PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Iodometric Determination of the Concentration of Copper(II) and Iron(III) in a Sample of Technological Solution

Reagents

- $K_2Cr_2O_7$, 0.008333 M
- KI, 20 % by mass.
- HCl, 1 M
- H_2SO_4, 1 M
- $Na_4P_2O_7$, 5 % by mass.
- Starch, 1 % by mass.
- $Na_2S_2O_3$ (should be standardized)
- The solution to be analyzed in 100 cm^3 volumetric flask.

Procedure

1. Standardization of $Na_2S_2O_3$ solution
   (1) 10 cm^3 of 1 M solution of H_2SO_4 and 2 cm^3 of 20 % KI solution are placed into an Erlenmeyer flask (the solution remains colourless).
   (2) 10.00 cm^3 of $K_2Cr_2O_7$ solution is added.
   (3) The Erlenmeyer flask is covered with a watch glass and kept in a dark place for 3 to 5 min.
   (4) 100 cm^3 of water is added to the flask.
   (5) The mixture is titrated immediately with $Na_2S_2O_3$ solution until the colour of mixture changes to pale yellow. Then 10 drops of starch solution are added. The titration continues until blue colour disappears completely.
   (6) It is recommended to repeat the titration (steps 1 through 5) two more times.

Do the following and fill in the answer sheet form

1.1 Write the reactions involved in the procedure of standardization of $Na_2S_2O_3$ solution

1.2 Calculate the concentration of $Na_2S_2O_3$ solution, and write your calculations.

2. The determination of copper

(1) The solution to be analyzed in a 100 cm^3 volumetric flask is diluted with water to the mark and stirred

(2) A 10.00 cm^3 aliquot of the solution is placed into an Erlenmeyer flask.

(3) 20 cm^3 of 5 % solution of $Na_4P_2O_7$, 7 cm^3 of 1 M solution of HCl, and 10 cm^3 of 20 % solution of KI are added. A precipitate may form upon the addition of $Na_4P_2O_7$.

(4) The Erlenmeyer flask is covered with a watch glass and left in a dark place for 3 - 5 min.

(5) The mixture is titrated immediately with $Na_2S_2O_3$ solution until the colour of suspension changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until the colour of suspension becomes clear white.

(6) It is recommended to repeat the titration (steps 2 through 5) two more times.

Do the following and fill in the answer sheet form

1.3 Write the reactions involved in the procedure of determination of Cu^{2+} ion.

1.4 Calculate the mass of copper in the solution under analysis, and write your calculations.

3. The determination of total amount of copper and iron

(1) A 10.00 cm^3 aliquot of the solution prepared in the item 2(1) is placed into an Erlenmeyer flask.

(2) 2 cm^3 of 1 M HCl solution and 10 cm^3 of 20 % KI solution are added.

(3) The Erlenmeyer flask is covered with a watch glass and kept in a dark place for 3 to 5 min.

(4) The mixture is titrated immediately with $Na_2S_2O_3$ solution until the colour of suspension changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until the colour of suspension becomes clear white.

(5) It is recommended to repeat the titration (steps 1 through 4) two more times.

Do the following and fill in the answer sheet form

1.5 Write the reactions involved in the procedure of determination of Fe^{3+} ion.

1.6 Calculate the mass of iron in the solution under analysis, and write your calculations.

SOLUTION

1.1

Equations:

$$Cr_2O_7^{2-} + 6\,I^- + 14\,H^+ = 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O$$

$$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$$

i

1.3

Equations:

$$2\,Cu^{2+} + 4\,I^- = 2\,CuI + I_2$$

$$4\,Fe^{3+} + 3\,P_2O_7^{4-} = Fe_4(P_2O_7)_3 \downarrow$$

$$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$$

1.5

Equations:

$$2\,Fe^{3+} + 2\,I^- = 2\,Fe^{2+} + I_2$$

$$2\,Cu^{2+} + 4\,I^- = 2\,CuI + I_2$$

$$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$$

PROBLEM 2 (Practical)

Qualitative Determination of Paracetamol in a Sample of Unknown Drug

Introduction

Three organic compounds are most widely used as pain relieving drugs: acetylsalicylic acid (ortho-acetoxybenzoic acid), phenacetine (*para*-ethoxyacetanilide), and paracetamol (*para*-hydroxyacetanilide). Paracetamol is now the most popular, being the base of a large number of well known patented pharmaceuticals (panadol, solpadeine, coldrex, calpol, efferalgan etc.), as it is now considered as the safest and highly efficient drug.

You were given a sample of unknown drug which claims to contain paracetamol. Your task is to prove or disprove this claim experimentally. To do this you shall have to prepare an authentic sample of *para*-hydroxyacetanilide, and run a thin layer chromatography test.

Reagents

- *Para*-aminophenol, 3.10 *g* in a weighing beaker
- Acetic anhydride, 4.00 cm^3 in an Erlenmeyer flask
- Ethanol
- Eluent (heptane : ethyl acetate : ethanol = 41 : 47 : 12 by volume)
- Sample of unknown drug in a test tube, 1 % solution in ethanol
- Water (use tap water for all purposes)

Procedure

Preparation of para-hydroxyacetanilide

A 50 cm^3 round bottom flask is equipped with reflux condensor and installed on a laboratory stand over a hot plate. Note that the space between the top of hot plate and the bottom of flask be about 1-1.5 cm. Use two clamps to properly support the flask and condenser. Remove the hot plate. Do not switch on the hot plate until you finish with adding reagents and reassembling the apparatus. With reflux condensor temporarily removed, 3.10 g of *para*-aminophenol is placed to the flask using a funnel (use a glass rod

to push it through the funnel, if necessary). Water (10 cm^3) is then added through the same funnel. The condenser is mounted back, and acetic anhydride (4.00 cm^3) is carefully poured to the reaction mixture through the condenser (*attention*! acetic anhydride has a strong irritating smell. In case of spill immediately wash hands with water and ask the supervisor to help with the disposal of spilled compound). Carefully stir the contents by slightly relieving clamps and waving the flask 2 - 3 times. Be careful as the mixture and the flask gets very hot due to the reaction heat. Place back the hot plate and switch it on. The reaction mixture is heated for 15 minutes beginning from the time when you switch on the hot plate. Then, the heater is switched off and removed from the apparatus. The mixture is allowed to cool first by immersing the flask into a bath with cold tap water. You may do this immediately after you remove the plate as the flask is made of highly durable glass. After approximately five minutes unattach the condenser and pour the contents into an empty 100 cm^3 pyrex glass beaker. Put the beaker into a metal dish filled with ice and water. Accurately rub the walls of beaker with spatula and observe the crystallization of crude product as small white crystals.

Assemble a suction filtration device: put the frit filter onto a rubber ring and a heavy-wall flask. Connect the flask to a suction vacuum pump and turn on water in the pump by turning tap. (*Attention*! Never turn off the water tap if your device is under vacuum. First always disconnect the flask from vacuum pump by carefully pulling off the rubber tubing from the inlet.)

The crystalline precipitate is quantitatively moved onto a filter by spatula. Remaining solid can be washed with small portions of ice cold water (as small as possible, as the compound possesses an essential solubility in water, and the losses of dissolved compound must not outweigh the losses due to incomplete transfer of product to the filter). The product in the filter is carefully washed with 2 - 3 portions of 2 - 3 cm^3 of cold water by a) connecting the vacuum suction flask to the atmosphere; b) addition of water and careful mixing it with the precipitate using a spatula; c) reapplying vacuum; d) pressing the precipitate with flat tip of a glass rod to squeeze out as much water as possible.

Several crystals of material are used for chromatography test (see below). All other precipitate is moved to a sheet of filtering paper in a Petri dish, and spread out over the filter in a thin layer, and allowed to dry on a shelf to exclude accidental spill. For rapid drying it is critical to spread it as thin as possible, to break all large pieces, and to stir it

and spread again every 3-5 minutes to expose all wet crystals to air. It is established after a numerous repetition of this procedure, that after 30 min the product contains no more than 5 % of water. Such wetness is considered as insignificant for evaluating the results of the preparation.

Chromatography test

(If for some reason you have failed to obtain *para*-hydroxyacetanilide, you can obtain a sample for chromatography from your supervisor.)

While still wet several crystals of the material obtained by you are dissolved in a tube in 1 - 2 cm^3 of ethanol. The unknown drug is already dissolved in ethanol and given to you as 1 % solution. These solutions are used for thin layer chromatography, as follows:

Prepare a sheet of chromatography plate covered with silica. Using a sharp pencil draw a start line and marks for sample spots. A small spot of each solution is placed on a chromatography plate using a capillary. The spots are allowed to dry for 1-2 minutes.

The plate is immersed into a beaker containing the eluent and allowed to be eluted. Use forceps to move the plate in and out of the beaker. After the elution, remove the plate from the flask, mark the front of eluent, and allow it to dry under the hood for 5 minutes. Examine the chromatogram under UV light in a special cabinet. Outline the dark spots (if there are any) with a sharp pencil.

Weighting of sample

After you complete the chromatography, your product usually is almost dry and is ready for weighting. Ask you supervisor to weight an empty weighing beaker. Put the dry product into a weighted beaker and give it to the supervisor for weighting. Weights are written in your answer sheet by the supervisor. Calculate the weight of the product.

Do the following and fill in the answer sheet form

2.1 Draw the structures of three main pain relieving drugs mentioned above.

2.2 Draw the reaction equation involved in the preparation of *para*-hydroxyacetanilide. Calculate the stoichiometric amounts of reagents needed for the reaction. How much acetic anhydride is taken in excess over the stoichiometry? The density of acetic anhydride is 1.08 g cm^{-3}.

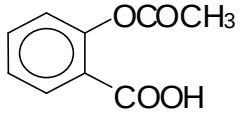
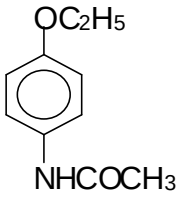
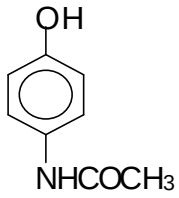
2.3 Calculate the yield of product obtained by you.

2.4 Calculate and compare the values of R_f of unknown drug and your product.

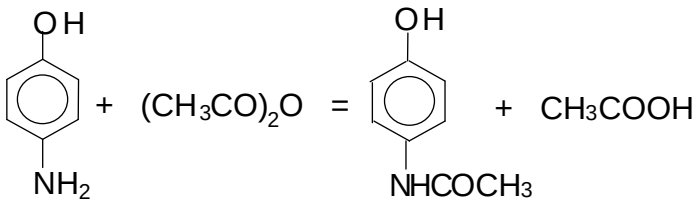
2.5 Is it likely that paracetamol is contained in the sample of drug?

SOLUTION

2.1

Acetylsalicylic acid	Phenacetine	Paracetamol
		

2.2



2.5 Yes, the sample is likely to contain paracetamol.