the solution, the instability constant of the complex can also be graphically determined approximately (Figure 1).

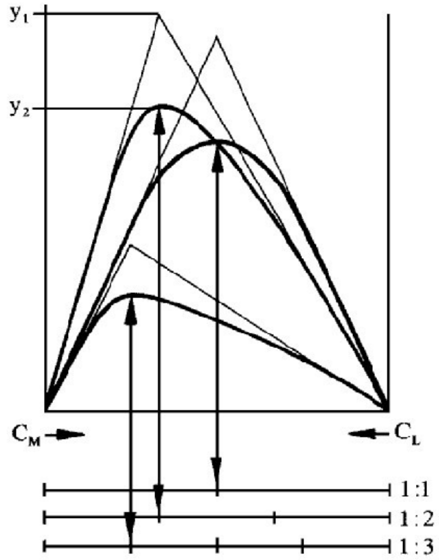

Figure 1.Grphical method for determining the instability constant of the complex.

The instability constant of particular coordination compound of composition, *e.g.* ML_n, is the equilibrium constant of dissociation occurring according to the scheme:

$$ML_n \rightleftharpoons M + nL$$

And can be written as:

$$K = \frac{c_M \cdot c_L^n}{c_{ML_n}} \quad (1)$$

If the overall concentration of the complex is c, and the degree of dissociation is α, then at equilibrium the concentrations of the reactants are:

$c_M = c \cdot \alpha$

$c_L = c \cdot n \cdot \alpha$

$c_{ML_n} = c(1 - \alpha)$

By applying the above with equation (1), we obtain:

$$K = \frac{c^n \cdot n^n \cdot \alpha^{n+1}}{1-\alpha} \quad (2)$$

To calculate the constant of instability from this equation, it is necessary to know the degree of dissociation of the complex, α. To determine α on the resulting graph (Figure 1), tangents are drawn at the points of intersection of the curve with the x-axis. The points of intersection of the tangents (y_1) corresponds to the overall concentration of the complex (if it had not dissociated), while the point of the maximum on the experimental curve (y_2) corresponds to its actual concentration. The degree of dissociation of the complex is therefore:

$$\alpha = \frac{y_1 - y_2}{y_1} \quad (3)$$

Experiment method

The aim of the exercise is to determine the molar ratio of the reactants in the reaction to form an iron-salicylate complex, and to determine the instability constant of this complex at pH = 1. Light adsorption is measured with a “Cecil” spectrophotometer in a cuvette 1 cm thick.

Procedure

From solutions of sodium salicylate and iron (III) sulfate, both of concentrations equal to 0.05 M, a series of solutions are prepared in 50 cm^3 flasks in such a way that in each case the sum of the volumes of the two starting solutions is constant and equal to 2 cm^3 and the rest is buffer solution.

(a) Start with an amount of 0.2 cm^3 of iron(III) sulfate in the first flask, in the next ones, increase this amount by 0.1 cm^3 and after reaching 1.4 cm^3 , by 0.2 cm^3. Accordingly, add 1.8 cm^3 of sodium salicylate in the first flask and decrease this amount by 0.1 cm^3 in the next ones and after reaching 1.4 cm^3, by 0.2 cm^3. Then fill the flasks with buffer solution to a volume of 50 cm^3.
(b) Reference solutions should be prepared by taking in each case the same volume of iron(III) sulfate as for the test solution and the remaining volume to 50 cm^3 should be filled with a buffer solution.
(c) Absorption measurements are taken at 520 nm.
(d) Then a graph of the dependence of absorption on the composition of the mixture is made and the value corresponding to the maximum (y_2) is read from it.
(e) The ratio of the concentrations of the reactants at this point equals the coordination number.
(f) Determine α and calculate the approximate value of K by applying the previously described graphical method.