B.Sc. CHEMISTRY LAB MANUAL

6th Semester

Prepared By

Pure & Applied Science Dept.

Chemistry

MIDNAPORE CITY COLLEGE

CHEMISREY HONOURS

[Choice Based Credit System]

SEMESTER-VI

C14P: LAB (Physical Chemistry)

Experiment 1: Study of kinetics of $K_2S_2O_8$ + KI reaction, spectrophotometrically

Theory:

Kinetics, the study of reaction rates, is an important area of chemistry. One of the factors that affect the rate of a reaction is the concentration of the reactant. This factor can be studied by verifying the concentration of the reactants in a systematic manner. An interesting kinetics aspect of kinetics is the order of a reaction. A reaction is a first order if an increase in concentration produces the same increase in rate, that is, if doubling the concentration of a reactant doubles the rate, the reaction is first order in that reactant. If doubling the concentration of a reactant causes a fourfold increase in the rate, then the reaction is second order in that reactant. If doubling the concentration of a reactant causes an eight fold increase in the rate, then the reaction is third order. The rate of a reaction can be followed spetrophotometrically if one of the reactants or products absorbs light strongly and distinctly from the other reactants or products. The rate of the reaction is represented by the slope of the line in a graph of absorbance vs. time. If one wishes to do so, standards may be prepared and the absorbance converted into concentration.

Purpose: the purpose of this experiment is to determine the rate of the reaction of potassium iodide ant potassium persulfate and to determine the order of each reactant and the overall order of the reaction.

Experiment:

Apparatus:

Spectrophotometer, cuvettes, 1 ml pipet, 2 small test tube, parafilm

Chemicals:

Potassium iodide, potassium persulfate,distilled water,

Procedure:

1. Turn on the spectrophotometer.
2. Place 2 ml of KI and 2 mL of water into a cuvette to serve as the blank.
3. Insert the blank into the spectrophotometer and set the wave length to 350 nm. Set the absorbance to zero.
4. Place the required amount of KI and water into a cuvette and place the required amount of potassium persulfate into a small test tube.
5. Quickly pour the contents of the test tube into the cuvette, convert the cuvette with parafilm and invert three times. Remove the cover from the sample compartment of the spectrophotometer, insert the cuvette and recover quickly.
6. Record the absorbance every 2 seconds for 2 minutes. Consider the absorbance at time 0 to be 0. Being taking reading 10 seconds after pouring the contents of the test tube into the cuvette.
7. When the run is complete, remove the cuvette and clean thoroughly. Prepare to do the second set. Repeat step 4-6 using as many sets as assigned by the instructor.
8. Plot each run on the same graph. Determine the slope of each run.

Data table:

Set#	Time(sec)	Absorbance
Vol. of KI	0	
Vol. of $K_2S_2O_8$	10	
Vol. of water	20	
	30	
	40	
	50	
	60	

Calculation:

	[KI]	[$K_2S_2O_8$]	Slope	Rate
Set 1				
Set 2				
Set 3				
Set 4				

Order: KI

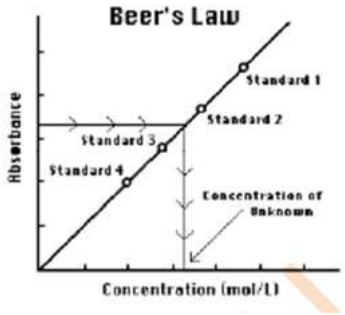
$K_2S_2O_8$

Experiment 2: Verification of Beer and Lambert's Law for KMnO4 and K2Cr2O7 solution

1. AIM: To verify Lambert – beer's law for $KMnO_4$ colorimetrically.

Theory:

The primary objective of this experiment is to determine the concentration of an unknown $KMnO_4$ solution. The $KMnO_4$ solution used in this experiment has a blue color, so Colorimeter users will be instructed to use the red LED. A higher concentration of the colored solution absorbs more light (and transmits less) than a solution of lower concentration.



You will prepare five of known concentration (standard solutions). Each solution is transferred to a small, rectangular cuvette that is placed into the Colorimeter or Spectrometer. The amount of light that penetrates the solution and strikes the photocell is used to compute the absorbance of each solution. When you graph absorbance vs. concentration for the standard solutions, a direct relationship should result. The direct relationship between absorbance and concentration for a solution is known s Beer's law. You will determine the concentration of n unknown KMnO4 solution by measuring its absorbance. By locating the absorbance of the unknown on the vertical axis of the graph, the corresponding concentration can be found on the horizontal axis. The concentration of the unknown can a so be found using the slope of the Beer's law curve.

Apparatus:

Colorimeter cuvette five 20 × 150 mm, test tubes, two 10 mL pipets or graduated cylinders, two 100 mL beakers, distilled water, test tube rack stirring rod, tissues (preferably lint-free)

Chemicals: 0. 01M KMnO4 solution

Procedure:

1. Obtain small volumes o0. 01M KMnO4f solution and distilled water in separate beakers.

2. Label five clean, dry, test tubes 1–5. Use pipets to prepare five standard solutions according to the chart below. Thoroughly mix each solution with a stirring rod. Clean and dry the stirring rod between uses.

Test tube	0.01 M $KMnO_4$	Distilled water	concentration
1	2	8	0.002
2	4	6	0.004
3	6	4	0.006
4	8	2	0.008
5	10	0	0.0100

Prepare a blank by filling a cuvette 3/4 full with distilled water. To correctly use cuvettes, remember:

- Wipe the outside of each cuvette with a lint-free tissue.
- Handle cuvettes only by the top edge of the ribbed sides.
- Dislodge any bubbles by gently tapping the cuvette on a hard surface.
- Always position the cuvette so the light passes through the clear sides.

You are now ready to collect absorbance-concentration data for the five standard solutions.

a. Using the solution in Test Tube 1, rinse the cuvette twice with ~1 mL amounts and then fill it 3/4 full. Wipe the outside with a tissue and place it in the device.
b. When the absorbance readings stabilize,
c. Discard the cuvette contents as directed. Using the solution in Test Tube 2, rinse and fill the cuvette 3/4 full. Wipe the outside and place the cuvette in the device (close the lid of the Colorimeter). When absorbance readings stabilize,
d. Repeat the procedure for Test Tubes 3 and 4. Trial 5 is the original 0.01M KMnO4solution. Note: Do not test the unknown solution until Step 9.

Determine the absorbance value of the unknown KMnO4 solution.

a. Obtain about 5 mL of the unknown KMnO4 in another clean, dry, test tube. Record the number of the unknown in your data table.

b. Rinse the cuvette twice with the unknown solution and fill it about 3/4 full. Wipe the outside of the cuvette, place it into the device. (Close the lid of the Colorimeter.)

c. Read the absorbance value displayed in the meter. When the displayed absorbance value stabilizes, record its value as Trial 6 in your data table.

d. Select Interpolate from the Analyze menu. Find the absorbance value that is closest to the absorbance reading you obtained in Step c above. Determine the concentration of your unknown KMnO4 solution and record the concentration in your data table.

e. Dispose of any of the remaining solutions as directed.

Data table:

Trial	Concentration (mol/L)	Absorbance
1	0.002	
2	0.004	
3	0.006	
4	0.008	
5	0.010	
6	Unknown number	

2. Verify Lambert – beer's law for $K_2Cr_2O_7$ colorimetrically.

Theory:

The primary objective of this experiment is to determine the concentration of an unknown $K_2Cr_2O_7$ solution. The $K_2Cr_2O_7$ solution used in this experiment has a blue color, so Colorimeter users will be instructed to use the red LED. A higher concentration of the colored solution absorbs more light (and transmits less) than a solution of lower concentration.

You will prepare five of known concentration (standard solutions).

Each solution is transferred to a small, rectangular cuvette that is placed into the Colorimeter or Spectrometer. The amount of light hat penetrates the solution and strikes the photocell is used to compute the absorbance of each solution. When you graph absorbance vs. concentration for the standard solutions, a direct relationship should result. The direct relationship between absorbance and concentration for a solution is known as Beer's law.

You will determine the concentration of an unknown $K_2Cr_2O_7$ solution by measuring its absorbance. By locating the absorbance of the unknown on the vertical axis of the graph, the corresponding concentration can be found on the horizontal axis. The concentration of the unknown can a so be found using the slope of the Beer's law curve.

Apparatus and chemicals:

Colorimeter cuvette, five 20 × 150 mm test tubes, two 10 mL pipets or graduated cylinders, two 100 mL beakers, 0. 01M $K_2Cr_2O_7$ solution, distilled water, test tube rack, stirring rod tissues (preferably lint-free).

Procedure:

1. Obtain small volumes of 0. 01M $K_2Cr_2O_7$ solution and distilled water in separate beakers.

2. Label five clean, dry, test tubes 1–5. Use pipets to prepare five standard solutions according to the chart below. Thoroughly mix each solution with a stirring rod. Clean and dry the stirring rod between uses.

Test Tube	0.01M $K_2Cr_2O_7$ (mL)	Distilled H2O (mL)	Concentration (M)
1	2	8	0.002
2	4	6	0.004
3	6	4	0.006
4	8	2	0.008
5	10	0	0.010

4. Prepare a blank by filling a cuvette 3/4 full with distilled water. To correctly use cuvettes, remember:

- Wipe the outside of each cuvette with a lint-free tissue.
- Handle cuvettes only by the top edge of the ribbed sides.
- Dislodge any bubbles by gently tapping the cuvette on a hard surface.
- Always position the cuvette so the light passes through the clear sides.

You are now ready to collect absorbance-concentration data for the five standard solutions.

a. Using the solution in Test Tube 1, rinse the cuvette twice with ~1 mL amounts and then fill it 3/4 full. Wipe the outside with a tissue and place it in the device (Colorimeter or Spectrometer). Close the lid on the Colorimeter.

b. When the absorbance readings stabilize,

c. Discard the cuvette contents as directed. Using the solution in Test Tube 2, rinse and fill the cuvette 3/4 full. Wipe the outside and place the cuvette in the device (close the lid of the Colorimeter). When the absorbance readings stabilize,

d. Repeat the procedure for Test Tubes 3 and 4. Trial 5 is the original 0.01M $K_2Cr_2O_7$ solution. Note: Do not test the unknown solution until Step 9.

e. When you have finished testing the standard solutions

Determine the absorbance value of the unknown $K_2Cr_2O_7$ solution

a. Obtain about 5 mL of the unknown $K_2Cr_2O_7$ in another clean, dry, test tube. Record the number of the unknown in your data table.

b. Rinse the cuvette twice with the unknown solution and fill it about 3/4 full. Wipe the outside of the cuvette, place it into the device. (Close the lid of the Colorimeter.)

c. Read the absorbance value displayed in the meter. When the displayed absorbance value stabilizes, record its value as Trial 6 in your data table.

d. Select Interpolate from the Analyze menu. Find the absorbance value that is closest to the absorbance reading you obtained in Step c above. Determine the concentration of your unknown $K_2Cr_2O_7$ solution and record the concentration in your data table.

e. Dispose of any of the remaining solutions as directed.

Data table:

Trial	Concentration (mol/L)	Absorbance
1	0.002	
2	0.004	
3	0.006	
4	0.008	
5	0.010	
6	Unknown number	

Experiment 3: Determination of CMC from surface tension measurements

Theory:

The determination of CMC is generally based on the localization of the position of a breaking point in the concentration dependencies of selected physical or chemical properties of surfactant solutions. Because of the surface activity of this substance, measurements of the surface tension of surfactant solutions represent the principal method of CMCs determination. However, it is rather tedious and time-consuming procedure. In the case of ionic surfactants, the utilization of electrochemical measurements is much more convenient, especially the measurements of the electrical conductivity of their solutions with varying concentration. The conductometric method is based on the finding of a breaking point on the curves, which describe the concentration dependence of conductivity. It is well-known, that the conductivity of any solution is directly proportional to the concentration of its ions. The point, where the micelle formation starts, is indicated on the concentration dependence of specific conductivity (κ) as a breaking point. It is easy to find the breaking point, because it marks a significant change the slope of the linear dependence:

$$\kappa = f(c)$$

The requested value of CMC is the intercept of two linear functions with mutually different slopes (**Figure 3a, b**).

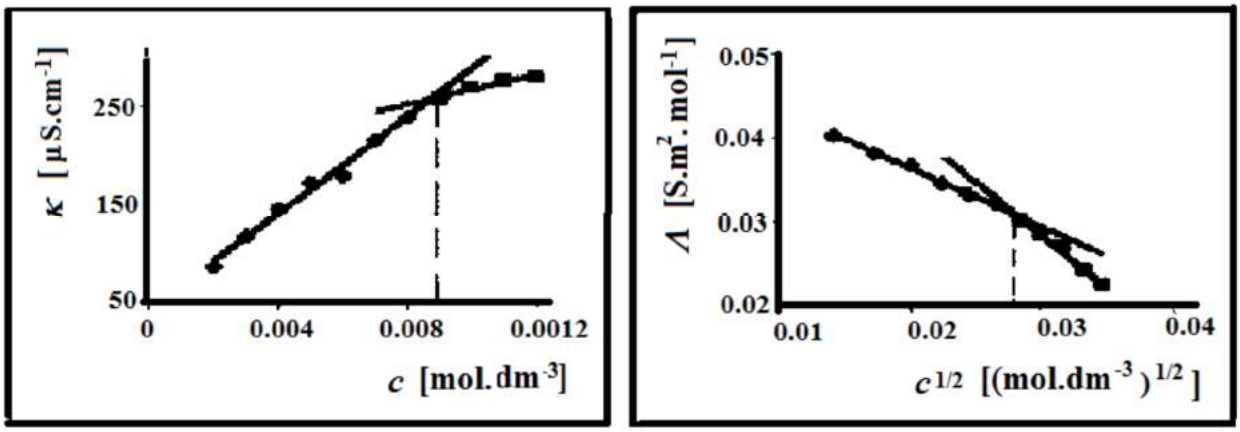


Figure: the specific conductivity (a) and molar conductivity (b) as a function of concentration

The dependence of the molar conductivity (Λ) on the second root of concentration (c) can be used for more precise determination of CMC of ionic surfactants Figure 3b.

The solution of surfactant, e.g. sodium dodecyl sulfate, behaves as the strong univalent type of electrolyte in the concentration range below the CMC and the linear function of dependence of the molar conductivity on the second root of concentration has a small negative slope. This concentration dependence of the molar conductivity is thus described by the Onsager equation:

$$\Lambda = \Lambda_0 - a.\sqrt{c} \qquad [S\ m^2\ mol^{-1}]$$

Where Λ0 - is the corresponding molar conductivity at the infinitive dilution

c - is the concentration of the studied surfactant

Values of the molar conductivity are calculated from the experimental values of specific conductivity (κ) and the molar concentration of solution. The basic unit of this quantity is S m^2 mol^{-1}.

$$\Lambda = \frac{\kappa}{c} \qquad [S\ m^2\ mol^{-1}]$$

Apparatus and chemicals:

Conductometer, conductivity electrode, thermometer, thermostat, stirrer, 25 ml analytical flask

Anionic surfactant: sodium dodecyl sulphate C12H25NaSO4, Mr = 288.38

Cationic surfactant: septonex C21H44NO2Br, Mr = 422.49

redestilled water

Procedure:

- Prepare the initial solution of the surfactant sodium dodecyl sulfate with concentration c = 0.012 mol dm-3 (or Septonex c = 0.0012 mol dm-3) in 25 ml volumetric flask.

- The calculated amount of the studied substance should be weighed using analytical balance directly in the volumetric flask.

- Dissolve the substance adding a small amount of redistilled water, and when it is fully dissolved add the remaining volume of redistilled water, as it is given with the marker on the volumetric flask.

- Use only a slow mixing motion to avoid the formation of a foam.

- Insert the stirrer and pour the solution in the conductivity vessel, which was previously cleaned and dried. Immerse the thermometer and the conductivity electrode. Set the thermostat to 25°C and switch on the electromagnetic stirrer. Turn on the conductometer.

The measurement:

1 After the temperature reaches 25°C, read the first conductivity data for the solution with

c = 0.012 mol dm-3 for sodium dodecyl sulphate (or c = 0.0012 mol dm-3for Septonex).

2 The next concentration of the surfactant solution should be prepared by diluting the current solution.

3 Calculate the necessary volume of the solution as it is outlined below, in the example

4. Now remove the calculated volume of the measured solution and then add the same volume of pure redistilled water.

5 After stabilization of the display on the instrument scale, read the conductivity data.

6 Repeat the steps 2-4 for each concentration in the series given in the Tables 1 or 2 below.

Please note, that at each measurement, the total volume of the measured solution in the conductivity vessel should be always 25 ml.

Table 1 Measured and calculated values for the determination of CMC of the sodium dodecyl sulphate

t = ...°C

c (mol dm^{-3})	c (mol m^{-3})	$\sqrt{c}$ (mol dm^{-3})$^{1/2}$	V (±ml)	κ (μS cm^{-1})	κ (S m^{-1})	Λ (S m^2 mol^{-1})
0.012						
0.011						
0.010						
0.009						
0.008						
0.007						
0.006						
0.005						
0.004						
0.003						
0.002						

CMC = ...mol dm^{-3}

Table 2 Measured and calculated values for the determination of CMC of the septonex

t = ...°C

c (mol dm^{-3})	c (mol m^{-3})	$\sqrt{c}$ (mol dm^{-3})$^{1/2}$	V (±ml)	κ (μS cm^{-1})	κ (S m^{-1})	Λ (S m^2 mol^{-1})
0.0012						
0.0011						
0.0010						
0.0009						
0.0008						
0.0007						
0.0006						
0.0005						
0.0004						
0.0003						
0.0002						

CMC = ...mol dm^{-3}

Data treatment

- To the Table 1 or Table 2 calculated$\sqrt{c}$ and Λ (according Equation 1)

- Prepare dependence κ = f(c) and Λ= f(√ c)

Experiment 4: Determination of surface tension of a liquid using Stalagmometer

Theory:

In the drop number method, the number of drops formed by equal volumes of two liquid is counted. If m_1 and m_2 is the mass of one drop of each of the liquid having densities d_1 and d_2 respectively. If n_1 and n_2 is the number of drops formed by volume v of the two liquids, then their surface tensions are related as

$\gamma_1 / \gamma_2 = (d_1/d_2)*(n_2/n_1)$

One of the liquid is water its surface tension and density are known. Then surface tension of the given liquid can be calculated.

Experiment:

Apparatus and chemicals:

Stalgmometer, specific gravity bottle, a small rubber tube with a screw pinch cork, distilled water, experimental liquid.

Procedure:

1. Clean the stalgmometer with chromic acid mix, wash with water and dry it

2. Attach a small piece of rubber tube having a screw pinch cock at the upper end of the stalgmometer.

3. Immerse the lower end of the stalgmometer in distilled water and suck the water 1-2cm above mark A. adjust the pinch cork so that 10-15 drops fall per minute

4.Clamp the stalgmometer allow the water drops to fall and start counting the number of drops when the meniscus crosses the upper mark A and stop counting when the meniscus passes mark B

5. Repeat the exercise to take three to four readings

6. Rinse the stalgmometer with alcohol and dry it

7. Suck the given liquid in the stalgmometer and count the drops as in case of water

8. Take a clean dry weighing bottle weighs it with water as well as with liquid.

9. Note the temp of water taken in a beaker.

Observations:

Room temp=t^{o}C

Density of water=d_w

Surface tension of water=γ dynes/cm

No of drops From a Fixed Volume				Mean
Liquid	1	2	3	n_1
Water	1	2	3	n_w

Weight of empty specific gravity bottle=$w_1$gram

Weight of specific gravity bottle+water=w_2 gram

Weight of empty sp.gravity bottle+liquid=$w_3$gram

Weight of water= (w_2-w_1) gram

Weight of liquid= (w_3-w_1) gram

Calculations:

Density of the liquid

Dl= (w_3-w_1) / (w_2-w_1) *d_w

Surface tension of liquid=

$\gamma_1 \gamma_2 = (d_l/d_w)*(n_w/n_l)* \gamma_w$

Result:

The surface tension of liquid is ……dynes/cm.

Experiment 5: Determination of pH of unknown buffer, spectrophotometrically

Theory:

The pH of an unknown solution can be determined by addition of an acid/base indicator of known K_a and spectrophotometric measurement of the relative concentrations of the acid and base forms of the indicator. This method has been used as a basis for continuous shipboard monitoring of seawater pH.1

The relationship between the two forms of the indicator in an aqueous solution is described by the equilibrium

$$HIn + H_2O \leftrightarrow H_3O^+ + In^-$$

for which

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

and

$$pH = pK_a + \log\frac{[In^-]}{[HIn]}$$

Thus if pK_a is known and [In-]/[HIn] is measured, the pH of the solution can be calculated.

In this exercise the indicator is bromocresol green, with K_a = 1.6 x 10-5. The spectra of the acid and base forms of bromocresol green overlap. The absorbance of the solution at a given wavelength is equal to the sum of the absorbances of the individual components in a mixture. For two overlapping components the absorbance must be measured at two wavelengths.

$$A_1 = \varepsilon_{a1} b C_a + \varepsilon_{b1} b C_b$$
$$A_2 = \varepsilon_{a2} b C_a + \varepsilon_{b2} b C_b$$

Where the subscripts 1 and 2 indicate the two wavelengths and the subscripts a and b indicate the acid and base forms of the indicator.

To determine the amount of each form in a mixture from the measured absorbances requires knowledge of the molar absorptivity of each form. In a preliminary experiment the absorption spectra of the acid and base forms of the indicator are measured separately. The wavelength of maximum absorbance for

each component is identified, and the molar absorptivities of each component at these two wavelengths are determined. The absorbance of the solution of unknown pH is measured at the same two wavelengths, and the concentrations of the two forms of the indicator in this solution are calculated by solving the two simultaneous equations describing the solution absorbances at the two wavelengths.

Experiment:

Apparatus:

WPA Biowave II or comparable benchtop UV-Visible spectrophotometer, Digital pH meter and pH electrode, plastic cuvette (1), 100 mL volumetric flask (1), 50 mL volumetric flasks (3), 5 and 10 mL pipets (1 each)

Chemicals:

Standard pH calibration buffer solutions (pH = 4.00 and pH = 7.00), bromocresol green, 0.10 M HCl, 0.10 M NaOH, 2.40 M acetic acid

Procedure:

Solutions

1. Bromocresol green. Dissolve 40.0 mg (to the nearest 0.1 mg) of the sodium salt of bromocresol green (720 g/mol) in water and dilute to 500 mL in a volumetric flask.

2. HCl, 0.5 M. Dilute about 4 mL of concentrated HCl to approximately 100 mL with water.

3. NaOH, 0.4 M. Dilute about 7 mL of 6 M NaOH to about 100 mL with water.

Determination of Individual Absorption Spectra

Transfer 25.00-mL aliquots of the bromocresol green indicator solution to two 100-mL volumetric flasks. To one, add 25 mL of 0.5 M HCl; to the other, add 25 mL of 0.4 M NaOH. Dilute to the mark with water and mix well.

Obtain the absorption spectra for the acid and conjugate-base forms of the indicator between 400 and 650 nm, using water as a blank. Record absorbance values at 10-nm intervals routinely and as needed to define maxima and

minima. Evaluate the molar absorptivity for HIn and In- at wavelengths corresponding to their absorption maxima.

Determination of pH of an Unknown Solution

Transfer 25.00 mL of the stock bromocresol green indicator to the 100-mL volumetric flask containing 50.0 mL of the unknown solution, dilute to the mark with water, and mix well. Measure the absorbance of the diluted solution at the wavelengths for which absorptivity data were calculated.

Experiment 6: Spectrophotometric determination of CMC

Theory: