5: The Paramagnetic Complex $Mn(acac)_3$ (Experiment)

Introduction

This experiment is from the textbook (pages 117-130). Further information and background information can be found there. The experiment is copied here verbatim for ease of use during lab.

Notes

1. The molar amount for $KMnO_4$ is incorrect. Instead of 0.027 mol it should say 0.023 mol.

2. Near the top of page 126, the instructions state that you should dry the crystals of $Mn(acac)_3$ for at least 30 minutes. Dry them for longer than that if possible.

3. The normal chemical shift of $CHCl_3$ is 7.26 ppm. In the presence of a paramagnetic complex it is shifted upfield.

4. The magnetic susceptibility balance (MSB) we use is slightly different from the Gouy balance used in the lab manual. With the MSB, you need to weigh the empty tube and then the filled tube (filled to 2.5 to 3.5 cm).

5. Because we are using an MSB instead of a Gouy balance, some of the questions do not apply. Please ignore Report question #1 and Problems #2, 5 and 10.

6. There is an error on page 122 in footnote "a" of the table. The number should be -13 x 10^{-6} cm^3 mol^{-1}. Also be careful when reading the table. For example, the entry for $acac^-$ is -52 x 10^{-6} cm^3 mol^{-1}.

7. The equation for calculating the susceptibility is explained in the manual for the magnetic susceptibility balance. The equation is:

$$\chi_g = \frac{C_{bal} \times l \times (R - R_0)}{10^9 m} \tag{5.1}$$

$$\chi_m = \chi_g \times M \tag{5.2}$$

C_{bal} = balance calibration constant = 1.006 cm^2

l = sample length (cm)

m = sample mass (g)

R = reading for tube plus sample

R_0 = reading for empty tube

M=molar mass of $Mn(acac)_3$

8. An alternative, and very accurate, method for determination of the magnetic susceptibility is the Evan's Method, based on ^1H NMR. A special NMR tube is needed to carry out this measurement. It is based on the chemical shift difference between pure $CDCl_3$ and a $CDCl_3$ solution of a known amount of the dissolved paramagnetic $Mn(acac)_3$.

Safety Precautions

Read all of the safety warnings in the text for this experiment.

Chloroform may be a carcinogen. Therefore **do not touch, inhale or ingest chloroform**. Use chloroform in a **fume hood**. **Wear gloves** which are resistant to chloroform (see chart earlier in this manual). The Viton and Silver Shield gloves are not disposable.

Waste disposal

All solid waste should be collected in the Experiment 12 solid waste container. Collect the filtrate in the Experiment 12 liquid waste container.

Experiment

Safety Precautions

Potassium permanganate is a strong oxidant. If you spill some on your skin, wash it off immediately with large amounts of water.

Tris(acetylacetonato)manganese(III), $Mn(acac)_3$

In a 250-mL beaker, prepare a solution of 3.75g (0.0237mol) of potassium permanganate, $KMnO_4$, and 75mL of distilled H_2O. Warm the stirred solution to 80ºC on a hot plate to dissolve all the solid. Then cool the solution to room temperature by packing the beaker with ice. When the solution has cooled, stir it rabidly and slowly add 17mL (16.6g, 0.166mol) of acetyl acetone in several aliquots over a few minutes. (If you add the acetyl acetone too quickly, the solution will generate large amounts of foam that may overflow the flask.) Note the color change. After the addition is complete, boil the solution for 5 minutes, and then chill the beaker in ice. Collect the shiny brown-black crystals on a course fritted filter (see Figure 13-1) and wash them tree times with 10-mL portions of distilled water. Dry the crystals thoroughly by pulling air through the frit for at least 10 minutes. If possible, dry the crystals under vacuum for at least 30 minutes.

Measurement of Magnetic Susceptibility by the Evans Method

Weigh a clean and dry NMR tube (5-mm outer diameter) on an analytical balance to the nearest 0.1mg (or the nearest 0.01mg if possible). Add between 2 and 5mg of $Mn(acac)_3$ to the NMR tube; this amount of $Mn(acac)_3$ is less than what is needed to cover the bottom of the tube. Reweight the NMR tube to determine exactly the amount of solid added.

If you will be using a NMR spectrometer equipped with and electromagnet, carry out the following procedure. Into the NMR tube, place a sealed capillary that contains pure chloroform, $CHCl_3$ (the capillaries that can be made by syringing $CHCl_3$ into a melting point capillary, and then sealing the open end in a flame). Make sure to insert the capillary so that the end filled with solvent is resting on the bottom of the NMR tube. With a syringe, add exactly 0.70mL of $CHCl_3$ to the NMR tube. Cap the tube and shake gently to dissolve the $Mn(acac)_3$ completely. When the solid is completely dissolved, record the NMP spectrum of the solution (see your instructor for directions concerning the use of the NME instrument). There should be two peaks near δ7: One of the two peaks is due to the $CHCl_3$ in the capillary and the other due to the $CHCl_3$ that has been paramagnetically shifted by the dissolved $Mn(acac)_3$. Determine the chemical shifts of these two peaks, and measure the separation between them in hertz. For example, if the spectrometer frequency is 100MHz and the two peaks are 0.3ppm apart, then the separation is 0.3 ×100 = 30Hz. The magnetic susceptibility of your sample can be determined from the weight of your sample, the volume of $CHCl_3$ used, the chemical shift difference $\Delta\nu$ between the two peaks. And radio frequency used. Use Eq. with Q=1.

If you will be using a NMR spectrometer quipped with a superconducting magnet, carry out the same procedure except use deuterated chloroform ($CDCl_3$) both in the capillary and as the solvent to dissolve the $Mn(acac)_3$. The measurement is conducted the same way; the only difference is that the two peaks near δ 7 are due to the small (about 0.1%) residual amounts of $CHCl_3$ in the $CDCl_3$ solvent. Determine the magnetic susceptibility of your sample from Eq 10 with Q=2.

Measurement of Magnetic Susceptibility by the Gouy Method

Scratch a horizontal line on the Gouy tube about 2cm from the top, if this has not already been done. For the weight measurements, the tube should always be filled to this line. To remove paramagnetic impurities from the tube, clean it with Nochromix cleaning solution (do not use chromic acid, which will add paramagnetic impurities!). Thoroughly rinse the tube with water and acetone, and dry it in the oven. Do not wipe the tube with a dry towel; this gives the tube a static charge that significantly affects the weighings.

Weigh the empty tube on the chain with the field off. With the field on, weigh the tube again. Although “pure class” is diamagnetic, paramagnetic impurities may cause the tube to be attracted by the field rather than repelled. The difference between these two weighings, on minus off, is and will be used to correct for the magnetism of the tube when the sample is weighed in the tube. It is necessary to maintain the same magnetic field for all measurements when the field is on. With electromagnetics this will require a constant electric current (and therefore field). Because the current will decrease as the coils begin to hear, the current will have to be adjusted frequently. Current regulators are available that will conveniently provide this control.

To correct for the magnetism of air when it is displaced by the sample, the volume occupied by the air must be determined. Fill the tube to the line with water at the existing temperature, the volume (V) may be calculated. The volume susceptibility of air is 0.029 $\times 10^{-6}$.

To determine the calibration constant for the apparatus, fill the dry tube to the line with the solid standard. The largest source of error in the Gouy method is inhomogeneously packed sample tubes. To minimize this problem, the sample should be finely powdered (sue a mortar and pestle) and introduced into the tube in small portions. After each addition, firmly tap the tube on the hard surface. Carfeul packing of the tube will require 20-30 minutes. Weigh the tube with the magnet off and again with the magnet on, using the same current as used previously. After each weighing of a solid sample with the field on, measure the temperature between the poles of the magnet. The difference in these two weighings (on minus off) is designated Δ and is a measure of the magnetic susceptibility of both the sample and the tube. From the magnetic susceptibility of both the sample and the tube. From the magnetic suspetibility per gram of the standard (χ), the mass in grams of the standard (*m*), and the values of δ, Δ, and *V*, the calibration constant (β) may be calculated

$$(\chi)(m) - (0.029 \times 10^{-6})V = \beta(\delta - \Delta) \tag{5.3}$$

For calibration, either $HgCo(NCS)_4$ or $[Ni(en)_3]S_2O_3$ where en=$NH_2CH_2CH_2NH_2$, has provided to be very satisfactory. These compounds may be prepared easily in high purity, are stable, are not hygroscopic, and pack very well. The susceptibility per gram of $HgCo(NCS)_4$ at 20°C is $\chi=16.44\times10^{-6}$ cm^3 g^{-1}. The susceptibility obeys the Curie-Weiss law with θ= -10K. The relativity high susceptibility of this compound sometimes causes the sample tube to cling to one of the poles of the magnet. This problem can be avoided by carefully positioning the sample tube midway between the poles. On the other hand, or $[Ni(en)_3]S_2O_3$ is rarely drawn toward a pole because of its lower susceptibility. Its values 20°C is $\chi=11.03\times10^{-6}$ cm^3 g^{-1}. It, too, obeys the Curie-Weiss law with θ= 43K.

After the values of β is obtained, the sample tube is cleaned and dries. The same procedure is repeated for the determination of the unknown, $Mn(acac)_3$. The empty tube is weighed with the field on and off to obtain δ. Then the tube is carefully packed with finely powdered $Mn(acac)_3$. The filled tube is then weighed with the field on and off to obtain Δ. These measurements will then permit the calculation of χ and the molar susceptibility χ_M.

Summarized below are the measurements that must be made first on the standard and then on the unknown:

A. Weight of the empty tube, field off _____ g

B. Weight of the empty tube, field on _____ g

C. Weight of the tube filled to line with water, field off _____ g

D. Weight of the tube filled to line with solid, field off _____ g

E. Weight of the tube filled to line with solid, field on _____ g

F. Temperature during measurements above _____ g

As given, these weights are related to the terms in Eq. 12.3 in the following manner:

$$V = \frac{(C - A)}{d} \tag{5.4}$$

d is the density of water (g/mL) at ambient temperature

$$\Delta = B - A \tag{5.5}$$

$$\delta = E - D \tag{5.6}$$

$$m = D - A \tag{5.7}$$

To determine the reproducibility of your value, repeat the evaluation for χ for $Mn(acac)_3$ at least one more time by emptying and repacking the tube and then making the necessary weighings.