الجامعة الألمانية الأردنية
German Jordanian University

School of Medical Sciences

Pharmaceutical and Chemical Engineering Department

Laboratory Manual

For

PHYSICAL CHEMISTRY LAB MANUAL

PCE272

Edition: 2021

Contents

Preface and safety

Course Objectives and Learning Outcomes
The practical part is designed to achieve a working knowledge through examination of some of the basic physicochemical principles covered in the lectures of CPE2282 in the delivery of drug and the design of pharmaceutical dosage forms.
Teaching and Learning Methods
Teaching Methods: Demonstration and general explanation

Course Content	
Topic	**No. of Lab.sessions**
Syllabus –Introduction, Safety regulations	1
Partial Molar volume	1
Boiling Point Elevation	1
Salt effect on solubility and dissociation effect	1
Reaction Rate and Activation Energy of the Acid Hydrolysis of Ethyl Acetate	1
Adsorption isotherm	1
Binary and ternary systems	3
Transfer of salicylic acid across polymeric membrane: Diffusion phenomenon	1
Determination of Distribution Coefficient of I2 and Stability Constant of I3-Complex	1
Critical Micelle Concentration	1

Assessment Policy*	
Type	**Weight (%)**
Reports and quizzes	60%
Final Exam(practical-theoretical)	40 %

*Make-up exams will be offered for valid reasons only with consent of the Dean. Make-up exams may be different from regular exams in content and format.

Regulations	
Attendance	There is one laboratory session per week (3 hours). Laboratory attendance is MANDATORY (NOT optional), unless special arrangements are made with your instructor (no more than two sessions), accompanied by a valid excused absence. There will be no make-up laboratories. The student will lose 5 marks of the total course grade for each missed laboratory session. Students are not allowed to leave the laboratory during the session without obtaining permission, to minimize their absence.
Laboratory notebook:	The week's experimental procedure will be sent periodically by e-mail. Students are required to read carefully the experimental procedure before coming to the lab. The lab report with completed lab work should be submitted to the lab TA at the end of each lab session in order to be signed and graded.
Safety measures:	-Lab Safety Lecture A mandatory introductory safety lecture FOR ALL GROUPS will be held on first session Each student must wear a clean, white laboratory coat at all times while in the laboratory. Each student must have a clean towel on hand at all times to keep his place or tools clean. All equipment and bottles should be returned to the proper place after use. Assume all chemicals used in the experiment are dangerous. Eating or drinking in the laboratory is prohibited. Do not pipette by mouth or carry reagents around the lab. Wash your hands thoroughly before leaving the lab. Take time to review the laboratory safety section and locate the following safety equipment in the laboratory. Safety Equipment Location Fire Extinguishers Fire Alarm Eye Wash Fountains Safety Shower First Aid Box Chemical Disposal

	There are large red buckets (or otherwise indicated by the TA) available for broken glassware in the lab. Please use them instead of the garbage, to respect the safety of the cleaning staff. There will be designated waste jars for hazardous waste and organic solvents in the fume hoods for each lab. Chemically inert waste (e.g. petrolatum) will gum up the drains, and are properly disposed of in the garbage. If you are unsure how to properly dispose something, ask your TA or instructor. Dress Code For your protection, you are required to wear the following protective gear, at all times during the lab: A lab coat Safety Goggles (even if you wear glasses) Closed-Toed Shoes (no sandals or open-toed shoes) Clothing that covers your legs Do not wear contact lenses Lab Check-Out Procedure Clean your lab bench and any dirty glassware; Throw out any remaining formulations or garbage; Return any extra glassware to the laboratory back shelves; Be assigned a special area in the lab to clean.
Laboratory structure	Students will work independently or in group according to the lab schedule. Students are required to read the theory and procedures of each experiment before coming to the lab. There will be a brief lecture-discussion on the theory and procedure before each new experiment After the completion of each experiment, a full report must be submitted individually to the TA. The laboratories start on times. You should expect a quiz at the beginning of each laboratory session. Assignment of Grades This laboratory has been assigned a 100% weight of the course grade. Performance in the laboratory will be evaluated from a combination of activities. In order to receive a grade for this laboratory, students have to submit work for each of the graded areas noted. The following are approximate percentages (% of total). Guidelines for Writing a Formal Laboratory Report

A formal individual laboratory report consisting of individual identified sections will be submitted according to the TA instructions after completion of the lab or one week after performing the lab.

Rationale of Laboratory Reports

The purpose of writing a scientific report is to communicate your findings with the outside world. Enough detail should be conveyed so that someone who did not do the experiment could repeat it and replicate your results. Writing laboratory reports (and technical writing in general) is an extremely useful and valuable skill to develop. Avoid providing one word answers and bullet points. Use sentence form, and summarize where appropriate. The ability to condense the purpose, observations, and results into an abstract will help the reader connect with the material, and will put your results in perspective for the reader. This process will help prepare you for writing scientific publications.

Typical Components of a Laboratory Report

1. Title Page (1%)
Please include lab number and title, Student name, date submitted,
Course code.
2. Abstract (10%)
No more than 200 words, an abstract is a mini-version of the entire lab report. It provides a brief introduction, purpose, a summary of results (not the raw data itself but parameters estimated), conclusions, and the relevance of the conclusions to the field of study. It is usually the last section that you will write, although it comes first in the report.
3. Introduction (5%)
This section should be 1-2 paragraphs long, and include the purpose of the experiment and a brief overview.
What is the main purpose of the lab? Which scientific principles are being investigated? What is the value of the results to the field of study? A good introduction will spark the interest of the reader and explain the purpose of the work.
4. Experimental part (10%): Mainly set up and speciality glassware(s) and devices. This section should be no more than one pages long, but depending on the experiment, may only be a few paragraphs. Do not copy and paste the methods section from the lab manual – this is a protocol. The purpose of the methods section is to summarize what you did with sufficient detail for someone to repeat the experiment, without getting into step-by-step instructions. Provide details of the chemicals you used. Key equipment (e.g. a UV spectrophotometer) should be mentioned; however, glassware (e.g. 100 mL graduated cylinder) should not unless it was integral to the method. Document what you actually did, not what you were supposed to do. If there was a change or deviation from the lab manual, describe it. Explain what you did in chronological order (the order that you did things in the lab).

5. Results and discussion (70%): Not more than two pages long (words excluding graphs and or the recorded readings; avoid blank pages)
-The length of your results section will depend on the experiment.
-All of your data and observations go into this section, in table form. Attach any graphs printed out in the lab. This should be the easiest section to write.
-Provide sample calculations for key elements of the lab: dilutions, standard curve use, etc.
-Make sure you:
1.Properly label all graph axes;
2-Always report the units with each measurement;
3-Report your parameters with the appropriate number of significant
Digits.

Then discuss your results:
a) Summarize the key scientific idea(s) behind the lab. If there was a key equation , report it here and describe its significance.
b) Did the results confirm or refute the scientific principles involved? Discuss the precision of your data (e.g. how good the r2 was of a fitted linear regression). Were the results obtained what you expected? Sometimes in the lab you may observe a trend opposite to what you were expecting. It is up to you to either re-evaluate your understanding of the phenomena, or try to identify the sources of error

6. Conclusions (4%)
Conclusions are relatively short compared to the discussion. They are typically 1-2 paragraphs, and serve as the bottom line of the lab. In sentence form, report the final estimated values of parameters, and summarize the results/discussions with a closing thought. Recommendations for future work or how the lab could change may also be included here.

7. References
Include literature references you referred to in this section. If you did not refer to the references, you do not need to include them here.
8. Appendices
You may include extra calculations, additional information, and supplementary analyses attached as appendices.

Make sure you staple your lab report together, and that you present your work neatly.

Cheating is defined as conduct (whether successful or not) aimed at deceiving the University into acknowledging a false level of attainment by a student. Cheating including assisting someone else to cheat (including attempting to assist someone else to cheat) may be subject to disciplinary action in accordance with the University's Disciplinary Procedure.
Any form of cheating is strictly forbidden under this regulation but, in order to assist understanding, a number of specific forms of cheating are described. These include but are not limited to the following examples:

Cheating regulations	Submitting other people's work as your own - either with or without their knowledge. This includes copying reports; using notes or unauthorized materials in examinations; submitting work you have paid for as your own; impersonation - taking an assessment on behalf of or pretending to be another student, or allowing another person to take an assessment on your behalf or pretend to be you.
	Plagiarism - taking or using another person's thoughts, writings or inventions as your own. To avoid plagiarism you must make sure that quotations from whatever source are clearly identified and attributed at the point where they occur in the text of your work by using one of the standard conventions for referencing.
	Collusion - except where written instructions specify that work for assessment may be produced jointly and submitted as the work of more than one student, you must not collude with others to produce a piece of work jointly, copy or share another student's work or lend your work to another student when it is likely that some or all of it will be copied.
	Duplication - submitting work for assessment that is the same as, or broadly similar to, work submitted earlier for academic credit, without acknowledgement of the previous submission.
	Falsification - the invention of data, its alteration, its copying from any other source, or otherwise obtaining it by unfair means, or inventing quotations and/or references.
	Custom Writing Services - this includes the use of any service which produces custom materials. The University may consider any request placed with any form of custom writing service to be a form of cheating, whatever use is then made of the material produced, and therefore to be an offence under the University Regulations.
	Assisting Others to Cheat - The University considers assisting others to cheat (including attempting to assist someone else to cheat) as a form of cheating.

References
1. Basic physical pharmacy, Josepha Ma and Boka Hadzija, Jones and Bartlett learning, USA.2013.
2. Martin's Physical Pharmacy and Pharmaceutical sciences, Edited by Patrick Sinko, Lippincott Williams & Wilkins. 6th Edition (2006,2011).

PARTIAL MOLAR VOLUME

Objectives

- Measure the densities of different Ethanol-Water mixtures of specified composition at room temperature with pyknometer.
- Calculate the real volumes and the mean molar mixing volumes of the investigated Ethanol-Water mixtures and also the partial molar volumes of each liquid for selected compositions. Compare them with the molar volumes of the pure substances at room temperature.

Theory

Due to the intermolecular interactions, the total volume measured when two real liquids (e.g. ethanol and water) are mixed deviates from the total volume calculated from the individual volumes of the two liquids (Volume contraction). To describe this non-ideal behavior in the mixing phase, one defines partial molar quantities which are dependent on the composition of the system. The values of these can be experimentally determined.

The volume v_{id} and the mean molar volume V_{id} of an ideal mixture of the components A and B can be calculated if the quantitative composition is known.

$$x_A = \frac{n_A}{n_A + n_B} \tag{1.1}$$

$$x_B = \frac{n_B}{n_A + n_B} \tag{1.2}$$

x_A, x_B :mole fraction of the components A and B, respectively

n_A, n_B : amounts of A and B respectively

V_A , V_B : molar volume of pure components which are independent of the composition.

$$V_{id} = \frac{v_{id}}{n_A + n_B} = V_A x_A + V_B x_B \tag{2}$$

However, the assumed additively in equation (2) loses its validity in cases of real mixtures (e.g. ethanol/water). The real volumes v_r and V_r deviate more or less strongly from the ideal

volumes due to volume contraction but can still be calculated if the molar volumes of the pure components A and B are replaced by the partial molar volumes, $\overline{V}_A$ and $\overline{V}_B$ which are dependent of the composition.

$$\overline{V}_A = \left(\frac{\partial v_r}{\partial n_A}\right)_{T,P,n_B} \tag{3.1}$$

$$\overline{V}_B = \left(\frac{\partial v_r}{\partial n_B}\right)_{T,P,n_A} \tag{3.2}$$

$$V_r = \frac{v_r}{n_A + n_B} = \overline{V}_A x_A + \overline{V}_B x_B \tag{4}$$

The difference between the mean molar volumes defined according to equations (2) and (4) is designated as the mean molar mixing volumes $\Delta_M V$ and is an intensive measure of the deviation of the mixture from the ideal behavior.

$$\Delta_M V = V_r - V_{id}$$

$$= \left[(\overline{V}_A - \overline{V}_B) - (V_A - V_B)\right] x_A + (\overline{V}_B - V_B) \tag{5}$$

The dependence of it on the composition is described by the following relationship:

$$\frac{d(\Delta_M V)}{dx_A} = \frac{dV_r}{dx_A} = \frac{dV_{id}}{dx_A} = (\overline{V}_A - \overline{V}_B) - (V_A - V_B) \tag{6}$$

Analogous correlations can be formulated for x_B due to the fact that $x_A = 1 - x_B$.

After substituting (6) in (5), the following relationships are obtained:

$$\overline{V}_B = \Delta_M V - \frac{d(\Delta_M V)}{dx_A} x_A + V_B \tag{7.1}$$

$$\overline{V}_A = \Delta_M V - \frac{d(\Delta_M V)}{dx_A} x_B + V_A \tag{7.2}$$

According to this, the partial molar volumes of the components A and B for the specific compositions (x_A, x_B) can be determined if the molar volumes of the pure substances (V_A, V_B) and their differential quotients $d\Delta_M V / dx_A$ are known. These can be obtained as the tangent to the graphical plot of $\Delta_M V$ versus x_A (Fig.2). This is, however, better calculated by deriving the functional correlation $\Delta_M V = f(x_A)$ for selected values of x_A.

The following procedure is recommended for this: First, calculate the exact mole fractional compositions from the weighed-out masses of ethanol (A) and water (B) using equation (1.1) or (1.2). Using pyknometer (small container whose volume is known accurately) and

the following data (m= mass of the liquid in the pyknometer; v=25 ml=pyknometer volume, the densities (ρ=m/v) of the mixtures) the volumes v_r corresponding to the total masses (m_A+ m_B) can be determined. These values can be converted into the mean molar volume v_r using equation (4) and then into the mean molar mixing volume $\Delta_M V$ in accordance with equations (2) and (5).

The molar volumes of the pure liquids required for these conversions are V_A = 58.277 ml.mol^{-1} (ethanol) and V_B= 18.073 ml.mol^{-1} (water) at T=293.15K. Plot the dependence of the mean molar mixing volume $\Delta_M V$ on the composition x_A and determine the differential quotients $d\Delta_M V/dx_A$ from the slope of the tangents for selected mole fractions x_B and the corresponding estimated values for $\Delta_M V$ from the curve itself.

[Note: the correlation between the variables can also be approximated by a polynomial of the second or higher degree using a computer-assisted method. By substituting arbitrary mole fractions x_A in the polynomial or its first derivative, the corresponding estimated value for $\Delta_M V$ and the differential quotients $d(\Delta_M V)/dx_A$ can be calculated.]

The partial molar volumes of both components are now accessible via equations (7.1) and (7.2).

Finally, calculate the mean molar volume V_r for a selected mixture which corresponds well to the experimental conditions from the partial molar volumes determined according to equation (4) and compare it with your experimental results.

Fig 1.1: Pyknometer

Apparatus / Reagents Needed

-Absolute Ethanol

- Distilled water

- 100 ml Beakers

- Volumetric Pipettes (5ml, 10ml, 25ml)

-5 Pyknometers with known volumes

-5 Reagent bottles with plastic stopper

- Analytical Balance

-Temperature controlled water bath

-Hot air gun

Procedure

- Prepare the ethanol-water mixtures in the narrow neck bottles on the laboratory balance using the approximate volume composition specified in Table 1, weighing ethanol into the predetermined mass of water (weighing accuracy 0.001g).

Volume of Ethanol (C_2H_5OH)	Volume of water
10	40
15	35
20	30
30	20
40	10

- Close the bottles immediately when the desired volume has been reached.
- Weigh dry pyknometers and record their weight.
- Fill dry pyknometer of known empty mass completely with the mixtures.
- Position the pyknometers in the temperature-controlled bath for about 30 min at 20°C for temperature equilibration.
- Remove pyknometers and weigh them after complete drying.

Data Sheet

	Wt. of dry pyknometer	Wt. of pyknometer + (A-B)mixture	Wt. of (A-B) mixture	Volume of Mixture=Volume of pyknometer	Density of mixture
Sample 1					
Sample 2					
Sample 3					
Sample 4					
Sample 5					

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EXPERIMENT 2

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BOILING POINT ELEVATION

Objective

- Measure the increase in boiling point of water as a function of the concentration of table salt, urea and hydroquinone.
- Investigate the relationship between the increase in boiling point and the number of pellets.
- Determine the molar mass of the solute from the relationship between the increase in boiling point and the concentration.

Theory

The boiling point of a solution is always higher than that of the pure solvent. The dependence of the temperature difference (elevated boiling point) on the concentration of the solute can be determined using a suitable apparatus.

A solution is a mixed-phase liquid which consists of a dissolved substance and a solvent. Only the solvent is capable of vaporization, the vapour pressure of a solute is partially zero. When a substance dissolves in solvent, additional forces results and these must be overcome by solvent molecules before they can pass into the gas phase. Less solvent molecules can therefore vaporize from a solution than from the pure solvent. In 1886, F.M. Raoult postulated the law that is named after him: The vapour pressure of a solution is given by the product of the vapour pressure of the pure solvent and the mole fraction of the solute.

$$P_s = \frac{n_2}{n_1 + n_2} \cdot P_o \qquad\qquad (1)$$

Where:

P_s: Vapour pressure of the solution.

P_o: Vapour pressure of the pure solvent

n_1: Amount of the pure solvent

n_2: Amount of dissolved substance

A liquid boils when its vapour pressure is the same as the ambient pressure. The vapour pressure of water reaches an ambient pressure of 1013 hPa at a temperature of 100ºC. When a substance

is dissolved in water, the vapour pressure is reduced, and is so less than 1013 hPa at 100ºC. Heat must now be supplied to increase the kinetic energy of the molecules, and so to raise the temperature so that the solution comes to boiling. The reason for the higher energy requirement for the solution than for the pure solvent is because additional forces, mutual attractive forces between solute and solvent, must be overcome in the solution. The solution does not boil at T_0, but at the higher temperature T_s. The difference between these two temperatures is the boiling point elevation ΔT_s

$$\Delta T_s = T_s - T_o \qquad (2)$$

From a quantitative point of view, the boiling point elevation is dependent on the amount to which the vapour pressure is lowered, and so on the concentration of the solute. Molality is used here as dimension, i.e. the number of moles of solute dissolved in 1 liter of solvent.

$$\Delta T = i . K_b . m$$
$$= \frac{K_b . m_2 . 1000}{M_2 m_1} \; i \qquad (3)$$

m_1: Mass of the pure solvent
m_2: Mass of the dissolved substance
M_2: Molar mass of the dissolved substance
K_b : Ebullioscopic constant (for water $K_b = 0.512$ (°C·kg·mol^{-1}))
i: depends on the number of particles in the solution (for non-electrolyte i=1)

Apparatus / Reagents Needed

-NaCl Compressed as pellets

- Distilled water

- Analytical balance

- 50 ml graduated cylinder

-250 ml graduated cylinder

- 50 ml beakers

-Boiling point elevation apparatus (Fig.2.1 shows the apparatus used in the experiment.)

Fig.2.1: The apparatus used in the experiment.

Procedure

- Weigh the dry inner vessel of the boiling point apparatus and note the exact mass.
- Fit the inner vessel into the outer vessel so that its inlet opening is located below the silicone rubber seal of the connecting cap.
- During measurement, steam is to enter the inner vessel through the lateral aperture, so pay attention that it is not covered. Fill the round flask with 150 to 200 ml of water and connected it to the assembled apparatus.
- Slip two short pieces of silicon tubing onto the two gas outlets of the outer vessel and place the lengths in a 250 ml glass beaker with free ends at about the middle of the beaker.
- Attach a pinch clip to the lower of the two tubes coming from the outer vessel, but for the time being leave it open.
- Pour approximately 40 ml of distilled water into the inner vessel. Close the vessel at the top by fixing the temperature probe in position.

Note: The substances to be used must be pressed into pellets in order to prevent any particles of them from sticking on the walls of the vessel while being added.

- Weigh out five portions of NaCl, each of approximately 1000 mg use a suitable presser to make it as pellets.
- Weigh the pellets to an accuracy of 1 mg. (The dependence of the boiling point elevation of water on the concentration can be demonstrated in a single experiment by successively adding known amounts of the same substance).

- Heat the solvent in the flask to boiling. The vapour evolved rises up into the outer vessel and heats up the inner vessel.
- Control the heating rate with the power control. The temperature in the inner vessel is displayed on the digital temperature meter in degrees Celsius.
- After some minutes, when the temperature in the inner vessel has nearly reached the boiling point and no longer increases, lower the heating hood for few seconds until boiling stops and the condensate on the outer vessel returns to the round flask. Then raise the heating hood again.
- When boiling recommences, close the pinchcock. The (slightly superheated) steam now flows through the water in the inner vessels. Set the digital temperature meter to measure the change in temperature ΔT over time with the tare function$< SET\ 0.00 >$. In this mode of operation, the resolution is tenfold better (0.01K).

- Wait until the value displayed remains constant. Now carefully open the inner vessel (screw cap), add the first substance pellet, and close the opening immediately. The temperature first drops slightly and then rises again while the pellet dissolves.
- When the value has again become constant, record it and repeat this procedure for the next portion of the substance.

- After five concentration steps have been measured, first open the pinchcock and then switch off the heating. This is important to avoid solution being sucked from the inner vessel into the flask containing water while cooling down.

- Remove the inner vessel, dry its outer surface, remove the temperature probe and re-weigh it. The mass of the water is now equal to the last measured value less the mass of the empty vessel and the masses of the five substances pellets.

- Plot the increase in boiling point against the quotient of the mass of the dissolved NaCl and the mass of water for each substance.
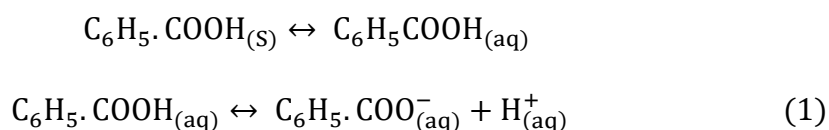
Data Sheet

Boiling point of pure water (^{O}C)		
Mass of NaCl (g)	**Boiling point of NaCl solution(^{O}C)**	**Boiling point elevation (^{O}C) =(T_S-T_O)**

EXPERIMENT 3

SALT EFFECT ON SOLUBILITY AND DISSOCIATION

Theory

Benzoic acid has a little solubility in H_2O. In a saturated solution we have the following equilibria:

$$C_6H_5.COOH_{(S)} \leftrightarrow C_6H_5COOH_{(aq)}$$

$$C_6H_5.COOH_{(aq)} \leftrightarrow C_6H_5.COO^-_{(aq)} + H^+_{(aq)} \tag{1}$$

Total solubility = [C_6H_5.COOH $_{(aq)}$] + [dissociated acid]

Or

$$y = [C_6H_5.COOH _{(aq)}] + x \tag{2}$$
$$x = [C_6H_5.COO^-] = [H^+] = 10^{-pH} \tag{3}$$

Total solubility is determined by titration against NaOH in the presence of ph.ph. Indicator.

The equilibrium in equation (1) can be described by two ways

   i. $K_c = \dfrac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH_{(aq)}]}$ (4)

Where K_c is affected by concentrations, and temperature.

   ii. $K_a = \dfrac{\gamma^-.\gamma^+}{\gamma} \cdot \dfrac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH_{(aq)}]}$ (5)

Where γ an activity coefficient, and Ka is a true thermodynamics constants that is constant at given temperature.

From equation 4, 5

$$K_a = \frac{\gamma^-.\gamma^+}{\gamma} \cdot K_c \tag{6}$$

$$\gamma^+\gamma^- = \gamma^{\pm^2}$$

$\gamma^\pm$: Mean activity coefficent of benzoic acid $\gamma = 1$ for benzoic acid

$\gamma^{\pm}$ Is affected by the ionic strength of the solution. The ionic strength (I) is defined as:

$$I = \frac{1}{2} \sum_i C_i Z_i^2 \qquad (7)$$

In this experiment, we will ignore the contribution of benzoic acid to I due to its small dissociation. If NaCl is used as an electrolyte in the experiment, then I for each solution is the molarity of NaCl in the particular solution

$\gamma^{\pm}$ is related to I by the Debye–Hückel limiting law:

$$log\gamma^{\pm} = -0.51|Z^+ Z^-|(I)^{\frac{1}{2}} \qquad (8)$$

Eq 6,8 give:

$$K_a = \gamma^{\pm^2} K_c \qquad (9)$$

$$log K_a + 1.02 \, (I)^{\frac{1}{2}} = log K_c \qquad (10)$$

Data Presentation and Calculations

a) For each solution , find K_c from equation (4) as follow:

$$K_c = \frac{(10^{-pH})^2}{(y - 10^{-pH})}$$

$$y = \frac{V_{NaOH} M_{NaOH}}{V_{sample}}$$

b) Plot log Kc on the y-axis and $(I)^{1/2}$ on the x-axis. Extrapolation to I=0. Gives K_a from intercept on the y-axis.
c) $\gamma^{\pm}$ should be calculated for each solution from the equations

$$log\gamma^{\pm} = \frac{1}{2}\{log K_a - log K_c\}$$

Plot $log\gamma^{\pm}$ on the y-axis and $(I)^{1/2}$ on the x-axis. Find the limiting slope.

Apparatus / Reagents Needed

-0.05 M NaOH
-Five Different concentrations of NaCl solution (0.05, 0.1, 0.3, 0.4, 0.5) M
-Benzoic acid
-KHP (potassium hydrogen phthalate)
-Phenolphthalein Indicator

- 100 ml Stopper flasks

-100 ml Graduated Cylinder

- 50 ml Burette

-250 ml Erlenmeyer flasks

-Funnel

-25 ml Volumetric Pipette

-100 ml Beakers

-Top loading balance

-Water bath with shaker

- PH meter

Procedure

1. Place about 1 gm of benzoic acid in each of 5 clean dry stoppered bottles.
2. In each bottle pour 100ml of NaCl solution prepared by using 100ml volumetric flask with the following concentrations:
   0.05, 0.10, 0.30, 0.40 and 0.50.
3. Stopper the bottles; place them in a 25°C thermostat with shaking for 1hr.
4. Filtrate each solution, Withdraw 25ml sample from each bottle using a pipette, and discharge each sample to 250ml Erlenmeyer flask.
5. Measure the pH for each solution in the bottles by using the pH meter.
6. Determine the concentration of benzoic acid in each solution by titrating with 0.05M NaOH (Standardized with KHP) using ph.ph. as Indicator.

Data sheet

Standardization of NaOH	Trial 1	Trial 1
Initial reading of burette =		
Final reading of burette =		
Volume of NaOH =		
Concentration of NaCl	PH	Volume of NaOH (ml)
0.05 M		
0.1 M		
0.3 M		
0.4 M		
0.5 M		
Volume of titrated benzoic acid solution =		

REACTION RATE AND ACTIVATION ENERGY OF THE ACID HYDROLYSIS OF ETHYL ACETATE

Objective

- Determine the reaction rate constant for the hydrolysis of ethyl acetate at two (or more) temperatures.
- Calculate the activation energy of the reaction from the temperature dependence of the measured rate constants.

Theory

In acid solution, ethyl acetate is hydrolyzed to equivalent quantities of ethanol and acetic acid according to pseudo-first order rate law. The alkali metric determination of the acetic acid formed enables conclusions to be drawn on the temporal concentration of ester.

The acid ester hydrolysis is described by the equilibrium

$$CH_3COOC_2H_5 + H_2O \xrightarrow{[H_3O^+]} CH_3COOH + C_2H_5OH$$
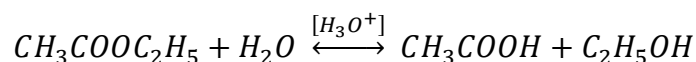
Under the given experimental conditions, equilibrium is shift quantitatively towards the reaction products. The reaction velocity (rate) v_R of this reaction is given by the rate law:

$$v_R = -\frac{dc_E}{dt} = kc_Ec_Wc_K \qquad (1)$$

Where:

k: Reaction rate constant

c_E, c_W, c_K: Concentration of ester, water and catalyst at time t

The rate of the reaction investigated is a function of the acid concentration and can be controlled by it.

As a result of the practical constancy of the concentrations of H_2O (Stoichiometric excess) and H_3O^+ (Catalyst), this reduces to

$$-\frac{dc_E}{dt} = k'c_E \qquad (1.1)$$

The rate of hydrolysis thus conforms to a pseudo-first-order time rule whose integration results in the following:

$$\ln\frac{c_{E,0}}{c_E} = k't \qquad (1.2)$$

The ester concentration $c_{E;0}$ and c_E at time t_0 and t can be replaced by the volumes of NaOH required for neutralization of the samples at the start ($v_{NaOH;0}$) during the reaction (V_{NaOH}) and after the complete conversion ($V_{NaOH;\infty}$):

$$\ln\frac{V_{NaOH,\infty} - V_{NaOH,0}}{V_{NaOH,\infty} - V_{NaOH}} = \ln Q = k't \qquad (1.3)$$

The volumes $V_{NaOH;0}$ and $V_{NaOH;\infty}$ can be experimentally determined (see 'set-up and procedure') or can be calculated using relationships (2.1) and (2.2):

$$V_{NaOH,0} = \frac{c_{HCl}V_1}{c_{NaOH}} \cdot \frac{100}{105} \qquad (2.1)$$

Where:

C_{HCl}: Concentration of the HCl solution (=1.0 mol/l)

C_{NaOH}: Concentration of the NaOH solution (=0.2 mol/l)

V_1: Sample volumes (=5 ml)

$$V_{NaOH,\infty} = \frac{\rho_E V_E V_1}{M_E V_S c_{NaOH}} + V_{NaOH,0} \qquad (2.2)$$

Where:

ρ_E: Density of ethyl acetate at T=298K (=0.895 g/ml)

M_E: Molar mass of ethyl acetate (=88.12 g/mol)

V_E: Volumes of ethyl acetate contained in the volume of the total system V_S=105 ml at time t_0 (= 5ml)

In accordance with equation (1.3), the plot of the expression $\ln\left[\frac{V_{NaOH;\infty}-V_{NaOH;0}}{V_{NaOH;\infty}-V_{NaOH}}\right]$ as a function of time results in a rising straight line with a slope of k'. The constant k includes the dependence of the reaction velocity on the binding conditions of the participating

molecules, the type of the reaction and the temperature. For two molecules to react, they must not only collide, but also have sufficient energy content.

The activation energy E_A is the difference between the average energy content prior to reaction and the energy required for reaction. The molecules obtain the energy that is needed for activation from heat supplied, from light and form the exchange of energy when collisions occur. Such take-up of energy activates the molecules (loosens bonds, polarization etc.) so that they can react. The portion of molecules with this increased energy content increases with increasing temperature. The greater the portion of the molecules capable of reaction, the more molecules that will react, and so the higher the activation energy velocity.

The activation energy can be determined using the empirical Arrhenius equation:

$$k' = k_{max}.\,e^{-\frac{E_A}{RT}} \qquad\qquad (3)$$

Where:

R: Universal gas constant (=8.31441 J.K^{-1}.mol^{-1})

k_{max}: Maximum rate constant at infinite temperature (frequency factor)

k_{max} is the velocity constant which would be given when every collision resulted in reaction, i.e. when the activation energy was 0. For two known pairs of values having the rate constant k'_1 and k'_2 and the temperatures T_1 and T_2, using

$$\ln k' = -\frac{E_A}{RT} + \ln k_{max} \qquad\qquad (3.1)$$

The following concrete relationships result:

$$\ln k'_1 = -\frac{E_A}{RT_1} + \ln k_{max} \qquad\qquad (3.11)$$

$$\ln k'_2 = -\frac{E_A}{RT_2} + \ln k_{max} \qquad\qquad (3.12)$$

From which, by subtraction

$$E_A = R.\frac{T_1 T_2}{T_2 - T_1}.\ln\frac{k'_2}{k'_1} \qquad\qquad (3.2)$$

If further regarding k' and T are available (i.e., measurements at a number of temperatures), then the activation energy can alternatively be determined from the slope of the linear relation between ln k' and 1/T according to equation (3.1)

Apparatus / Reagents Needed

-0.20 M NaOH
-Ethyl acetate
- 1M HCl
-KHP (potassium hydrogen phthalate)
-Phenolphthalein Indicator
- 2 Stopper flasks (250 ml)
-100 ml Graduated Cylinder
- 50 ml Burette
-250 ml Erlenmeyer flasks
-Funnel
-5 ml Volumetric Pipette
-100 ml Beakers
-Top loading balance
-Water bath with shaker
-Ice bath

Procedure

- Prepare 0.2 molar NaOH solution by pipetting 200 ml of 1.0 molar sodium hydroxide solution into a 1000 ml volumetric flask and filling up to the calibration mark with water. Fill the burette with 0.2 molar NaOH solution.

- Pipette 100 ml of 1.0 molar hydrochloric acid solution into an Erlenmeyer flask, seal it with a stopper, and temperature equilibrate it for approximately 15 minutes at 30ºC (measure the exact temperature T_1).

- Start the reaction by adding 5 ml of ethyl acetate (room temperature). Shake the flask briefly, and then replace it in the temperature controlled bath.
- After 10 minutes and at further intervals of 10 minutes, take 5 ml samples and transfer those into a wide neck Erlenmeyer flask containing 100 ml of cold water. This will stop the reaction immediately. Titrate the solutions with as little delay as possible with the 0.2 molar sodium hydroxide solution, using phenolphthalein as indicator.

- Terminate the measurement series after a reaction time of 50 minutes. Repeat the above procedure at a temperature of 45ºC (T_2).
- The volumes of NaOH at time t_0 ($V_{NaOH;0}$, neutralization of the constant quantity of HCl) and subsequent to complete conversion ($V_{NaOH;\infty}$) are required for the evaluation. They can either be calculated or be determined experimentally as follows.

- The determine $V_{NaOH;\infty}$, after concluding the first measurement series, heat the solution which was converted to the greatest extent to approximately 70°C in a water bath on the magnetic stirrer. The reaction will go to completion at this temperature.

- Allow the solution to cool, then titrate it with 0.2 molar NaOH solution as described above.

- To determine the initial consumption $V_{NaOH;0}$ titrate 5 ml of the 1.0 molar hydrochloric acid solution used, whereby the volume must be corrected by the factor of 100/105 for the ester portion which is absent here.

Data sheet

Standardization of NaOH		Trial 1	Trial 1
Initial reading of burette =			
Final reading of burette =			
Volume of NaOH =			
T = 25 °C		T = 45 °C	
Time (min)	Volume of NaOH	Time (min)	Volume of NaOH
10		10	
20		20	
30		30	
40		40	
50		50	
$V_{NaOH,0}$ =		$V_{NaOH,\infty}$ =	

EXPERIMENT 5

ADSORPTION ISOTHERM

Objective:

Determine the residual equilibrium concentrations of acetic acid after stirring solutions of differing initial concentrations with a constant mass of active carbon. Using the measured results, determining the adsorption isotherm, which is valid for the given system.

Theory:

Phenomenon whereby molecules or ions are adhered to surface of a solid due to forces of attraction is called adsorption. The solid phase is called the adsorbent and the molecules that are adsorbed on the adsorbent are called the adsorbed phase or adsorbate. The adsorbate can be either a gas (molecules) or a solute (molecules or ions) in solution. There are two types of adsorption i.e. physical adsorption in which the particles are held by physical forces such as dipole and Van der Waals forces and chemical adsorption (or chemisorption) where chemical bonds are formed between the particles and the surface.

Adsorption is different from absorption, a process in which the material transferred from one phase to another interpenetrates the second phase to form a "solution". The term 'sorption' is a general expression encompassing both adsorption and absorption.

The adsorption of acetic acid on charcoal is studied using both the Freundlich isotherm and the Langmuir isotherm. This is an example of physical adsorption, where dipole and van de Waals forces are the predominant sources of attraction, and the heat of adsorption is typically less than 50 kJ/mol.

The amount of acetic acid (adsorbate) adsorbed per gram of charcoal (adsorbent) will depend on the surface area of the charcoal, the temperature of the solution, and the adsorbate concentration in solution. The adsorption will be followed by titrating the acetic acid not adsorbed by the charcoal, then determining the amount adsorbed by difference. Isotherms (plots of moles of adsorbate adsorbed per gram of adsorbent versus solution concentration) will be constructed, then compared with two models: The Freundlich isotherm and the Langmuir isotherm.

In general, the term adsorption is used to describe the attachment of gasses or dissolved substances to the surface of a solid (or liquid interfaces). At a constant temperature the quantity of absorbed substances is a function of the type of system investigated and the partial pressure and/or the concentration of the substance in question. This correlation is described by great numbers of adsorption isotherms: their validity is to be investigated experimentally.

As a result of the action of attractive forces between the exposed particles, gases or dissolved substances B attach themselves (adsorbate) reversibly to the surfaces of solid phases A (adsorbing agents) (adsorption).

$$A + B \leftrightarrow AB_{ads}$$
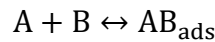
The extent of adsorption is normally expressed by the quantity of adsorbed substance (adsorbate) $n_{B,ads}$ referred to the surface area of or the mass m_A of the absorbing agent:

$$\gamma = \frac{n_{B,ads}}{m_A} \tag{1}$$

In cases of monolayer formation, the quotient of the real γ and the maximum γ_{max} adsorption molality is defined as the degree of coverage θ.

$$\theta = \frac{\gamma}{\gamma_{max}} \tag{2}$$

The type and degree of adsorption (γ, θ) are function of the chemical nature of the investigated system (adsorbing agent and adsorbate), among other things, as well as of the temperature and partial pressure (gasses) or the concentration (dissolved substances) of the adsorbate.

The correlation between the adsorption molality and the free equilibrium concentration of B at constant temperature is described by great numbers of adsorption isotherms of limited validity.

From kinetic consideration of the adsorption rate $-\frac{dc_B}{dt}$:

$$-\frac{dc_B}{dt} = K_{ads} c_B (1 - \theta) - K_{des} \theta \tag{3}$$

Where:

c_B: concentration of B in the solution.

K_{ads} and K_{des}: rate constants of the adsorption and desorption, respectively.

For the case of an established adsorption $(-\frac{dc_B}{dt} = 0)$ with the function (2), Langmuir's adsorption isotherm follows:

$$\gamma = \frac{(\gamma_{max})(c_{B,eq})K}{1 + (c_{B,eq})K} \qquad (4)$$

Where:

$c_{B,eq}$: equilibrium concentration of B in solution.

$K = K_{ads}/K_{des}$ = constants.

This simplifies for very low equilibrium concentration ($Kc_{B,eq} < 1$) to:

$$\gamma = \gamma_{max}Kc_{B,eq} = K'c_{B,eq} \qquad (4.1)$$

Thus, the adsorption molality γ should be linearly correlated with $c_{B,eq}$ (Henry's isotherm).

In contrast, the adsorption molality tends toward a concentration independent limiting value γ_{max} at very high equilibrium concentrations ($Kc_{B,eq} < 1$):

$$\gamma = \gamma_{max} \qquad (4.2)$$

In the region of validity of the isotherm (4) the correlation between adsorption molality and equilibrium concentration can be linearized by simple rearranging:

$$\frac{1}{\gamma} = \frac{1}{\gamma_{max}K} \cdot \frac{1}{c_{B,eq}} + \frac{1}{\gamma_{max}} \qquad (4.3)$$

Consequently, the graphic plot $1/\gamma$ as a function of the reciprocal equilibrium concentration $1/c_{B,eq}$ gives a straight line with a slope of $\frac{1}{\gamma_{max}K}$ and the ordinate segment $1/\gamma_{max}$. The initial region of the adsorption isotherm is described by the Freundlich's empirically determined adsorption isotherm for many systems:

$$\gamma = \alpha c_{B,eq}^{\beta} \qquad (5)$$

Where:

α, β = system-dependent constants,

Whose logarithmic expression is as follow:

$$\log\gamma = \beta\log c_{B,eq} + \log\alpha \qquad (5.1)$$

This form allows a simple graphic evaluation and thus the determination of the constants α and β. Plot $\log\gamma$ Vs $\log c_{B,eq}$, the slope will be β and the intercept will be $\log\alpha$.

Apparatus / Reagents Needed

-0.10 M NaOH
-Five different concentrations of acetic acid solutions 0.03, 0.05, 0.09, 0.15, 0.2 M
-KHP (potassium hydrogen phthalate)
-Phenolphthalein Indicator
-100 ml Graduated Cylinder
- 50 ml Burette
-250 ml Erlenmeyer flasks
-Funnel
-25 ml Volumetric Pipette
-100 ml Beakers
-Top loading balance
-Hot plate with stirrer
-5 magnetic bars

Procedure

1. Prepare the following solutions of acetic acid 0.20, 0.15, 0.09, 0.05, 0.03 M.

2. Transfer 100 ml of each of the above solutions to a 250 ml Erlenmeyer flask, and then add about 1.0g of activated charcoal to each flask (record exact weight). Stopper the flasks, shake the contents.

3. Place the flasks on a hot plate with intermitted shaking for about one hour to reach equilibrium state. (*)

4. Separate the acetic acid solution in each flask from charcoal by using a filter paper into another flask (discard the first 5-10 ml of each filtrate sample).

5. Take two 25.0 ml samples of each filtrate and titrate with standard 0.10M NaOH using ph.ph. as an indicator, record the volume of NaOH for each trial.

(*) During this time prepare 0.10M NaOH in 500ml volumetric flask and standardize with KHP to calculate the exact concentration of NaOH.

Data and Calculations:

Table (1): Adsorption molality for acetic acid-charcoal.

Soln. no.	C^o_{HAC}(mol/L)	V_{NaOH}(ml)
1	0.20	
2	0.15	
3	0.09	
4	0.05	
5	0.03	

$\gamma = \dfrac{\text{moles adsorbed}}{\text{wt.charcoal (Kg)}} = $ adsorption molality (adsorption capacity).

- Plot γ Vs. C_{HAc} Discuss.

- $\dfrac{1}{\gamma} = \dfrac{1}{\gamma_{max}K} \cdot \dfrac{1}{C} + \dfrac{1}{\gamma_{max}}$ Plot 1/γ vs. 1/C
- Logγ=βlogC+logα   Plot logγ vs. Log C

Data sheet

Standardization of NaOH	Trial 1	Trial 1
Initial reading of burette =		
Final reading of burette =		
Volume of NaOH =		
Initial Concentration of Acetic Acid	Volume of NaOH (ml) (trial 1)	Volume of NaOH (ml) (trial 2)
0.2 M		
0.15 M		
0.09 M		
0.05 M		
0.03 M		

EXPERIMENT 6

BINARY WATER - PHENOL MIXTURE

Objectives

- Determination of the Critical Solution Temperature, CST of Phenol-Water system.
- Measuring the miscibility temperatures of several water-phenol mixtures of known composition will be measured.

Theory

The study of the possible ways in which various materials can exist by themselves or in contact with others, as a function of temperature, pressure, and time, is a very important part of Materials Science. The reason is that we have to be able to tell what the stability of materials will be in all sorts of environments, since the mechanical performance of these materials depends very much on this. These changes in phase, called phase transformations, can be recorded in diagrams called PHASE DIAGRAMS. The phase diagram is a type of map that allows us to predict what will happen when we change the temperature or the overall composition of the material.

Binary systems are two-component systems. There are three types of liquid pairs:

A) Those which are completely soluble in each other in all proportions. (Alcohol and Water).
B) Those which are soluble in each other in definite proportions. (Phenol and Water)
C) Those which are not soluble in any proportion. (Castor oil and Water)

At low and high percentages of phenol, water and phenol mix completely, forming a single liquid phase. However, at intermediate compositions (and below the critical temperature) mixtures of phenol and water separate into two liquid phases. Above the critical temperature, phenol and water are completely miscible. The independent variable in the phase diagram is composition. Composition is sometimes given as mass percent (w/w%).

➢ **Binary phase Diagram:**

Knowledge of the phase diagrams of binary systems is necessary for an understanding of the nature of the interaction of the components and the practical use of such systems.

The binary phase graph is obtained by drawing a curve of the temperature at which transition between a one phase and a two phase system occures VS Composition.the maximum temperature on this curve is called upper CST. Above which a homogeneous solution occures regardless of the composition of the mixture. The region within the curve will represent a two-phase system while the region outside the curve will represent a one phase system.
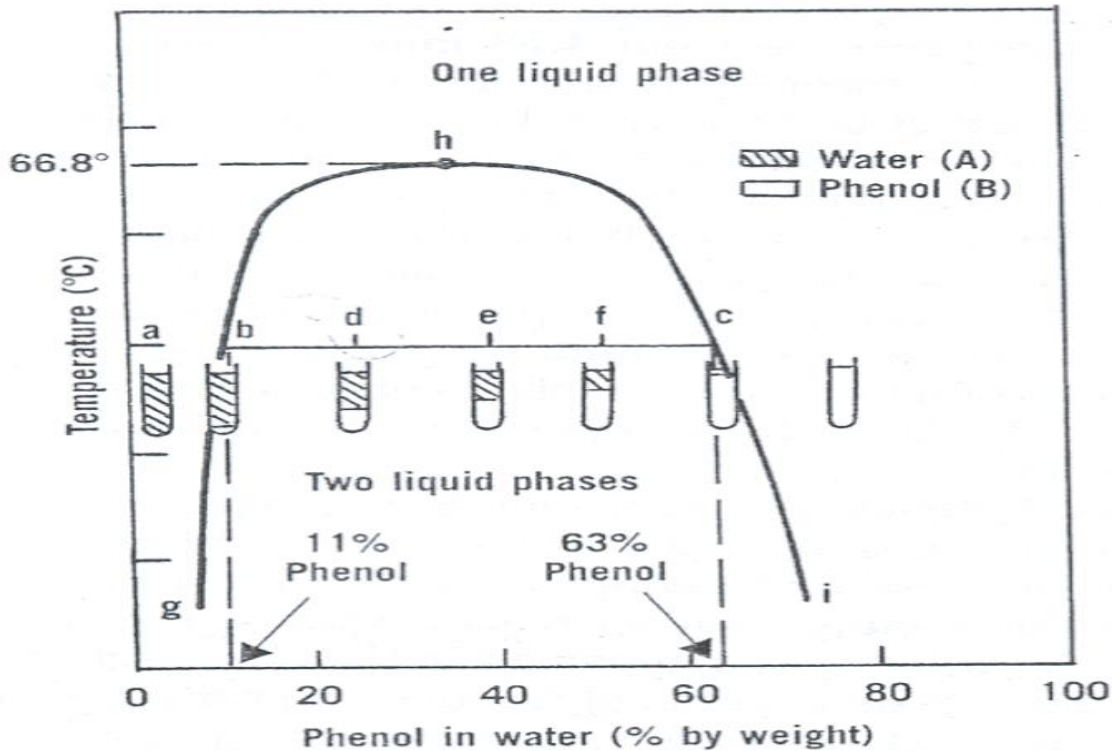
A horizontal line (parallel to the baseline) drawn across the curve (called tie line) will represent the effect of varying composition at a constant temperature. Before crossing the curve, at low %phenol, we will have a single water-rich phase until the solubility of phenol in water at that temperature is reached at the point here the tie line intersects with the curve. At this point, a minute amount of a second, phenol-rich, phase will appear in which we will have a smaller amount of water dissolved in a larger amount of phenol with% water equal to the solubility of water in phenol at that temperature. The two phases (termed conjugate phases)will be in equilibrium along the tie-line, and as %phenol is increased we will have less of the water-rich phase and more of the phenol rich phase, but the composition of each phase will remain constant, as long as we have a two-phase system, and will correspond to the solubility of each component in the other at that temperature. For example, in the above diagram, at 50 º C, the solubility of phenol in water, determined from the point B, is 11% w/w, while the solubility of water in phenol as determined from the point C is 37% w/w. so, along the entire length BC we will have:

A) A water-rich phase containing: 11%phenol and 89% water by weight in equilibrium with:

B) A phenol-rich phase containing 63% phenol and 37% water by weight

After the tie line intersects with the curve again, we will get a one-phase system consisting of a single phenol-rich phase.

Now, how can you determine the weight of each phase at any point on the tie-line? By taking point F, for example:

Weight of Phase A (water-rich phase) / Weight of Phase B (phenol-rich phase) = Length FC/Length of BF

Then we can calculate the weight of each component in each phase by simply multiplying the weight of each phase by the %w/w of each component in it.

Some systems show a decrease in miscibility with increasing temperatures and their curves show a lower CST appearing as a minimum point on the curve which will, compared to the phenol-water system phase diagram, look inverted like in case of the triethylamine-water system. Other systems will show both upper and lower CST's and their phase diagrams will give a closed loop like in the case of the nicotine-water system. However, there are solutions that do not exhibit CST's

EXPERIMENTAL PART:

Materials

76% wt/wt Phenol solution, Distilled water.

Apparatus:

11Test Tubes, Test Tube Holder, Burette, Beakers, Funnel, Water Bath, Thermometer.

Procedure:

Note:

Phenol is poisonous; the phenol-water mixtures used in this lab are concentrated and dangerous by contact or ingestion.

Phase diagram construction:

1-Prepare the following Concentrations of phenol in water mixtures (5ml each):

Volume (ml)	
phenol	**Water**
0.3	4.7
0.4	4.6
0.5	4.5
1.0	4.0
1.5	3.5
2.0	3.0
2.5	2.5
3.0	2.0
3.5	1.5
4.0	1.0
4.5	0.5

2- Heat each concentration separately on a water bath until you have a homogenous solution of phenol in water while gently stirring with the thermometer

3- Keep the thermometer inserted in the mixture; observe the temperature of the complete miscibility, indicated by the complete disappearance of any turbidity and the formation of one phase system.

4- Take the test tube outside the water bath, while gently stirring; observe the solubility temperature again, but this time by the first appearance of turbidity or two-phase system. Record

the solubility temperature in the table. If you missed the exact temperature, you can repeat the observation using the same mixture.

RESULTS AND CALCULATIONS:

Knowing that:

wt /wt % phenol = $\dfrac{\text{volume of phenol solution} \times \text{solution density} \times \text{phenol\% in stock solution}}{(\text{volume of phenol solution} * \text{solution density}) + (\text{volume of added water} * \text{water density})}$

Fill the table below with temperature of miscibility for each phenol- water mixture:

Sample	A	B	C	D	E	F	G	H	I	M	N
Temperature ^{0}C											
Phenol Conc.(wt/wt)%											

1. Plot the temperature of complete miscibility against composition.
2. Determine CST from the curve.
3. Determine the solubility of phenol in water and solubility of water in phenol at 45°C.
4. Calculate the composition of each phase of a 55% w/w phenol water mixture at 45°C.

Note:

Density of phenol solution =1.05 g/ml

Density of Water =1.00 g/ml

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TERNARY SYSTEMS

Objectives

- To construct the phase diagram of a ternary system.
- To illustrate the effect of solvent composition on the solubility of a third substance.

Theory

A ternary system is defined as a physicochemical system consisting of three components. Examples of ternary systems with practical importance are metal alloys, molten salts, oxides (slags), and sulfides (mattes), and systems of water and two salts with a common ion.

According to the phase rule, the variance, or number of thermodynamic degrees of freedom, of condensed ternary systems (those not containing a gaseous phase) at constant pressure is determined from the formula $F = C - P + 2$, where P is the number of phases in the system, and C is the number of components in the system.

Degrees of freedom are defined as: the least number of independent (intensive) variables that must be fixed to completely describe the system.

Example: for a system containing 3 components (ternary system) but only one phase:

$$F = 3 - 1 + 2 = 4$$

These four intensive variables are pressure, temperature and concentration of two of the three components.

Like in the previously mentioned example, we need four intensive variables to describe such a system. However, it is not practically possible to deal with four different variables at the same time. Therefore, in this experiment, we will work under constant pressure (condensed system) and constant temperature. In this case, we will deal only with the effects of the two remaining variables, which are the concentration of two of the three components.

Ternary phase Diagram:

Knowledge of the phase diagrams of ternary systems is necessary for an understanding of the nature of the interaction of the components and the practical use of such systems.

As seen in the graph, we can see a bimodal curve which represents the phase boundary (miscibility envelope). Above this curve we have one-phase region and below it we have two phase region. The two phases below the bimodal curve are taken to be a water-rich phase and a chloroform-rich phase, with acetic acid distributed between these two phases.

Acetic acid - Water - Chloroform

Taken as three different two-component systems, we find that water and acetic acid are miscible in all proportions, as are chloroform and acetic acid. However, water and chloroform are only partially miscible. This is represented by the two-phase region that lies on the chloroform/water base of the triangle. Note that the compositions on the base represent the compositions of water-rich and chloroform-rich phases in equilibrium at this Temperature and Pressure.

Not like the binary phase diagram, tie lines in ternary phase diagram are not necessarily parallel to each another or to the base line. In fact, the directions of tie lines are related to the shape of the bimodal curve; which in turn depends on the relative solubility of the third component (acetic acid) in the other two components. Even though, they never cross each other. Other properties of tie lines discussed previously in binary phase diagrams still apply.(in relation to compositions and relative amounts of conjugate phases)
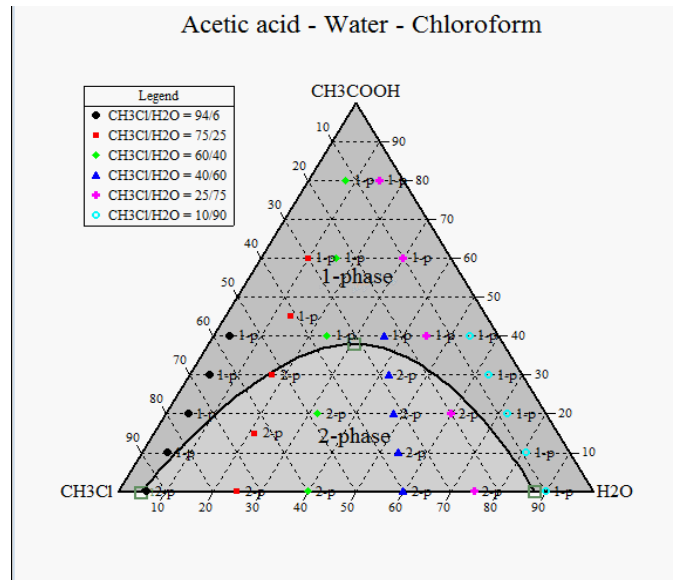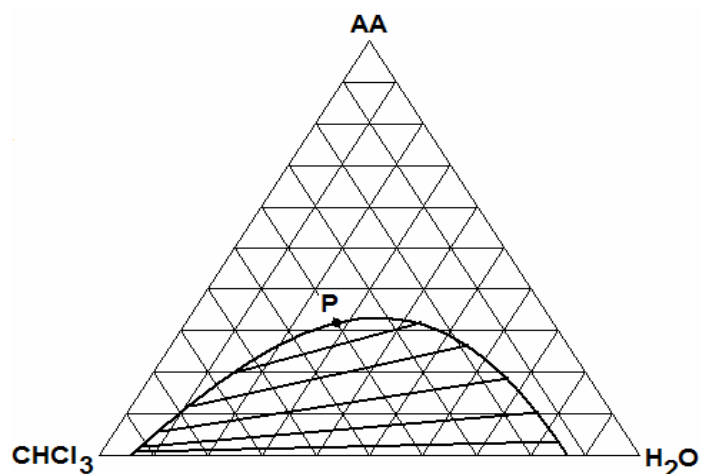
EXPERIMENTAL PART:

Materials:

Chloroform, GAA, Distilled water, Phenolphthalein, 1 M NaOH.

Apparatus

5 ml Volumetric pipettes, Bulb, Erlenmeyer Flasks, Beakers, Burette, Separatory funnel

Procedure:

Notes:

- G. Acetic Acid and Chloroform must be handled inside the fume hood.

- All volumes must be measured accurately.

Phase diagram construction:

1. Prepare the following solutions of glacial acetic acid (G.A.A) in water (20 ml each):

Conc. Of G.A.A (%v/v)	Volume (ml)	
	G.A.A	Water
10		
25		
45		
60		

2. Titrate each of the previous solutions with chloroform to the point of appearance of a second liquid phase.
3. Prepare the following solutions of glacial acetic acid in chloroform (20 ml each):

Conc. Of G.A.A (%v/v)	Volume (ml)	
	G.A.A	Chloroform
10		
15		
40		
60		

4. Titrate each of the previous solutions with water to the point of appearance of a second liquid phase

Tie lines construction:

1. Prepare 40 ml of each of the following mixtures: (calculate volume first)

Concentration % (v/v)			Volume (ml)		
G.A.A	Chloroform	Water	G.A.A	Chloroform	Water
10%	45%	45%			
20%	45%	35%			
30%	45%	25%			
40%	45%	15%			

2. Shake the mixtures in a separatory funnel for two minutes and leave for five minutes to separate.
3. Separate the two phases present in each mixture.
4. For each phase (separated in each step):
   a. Prepare a clean empty flask, and record the weight of this empty flask.
   b. Take 10 ml (accurately measured) from the solution, fill in the pre-weighed flask, and record the weight of the filled flask.
   c. Titrate the (10 ml solution) with 2 M NaOH using phenolphthalein as indicator.

RESULTS AND CALCULATIONS:

You will need the following information and table to construct the phase diagram:

- Density (chloroform):=1.477 g/ml
- Density (G.A.A)= 1.0495 g /ml
- Molar Mass (G.A.A) = 60 g/mol

1. **Acetic acid in water :**

G.A.A	Volume (ml)			Weight(g)				% w/w		
	G.A.A	Water	Chloroform	G.A.A	Water	Chloroform	Total	G.A.A	Water	Chloroform
10%										
25%										
45%										
60%										

2. **Acetic acid in chloroform:**

G.A.A	Volume (ml)			Weight(g)				% w/w		
	G.A.A	Chloroform	Water	G.A.A	Chloroform	Water	Total	G.A.A	Chloroform	Water
10%										
15%										
40%										
60%										

3. **Mixture system points:**

G.A.A %v/v	Volume (ml)			Weight(g)				% w/w		
	G.A.A	Chloroform	Water	G.A.A	Chloroform	Water	Total	G.A.A	Chloroform	Water
10%										
20%										
30%										
40%										

4. For each system:

| Phase	Flask Weight (g)		End Point (ml)	# moles G.A.A	Weight (g)		% w/w G.A.A
	Empty	Filled			G.A.A	Solution	
Aqueous							
Organic							

Using a triangular graph paper, plot the following:

1. Phase diagram for our ternary system.
2. The points representing each of the systems prepared in tie line experiment.
3. The tie lines.

Answer the following question in your report:

1. When do you expect to have symmetrical bimodal curve and parallel tie lines in ternary phase diagram?

Rules of Triangular Diagrams
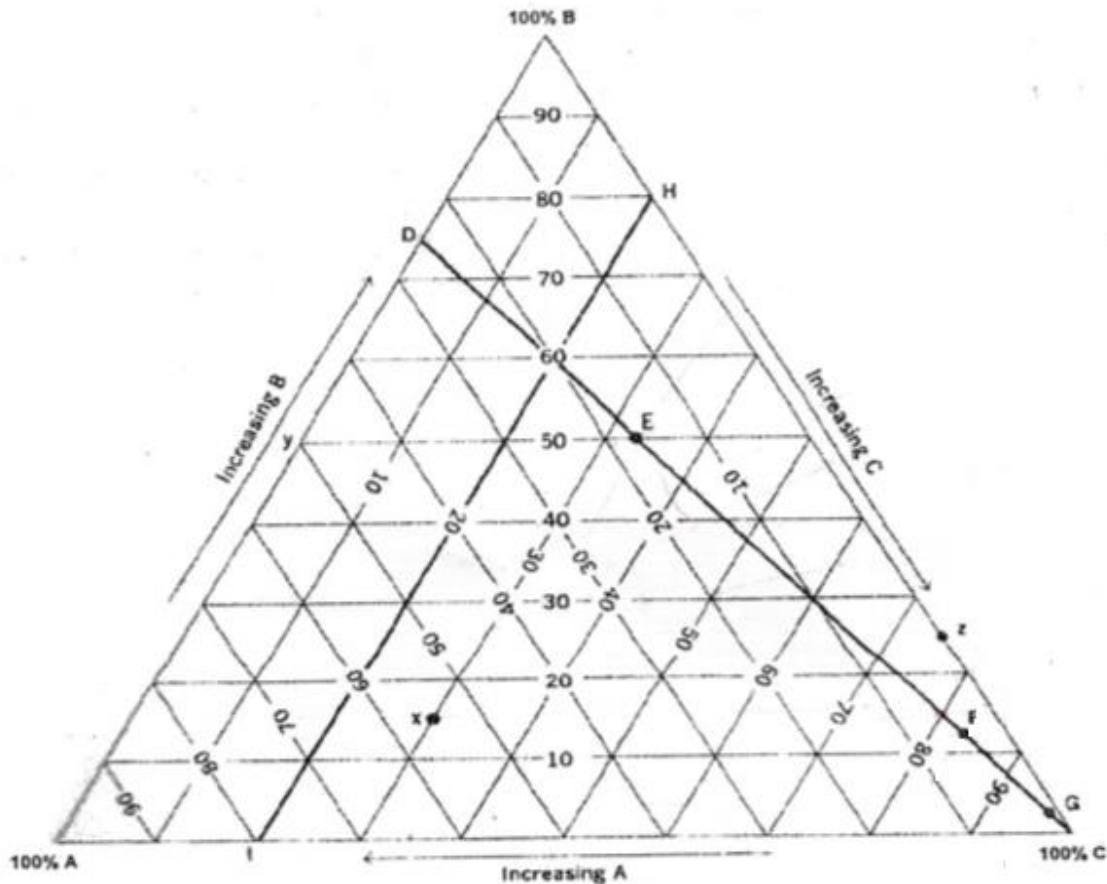
1. The composition of any system should be expressed as %w/w.
2. The percentage of the three components at any point should add up to a total of 100%.
3. For determining the % of a component (B for example) in any point, we start counting from the baseline opposite to its apex (line AC in this case) which represents 0% of this component. While moving toward the apex, the concentration of B increases until reaching 100% at the Apex.
4. When drawing a point representing a certain system, we take the intersection of the two lines representing the % of two of the components in this system.
5. Each of the three corners or apexes of the triangle represents 100% of one component (A, B, or C). As a result, that same apex will represent 0% of the other two components.
6. The three sides joining the corner points represents two-compartment mixtures of the three possible combinations of A, B, and C, (e.g. any point at the line AC represents a binary mixture of component A and components C). By dividing each line by into 100 equal units. The location of a point along the line can be directly related to the percent concentration of one component in a two component system, (e.g. point H represents 0% A, 80% B, and 20% C)

7. We divide the triangle from base to apex by equal parallel lines (100 lines >> from each base to the corresponding apex).
8. The area within the triangle represents all possible combinations of A, B, and C to give three-component systems, (e.g. point X represents 55% A, 15% B, and 30% C).
9. Any line drawn parallel to a side of the triangle represents systems containing a constant % of one of the three components, (e.g. any system at line HI will contain 20% of component C).
10. Any line drawn from an apex toward a baseline represents systems containing a constant ratio of two components, (e.g. any system at line DC will contain a constant ratio of A to B, i.e. %A/%B in any system at this line is 1 to 3)

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EXPERIMENT 8

DETERMINATION OF DISTRIBUTION COEFFICIENT OF I_2 AND STABILITY CONSTANT OF I_3^- COMPLEX

Objectives

- Determine the Distribution Coefficient (K_d) of molecular iodine between water and Ethyl Acetate.
- Determine the Stability Constant (K_s) of Iodine-Iodide complex.

Theory

The distribution Coefficient:
If an excess amount of a certain substance, is added to a mixture of two immiscible phases (i.e. liquids), it will distribute itself between the two phases so that each of them becomes saturated; provided that the substance is soluble in both phases.

If the substance is added in an amount insufficient to saturate each of the two phases, it will still become distributed between the two phases in a definite concentration ratio. This ratio is called Distribution (or Partition) Coefficient.

Distribution Coefficient (K_d) = Concentration in the first phase/ concentration in the second phase= C_1/C_2

For instance; if a substance is added to ethyl acetate/water mixture, then K_d of this substance is:

$K_d = C_{ethyl\ acetate}/ C_{water}$

Distribution coefficient is a function of:

1. Nature of the solute.
2. Type of the two immiscible phases.
3. Temperature of the system. (Why?)

Distribution coefficient governs the concentration ratio of the solute species common to both phases (i.e. in the same molecular condition). To better understand this idea, suppose that we have benzoic acid added to octanol/water mixture. This weak acid will be present in the aqueous phase in two different forms, which are dissociated form $[A^-]_w$ and un-dissociated $[HA]_w$. On

the other hand, it can be present in the organic phase in the un-dissociated form $[HA]_0$ and in the dimer form $[2HA]_0$.

In this case: $K_d = [HA]_0 / [HA]_w$

Distribution phenomenon is involved in several areas of pharmaceutical interest, which includes:

1) Preservation of oil-water systems (i.e. emulsions).
2) Drug actions at nonspecific sites.
3) The absorption and distribution of drugs throughout the body.
4) Chromatographic separation technique.
5) Extraction purposes.
6) Determination of complex stability constant.

The stability constant:
Complexes are structures that result from a donor-receptor interaction between two or more different chemical constituents.

Intermolecular forces involved in the formation of these complexes are:

1. Covalent bonds.
2. Van der Waal forces.
3. Dipole or induced Dipole bonds.
4. Hydrogen bonds.
5. Charge transfer and hydrophobic interactions.

Complexes can be divided into three broad classes, which are:

1. Metal Ion Complexes.

In which a central metal ion is bonded to one or more ligands by a coordinate bond, for example: chelate complexes.

2. Organic Molecular Complexes.

Molecular complexes consist of constituents held together by weak forces. For example: Caffeine with acidic drugs.

3. Inclusion/Occlusion Compounds.

In which one of the constituents is trapped in the open lattice or cage-like structure of the other to yield a stable arrangement. For example: Cyclodextrins with hydrophobic drugs.

Determination of the stoichiometric ratio of ligand-to-metal or donor-to-acceptor, and of a quantitative expression of the stability constant (K_s) for complex formation are important in the study and application of complexes.

In this experiment, we are going to use the 'Distribution Method' to determine the stability constant (K_s) of iodine-iodide complex.

$$I_2 + I^- \longleftrightarrow I_3^-$$

The complex stability constant determined at equilibrium is given by:

$K_s = [I_3^-]_{complex} / ([I_2]_{free} \times [I^-]_{free})$

The concentrations of the above species can be determined from the initial concentrations, the distribution coefficient (K_d) of molecular iodine between two immiscible solvents, and from the fact that only molecular iodine will be present in the organic phase, while both ionized and molecular iodine will be present in the aqueous phase.

Experimental Part

Materials and apparatus:

0.04 M I_2/Ethyl Acetate, 0.1 M NaI, Distilled water, pure Heptane, 0.1 M $Na_2S_2O_3$, 0.01 M $Na_2S_2O_3$, conical flasks, burets, volumetric pipets(10 ml and 25 ml), beakers, separatory funnel, measuring cylinder, pipette filler.

Procedure

Important Note: during the titration of organic phase, very good shaking is required after each addition of $Na_2S_2O_3$ in order to extract I_2 from the organic phase; because the interaction between them takes place in the aqueous medium.

K_d Determination:

1. Take 20 ml of 0.04 M I_2/Ethyl Acetate solution (organic phase), place in separatory funnel, add 100 ml distilled water (aqueous phase).
2. Shake at intervals for about 10 min.
3. Allow the equilibrium to establish in the system at room temperature.
4. Separate the two layers.

Titration of organic layer:

1. Using a pipet transfer 10 ml of the organic layer to a conical flask containing 10 ml of 0.1M NaI.
2. Titrate with 0.1 M $Na_2S_2O_3$ until the disappearance of color.
3. Note that the chemical reaction that occurs is : $2Na_2S_2O_3 + I_2 \longrightarrow 2\ NaI + Na_2S_4O_6$

Titration of aqueous layer:

1. Transfer 25 ml of aqueous layer to an Erlenmeyer flask containing 10 ml of 0.1M NaI.
2. Add 1 ml of Heptane, which will act as an indicator, and shake the solution (heptane will extract I_2 and appear as pink droplets).
3. Titrate with <u>0.01 M</u> $Na_2S_2O_3$ until the disappearance of pink color (of heptane droplets).

K_s Determination:

Repeat the previous procedures using 0.1 M NaI instead of distilled water as an aqueous phase and 0.04 M I_2/ ethyl acetate as an organic phase.

Results and calculations

K_d Determination:

End Point		[I_2], M		K_d
Organic	Aqueous	Organic	Aqueous	

K_s Determination:

End point		[I_2], M				K_s
		Organic	Aqueous			
Organic	Aqueous	[I_2] free	[I_2]free	[I_3^-]complex	[I^-]free	

EXPERIMENT 9

TRANSFER OF SALICYLIC ACID ACROSS POLYMERIC MEMBRANE

Objectives

- To demonstrate the diffusion characteristics of salicylic acid across polymeric membrane.

Theory

Diffusion can be defined as the spontaneous flow of molecules from a region of high concentration to a region of lower concentration as a result of the solute molecules' Brownian movement. The flow of molecules is described by Fick's law:

$$J = dM / S.dt$$

Where J is the solute flux. The flux J, is the amount of material, M, flow through barrier unit cross section area, S, in unit time, t.

If a drug of a concentration Cd is placed in a donor compartment and separated from a receptor compartment by a membrane of thickness, h , then the flux of the drug from the donor to the receptor compartment, when steady state **sink condition** (in in vivo absorption, sink conditions are brought about by the movement of drug molecules away from the absorption site in the blood stream, thus, in in vitro diffusion experiments, there should be a way of maintaining sink conditions) are assumed, is given by:

$$dM/ Sdt= DK Cd/h \qquad dM = (SDK Cd/ h) dt$$

If the membrane permeability coefficient, P is given by:

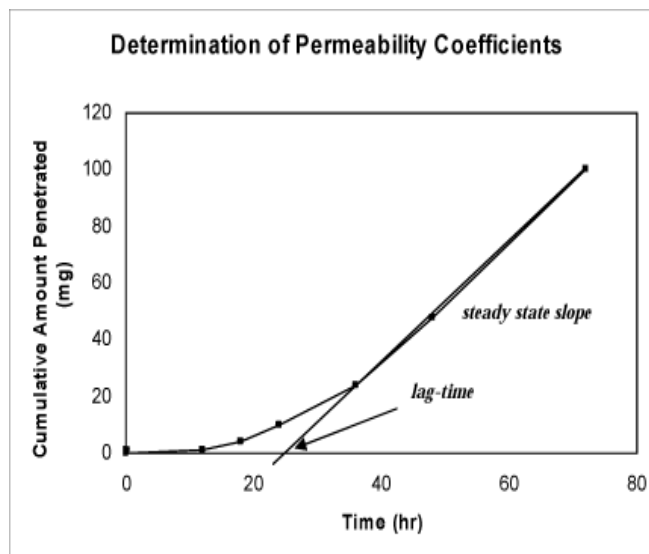$$P= DK/h \quad then \quad dM= PS Cd dt \qquad or M= P S Cd t$$

Where D= the diffusion coefficient of the drug

K= partition coefficient of the drug between the membrane and the solvent.

If also the donor compartment concentration does not change appreciably during diffusion, then Cd will be constant and the plot of M vs. Time will take the following form:

Determination of Permeability Coefficients

Initially, the flux (given by the slope divided by the surface area) will be increasing until the diffusing species gets equilibrated throughout the membrane. Afterwards, steady state conditions are established, and flux will be constant as well as we have a constant concentration gradient across the membrane. Therefore, the latter portion of the curve will be linear. Extrapolation the curve to the time axis will give the lag time

(t_{lag}) which is related to the time required for the before mentioned diffusing species equilibration across the membrane to be achieved. The slope of this linear portion will equal the flux, J, multiplied by the surface area, S, therefore:

$$\textbf{Slope} = \textbf{\textit{J S}} = \frac{\textbf{\textit{D}}\times\textbf{\textit{S}}\times\textbf{\textit{K}}\times\textbf{\textit{C}}_{\textbf{\textit{d}}}}{\textbf{\textit{h}}} = \textbf{\textit{P S C}}_{\textbf{\textit{d}}}$$

Experimental Part

Materials and apparatus:

Phosphate buffer pH= 7.4, distilled water, saturated solution of salicylic acid, scissors, Teflon tape, thread, polymeric membrane, volumetric pipettes, stop watch, beakers, test tubes, measuring cylinders, burette, volumetric flasks.

Procedure:

1. Prepare your solution reservoir using a test tube covered by the polymeric membrane. Fix the latter using thread and a Teflon tape.
2. Take by pipettes 10 ml of saturated solution of salicylic acid and place them into reservoir. Put the system inside a beaker containing 30 ml of phosphate buffer pH 7.4 (receiving medium).
3. Bring the reservoir in contact with the receiving medium, 5 ml sample is taken by pipette from the receiving medium as soon as possible, the time is recorded, then 5 ml is taken by pipette

after 3,5,10,15,30,45,60,75,90 minutes. 5 ml phosphate buffer pH 7.4 should be added to the receiving medium after each sampling to keep the volume of the later constant.

4. Stirring should be carried out at all the time of the experiment since it is very important factor in diffusion process, start stirring in a very slow, vertical and continuous movement, to prevent the formation of air bubbles and to ensure good mixing.
5. Measure the absorbance of each sample using the spectrophotometer at 296 nm wavelength. Dilute if necessary
6. Calculate the drug concentration in each sample using the calibration equation.

Results and calculations:

Record your own sampling time whenever it differs from the listed times.

Time (min)	Absorbance	Conc. (µg /ml)	Amount in 5 ml sample taken (mg)	Amount present is the receptor compartment (mg)	Total amount removed from the receptor compartment for sampling prior to taking this sample (mg)	Total amount, M, that has diffused from the donor compartment (mg)

➢ **Required tasks in the report:**

- **Construct your own calibration curve according to the following instructions**
1. Take 1 ml of the saturated salicylic acid solution (conc. = 2.2 g/L) and dilute up to 100 ml with the buffer.
2. From the resulting solution, take 2, 4, 6 and 8 ml and dilute each up to 10 ml.
3. Measure the absorbance of each solution.
- Use the calibration curve, or the calibration equation, to calculate the drug concentration.
- When diluting any sample, consider the dilution factor in your calculations.
- Record the diffusion surface area S as ………….. cm^2

- Plot the amount, M, of salicylic acid versus time using regular graph paper.
- From the plot calculate the value of P.
- The time taken for the equilibrium concentration of the drug to be established in the membrane is known as the lag time, if you were able to detect this time, use the equations:

$T_{lag} = h^2 / 6D$ and $t_{lag} = h/6p$ to calculate approximate values for h and D.

$T_{lag} =$ h=   D=

Questions:

1. Sink conditions are assumed when Cd>> Cr, according to the results of your experiment can you consider it as sink condition? Why?
2. What factors contribute to creating sink conditions in our experiment?
3. What would be the factors affecting the diffusion rate and the lag time?

References:

- 2015:https://www.google.jo/search?q=concentration+vs+time+flux&safe=active&biw=1680&bih=955&source=lnms&tbm=isch&sa=X&ei=vufiVKfZDpGLaIOcgtAK&ved=0CAYQ_AUoAQ#safe=active&tbm=isch&q=concentration+vs+time+flux+lag+time&imgdii=_&imgrc=myNd3Z-Fg83btM%253A%3Bxlwo5LSgzjqVIM%3Bhttp%253A%252F%252Fwww2.mst.dk%252Fudgiv%252Fpublications%252F2009%252F978-87-7052-980-8%252Fhtml%252Fimages%252Fs21.gif%3Bhttp%253A%252F%252Fwww2.mst.dk%252Fudgiv%252Fpublications%252F2009%252F978-87-7052-980-8%252Fhtml%252Fhelepubl_eng.htm%3B432%3B314

EXPERIMENT 10

CRITICAL MICELLE CONCENTRATION

Objectives

    a. To learn the process involved in CMC determination of a surfactant using surface tension measurements and conductivity method.

    b. To recognize the pharmaceutical applications of surfactants.

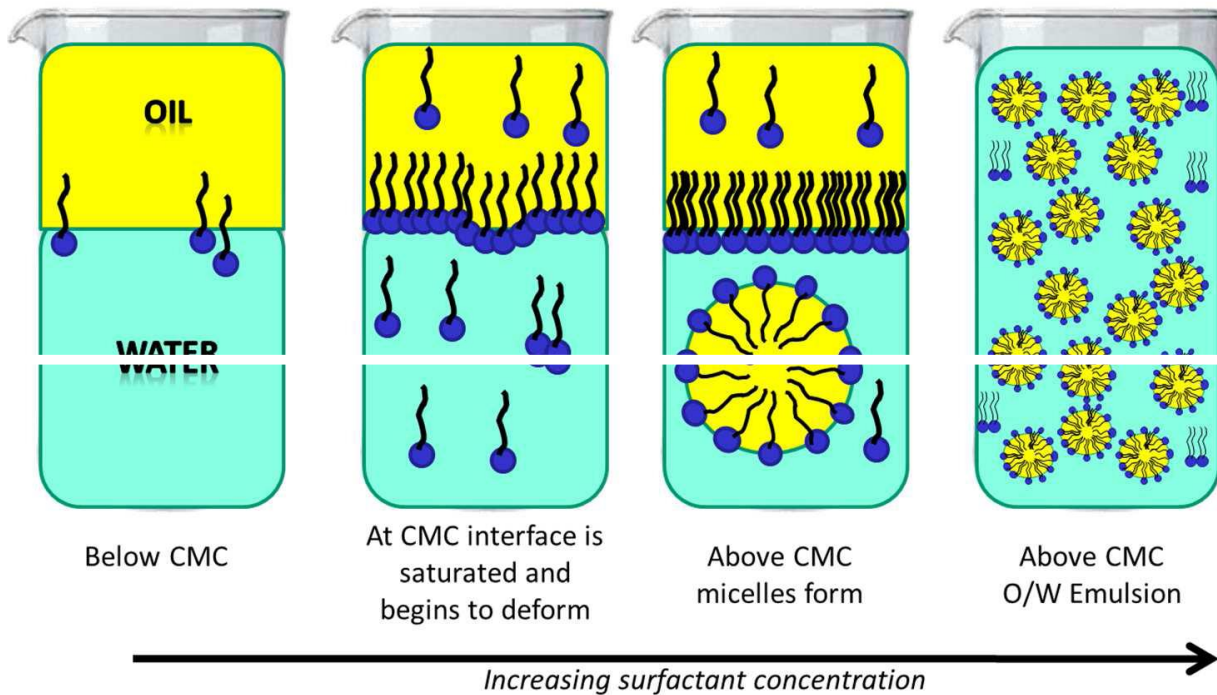   c. To be familiar with the concept of phase inversion.

Theory

Surfactants are amphiphilic molecules that possess both hydrophobic and hydrophilic properties. A typical surfactant molecule consists of a long hydrocarbon 'tail' that dissolves in hydrocarbon and other non-polar solvents, and a hydrophilic 'headgroup' that dissolves in polar solvents (typically water), the hydrophilic part could be anionic, cationic, ampholytic or non-ionic. There are two general types of surfactants: nonionic and ionic surfactants. Glyceryl monostearate is a nonionic surfactant, whereas sodium lauryl sulfate is an ionic surfactant. In order to reduce the free energy of the system, the surfactant molecule will orient itself so that the hydrophobic (water-hating)/lipophilic (oil-loving) group will be positioned at the surface facing the air, and the hydrophilic (water-loving) group will be positioned facing water. When the surfactant concentration increases so that the water surface is fully occupied, the added molecules will go into bulk solution forming aggregates called micelles, where the surfactant molecules orient themselves so that the hydrophilic groups are located at the surface facing water while the hydrophobic groups are located in the interior away from water forming a hydrophobic core. This concentration is called the critical micelle concentration (CMC).
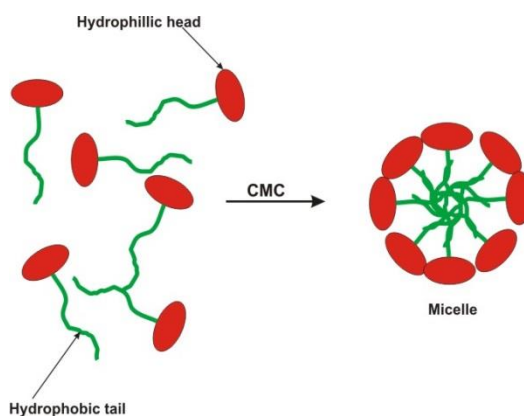
CMC determination is based on the fact that different properties of a surfactant solution are affected by its concentration in a different manner before and after reaching the CMC because, prior to reaching CMC, the surfactant molecules are present as monomers, while, after reaching CMC, micelles form and exist in equilibrium with the monomers. Examples on such properties are the surface tension and conductivity.

Surface-active agents (surfactants) form micelles in aqueous solution above a critical concentration called the critical micelle concentration (CMC). Since the surfactant molecules would much rather live at an interface than be in either solution alone, when the interface is saturated, the surfactant molecules create more interface by increasing the surface area real estate by creating micelles. In aqueous solution, the micelle has a hydrophobic core and a dielectric gradient towards the surface of the micelle making the micelle surface hydrophilic.

Thus, the micelle can act as a soluble phase for non-polar solutes (core), semi-polar solutes (palisade layers) and polar solutes (surface). As a result, the efficiency of a particular surfactant as a solubilizing agent varies from substance to substance. The process of increasing the water solubility of a solute (drug) using a surfactant is called micellar solubilization.

Below CMC | At CMC interface is saturated and begins to deform | Above CMC micelles form | Above CMC O/W Emulsion

Increasing surfactant concentration

Surface tension: the molecules at the surface of a liquid are much more strongly attracted to their counterparts below or adjacent to them than to air, leading them to experience a net inward drag force into the bulk. This force pulls the surface molecules together contracting the surface and so giving rise to surface tension.

Surface tension can be **defined as** the force per unit length that has to be applied parallel to surface in order to counterbalance the aforementioned pull force. Or, it could be defined as the work (surface free energy increase in this case) per unit increase in surface area required for expanding the area of the liquid surface.

Examples on methods of measuring surface tension include the Du Nouy tensiometer and the capillary rise methods.

The Du Nouy tensiometer will measure the force required to detach a platinum-iridium ring immersed at the surface which is directly proportional to the surface tension.

Capillary rise method is based on the fact that if the forces of adhesion between the liquid molecules and the glass surface exceed the cohesive forces among the liquid molecules, the liquid will spread over the capillary wall and its surface tension will result in an upward drag force resulting in the liquid level rising through the capillary until this upward force is balanced by the downward gravitational force. That's why water rises and forms a concave surface in glass capillaries. It is clear that the greater the surface tension, the greater is the capillary rise. Surface tension can be calculated from capillary rise by the following equation:

$Y = 0.5 * r * p * g * h$

Where Y is the surface tension, r is the capillary radius, p is the density of the liquid, g is the acceleration due to gravity and h is the capillary rise (make sure to use the right units). If the surface tension of any material, like water in our case, is known, and its capillary rise is determined at the same conditions as our solution of interest, then:

$Y_{solution} / Y_{water} = p_{solution} h_{solution} / p_{water} h_{water}$

Upon adding surfactant, the surface tension will decrease as the surfactant molecules accumulate at the surface because the attractive forces between the hydrophobic groups are less than that between water molecules, so that the surface tension of water will be decreased as more surfactant molecules are added to the surface until the CMC is reached. The decrease in surface tension will be linear in relation to the logarithm of surfactant concentration. But, after reaching
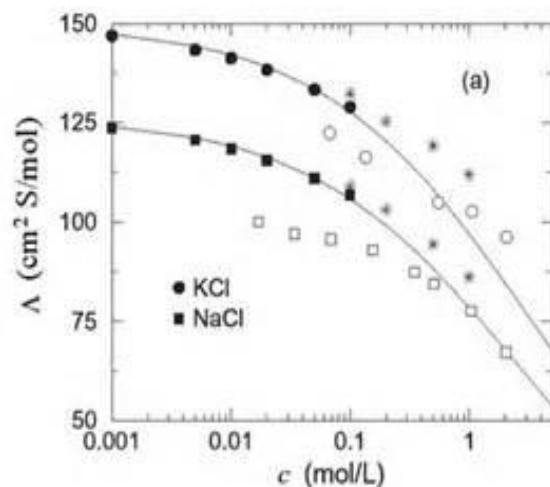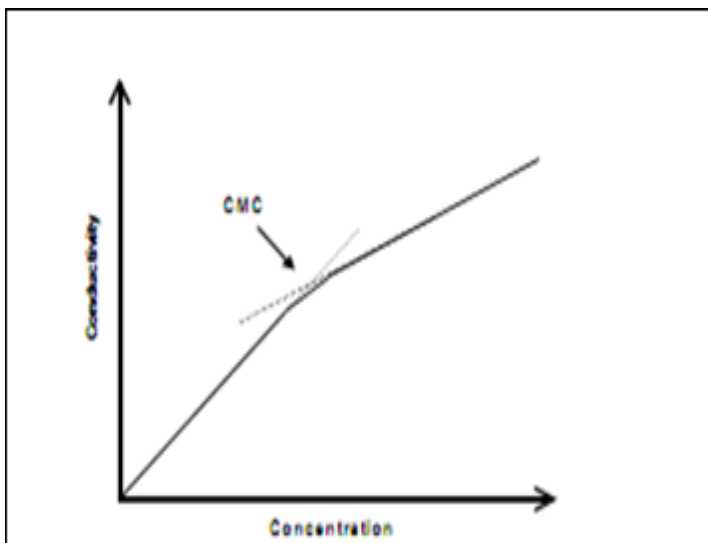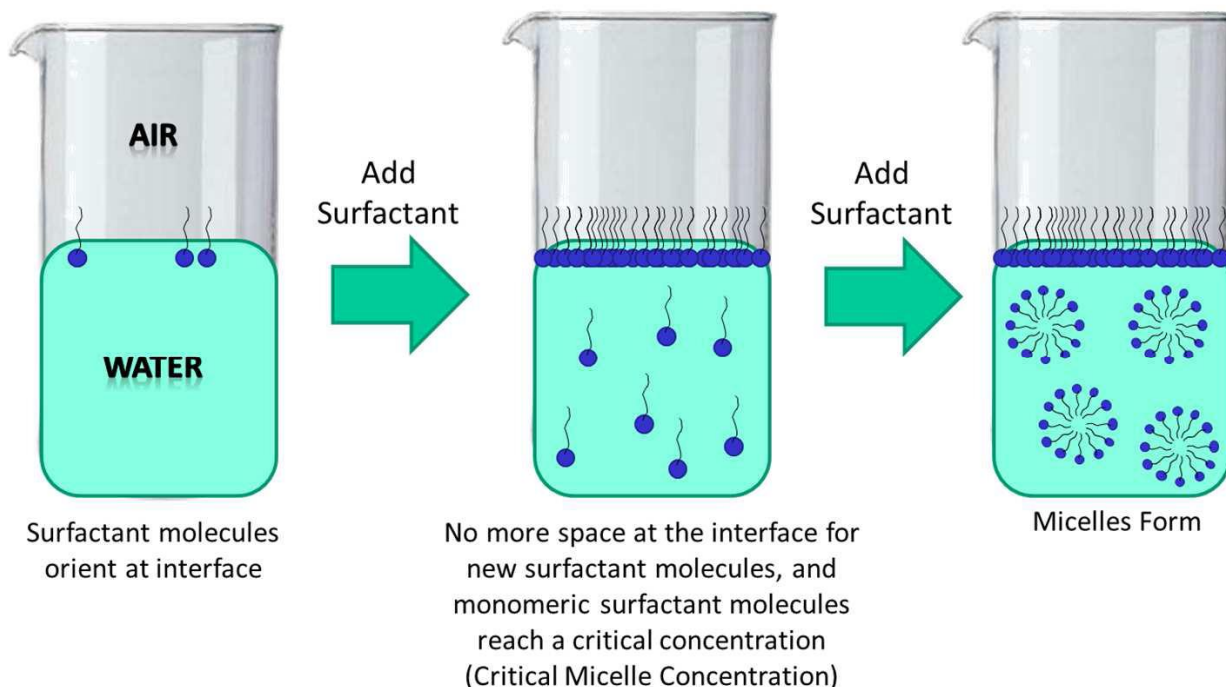
CMC, most of the added surfactant molecules will go to the micelles in the bulk resulting in a drastically reduced slope of the decrease.

For ionic surfactants, electrical conductivity measurements may be used. Specific conductance increases with an increasing ionic surfactant concentration due to the increase in the number of ions in the solution, but, after reaching CMC, this increase becomes less steep, since, due to their size micelles are less capable of conducting electricity. As for equivalent/molar conductance, which is defined as the conductance of a solution of a concentration c (expressed in units of normality/molarity) of sufficient volume to contain one equivalent/mole of the solute when measured in a cell in which the electrodes are spaced 1 cm apart. It decreases linearly with square root of the concentration since the ions get more hindered by their neighbors in more concentrated solutions. At concentration above CMC, the decrease in equivalent/molar conductance becomes steeper as micelles; due to their size will even more hinder the mobility of their neighbors. In addition, its relationship with the square root of concentration often deviates from linearity at concentrations above CMC especially at very high concentrations. **Note that conductivity methods can be applied only to ionic surfactants.**

Surfactants in a Water-Only System

In the second part of this laboratory, we are examining the effect of increasing surfactant concentration on electrical conductance of the solution. This is because the solvent more strongly interacts with the hydrophilic moiety of the surfactant molecule. As there is no oil phase in this system, at low concentrations the surfactant molecules will tend to orient at the air-liquid interface. Like the Oil-Water diagram, as the surfactant concentration is increased, the interface will become saturated with surfactant, and eventually superstructures of surfactant molecules will form in solution:

Surfactant molecules orient at interface

No more space at the interface for new surfactant molecules, and monomeric surfactant molecules reach a critical concentration (Critical Micelle Concentration)

Micelles Form

Superstructures of surfactant are concentration-dependent. Above the CMC, other structures also form, including cylinders and sheets.
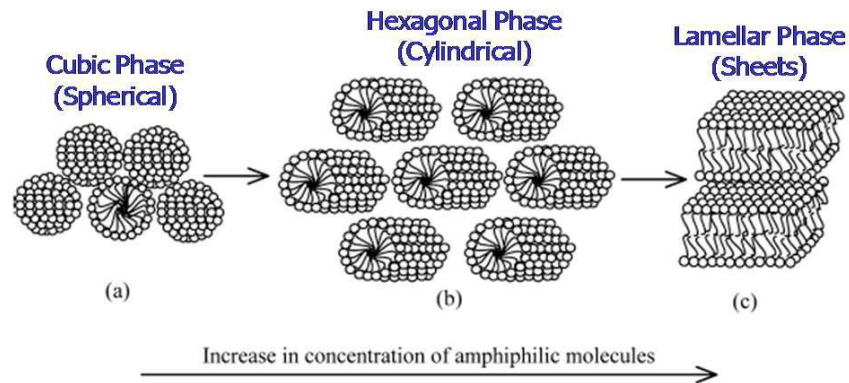
An important feature of the CMC is that at surfactant concentrations below it, the osmotic properties of the liquid change drastically with surfactant concentration. However, once the air liquid interface is saturated, changes in osmolarity, solution conductance, and surface tension are much less pronounced. Consequently, the CMC may be found by measuring these properties as a function of surfactant concentration.

> **Pharmaceutical Applications.**

The vast majority of drugs are hydrophobic. However, often aqueous solutions, suspensions, or emulsions are required (e.g. intravenous and topical formulations). Surfactants, when organized into micelles, solibilize drugs by entrapping them in their hydrophobic core. Drugs which would never exist in aqueous solution can be wetted and effectively dissolved using an appropriate type and concentration of surfactant. Micelle formation and phase inversion is depending upon the surfactant's concentration. Too low a concentration will leave surfactant only at the interface of the formulation.

Particularly with emulsions, compounding must involve knowledge of the concentration of surfactant required in order to achieve the desired emulsion (e.g. O/W, W/O, O/W/O, W/O/W) as well as the target micellar size.

Hydrophile-Lipophile Balance (HLB) System

The orientation and positioning of a surfactant molecule at the oil-water interface would depend on the interactions of the hydrophilic and lipophilic segments with the environment. The molecules' hydrophilic portion can be expected to dissolve in, or associate with the aqueous phase of the system. On the other hand, the lipophilic portion would dissolve in the oil phase. The balance between the hydrophilic and lipophilic properties of a surfactant has been codified by the hydrophile-lipophile balance (HLB) system. Griffin, almost 40 years ago, established an empirical scale of HLB values for a variety of nonionic surfactants. The original concept defined HLB as the percentage (by weight) of the hydrophile, divided by 5 to yield more manageable values:

(1) HLB = wt. % hydrophile / 5

The HLB system provides a rational means for identifying combinations of emulsifiers and facilitates the formulation of stable emulsion. Surfactants with a high HLB dissolve or disperse in water, while those with a low HLB dissolve or disperse in oil.

· Surfactants with an HLB from 1-10 are considered lipophilic.

· Surfactants with an HLB from 10-20 are considered hydrophilic.

A list of the average HLB values of some common surfactants is provided in the appendix of this manual. The HLB of a surfactant will help determine what application it will be most useful for:

Experimental Part:

This experiment will be divided into two parts:

Part A where you will determine the CMC using the capillary method

Part B where you will determine the CMC using conductivity.

❖ <u>Part A:</u>

Materials and equipment

Capillary tubes, beakers, graduated ruler, rubber band, v. pipette, pipette filler, volumetric flasks 50 ml.

Procedure

- Prepare the following concentrations of sodium lauryl sulfate solutions: 0.005M, 0.006M, 0.0082M, 0.010M, 0.015M, 0.020M
- Clean the ruler very well with distilled and dry it very well.
- Attach a perfectly clean capillary to the ruler using a rubber band.
- Place the capillary attached to the ruler in a 50 ml beaker containing 25 ml of the liquid.
- Measure the difference in height between the liquid surface in the beaker and the capillary and record it.
- Repeat for the other solutions.
- Estimate the density of each solution by measuring the weight of a small beaker before and after pipetting 10 ml of the solution into it.

Results

Fill the table:

Surfactant conc. (mol/L)	Capillary rise (cm)	Surface tension, dyne/cm capillary
Pure water		
0.005		
0.006		
0.0082		
0.010		
0.015		
0.020		

> ➢ **Calculations and Graphs**:
> 1. Plot surface tension versus surfactant concentration on a semi-log paper.
> 2. From the graph determine the CMC.

❖ Part B:
- **Materials and Special Equipment:**

Sodium Lauryl Sulfate, 150 mL Beaker, 100 mL Volumetric Flasks, Conductivity Meter.

- **Part 1. Preparing the Solutions**

Water acts as an insulator. As a charged species is added, the current may more readily flow between the electrodes. The amount of current that flows can be proportional to the concentration of ionic species present. Below the CMC, the addition of amphiphiles causes an increase in charge carriers, and we observe an increase in current. Above the CMC, there is an increase in micelle concentration, and the monomer concentration stays the same. Hence the relative leveling of the curve with the break occurring at about the point that [C] = CMC.

1. Prepare the following solutions in de-ionized water in 100 mL volumetric flasks:

Concentration Of SLS	Conductivity
0.005 M	
0.006 M	
0.0082 M	
0.010 M	
0.015 M	
0.020 M	

NOTE: When you are working with SDS solutions, avoid shaking them. Agitate gently, in order to minimize bubble formation. Pour slowly and on an angle. When diluting to the mark, do not use the top of the bubbles as a guide. Wait for a clear liquid meniscus to form, and add fluid until the etched line at the neck of the volumetric mark.

2. Using the conductivity meter, measure the conductivity of each of the solutions prepared.
3. Plot conductivity vs. concentration of the surfactant

Questions

1. If a non-ionic surfactant were used in Part B of this experiment, would the experimental design have to change? If so, how?

References:

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- 2015: http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Rate_Laws/The_Rate_Law
- 2015: http://en.wikipedia.org/wiki/Critical_micelle_concentration