PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determination of Fatty Acids

A mixture of an unsaturated monoprotic fatty acid and an ethyl ester of a saturated monoprotic fatty acid has been dissolved in ethanol (2.00 cm^3 of this solution contain a total of 1.00 g acid plus ester). By titration the acid number[1)], the saponification number[2)] and the iodine number[3)] of the mixture shall be determined. The acid number and the saponification number shall be used to calculate the number of moles of free fatty acid and ester present in 1.00 g of the sample. The iodine number shall be used to calculate the number of double bonds in the unsaturated fatty acid.

Note: The candidate must be able to carry out the whole exam by using the delivered amount of unknown sample (12 cm^3). There will be no supplementation.

1) Acid number: The mass of KOH in milligram that is required to neutralize *one* gram of the acid plus ester.
2) Saponification number: The mass of KOH in milligram that is required to saponify *one* gram of the acid plus ester.
3) Iodine number: The mass of iodine (I) in g that is consumed by 100 g of acid plus ester.

Relative atomic masses:

A_r(I) = 126.90 A_r(O) = 16.00

A_r(K) = 39.10 A_r(H) = 1.01

1) Determination of the Acid Number

Reagents and Apparatus

Unknown sample, 0.1000 M KOH, indicator (phenolphthalein), ethanol/ether (1 : 1 mixture), burette (50 cm^3), Erlenmeyer flasks (3 x 250 cm^3), measuring cylinder (100 cm^3), graduated pipette (2 cm^3), funnel.

Procedure:

Pipette out aliquots (2.00 cm^3) from the unknown mixture into Erlenmeyer flasks (250 cm^3). Add first ca. 100 cm^3 of an ethanol/ether mixture (1:1) and then add the indicator (5 drops). Titrate the solutions with 0.1000 M KOH.

Calculate the acid number.

2) Determination of the Saponification Number

Reagents and Apparatus

Unknown sample, 0.5000 M KOH in ethanol, 0.1000 M HCl, indicator (phenolphthalein), volumetric flask (50 cm^3), round bottom flask (250 cm^3), Liebig condenser, burette (50 cm^3), Erlenmeyer flasks (3 x 250 cm^3), volumetric pipette (25 cm^3), volumetric pipette (10 cm^3), graduated pipette (2 cm^3), funnel, glass rod. The round bottom flask and Liebig condenser are to be found in the fume hoods.

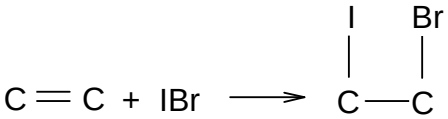
Procedure

Pipette out a 2.00 cm^3 aliquot of the unknown sample into a round bottom flask (250 cm^3) and add 25.0 cm^3 0.5000 M KOH/EtOH. Reflux the mixture with a heating mantle for 30 min in the fume hood (start the heating with the mantle set to 10, then turn it down to 5 after 7 min.). Bring the flask back to the bench and cool it under tap water. Transfer quantitatively the solution to a 50 cm^3 volumetric flask and dilute to the mark with a 1:1 mixture of ethanol/water. Take out aliquots of 10 cm^3 and titrate with 0.1000 M HCl using phenolphthalein as indicator (5 drops).

Calculate the saponification number.

3) Determination of the Iodine Number

In this experiment iodobromine adds to the double bond.



The Hanus solution (IBr in acetic acid) is added in excess. After the reaction is complete, excess iodobromine is reacted with iodide forming I_2, ($IBr + I^- \rightarrow I_2 + Br^-$) which in turn is determined by standard thiosulphate solution.

Warning: Be careful when handling the iodobromine solution. Treat any spill immediately with thiosulphate solution.

Reagents and Apparatus

Unknown sample, 0.2000 M Hanus solution, dichloro-methane, 15 % KI solution in distilled water, distilled water, 0.2000 M sodium thiosulphate, starch indicator, Erlenmeyer flasks (3 x 500 cm^3), buret (50 cm^3), graduated pipette (2 cm^3), measuring cylinders (10 and 100 cm^3), volumetric pipette (25 cm^3), aluminium foil.

Procedure

Pipette out aliquots (1.00 cm^3) of the unknown mixture into Erlenmeyer flasks (500 cm^3) and add 10 cm^3 of dichloromethane. With a pipette add 25.0 cm^3 Hanus solution, cover the opening with aluminium foil and place your labelled flasks in the dark in the cupboard (under the fume hood) for 30 min. with occasionally shaking. Add 10 cm^3 of the 15 % KI solution, shake thoroughly and add 100 cm^3 of dist. water. Titrate the solution with 0.2000 M sodium thiosulphate until the solution turns pale yellow. Add starch indicator (3 cm^3) and continue titration until the blue colour entirely disappears.

Calculate the iodine number.

4) Use the results from 1) 2) and 3) to:

i) Calculate the amount of ester (in mol) in 1 g of the acid plus ester.

ii) Calculate the number of double bonds in the unsaturated acid.

PROBLEM 2 (Practical)

Volumetric Determination of Bromide by Back-titration with Thiocyanate after Precipitation with Silver Ions in Excess

Moments worth considering:

- The candidates must consider the number of significant figures that will be reasonable in the results.
- The candidates must be able to carry out the whole analysis by using the delivered portions of silver nitrate and potassium thiocyanate. Supplementation of these two solutions will not be available.
- Only *one* 25 cm^3 pipette will be at disposal for each candidate.

Principle

Bromide is precipitated as silver bromide after a known amount of silver ions has been added in excess.

$$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s) \qquad \text{(faint yellow-green)}$$

The excess of silver ions is titrated with thiocyanate with a known concentration, after a previous standardization of the thiocyanate solution.

During the titration of the following reaction takes place resulting in the precipitation of silver thiocyanate:

$$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(s) \qquad \text{(white)}$$

Fe(III) is added as indicator producing a red-coloured ion at the equivalence point:

$$Fe^{3+}(aq) + SCN^-(aq) \rightarrow FeSCN^{2+}(aq) \qquad \text{(red)}$$

a) ***Procedures***

Every candidate has got a 0.5 dm^3 brown bottle with screw cap, containing the potassium thiocyanate solution (about 0.08 M) and also a 0.25 dm^3 brown bottle with screw cap, containing the silver nitrate solution. The concentration of this solution is 0.1000 M. The exact concentration of the KSCN solution is to be determined by the candidates.

i) ***Determination of bromide in the unknown sample solution***

Fill the 250 cm^3 volumetric flask containing the bromide sample solution to the mark with water. Transfer three 25.00 cm^3 portions (pipette) of the sample solution to three Erlenmeyer flasks. Add about 5 cm^3 of 6 M nitric acid (measuring cylinder) to each flask. Transfer 25.00 cm^3 (pipette) of the accurately known silver solution and about 1 cm^3 of iron(III) indicator (ind.) (measuring cylinder) to each solution.

Titrate the contents of the three aliquots with the potassium thiocyanate solution. The end-point of the titration is detected when the solution (including the precipitate) becomes permanently *very faint* brownish. It is important to shake the contents vigorously near the end-point and rinse the walls of the flask with water. The colour should be stable for at least one minute.

ii) ***Standardization of the potassium thiocyanate solution***

Transfer 25.00 cm^3 (pipette) of the silver nitrate solution to an Erlenmeyer flask, add about 5 cm^3 of 6 M nitric acid and about 1 cm^3 of the iron(III) indicator solution and about 25 cm^3 of water (use measuring cylinders for these solutions). Titrate the contents with the thiocyanate solution and determine the end-point according to the instruction given in the "Determination" procedure.

Atomic mass: $A_r(Br) = 79.90$

b) ***Exercise***

At the equivalent point the solution is saturated with respect to both AgBr and AgSCN. Find the molar concentration of free (unprecipitated) Br^- in this solution:

$$K_{sp}(AgBr) = 5.00\times10^{-13} \qquad K_{sp}(AgSCN) = 1.00\times10^{-12}$$

Ignore the effect of *pH* and Fe(III) species.

Note:

On the answer sheet, not only the required final results shall be given, but also examplifications of how the calculations are carried out.