Exam Procedure

- **The time allowed** for the exam is **5 hours**. There will be an additional **15 minutes reading time** at the start. **DO NOT** begin practical work until the **START** command is given.
- **When the announcement is given to stop working at the end of the 5 hours you must do so immediately. A delay in doing this may lead to your disqualification from the examination.**
- After the signal to stop working has been given, **wait in your lab space**. A supervisor will come to you and check off the following items as being **left behind:**
  - These 'Practical Exam' instructions.
  - All your answer sheets *plus* the sheet of graph paper from Task 3 in the envelope labelled with your student code. Do not seal the envelope.
  - Your chosen TLC plate in the Ziploc bag labelled with your student code.
  - The sample labelled 'RPA' from Task 1.
- **Do not leave** the examination hall until instructed to do so by the supervisors.

General Information

- **Safety** is of paramount importance in the laboratory. You should be following the safety rules given in the IChO regulations. **Safety glasses** and **lab coats** must be worn at **ALL TIMES**. **Gloves** should be worn during Task 1.
- If you behave in an unsafe way, you will be warned **once** before you are asked to leave the laboratory. You will not be allowed to return and will receive a score of zero for the entire experimental examination.
- The **problem booklet** is made up of 14 pages, within which there are **3 tasks**. You may do the tasks in any order you choose.
- The **answer booklet** is made up of 11 pages. You should write **your name and student code onto every answer sheet**. Do not attempt to separate the sheets.
- Your answers and working must **only be written in the spaces provided for them**. Anything written elsewhere will not be marked. Any calculations must be shown (calculators may be used). If you need to do **rough working**, use the back of the sheets.
- Numerical answers are meaningless without the appropriate units. You will be heavily penalised if units are not given where required.
- Use only the pens, pencil, rubber, ruler and calculator provided.
- If you make an error or break something and require **extra equipment, or chemicals**, ask a supervisor. Whatever you have requested will be provided, but after the first request **there will be a penalty of 1 of the 40 available practical points for each subsequent request.** Additional sheets of graph paper will be provided on request with no penalty.
- If you have any **questions** regarding the tasks or require a **refreshment/toilet break**, ask a member of staff.
- If you need to re-use glassware during the exam, clean it carefully at the closest sink to you.
- Solutions may be disposed of into the sink, **except EDTA and those containing copper or silver**. Please leave these on your bench or dispose of into the containers provided.
- The official English version of this examination is available on request if clarification is required.

Periodic table with relative atomic masses

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.102	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.55	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	57 La* 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.98	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac+															

***Lanthanides**	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
+Actinides	90 Th 232.01	91 Pa	92 U 238.03	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Apparatus per Student

Apparatus	Number
Task 1:	
Glass beaker (25 cm^3)	1
Large metal spatula	1
Small metal spatula	1
Flat ended glass rod	1
Suction pump	1
Buchner flask (250 cm^3)	1
Rubber ring seal for Buchner flask	1
Hirsch funnel	1
Vial for crude product A, labelled 'CPA'	1
TLC jar and lid with filter paper inside	1
TLC plates (in Ziploc bag labelled with student code)	3
TLC spotters	6
Conical flask (100 cm^3)	3
Magnetic stirring bar	1
Stirrer hotplate	1
Glass funnel (75 mm)	1
Spring test tube holder	1
Buchner funnel	1
Polystyrene tray (ice bath)	1
Vial for recrystallised product A, labelled with student code and 'RPA'.	1
Ziploc bag containing:	1
• pH paper and chart	1
• Filter paper for Hirsch funnel	2
• Filter paper for hot filtration	2
• Filter paper for Buchner funnel	2
Task 2:	
Burette (50 cm^3)	1
Measuring cylinder (25 cm^3)	1
Conical flask (250 cm^3)	4
Plastic funnel (40 mm)	1

Task 3:	
Tall plastic vessel	1
Conductivity meter	1
Rubber Pipette bulb (50 cm^3)	1
Pipette (50 cm^3)	1
Volumetric flask (250 cm^3)	1
Burette (50 cm^3)	1
Plastic funnel (40 mm)	1
Sheet of graph paper with labelled axes	1
For use in more than one task:	
Pencil	1
Marker pen	1
Envelope labelled with student code	1
Wash bottle containing distilled water (500 cm^3)	1
Bosshead	4
Clamps	4
Retort stand and rod (Zoology only)	3
Measuring cylinder (10 cm^3)	1
Tissue paper for cleaning	
Disposable plastic pipette (3 cm^3)	8
Shared equipment:	
UV lamp	
Balance (to 3 decimal places)	
Labelled waste containers for EDTA, copper, and silver waste	
Purple nitrile gloves in all sizes	

Chemicals on Each Desk

Chemical	R phrases	S phrases
Task 1:		
3,4-dimethoxybenzaldehyde: 0.50 g pre-weighed in vial labelled 'DMBA 0.5 g'.	22-36/37/38	22-24/25
1-indanone: 0.40 g pre-weighed in vial.	22	–
NaOH: 0.10 g pre-weighed in vial.	34-35	26-36-37/39-45
HCl (3.0M aqueous): 10 cm^3 in a 30 cm^3 bottle.	34-37	24-26-36-45
Diethyl ether:Heptane (1:1): 25 cm^3 in a 30 cm^3 bottle labelled 'Et_2O:Heptane (1:1)'.	Diethyl ether: 12-19-22-66-67; Heptane: 11-38-50/53-65-67	Diethyl ether: 9-16-29-33; Heptane: 9-16-23-29-33-60-61-62
Ethyl ethanoate: 1 cm^3 in a small vial.	11-36-66-67	16-26-33
Sample of 1-indanone dissolved in ethyl ethanoate: 1.0 cm^3 in small vial labelled '1-indanone in ethyl ethanoate'.	See above	See above
Sample of 3,4-dimethoxybenzaldehyde dissolved in ethyl ethanoate: 1.0 cm^3 in small vial labelled 'DMBA in ethyl ethanoate'.	See above	See above
Ethyl alcohol (9:1 mixture with H_2O): 100 cm^3 in a 125 cm^3 bottle labelled 'EtOH:H_2O (9:1)'.	11	7-16
Task 2:		
Inorganic complex: three samples of approximately 0.1 g, accurately pre-weighed in vials labelled 'Sample 1', 'Sample 2', 'Sample 3'.	22-25-36/37/38	26-28-37/39-45
Inorganic complex: three samples of approximately 0.2 g, accurately pre-weighed in vials labelled 'Sample 4', 'Sample 5' and 'Sample 6'.	22-25-36/37/38	26-28-37/39-45
pH 10 ammonia buffer: 10 cm^3 in a 30 cm^3 clear glass bottle labelled 'pH 10 ammonium buffer'.	20/21/22-36/37/38	26-36
Murexide indicator (solution in H_2O): 10 cm^3 in a 30 cm^3 clear glass bottle.	–	24/25
EDTA disodium salt (0.0200 M solution in H_2O): 150 cm^3 in a 250 cm^3 clear glass bottle.	22	36
Ethanoic acid: 10 cm^3 in a 30 cm^3 clear glass bottle.	10-35	23-26-45
2,7-Dichlorofluorescein indicator (solution in 7:3 EtOH:H_2O): 10 cm^3 in 30 cm^3 clear glass bottle.	36/37/38	26-36-37/39
Dextrin (2% in H_2O): 25 cm^3 in a 30 cm^3 bottle.	–	24/25
Silver nitrate (0.1000M solution in H_2O): 150 cm^3 in a 250 cm^3 brown glass bottle.	8-34-50/53	26-36-45-60-61
Task 3:		
Sodium dodecyl sulfate (99%): approximately 4.3 g, accurately pre-weighed in vial labelled 'SDS'.	22-36/37/38	26-36/37
Conductivity solution 'HI 70031': 20 cm^3 in pouch.	Non hazardous product	Non hazardous product

Risk Phrases

Indication of Particular Risks

R Number	Meaning
8	Contact with combustible material may cause fire.
10	Flammable.
11	Highly flammable.
12	Extremely flammable.
19	May form explosive peroxides.
22	Harmful if swallowed.
25	Toxic if swallowed.
34	Causes burns.
35	Causes severe burns.
36	Irritating to eyes.
37	Irritating to the respiratory system.
38	Irritating to skin.
65	Harmful: may cause lung damage if swallowed.
66	Repeated exposure may cause skin dryness or cracking.
67	Vapours may cause drowsiness and dizziness.

Combination of Particular Risks

R Numbers	Meaning
20/21/22	Harmful by inhalation, in contact with skin and if swallowed.
36/37/38	Irritating to eyes, respiratory system and skin.
50/53	Very toxic to aquatic organisms; may cause long term effects in the aquatic environment

Safety Phrases

Indication of Safety Precautions Required

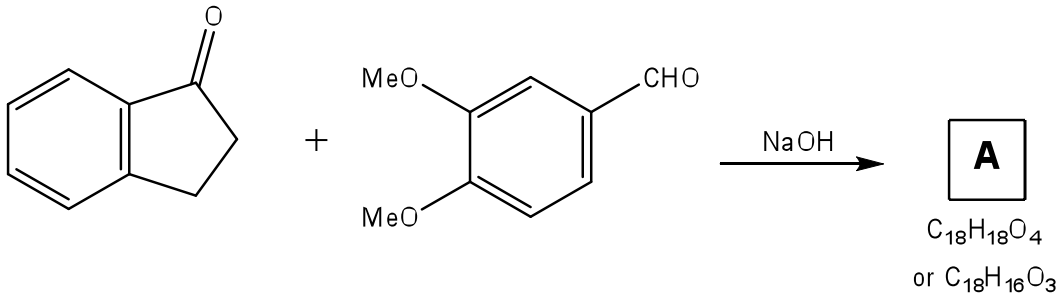
S Number	Meaning
7	Keep container tightly closed.
9	Keep container in a well ventilated place.
16	Keep away from sources of ignition. No smoking.
22	Do not inhale dust.
23	Do not inhale gas/fumes/vapour/spray.
24	Avoid contact with the skin.
26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
28	After contact with skin, wash with plenty of water.
29	Do not empty into drains.
33	Take precautionary measurements against static discharges.
36	Wear suitable protective clothing.
45	In case of accident or if you feel unwell, seek medical advice immediately (show label where possible).
60	This material and/or its container must be disposed of as hazardous waste.
61	Avoid release to the environment.
62	If swallowed, do not induce vomiting: seek medical advice immediately and show this container or label.

Combination of Safety Precautions Required

S Numbers	Meaning
24/25	Avoid contact with skin and eyes.
36/37	Wear suitable protective clothing and gloves.
36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
37/39	Wear suitable gloves and eye/face protection.

Task 1 – An Environmentally Friendly Aldol Condensation

In attempts to become more environmentally friendly, increasing attention is being paid to minimising the large amounts of solvents used in chemical reactions. In the following experiment, an aldol condensation reaction is carried out in the absence of solvent.



1. Add 3,4-dimethoxybenzaldehyde (DMBA 0.50 g, 3.0 mmol) and 1-indanone (0.40 g, 3.0 mmol) to a 25 cm^3 beaker. Use a metal spatula to scrape and crush the two solids together until they become a clear oil.

2. Add NaOH (0.1 g, 2.5 mmol) to the reaction mixture, crush any lumps formed and continue scraping and crushing until the mixture becomes solid.

3. Allow the mixture to stand for 20 minutes. Then add 4 cm^3 HCl (3 M aqueous) and scrape around the beaker so as to dislodge all product from the walls. Use a flat-ended glass rod to crush any lumps present.

a) Measure and <u>record</u> the pH of the solution.

4. Isolate the crude product using vacuum filtration through a Hirsch funnel. Rinse out the beaker with 2 cm^3 HCl (3 M aqueous) and pour over the crude product in Hirsch funnel to wash, continuing to pull air through the solid for 10 minutes to facilitate drying.

b) <u>Report</u> the mass of the crude product (which may still be a little wet), using the vial labeled 'CPA' as a container.

5. Take a TLC to assess whether the reaction is complete, using Et_2O:heptane (1:1) as the eluant. Solutions of both starting materials in ethyl ethanoate are provided. The crude product is soluble in ethyl ethanoate. [Note: three TLC plates are provided. You may use them all, but you must only submit *one* in your labelled Ziploc bag. This should be the plate that you draw in your answer booklet.]

c) Using UV light to visualize, draw around the spots on the plate in pencil to show where they are, copy your plate onto the answer sheet, and place your plate in the Ziploc bag labeled with your student code. Determine and record the relevant R_F values.

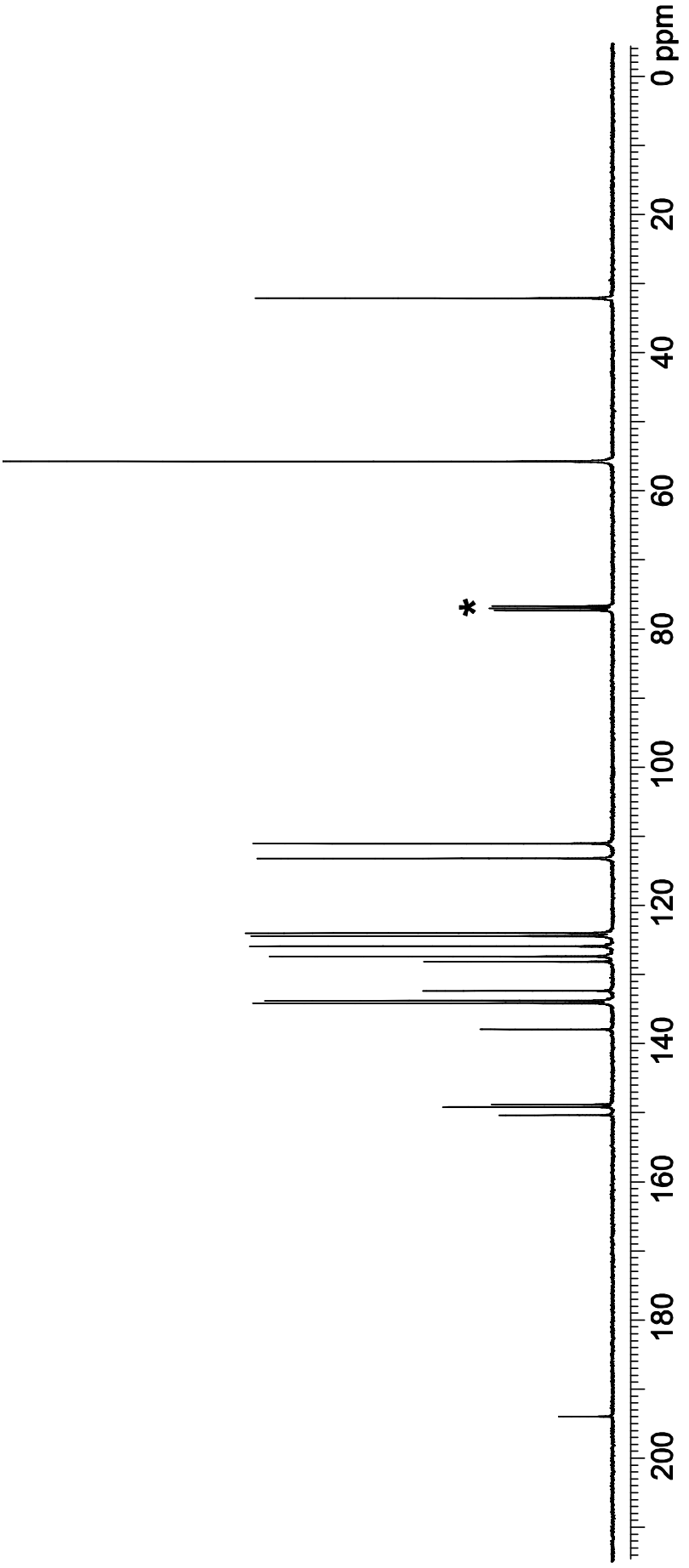
6. Using a 100 cm^3 conical flask with a stir bar in the bottom, recrystallise the product from 9:1 EtOH:H_2O (N.B. A hot filtration, using the glass funnel provided, is required as part of this process to remove small amounts of insoluble impurities). Any lumps may be crushed using the flat-ended glass rod. Allow the conical flask containing the filtered solution to cool to room temperature and then cool in an ice bath (use the polystyrene tray to make the ice bath in) for one hour before filtration through a Buchner funnel to collect your product. Suck air through for 10 minutes to dry the product. Place your product in the vial marked with your code and labeled 'RPA'.

d) Report the mass of the purified product.

e) Determine the potential structures for Product **A**, using the information on the answer sheet.

f) The ^{13}C NMR spectrum for **A** is shown on the next page. Peaks due to the solvent, $CDCl_3$, are marked with an asterisk. With the aid of the spectrum, decide which is the correct formula for **A**. Mark your answer on the answer sheet.

g) Calculate the percentage yield of the purified product, based on the formula you gave for its structure.


0 ppm
20
40
60
80
100
120
140
160
180
200
*

Task 2 – Analysis of a Copper(II) Complex

You are provided with a sample of an inorganic copper(II) complex, the anion of which is made from copper, chlorine, and oxygen. The counter ion is the tetramethyl ammonium cation. There is no water of crystallisation. You are required to determine proportions of copper ions and chloride ions by titration and hence determine the composition of the complex

Titration to determine the proportion of copper ions

1. You are provided with three accurately pre-weighed samples of copper complex, each of approximately 0.1 g. These are labeled "Sample 1", "Sample 2", "Sample 3", together with the exact mass of the copper complex. Take the first of these, note down the mass of the sample and quantitatively transfer the contents to a 250 cm^3 conical flask using approximately 25 cm^3 of water.

2. Add pH 10 ammonia buffer solution until the precipitate which forms initially just redissolves (about 10 drops).

3. Add 10 drops of the murexide indicator.

4. Titrate with the 0.0200 mol dm^{-3} EDTA solution until the solution turns violet and the colour persists for at least 15 seconds. Record the volume of solution used in the titration.

5. Repeat if necessary with samples 2 and 3.

Note: you will be marked only on a single value you report in the answer booklet. This may either be an average value, or a single value you feel most confident in.

a) Calculate the volume of EDTA solution needed to react completely with 0.100 g of complex.

b) Give an equation for the titration reaction.

c) Calculate the percentage by mass of copper in the sample.

You will need to wash out your burette before you start the titration for the determination of chloride ions. Any remaining EDTA solution may be disposed of into the waste containers labelled 'EDTA'.

Titration to determine the proportion of chloride ions present

1. You are provided with three accurately pre-weighed samples of copper complex each of approximately 0.2 g. These are labeled "Sample 4", "Sample 5", "Sample 6", together with the exact mass of the copper complex. Take the first of these, note down the mass of the sample and quantitatively transfer the contents to a 250 cm^3 conical flask using approximately 25 cm^3 of water.

2. Add 5 drops of ethanoic acid, followed by 10 drops of dichlorofluorescein indicator and 5 cm^3 dextrin (2% suspension in water). N.B. Shake the bottle well before adding the dextrin suspension.

3. Titrate with the 0.1000 mol dm^{-3} silver nitrate solution, swirling constantly until the white suspension turns pink and the colour does not disappear after swirling.

4. Repeat if necessary.

Note: you will be marked only on a single value you report in the answer booklet. This may either be an average value, or the value you feel most confident in.

d) Calculate the volume of silver nitrate solution needed to react completely with 0.200 g of complex.

e) Give an equation for the titration reaction.

f) Calculate the percentage by mass of chloride ions in the sample.

The percentage of carbon, hydrogen and nitrogen in the complex was determined by combustion analysis and found to be as follows:

Carbon: 20.87 %	Hydrogen: 5.17 %	Nitrogen: 5.96 %

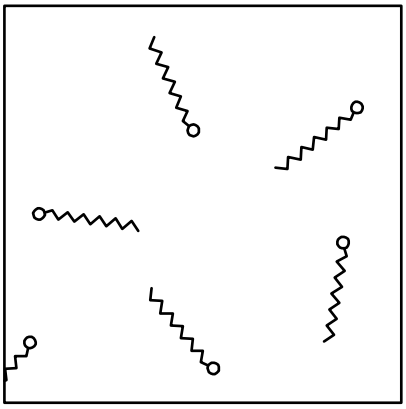
g) Mark in the answer booklet, which element in the complex has the greatest percentage error in the determination of its proportion.

h) Determine the formula of the copper complex. Show your working.

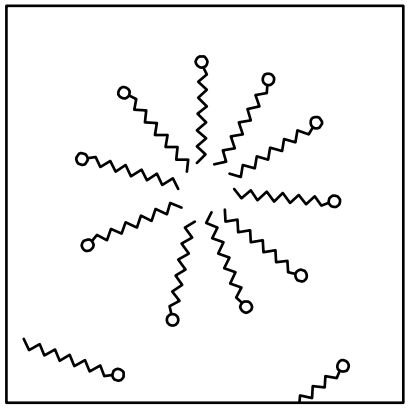
Task 3 – The Critical Micelle Concentration of a Surfactant

Surfactants are used extensively in many everyday cleaning products, such as shampoos or detergents for washing clothes. One such surfactant is SDS, sodium *n*-dodecyl sulfate, $CH_3(CH_2)_{11}OSO_3Na$ (Relative Molecular Mass: 288.37).

Very dilute aqueous solutions consist of solvated individual molecules of SDS. However, if the concentration is gradually increased beyond a specific concentration, the concentration of monomeric SDS does not change, but instead the surfactant begins to form clusters known as *micelles*. It is these micelles that assist in the removal of grease and dirt. The concentration at which the micelles form is called the *critical micelle concentration*. This process is shown schematically in the figure below.



low SDS concentration
free monomer only



high SDS concentration
micelles and some free monomer

In this experiment, you will determine the critical micelle concentration of SDS by measuring the conductivity of different concentrations of SDS.

1. You are provided with approximately 4.3 g SDS, accurately pre-weighed in a vial, a 250 cm^3 volumetric flask, a 50 cm^3 burette, 50 cm^3 bulb pipette, a conductivity meter, conductivity solution (used only for calibration), and a tall plastic vessel.

2. You need to measure the conductivity (σ, in $\mu S\ cm^{-1}$) of various concentrations of aqueous SDS (c, up to 30 mmol dm^{-3}). [Note: you may assume all volumes are additive.]

a) Give the concentration of your stock SDS solution.

b) Use the table given in the answer booklet to record your results and plot a suitable graph to determine the critical micelle concentration (CMC) on the paper provided.

c) State the concentration at which micelles begin to form (the critical micelle concentration).

Notes

1) Solutions of SDS readily form bubbles if shaken.

2) The conductivity meter needs at least 50 cm^3 of solution to be inside the plastic vessel in order to work correctly.

3) To calibrate the meter:

   - Switch the meter on by pressing the ON/OFF button once.
   - Press and hold the ON/OFF button again, this time for about 3 seconds, until you see the letters 'CAL' on the screen, indicating that the calibration mode has been entered. Let go of the ON/OFF button and '1413' will start blinking on the display. To calibrate, carry out the next step immediately, before the meter has reverted back to reading '0' on the screen (meaning you have exited the calibration mode)
   - Immerse the probe in the pouch containing the 'HI 70031' calibration solution, without exceeding the maximum immersion level.
   - Stir gently and wait for about 20 seconds to confirm the reading.
   - Once the display stops blinking, the meter is calibrated and ready for use.
   - Rinse the meter with distilled water and dry before making measurements.

4) To record the reading:

   - Switch the meter on by pressing the ON/OFF button
   - Immerse the probe in the sample without exceeding the maximum immersion level and being above the minimum immersion level.
   - Stir gently and wait for the reading to stabilize. The meter automatically compensates for temperature variations.
   - The conductivity value of the sample will be shown on the LCD.