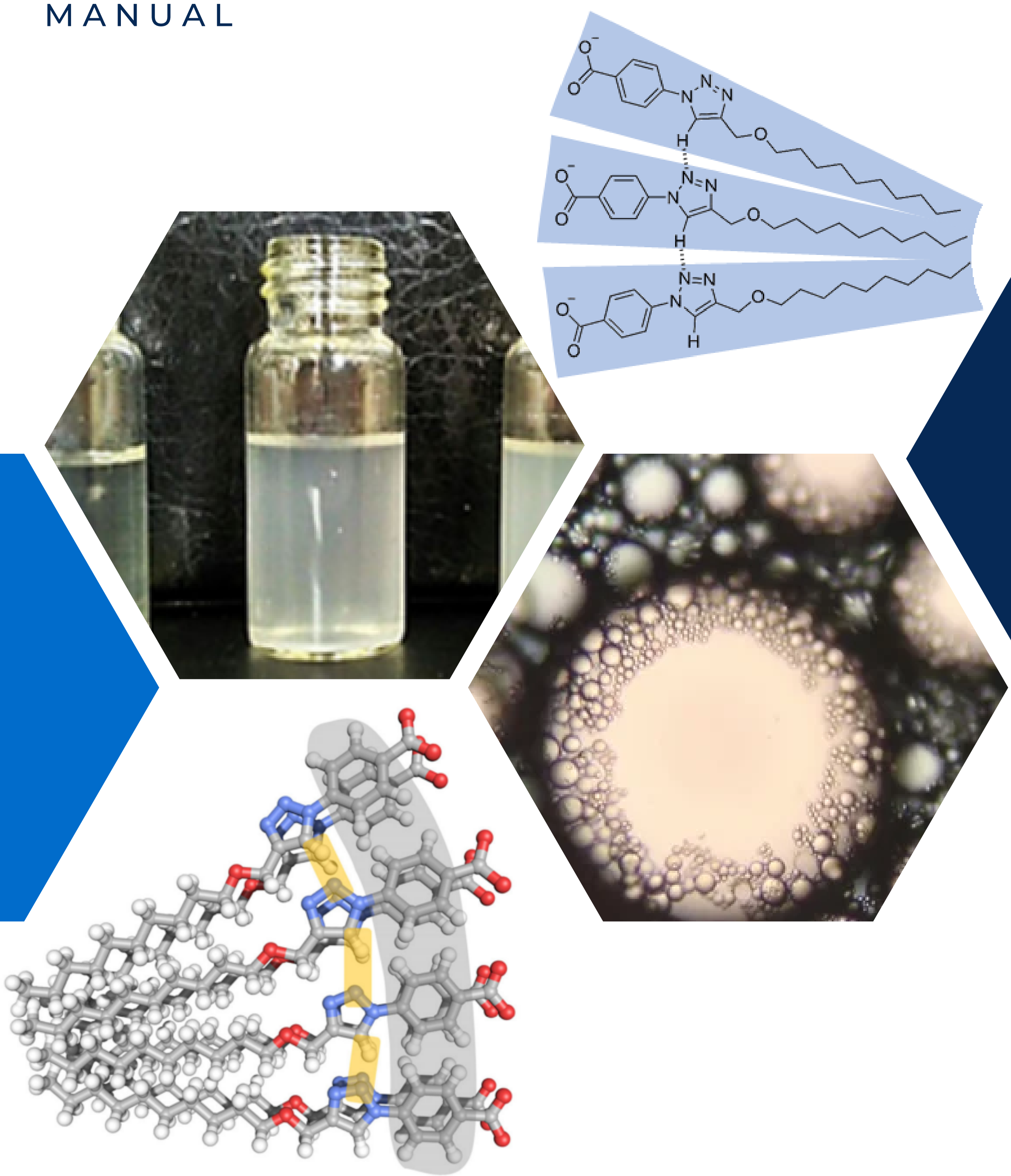
UNIVERSITI
MALAYA

SIC3042
COLLOID CHEMISTRY

LABORATORY
MANUAL



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Introductory Note

An experiment in physical chemistry is designed with the aim to illustrate the basic principles in chemistry. Typically, every experiment will be accompanied by its background and underlying theory, detailed experimental procedure and suggestions on methods to analyse the results followed by a brief discussion.

Before the laboratory session, please **READ** the General Laboratory Instruction which provides the basic principles in physical methods. In the General Laboratory Instruction, you will first be introduced to the basic idea of measurements, standards and associated quantitative aspects such as units, dimensionalities, symbols, and uncertainty. This is followed by accuracy, precision, data analysis, error estimation, general equipment and tools, and scientific writing. It intends to give the necessary background discussion which you MUST read before entering the laboratory. It is also important that you continue to practice the advice given here not only during your study but throughout your lifetime as a scientist. Of course, the brief manual is by no means complete. You may refer to a more elaborate introduction on similar subject in most general chemistry textbooks. There are also many sources on the Internet which you can browse through.

The colloid chemistry experiments designed here are to accompany the colloid chemistry lecture courses. Through these experiments you will experience measuring some of the physical properties of interest with known precision. Moreover, they will allow you to understand the concept behind the measurements and how to relate experimental results to the basic concepts in the lecture courses.

The quantitative measurements you have made produces numerical values which are subject to error due to many reasons such as the nature of the instrument and how the experiment is designed. Thus, it is equally important to repeat the experimental procedure a few times until the result is consistent. Sometimes the experimental procedure may be varied to check for convergence of the values by different methods. In addition to these, a physical chemist must estimate the value of error in his measurement to get improved accuracy of the measured value compared to a standard value.

A good laboratory practice is to process the raw data immediately to get a rough idea of the results of the experiment immediately. By doing so, anything which deviates from expectation may be checked immediately before dismantling the experimental set up. For example, graph should be plotted roughly during the laboratory. Should a linear behavior be expected and some points are found to deviate, then the experiments related to these odd data points may be repeated immediately.

Laboratory report should be processed immediately for two obvious reasons. First, if the processed result is unsatisfactory, the experiment may be repeated immediately. Secondly, since the detail information about the experiment is fresh in memory a better report will be produced.

Important Information

Further information about the details of the safety and health practice in Universiti Malaya can be found at:

Occupational Safety & Health and Environment (OSHE), Universiti Malaya

Universiti Malaya Laboratory Safety Guidelines

Manual Keselamatan dan Kesihatan Pekerjaan, Universiti Malaya

The University has a statutory obligation to comply with the safety requirements and you, as a student, have a duty to abide by the regulations. The following notes are to guide you in good laboratory practice and to familiarise yourself with the safety aspects of your laboratory work.

Emergency Telephone Numbers

National Emergency Number	999 (Mobile phone, dial 112)
Universiti Malaya Security Office	+603 7967 7070
Universiti Malaya Medical Centre (UMMC) Emergency Department	+603 7949 2892
Universiti Malaya Students' Health Clinic	+603 7967 6445
Occupational Safety & Health and Environment (OSHE)	+603 7967 6597
Department of Chemistry Office	+603 7967 4204
Pantai Fire Station (Jalan Pantai Baharu)	+603 2282 4444
Pantai Police Station (Jalan Pantai Baharu)	+603 2282 2222

Laboratory Safety Rules

Safety is the primary concern in any chemical laboratory. Chemicals, particularly organic chemicals, are almost all potentially hazardous. Fortunately, with sensible and correct precautions, the risks can be minimised if certain basic safety practices are followed. The responsibility for laboratory safety lies with everyone working in the particular laboratory. Sensible laboratory conduct does not mean memorizing a list of rules! The true test is the actual conduct in the laboratory and safety rules apply to all laboratory activities. Each person's safety is affected by the action of fellow workers in the laboratory. Therefore, it is in everyone's best interest to follow safety work practices. The guidelines below are recommended for working safely in the laboratory:

- Know the location of all exits for the laboratory and the building.
- Know the location of the alarm and fire extinguishers and how to operate them.
- Know the location and use of safety showers, eye-washes and safety aid boxes.
- Know the location of the nearest telephone that can be used during an emergency.
- Never work alone in the laboratory. If you must work alone, make someone is aware of your location and let him or her call or check on you periodically.
- **Safety glasses or goggles *must be worn at all times.*** You might find them a nuisance to wear, but your eyes are very precious.
- If you wear contact lenses, try to avoid wearing them in the laboratory. If you must wear contact lenses, your goggles must seal particularly well to your face.
- Do not eat, drink or smoke in the laboratory.
- Wear protective clothing in the laboratory. Basically this includes laboratory coats, safety glasses, proper shoes and gloves (if necessary).
- Long hair should be tied back. Other articles of clothing that may become entangled should also be secured.
- Do *NOT* smell or taste chemicals. If your need to determine the odor of any chemical, waft it gently towards your nose with your hand – do not stick your nose in the container and inhale.
- Know the potential hazards of the materials and equipment with which you will work.
- Follow good housekeeping practices, that is, clean up as you go. Work areas must be kept clean. Do not clutter the work areas, aisles and exits.
- Store away apparatus that are not in immediate use, either in a cupboard or storeroom.
- Wash hands carefully before leaving the laboratory.
- Do not wear laboratory coats, gloves or other personal protective clothing out of the laboratory and into non-laboratory areas. This clothing may have become contaminated.
- Report all accidents and injuries, however small, immediately to the lecturer-in-charge or demonstrator or the laboratory assistants.
- In the interest of safety and security, work is permitted only during scheduled laboratory periods.
- Dispose of organic chemicals only in designated waste bottles. Chemical wastes are segregated into three groups and stored separately, viz, halogenated wastes (examples are chloroform, dichloromethane, carbon tetrachloride), non-halogenated wastes (examples are acetone, alcohol, toluene, xylene) and other wastes such as mercury and organometallics.

Additional Guidelines for Students

Remember that in a laboratory you have fellow students opposite you and by the side of you. They do not know what you are doing, but they hope and expect that what you are doing is sensible and safe. Always think carefully about what you are about to do:

- Know the lecturer-in-charge and the laboratory workers of the laboratory.
- Undergraduates are not allowed to work or even be in any of the teaching laboratories at any time outside of the specified laboratory hours, unless they have explicit permission from the lecturer-in-charge. This includes before and after class and during lunch hour.
- Come to laboratory periods on time and be prepared by studying the experiment and planning your activities before you come to the laboratory.
- Write everything you do and see in your notebook so that you can trace your actions and make corrections if necessary.
- Do **NOT** use cracked or broken glassware. Check glassware before using it.
- Never use open flames, unless instructed by the lecturer-in-charge. If flames are permitted, plan your experiments so that you never leave your flame unattended. There are other sources of heat such as steam-baths and hot plates.
- Handle all chemicals with care and read labels before attempting to get them.
- Use a spatula to get solid chemicals. *Never* use your fingers.
- Be careful not to contaminate reagents with your spatulas or droppers. If you take too much of a chemical or reagent, give it to a fellow student - do no return it to the bottle.
- Do not wander off with the only bottle of a reagent that everyone needs; keep it in its assigned location. Do not pipette by mouth. Use only mechanical pipetting devices.
- Never look directly into the mouth of a flask containing a reaction mixture.
- Never point a test tube or reaction flask towards yourself or your neighbour.
- When using a separating funnel, vent frequently and remove the stopper immediately upon setting it upright for separation.
- **Never use a thermometer as a stirrer!** If a mercury thermometer breaks, immediately contact the lecturer-in-charge or the demonstrator.
- Turn off water, burners or electrical equipment when not in use.
- Wash your glassware at the end of the laboratory day. You will have clean and dry glassware ready to go for the next laboratory class.
- Make sure glassware or equipment is kept in the correct locker - your personal locker or the common locker.
- Clean your work area and equipment used before leaving the laboratory.

Contents

Experiment 1: Adsorption from Solution

Theory

An important phenomenon of interface or surface is that known as *adsorption*. It describes the tendency of a chemical species to accumulate in the immediate vicinity of an interface. The result is that a higher concentration of the chemical species will be found at the interface compared to that in the bulk of the medium. Thus, when a solid is in equilibrium with a gas, the gas is usually more concentrated in the region of the solid surface than in the free gas phase. The process by which this surface excess is formed is termed *adsorption*. The chemical species adsorbed (e.g. gas molecules) are called **adsorbates** whereas the adsorbing materials (e.g. the solid) are termed **adsorbents**.

The nature of the forces between the adsorbed molecules and the adsorbent is the main factor in determining the type of adsorption process. These forces may be of the van der Waals type or they may arise from the formation of chemical bonds between the adsorbed molecules and the adsorbent. In the former, the adsorption is called *physisorption* (physical adsorption) whereas the latter is termed *chemisorption* (chemical adsorption).

Adsorption from solution can take place at any of the three interfaces: liquid-vapour, liquid-liquid and liquid-solid. Different experimental methods of measuring adsorption are used for the above. For the liquid-solid interface, emphasis is centred on the change in concentration of the bulk liquid, whereas for the other two interfaces, the emphasis is on interfacial (surface) tension, a property of the interface itself.

Most studies of adsorption from solution have been concerned with equilibrium conditions. The amount of substances adsorbed at the liquid-solid interface decreases with rise of temperature. Since all adsorption increases with the concentration of the adsorbate, the relationship between the amount adsorbed (x) and the equilibrium concentration (c) is known as the **adsorption isotherm**. The adsorption isotherm describes the variation of the surface coverage with the adsorbate concentration at a chosen temperature.

Isotherms are essentially plots of the free energy change as a function of the amount adsorbed. Their shape can yield qualitative information about the adsorption process and a semi-quantitative measure of the fraction of the surface covered by the adsorbate. Numerous attempts have been made at developing mathematical expressions from postulated adsorption mechanisms to fit the various experimental adsorption isotherms. The *Freundlich* and the *Langmuir* isotherms are two such expressions.

The Freundlich isotherm is one of the first equations proposed to relate the amount of material adsorbed to the equilibrium concentration of the material in the solution:

$$x = Kc^n \tag{1}$$

where x is the amount adsorbed per g of adsorbent, K and n are constants at a fixed temperature and are characteristic of the particular system which is studied. The Freundlich isotherm fails if the concentration of the adsorbate is too high.

On the other hand, the Langmuir isotherm can be derived from a kinetic consideration of the condensation and evaporation of gas molecules from the surface under certain assumptions. It takes the following form:

$$\begin{aligned} \frac{x}{x_m} &= \frac{\alpha c}{1+\alpha c} \\ \alpha &= \frac{k_a}{k_d} \end{aligned} \tag{2}$$

where x_m is the amount adsorbed per g of adsorbent upon a completion of a monolayer, α is a constant known as the adsorption coefficient, k_a and k_d are the adsorption and desorption rate constants, respectively.

Equation (2) may be rearranged to give:

$$\frac{1}{x} = \frac{1}{x_m} + \frac{1}{\alpha x_m} \cdot \frac{1}{c} \tag{3}$$

Both isotherms were originally derived for the adsorption of gases upon solid surfaces. However, the Langmuir isotherm is generally more successful in interpreting the data than is the Freundlich isotherm if only a monolayer is formed.

This experiment involves the study of the adsorption of (a) oxalic acid and (b) acetic acid from solution onto a charcoal powder. The aim of the experiment is to test the validity of the Freundlich and Langmuir isotherms for these systems.

Procedure

Adsorption of Oxalic Acid

Prepare 500 mL of 0.1 M oxalic acid solution and titrate 10 mL portions with approximately 0.02 M $KMnO_4$ solution in the normal way (adding equal volume of dilute sulphuric acid into the oxalic acid solution and warming to 80 °C). Hence, standardise the $KMnO_4$ solution.

Clean and dry 7 stoppered bottles and weigh accurately into each about 0.5 g of granulated charcoal. To the first bottle, add 50 mL of oxalic acid and 50 mL of distilled water. Place the bottle in a shaker and shake for successive 15-minute periods. Pipette out a 10 mL sample after each shaking and titrate with the standardised $KMnO_4$ solution (These tests will show how rapidly adsorption is achieved). Note the time required for a constant concentration to be achieved. In the main set of experiments, shake the bottles for at least 50% longer than the minimum time indicated above.

Meanwhile, into the other 6 bottles add 100, 80, 60, 20, and 10 mL of oxalic acid solution by burette and make up to 100 mL with appropriate amounts of distilled water. Shake the bottles for the time mentioned above and filter the contents through small filter papers, rejecting the first 10-20 mL of filtrate in case there should be any adsorption of oxalic acid or water on the filter paper. Titrate two 20 mL portions from each bottle and hence calculate the number of moles of acid adsorbed per g of charcoal. For each titration, add equal volume of dilute H_2SO_4 solution to the flask warmed to 80 °C and titrate against standard $KMnO_4$ solution from the burette. End point will be marked by the appearance of a light pink colour.

Adsorption of Acetic Acid

Use the standard acetic acid solution provided to standardise the sodium hydroxide solution using phenolphthalein indicator. Weigh out 0.50 ± 0.02g of granulated charcoal into each of the 8 clean, dry stoppered bottles and by means of a burette, add standard acetic acid solution and distilled water as follows:

Table 1 Volume of acetic acid and water required

Bottle	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Volume of acetic acid / mL	100	70	40	30	20	10	5	0
Volume of water / mL	0	30	60	70	80	90	95	100

Stopper each bottle and shake contents for 45 minutes. Each solution should be in contact with the charcoal for the same period of time. Filter each solution through a dry filter paper, rejecting the first 10 mL of each filtrate. Titrate 10 or 20 mL of each filtrate in turn against the standardised NaOH solution. Carry out each titration in duplicates.

Calculate the total amount of g of free acetic acid in 100 mL of each of solution 1-7 (after allowing for the acid titration in water) when in equilibrium with the charcoal, and hence determine the amount adsorbed.

Report

The applicability of the Freundlich and Langmuir adsorption isotherms should be tested by appropriate plots and the respective constants obtained.

Explain how the experiment could be adopted to determine the heat of adsorption of oxalic acid onto charcoal.

Experiment 2: Investigation of the Properties of a Colloidal Surfactant. I. Effect of a Second Component on the CMC of a Surfactant

Theory

Colloidal surfactants are comprised of molecules possessing both lyophobic (solvent-hating) and lyophilic (solvent-liking) properties and may be anionic, cationic, non-ionic or amphoteric. Typical examples are shown in Table 2:

Table 2 Classification and examples of surfactants

Surfactant Type	Example
Anionic	Sodium dodecyl sulphate $C_{12}H_{25}SO_4^-Na^+$
Cationic	Dodecyl trimethyl ammonium bromide $C_{12}H_{25}N^+(CH_3)_3Br^-$
Non-ionic	Polyoxyethylene dodecyl ether $C_{12}H_{25}O(CH_2CH_2O)_nH$
Amphoteric (or zwitterionic)	Sodium dodecyl amino propionate $C_{12}H_{25}NHCH_2CH_2COO^-Na^+$

Studies of ionic surfactant solutions have revealed a most unusual phenomenon. At low concentrations, they behave as strong electrolytes. However, as the concentration is increased, a point is reached when the physical properties such as surface tension, conductivity, turbidity and osmotic pressure abruptly change. From observation of osmotic pressure values, it seemed that considerable association must be taking place as the values of the molecular weight evaluated were considerably higher than that for a single molecule. At the same time, however, the conductivity was still high showing that ionic dissociation was still in force.

McBain suggested that this seemingly anomalous behaviour could be explained by the formation of organised aggregates of the surfactant molecules known as *micelles.* The micellisation process is a direct consequence of the dual character of the surfactant molecules. The concentration above which micelle formation begins is termed the *critical micelle concentration* (CMC). Further increase in the concentration of surfactant beyond this point increases the number of micelles while the concentration of simple surfactant species remains constant.

The ease with which surfactant molecules form micelles is to a great extent dependent on its molecular structure. Factors such as electrostatic repulsion between polar head groups, hydrocarbon-water interfacial energy and the tendency of the solvent to hydrogen bond all affect the micellisation process. Other factors which affect the values of the CMC in aqueous solutions are temperature, pH and additives. The effects of numerous additives on the CMC have been studied (e.g. a second surfactant, alcohols, hydrocarbons, simple electrolytes, etc.). An understanding of the effects of a second surfactant is important in that most commercially prepared surfactants are mixtures of two or more homologs. Many such surfactants also contain long-chain alcohols as impurities, small quantities of which can considerably affect the properties.

A study of the effects of short-chain alcohols helps in understanding some of the factors involved in micellisation. In short, the CMC change gives us information on the effect of additives on the surface activity of the additives and provides a clearer understanding of the action of surfactants.

The methods available for the determination of CMC values are many and varied. Most of the physicochemical property changes can be used for its determination, provided the measurements of the particular property can be carried out accurately. In this experiment, the CMC of sodium dodecyl sulphate (SDS) aqueous solution will be determined using **one** of the methods given below. The effect of simple electrolyte on the CMC of this surfactant will then be investigated.

Procedure

For this experiment, all glassware must be thoroughly cleaned with chromic acid solution, followed by rinsing with distilled water. Excess water should be drained off and the last drop removed by touching with a slip of filter paper.

Method A: Surface Tension Measurement by du Nouy Tensiometer

An approximately 5.0×10^{-2} mol dm^{-3} solutions of SDS should be prepared by dissolving an accurately weighed amount of surfactant in distilled water using a 100-mL graduated flask. To aid dissolution, the solution may require warming to about 40 °C. A further 8 solutions (50 mL each) should be prepared in the range 2.5×10^{-2} to 5.0×10^{-4} mol dm^{-3} by appropriate dilution of the stock solutions. Repeat with another two series of 9 solutions of SDS in the presence of 1×10^{-2} and 1×10^{-1} mol dm^{-3} sodium chloride, respectively.

The du Nouy tensiometer should be zeroed and calibrated before hand following the instructions in the instrument manual (available upon request from the Laboratory Assistant).

The glass vessel, containing a little of the most dilute surfactant solution, should then be placed on the circular table. After about 5 minutes, a steady value of surface tension should be measured by the method given in the manual. At least three readings of the surface tension should be taken and a mean value calculated. The measurements are to be repeated with the other solutions.

Construct a plot of surface tension versus log[SDS] and deduce the CMC from the discontinuity in the curve.

NOTE: All pure surfactants are *expensive* chemicals. So, be extremely *thrifty* about them. DO not throw away the SDS solution containing no sodium choride. They can still be used to prepare those in the presence of 1×10^{-2} mol dm^{-3} sodium chloride.

Method B: Spectral Change of a Dye

Surfactants may cause the absorption spectrum of a dye solution to change in such a way that the CMC of the surfactant may be determined from the changes. The spectral changes may be followed spectrophotometrically.

Prepare all your SDS and their dilution with the 1×10^{-5} mol dm^{-3} methylene blue solution provided instead of distilled water. Prepare in this manner 8 SDS solutions of concentration ranging from 5.0×10^{-2} to 5.0×10^{-4} mol dm^{-3} (use 25 mL standard flasks except the stock solution (50 mL) of 3.0×10^{-2} $\mathrm{mol\,dm^{-3}}$ SDS). All these solutions will then contain a fixed concentration of methylene blue (i.e. 1×10^{-5} $\mathrm{mol\,dm^{-3}}$). Record the absorbance of these solutions over the wavelength range of 600-700 nm with an Ultraviolet-Visible (UV-Vis) spectrophotometer (1 cm cells). Construct a plot of absorbance at 660 nm of methylene blue versus SDS concentrations. Deduce CMC values of SDS from the discontinuity in the curve.

Repeat with another two series of 9 solutions of SDS in the presence of 1×10^{-2} $\mathrm{mol\,dm^{-3}}$ sodium chloride, respectively. The concentration range for the SDS is the same as that indicated in Method A. Obtain the UV-Vis spectra of all these solutions as outlined above. Deduce the CMC and plot ln(CMC) vs ln(counterion concentration). Comment on the shape of the curve.

Consult the lecturer as to which of the two methods should be employed for your experiment.

Experiment 3: Investigation of the Properties of a Colloidal Surfactant. II. Effect of Temperature on the Micellisation by Conductivity Measurement

Theory

One property common to all surfactants is their ability to aggregate in solution to form particles of colloidal dimensions called *micelles*. In addition, the majority of them also ionise in solution, and thus the term "Colloidal Electrolyte" is frequently applied to them. These materials are characterised by both lyophobic and lyophilic regions in their chemical structure. The surface active ion arises from the ionisation of such a molecule is termed an *amphipathic ion* by Hartley.

At very low concentrations, the ionic surfactant behaves like any other strong electrolyte. It is completely dissociated and its physical properties approach ideality at infinite dilution. Thus in this region, the molar conductivity falls in accordance with the predictions of the Debye-Hückel-Onsager theory for strong electrolytes. On reaching the CMC, a sharp fall in the molar conductivity occurs due to micelle formation. Thus, the CMC can be deduced from the intersection of the straight lines extrapolated from conductivity measurements obtained below and above the CMC. In practice, a curvature instead of a sharp break in the curve at the CMC region is observed, indicating that micelles actually form over a *narrow* concentration region rather than at a particular concentration, and the quoted CMC is an average value for the region. From a detailed study of the transport numbers of the amphipathic ion and the counter ion, and the overall molar conductivity, Hartley was able to learn much about the structure of micelles.

The behaviour of the conductivity of sodium dodecyl sulphate (SDS) as a function of concentration will be investigated in this experiment. The experiment is then repeated at two different temperatures. Increased thermal motion of surfactant molecules in solutions at higher temperatures may generally be expected to decrease the tendency to form micelles and hence increase the CMC. From the experimental data, the enthalpy and entropy of micellisation can be calculated.

Procedure

All glassware must be thoroughly cleaned with chromic acid solution followed by rinsing with distilled water.

An approximately 2×10^{-2} mol dm^{-3} solution of SDS should be prepared by dissolving an accurately weighed amount of surfactant in 0.01 mol dm^{-3} sodium chloride solution using a 250 mL graduated flask. To aid dissolution, the solution may require warming up to ca. 40 °C.

A further 8 solutions should be prepared in the range 1.5×10^{-2} to 5.0×10^{-4} mol dm^{-3} by appropriate dilution of the stock solution with 0.01 mol dm^{-3} NaCl solution as before.

Determine the conductivity of each solution using the conductivity meter at 30, 40 and 50 °C. This can be done by placing a glass vessel containing a sufficient volume of the solution in each thermostatted water-bath. Dip the conductivity cell into each glass vessel in turn to enable conductivity reading to be taken when the solutions are well-equilibrated. The instruction for the operation of the conductivity meter is provided. Read this carefully before operating the instrument. You should begin with the solution of the lowest SDS concentration.

Data Treatment

Plot both the conductivity and the molar conductivity against the square root of the SDS concentrations. Explain the shape of the curves and deduce the CMC of the SDS for each temperature.

The heat of micelle formation (ΔH_m) can be calculated from the temperature dependence of the CMC. If we assume that micelles can be treated as a phase and that the CMC is a saturation concentration of molecularly dispersed molecules, we obtain

$$\Delta H_m = -nRT^2 \left(\frac{\partial \ln(\mathrm{CMC})}{\partial T} \right)_P \tag{4}$$

for an ionic surfactant, where n is 1 for complete ion exchange and 2 when no ion exchange occurs (i.e. the micelle has the same number of counterions and amphipathic ions). When excess salt is present with one ion in common with the surfactant, the concentration of counterions does not change with the CMC, and the micelle forming ion will have a constant activity coefficient independent of ion exchange and equation (4) becomes

$$\Delta H_m = -RT^2 \left(\frac{\partial \ln(\mathrm{CMC})}{\partial T} \right)_P \tag{5}$$

It follows that the Gibbs free energy of micellisation, ΔG_m is

$$\begin{aligned} \Delta G_m &= RT \ln(\mathrm{CMC}) \\ \text{and} \quad \Delta G_m &= \Delta H_m - T\Delta S_m \end{aligned} \tag{6}$$

where ΔS_m is the entropy of micellisation.

Plot ln(CMC) against temperature for the above system. From the curve, deduce both the enthalpy and entropy of micellisation for SDS.

Experiment 4: Steric and Electrostatic Stabilisation Mechanisms of Colloidal Dispersions

Theory

DLVO theory (named after Boris Derjaguin and Lev Landau, Evert Verwey and Theodoor Overbeek) suggests that the stability of a colloidal system is determined by the sum of the van der Waals attractive (V_A) and electrical double layer repulsive (V_R) forces that exist between particles as they approach each other due to the Brownian motion they are undergoing. This theory proposes that an energy barrier resulting from the repulsive force prevents two particles approaching one another and adhering. But if the particles collide with sufficient energy to overcome that barrier, the particles adhere together (Figure 1).

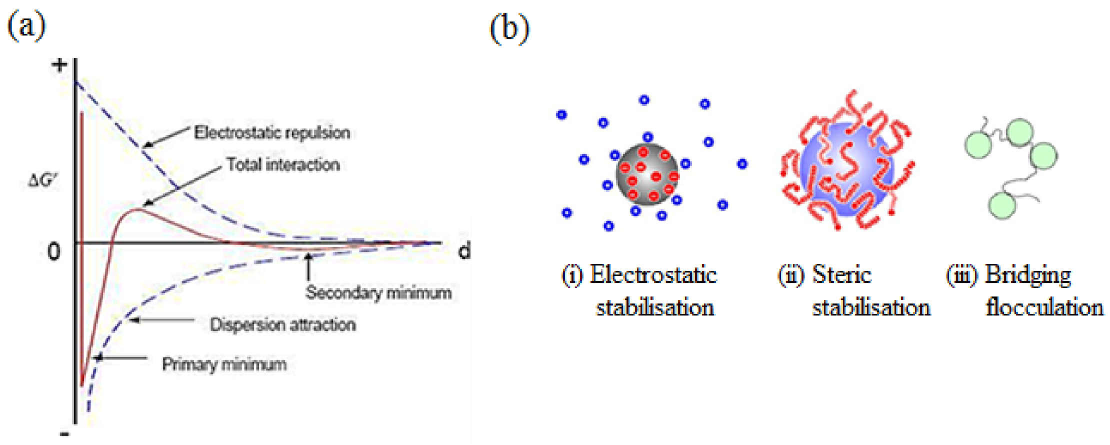

Figure 1: (a) DLVO theory assumes that the stability of a particle in solution is dependent upon its total potential energy function V_T, (b) Mechanisms of stabilisation for colloidal dispersions.

The charge, which is carried by surface determines its electrostatic potential. For this reason, they are called the potential-determining ions. We can calculate the surface potential on the crystals of silver halides by considering the equilibrium between the surface of charged crystal and the ions in the surrounding solution:

$$\begin{aligned} \Psi_0 &= \frac{kT}{ze}\left(\ln a - \ln a_{pzc}\right) \\ \text{or} \quad \Psi_0 &= 59 \times \left(p\mathrm{Ag}^+ - p\mathrm{Ag}^+_{pzc}\right)\,\mathrm{mV} \\ \text{or} \quad \Psi_0 &= -59 \times \left(p\mathrm{Cl}^- - p\mathrm{Cl}^-_{pzc}\right)\,\mathrm{mV} \end{aligned} \tag{7}$$

Note:

$$\begin{aligned} p\mathrm{Ag}^+ &= -\log_{10}\left[\mathrm{Ag}^+\right], \\ \text{and} \quad \ln\left[\mathrm{Ag}^+\right] &= 2.303 \times \log_{10}\left[\mathrm{Ag}^+\right] \end{aligned}$$

where Ψ_0 is the surface potential, a is the activity of the potential-determining ion, a_{pzc} is the concentration at point of zero charge.

The solubility product for AgCl, $K_{sp} = 1.8 \times 10^{-10}$, where

$$\begin{aligned} p\mathrm{Ag}^+_{pzc} &= 4.5 \ \left(\left[\mathrm{Ag}^+_{pzc}\right] = 2.9 \times 10^{-5}\ \mathrm{M}\right) \\ \text{and} \quad p\mathrm{Cl}^-_{pzc} &= 5.2 \ \left(\left[\mathrm{Cl}^-_{pzc}\right] = 6.3 \times 10^{-6}\ \mathrm{M}\right) \end{aligned}$$

This experiment involves the study of steric and electrostatic stabilisation in silver chloride sol. The aim of the experiment is to test the effect of polyvinyl alcohol in promoting steric stabilisation. Moreover, the effect of electrostatic stabilisation is also evaluated by varying the amount of Ag^+ and Cl^- in the sol.

Procedure

Chemicals and Materials

0.05% PVA solution, 0.0005 M $AgNO_3$ and 0.0005 M KCl solutions, deionised water, glass tubes, pipettes and optical cuvette.

Experimental

1. Prepare 50 mL 0.05% w/w PVA solution by dissolving 0.025 g of PVA in 49.975 grams of warm deionised water. Stir the solution continuously.
2. Prepare 50 mL 0.005 M $AgNO_3$ by dissolving appropriate amount of $AgNO_3$ in deionised water.
3. Prepare 50 mL 0.005 M KCl solution by dissolving appropriate amount of KCl in deionised water.
4. Calibrate the spectrophotometer at 350 nm with deionised water.
5. By using the solutions prepared in Step 1 to Step 3, prepare 5 mL A solution and 5 mL B solution according to Table 3. To form Sol I, pour the prepared B solution into A solution and back.

Table 3 Sample preparation

		Solution A / mL			**Solution B / mL**	
Sol	**Mixing Sequence**	**PVA 0.05%**	**Cl^- 0.005 M**	**Water**	**Ag^+ 0.005 M**	**Water**
I	Pour **B** into **A** and back	0.00	1.00	4.00	1.00	4.00
II	Pour **B** into **A** and back	1.00	1.00	3.00	1.00	4.00
III	Pour **B** into **A** and back	0.10	1.00	3.90	1.00	4.00
IV	Pour **B** into **A** and back	0.00	1.10	3.90	0.90	4.10
V	Pour **A** into **A** and back	0.00	0.95	4.05	1.05	3.95
VI	Pour **A** into **A** and back	0.00	0.90	4.10	1.10	3.90

6. Immediately without delay, fill in the cuvette with Sol I, start the timer and record the % Transmittance at 350 nm. Continue to monitor and record the % Transmittance every 2 minutes for a period of about 15 minutes.
7. Repeat Step 5 and Step 6 for Sol II to Sol VI.

Report

Plot the six %T versus time curves on the same graph. Compare the curves. Calculate the nominal surface potentials. Compare and discuss the colloid stability of the sols:

Sol	a_{Ag}	Ψ_0	**Observation**
I			
II			
III			
IV			
V			
VI			

In your report, answer the following questions:

- Write the definition of the point of zero charge.
- What kind of relation is there between the colloid stability and the zeta potential (ζ) of lyophobic colloids?
- What is the origin of the charge of the silver halide sols?
- How charged is a stoichiometric silver chloride?