Course Manual

M. Sc. (Integrated) - III Semester
Physical Chemistry Laboratory (CY 202)

School of Chemistry
University of Hyderabad

Preparation for the laboratory class and

Laboratory practices

1. Read the instruction manual carefully; discuss with the instructors any point that is not clear.
2. Read and understand the principles of the experiment before coming to the laboratory class.
3. You must arrive for the laboratory on time; late entry into the laboratory is not allowed.
4. Follow strictly, the instructions given in the laboratory by the instructors.
5. Safe practices in the laboratory are of utmost importance. Wear shoes that cover your feet properly. Wear preferably cotton clothing; clothing made of easily inflammable materials such as silk should be avoided.
6. Inside the laboratory, maintain absolute discipline in your behaviour and focus full attention on the experiment you are carrying out. Do not engage in any conversations and discussions. Do not compare your experimental observations and results with those of others; you are supposed to report your genuine results.
7. Keep your laboratory bench clean and organized; careless and disorderly handling of chemicals, glassware or equipment can lead to major laboratory accidents.
8. Maintain your laboratory notebooks properly. You must have two notebooks; (i) the Observation Notebook for recording the various observations and data during the experiment in the laboratory class and (ii) the Record Notebook for reporting the details of the experiments, observations and conclusions in the following laboratory class.
9. After you finish the experiment, ensure that you obtain the signature of the course instructor on the data/observations recorded in your Observation Notebook. The same observations along with details of the experiment, analysis, results and conclusions must be recorded neatly in the Record Notebook and submitted promptly at the very beginning of the following laboratory class. If this is not followed strictly, the grade for the specific experiment will not be awarded.
10. At the end of the laboratory class, hand over to the laboratory staff, the glassware, chemicals, equipment etc. after proper cleaning.
11. Reagent bottles and their stoppers should not be left at the work bench. They should be returned to their proper place upon the shelves immediately after use. If a reagent bottle is empty, bring it to the attention of laboratory staff.
12. Use the chemicals/samples provided to you very carefully, without wasting any material; extra samples will not be given under any circumstance.

Course evaluation / grading

Step 1. Continuous assessment (60 marks): All experiments will be given equal weightage. The grading for each experiment will be based on an assessment (for that experiment) of: (a) your performance and experimental work in the laboratory, (b) quality and correctness of your observations and recording of data, (c) presentation in the Record Notebook and (d) your response to questions during the evaluation of the Record Notebook in the following week.

Step 2. End semester practical examination (20 marks): Grading will be based on the evaluation of one experiment you will carry out (chosen by draw) from among the experiments carried out during the semester.

Step 3. End semester written examination (20 marks): This will be a 1 h examination to assess your understanding of the basic theory and conceptual details of all the experiments carried out during the semester.

Additional reading

Basic text books in Physical Chemistry: for example, P. Atkins, J. de Paula, *Atkin's Physical Chemistry*, 9th Edition, Oxford University Press, 2010

Experiments

Apparatus and Materials Required

No.	Experiment	Apparatus	Materials
1	Molecular weight by viscometry	Viscometer, Volumetric flask (4 × 10 mL), Beaker, Syringe, Pipette, Burette stand, Watch (precision = 1 s)	Dry polystyrene powder, Toluene
2	Heat of solution	Beaker, Thermal isolation chamber, Weighing balance, Thermometer (precision = 0.1°)	Calcium chloride, Distilled water
3	Phase diagram : Phenol - Water	Hard glass test tubes, Glass stirrer, Beaker, Burette and Thermometer (precision = 0.1°)	Phenol, Distilled water, Ice
4	pH titration	pH meter, Beaker, Burette, Pipette, Volumetric flask, Conical flask, Funnel	Standard buffers (pH 4, 7 and 10), glycine, 0.1 N NaOH solution, 0.1 N standard HCl solution, Phenolphthalein
5	Job's method	Colorimeter, Stoppered glass tube (test tube type)	N/500 HCl solution, Ferric ammonium alum, Salicylic acid
6	Conductometric titration	Conductivity meter + Cell, Beaker, Burette, Pipette, Volumetric flask, Conical flask, Funnel	0.1 N oxalic acid solution, 0.5 N NaOH solution, 0.1 N HCl solution, Phenolphthalein
7	Rate constant of hydrolysis	Burette, Pipette, Bottle, Conical Flask, Glass trough, Stopwatch	Ethyl acetate ester, 0.5 N HCl solution, 0.025 N HCl solution, 0.05 N NaOH solution, Phenolphthalein
8	Conductometric titration	Conductivity meter + Cell, Beaker, Burette, Pipette, Volumetric flask, Funnel	0.02 N $AgNO_3$ and HCl solutions, 0.1 N KCl solution
9	Solubility product	Stoppered bottle, Volumetric flask, Pipette, Burette, Beaker, Conical flask, Funnel	Potassium hydrogen tartrate, 0.03 N KCl solution, 0.1 N oxalic acid solution, 0.05 N NaOH solution, Phenolphthalein
10	Partition coefficient	Stoppered bottle, Volumetric flask, Pipette, Burette, Beaker, Conical flask, Funnel	0.1 N oxalic acid solution, 0.1 N NaOH solution, Benzoic acid, Toluene, Phenolphthalein

Experiment 1

Molecular weight of a polymer by viscometric method

The viscosity average molecular weight ($\overline{M_V}$) of a polymer is determined by measuring the viscosity of its solutions having a range of concentrations; polystyrene prepared by emulsion polymerization technique is used in the experiment.

Basic concepts

Average molecular weight of polymers

The properties of polymers are dependent on their molecular weight. Unlike small molecules, polymers do not have a unique molecular weight, as there is usually a distribution of molecular sizes. Different kinds of average molecular weights can be defined for polymers; number average molecular weight, $\overline{M_N}$, weight average molecular weight, $\overline{M_W}$, viscosity average molecular weight, $\overline{M_V}$. They are defined as follows:

$\overline{M_N} = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i}$ N_i molecules of the polymer have molecular weight M_i

$\overline{M_N} = \sum_{i=1}^{\infty} X_i M_i$ X_i is the number fraction of molecules with molecular weight M_i

$\overline{M_W} = \sum_{i=1}^{\infty} w_i M_i$ w_i is the weight fraction of molecules with molecular weight M_i

$\overline{M_w} = \frac{\sum_{i=1}^{\infty} N_i {M_i}^2}{\sum_{i=1}^{\infty} N_i M_i}$ (Prove this)

$\overline{M_V} = \left(\frac{\sum_{i=1}^{\infty} N_i {M_i}^{1+a}}{\sum_{i=1}^{\infty} N_i M_i}\right)^{1/a}$ a is a constant depending on the polymer/solvent pair used in the viscosity experiment

Viscosity measurements

Time of flow for the solvent (t_0) and polymer solution are measured in a viscometer. The **relative viscosity** is determined: $\eta_{rel} = \frac{t}{t_0}$

Specific viscosity is defined as : $\eta_{sp} = \eta_{rel} - 1 = \frac{t-t_0}{t_0}$; the value is generally 0.2 – 0.6

Reduced viscosity is defined as : $\eta_{red} = \frac{\eta_{sp}}{c}$ where c is the concentration of the solution, usually expressed as g dL^{-1} (then the unit of η_{red} is dL g^{-1}.

Intrinsic viscosity is defined as : $[\eta] = \left(\frac{\eta_{sp}}{c}\right)_{c=0}$; it is obtained by extrapolating reduced viscosity to zero concentration, as per the following equation:
$\eta_{red} = [\eta] + k[\eta]^2 c$ *Huggins equation*; k is known as the Huggins constant.

$[\eta]$ depends on the viscosity average molecular weight as :
$[\eta] = K\overline{M_V}^{a}$ *Mark-Houwink equation*; K and a are constants for a polymer-solvent pair; for polystyrene-toluene pair, K = 1.74 × 10 $^{-4}$ dL g^{-1} and a = 0.69.

Apparatus

Viscometer, Volumetric flask (4 × 10 mL), Beaker, Syringe, Pipette, Burette stand, Watch (precision required = 1 s)

Materials

Dry polystyrene powder, Toluene.

Experimental procedure

1. Clean and dry the viscometer; fix it on a burette stand securely and with the graduated tubes vertical
2. Using a pipette, transfer 10 mL toluene into the viscometer
3. Determine the flow time of the solvent, toluene (t_0). Make at least three readings; the variation should be within 1 s. If not, repeat the measurements until such consistent times are obtained. The mean value of the three close readings is t_0.
4. Remove the viscometer from the stand, drain the solvent and allow it to dry.
5. Prepare 10 mL of 1 % (w/v) solution of polystyrene in toluene.

6. Repeat Steps 1 – 4 and determine the flow time (t) for the polymer solution.
7. Prepare at least three more solutions with different concentrations (0.5%, 0.25% and 0.12% w/v) by successive dilution from the higher concentration solution.
8. Repeat Steps 1 – 4 and determine the flow time (t) for each polymer solution.
9. Prepare a Table as shown below, entering all the data observed. Calculate the different viscosity measures as shown in the Table, and estimate the viscosity average molecular weight as discussed.

Data analysis

1. Note the flow time data and construct the table using the equations given earlier.

Concentration (g dL^{-1})	**Flow time (s)**		**Mean flow time (s)**	$\boldsymbol{\eta_{rel}}$	$\boldsymbol{\eta_{sp}}$	$\boldsymbol{\eta_{red}}$ (dL g^{-1})
0						

2. Plot η_{red} versus concentration and measure the intercept; the intercept is [η].
3. Calculate $\overline{M_V}$ using the Mark – Houwink equation.

Experiment 2

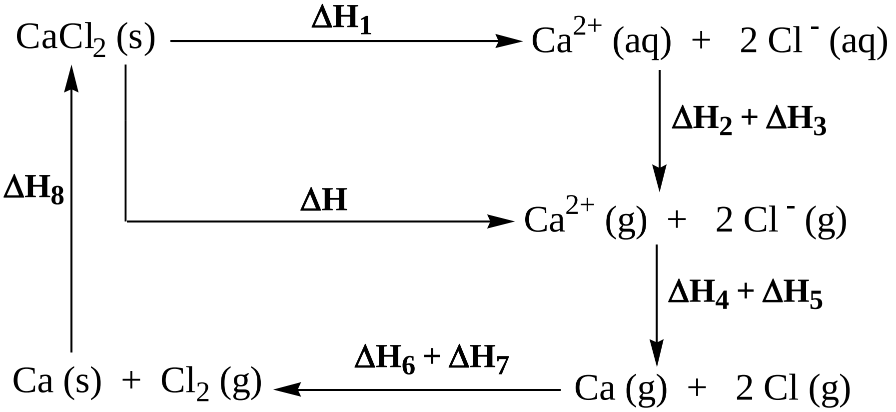
Heat of solution and lattice energy

Following the calorimetric measurement of the heat of solution the Born-Haber cycle is used to determine the lattice energy of calcium chloride.

Basic concepts

Born-Haber cycle

Total enthalpy change in a process can be written as a sum of the enthalpy changes of the constituent steps (*Hess's law*). Application of this concept to an ionic solid forms the basis of the Born-Haber cycle. The following is a representation of this concept to calcium chloride ($CaCl_2$); the table below gives some of the enthalpy values.



	Enthalpy change for	**process**	**value**
ΔH_1	dissolving $CaCl_2$ (s) in water	heat of solution	**?**
ΔH_2	Ca^{2+} (aq) → Ca^{2+} (g)	-1 × heat of hydration	+1579 kJ mol^{-1}
ΔH_3	$2Cl^-$ (aq) → $2Cl^-$ (g)	-2 × heat of hydration	+715.5 kJ mol^{-1}
ΔH_4	Ca^{2+} (g) → Ca (g)	-1 × ionization energy	-18 eV
ΔH_5	$2Cl^-$ (g) → 2Cl (g)	2 × electron affinity	2 × 3.64 eV
ΔH_6	Ca (g) → Ca (s)	-1 × heat of sublimation	-178.2 kJ mol^{-1}
ΔH_7	2Cl (g) → Cl_2 (g)	-1 × dissociation energy	-242.7 kJ mol^{-1}
ΔH_8	Ca(s) + Cl_2 (g) = $CaCl_2$ (s)	heat of formation	**?**
ΔH	Lattice energy		**?**

The Born-Haber cycle shows that the lattice energy, $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$, can be estimated using the measured value of the heat of solution, ΔH_1 and the values of ΔH_2 and ΔH_3 provided in the Table. The heat of formation of $CaCl_2(s)$ can also be estimated from the measured value of ΔH_1 and the other enthalpy values provided in the Table.

Calorimetry

If a body with mass, m and specific heat, s is heated through a temperature change, ΔT, the heat absorbed, $q = m \times s \times \Delta T$. The product, $m \times s$ is called the water equivalent of the body, as it represents the mass of water which absorbs the same quantity of heat when heated through the same temperature difference.

Apparatus

Beaker, Thermal isolation chamber, Weighing balance, Thermometer (precision = 0.1^o).

Materials

Calcium chloride, Distilled water.

Experimental procedure

Determination of the water equivalent of the beaker

1. Weigh a 250 mL beaker (w_1). Take ~ 100 mL of distilled water in it and weigh again (w_2). Insulate the beaker from the outside environment by placing in a thermal isolation chamber; measure the temperature of the water (T_1).
2. Heat some water separately to ~ 80^oC; measure the temperature (T_2). Add ~ 50 mL of this hot water to the water taken in the beaker in Step 1, kept inside the thermal isolation chamber. Wait for the temperature to stabilize and measure it (T_3).
3. Take the beaker out of the isolation chamber and let it equilibrate with the outside environment; weight it (w_3).

4. Using the various values measured above, determine the water equivalent of the beaker, W.

Determination of the heat of solution

5. Repeat Step 1; the weight of beaker (w_1), weight of beaker+water (w_2) and initial temperature (T_1) are measured.
6. Take ~ 8 g $CaCl_2$ and weigh it accurately (w); add this to the water in the beaker and stir. Note the final temperature (T_4).
7. Determine the heat of solution for the solid added.
8. Repeat Step 6 with ~ 9 g of $CaCl_2$.

Data analysis

1. First part of the experiment
   - (i) Equate the heat gained by the beaker+water with the heat lost by the added hot water. $[W+(w_2-w_1)]\times[T_3-T_1] = (w_3-w_2)\times[T_2-T_3]$
   - (ii) Determine W from the above equation.
2. Second part of the experiment
   - (i) Heat of solution released when $CaCl_2$ is dissolved is given by the heat gained by the beaker+water. $Q = [W+(w_2-w_1)]\times[T_4-T_1]$.
   - (ii) Using the weight of $CaCl_2$ added (w) and its molecular weight, determine the molar heat of solution, ΔH_1.
   - (iii) Repeat the analysis above, for the experiment with different weight of $CaCl_2$.
3. Using the ΔH_1, and the enthalpies values provided in the Table, determine
   - (i) lattice energy of $CaCl_2$
   - (ii) enthalpy of formation of $CaCl_2$.

Experiment 3

Phase diagram and the critical solution temperature of phenol – water system

The phase diagram of a 2-component system made up of partially miscible liquids is determined by observing the temperature at which the two become miscible

Basic concepts

For two liquids that do not react, three types of miscibility behaviour are possible:

- (i) immiscible at all temperatures (*eg.* mercury and water)
- (ii) miscible in all proportions at all temperatures (*eg.* ethanol and water)
- (iii) partially miscible under some temperature conditions (*eg.* phenol and water)

In case (iii), the solubility varies with temperature and the solubility (or miscibility) curve can be constructed. Above a certain temperature (called the critical solution temperature, CST), the two components become completely miscible in all proportions. A 2-component system may have an upper, lower or both upper and lower critical solution temperatures. Phenol and water has only an upper CST; above this temperature, phenol and water are miscible in all proportions. CST is greatly influenced by impurities. Commercial phenol gives a higher value than a sample of purified phenol. Phenol is corrosive; handle it carefully.

Apparatus

Hard glass test tubes, Glass stirrer, Beaker, Burette and Thermometer (precision = 0.1^o).

Materials

Phenol, Distilled water, Ice.

Experimental procedure

1. Weigh accurately 2 - 3 g of phenol in a weighing bottle; transfer it to a hard glass test tube fitted with an outer larger hard glass test tube by means of ring cork to provide an air jacket. Add to it, 1 mL of water from a burette.
2. Clamp the test tube assembly inside a large beaker fitted with a glass stirrer. Insert a thermometer into the test tube.
3. Heat the water of the beaker slowly and uniformly over a low flame stirring it all the time. The mixture, which was initially turbid, suddenly becomes clear at a particular temperature. Note the temperature. Remove the flame and allow the liquid to cool slowly. Note the temperature at which turbidity reappears. Take the mean of both the temperatures.
4. Go on adding 0.5 mL portions of water and repeating step 3 until 5 mL of water have been added. Thereafter, go on adding 1 mL portions of water and repeating step 3 until 16 mL of water have been added.
5. Find the weight percentages of phenol and water.
6. Draw a smooth curve by plotting temperature against the percentage of phenol. Find the point which just touches a horizontal line in the graph paper. The ordinate of the point gives the critical solution temperature of the system and the abscissa gives the composition

Data analysis

Density of water = 1 gm/ml

Weight of phenol transferred = g

No. of observation	**Volume of water added (mL)**	**Weight percentage of phenol**	**Miscibility temperature (°C)**		**Temperature Mean (°C)**
			Turbidity disappearance	**Turbidity reappearance**	

From the graph

Critical solution temperature = _____°C; Critical composition = ______

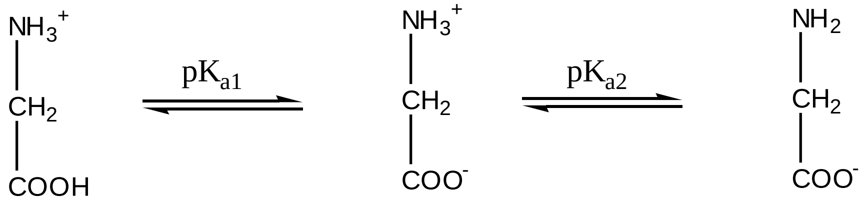
Experiment 4

pH titration of an amino acid

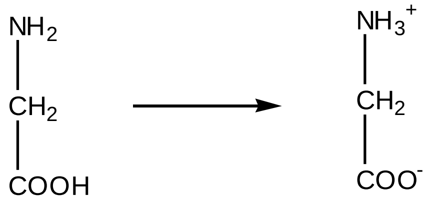
The pK_a values and the isoelectric point of an amino acid (glycine) are determined using a pH titration against acid and base.

Basic concepts

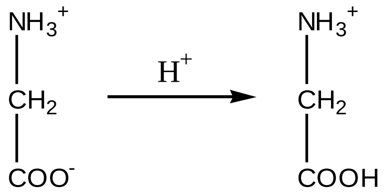
Amino acids possess at least two protolyzable functional groups, carboxylic acid and ammonium. In addition, they may have other functional groups on the "side chain" capable of receiving or donating a proton. Glycine, the simplest amino acid, has the COOH and α-NH_3^+ groups that can donate H^+.

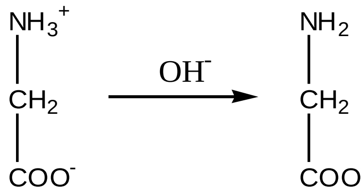


When a water soluble amino acid is dissolved in water, it undergoes self-proteolysis, whereby the more acidic group (COOH) transfers a proton to the more basic (NH_2 group) to yield the zwitterionic structure that has positively and negatively charged groups, but is overall neutral. The process is shown for glycine below.



The zwitterion in its neutral form exists at the pH corresponding to the isoelectric point (pH = pI). The following processes occur when an aqueous solution of glycine is treated with acid or base.





Titration of a weak acid / base with strong base / acid leads to buffer formation and a nearly constant pH over a range of addition of the titrant. The Henderson – Hasselbalch equation shows that, at the midpoint of these regions where [A-] = [HA], pH = pK_a.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad\qquad pH = pK_a + log\frac{[A^-]}{[HA]}$$

This concept can be used to determine the pK_a values of the amino acid, by titrating against strong base and acid. Prominent increase or decrease of the pH curve gives the equivalence points in the reaction.

Apparatus

pH meter, Beaker, Burette, Pipette, Volumetric flask, Conical flask, Funnel

Materials

Standard buffers (pH = 4, 7, 10), Glycine, 0.1 N NaOH solution, 0.1 N HCl solution (standard), Phenolphthalein

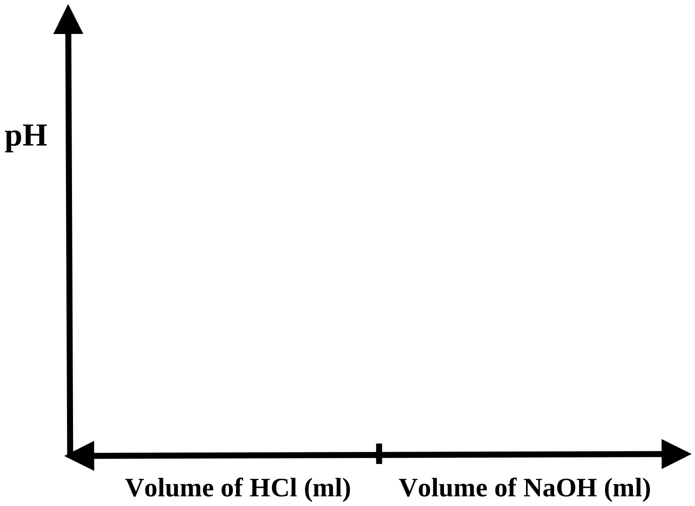
Experimental procedure

1. Prepare ~ 250 mL ~ 0.1 N HCl solution (the concentration should be known exactly, as this solution is used to standardise other solutions).
2. Prepare ~ 250 mL of ~ 0.1 N NaOH solution and standardise it against the HCl solution using phenolphthalein as indicator.
3. Prepare ~ 250 mL of an ~ 0.1 M glycine solution.
4. Rinse the pH cell and the beaker with distilled water.
5. Set up and calibrate the pH meter with standard buffers (pH = 4 and 7).
6. Pipette out 25 mL of 0.1 M glycine solution into a 250 mL beaker; measure the pH.
7. Add the standard HCl solution from a 50 mL burette in small amounts (~ 0.5 mL), stir well and determine the pH after each addition.

8. Continue the addition of HCl and stirring and pH measurement till the pH of the solution reaches ~ 1.4 (refill the burette if required).
9. Wash the electrodes carefully with distilled water from a wash bottle, dry with tissue paper.
10. Calibrate the pH meter again, now at pH 7 and 10.
11. Repeat the experiment in Step 7, now by adding the NaOH solution until the pH reaches ~ 12.

Data analysis

1. Tabulate the volumes and pH measured from the experiment.
2. Make a plot of the pH *vs* the volume of NaOH and HCl solution.



3. From the plot, determine the pK_{a1} and pK_{a2} for glycine.
4. Calculate the isoelectic point of glycine.
5. Using the data from the titration of glycine with base, calculate the exact concentration of glycine in the solution prepared. Compare with the value obtained from the titration with acid.

Experiment 5

Stoichiometry of ferric-salicylic acid complex by Job's method

Stoichiometry of Fe^{3+} - Salicylic acid complex is determined using colorimetry and the Job's method of continous variation

Basic concepts

When equimolar solutions of two reactants are mixed in varying proportions, the maximum amount of the complex at equilibrium is formed when the proportion of the reactants corresponds to the empirical formula of the complex. In $aA + bB \rightleftharpoons A_aB_b$, the maximum amount of A_aB_b is obtained when a parts of X molar solution of A is mixed with b parts of X molar solution of B (Job's method of continuous variation). If a : b = 1 : 1, the composition of the complex is AB. Several phenolic compounds (for example, 2-hydroxybenzoic acid or salicylic acid) form colored complexes with Fe^{3+} salts. In aqueous solution, the equilibrium may be written as:

$$[Fe(H_2O)_6]^{3+} + Sal \rightleftharpoons \left[Fe(H_2O)_x(Sal)_y\right]^{n+}$$

The stoichiometry of the complex (1 : y) can be determined by the Job's method. The optimum pH for the stability of the ferric-salicylic acid complex is 2.6 – 2.8.

Apparatus

Colorimeter, Stoppered glass tube (test tube type)

Materials

0.002 N HCl solution, Ferric ammonium alum, Salicylic acid

Experimental procedure

1. Prepare 0.002 N HCl.

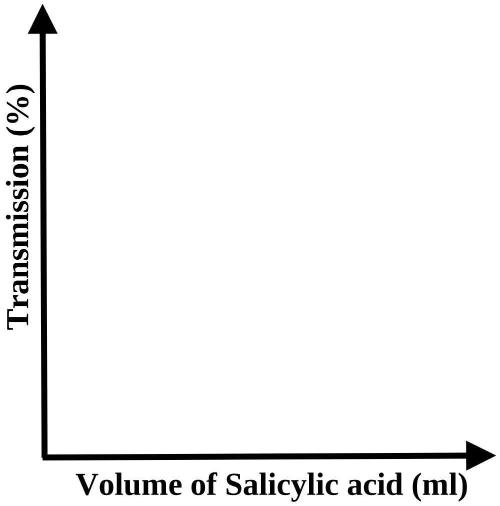
2. Prepare 1 mM solutions of the reactants in 0.002 N HCl (providing the required pH).
3. Mix the Fe^{3+} and salicylic acid solutions in different proportions (see Table below) in properly labeled stoppered glass tubes (test tube size).
4. Measure the transmission (or optical density) for a particular solution (say solution No. 4), using different filters (*ie.* at different wavelengths) and thus choose the filter corresponding to the λ_{max}.
5. Using that filter, measure the transmission (or optical density) of each solution.

Data analysis

Filter (corresponding to $\lambda_{max.}$) = ______________________

1. Tabulate the transmission data collected in Step 4 and plot them as follows.

Solution No.	**Volume of Fe^{3+} solution (mL)**	**Volume of Salicylic acid solution (mL)**	**Transmission (%) or Optical Density**
1	1	9	
2	2	8	
3	3	7	
:	:	:	
9	9	1	



2. Determine the stoichiometry of the complex from the peak of the curve in the plot.

Experiment 6

Conductometric titration : hydrochloric acid with sodium hydroxide

Conductometry is the measurement of conductivity of electrolytes or electrolytic conductance. Conductometric titrations are used to monitor the progress of a reaction based on the conductivities of the ions being exchanged and hence the resultant conductivity of the reaction mixture. In this experiment, the reaction of HCl (strong acid) with NaOH (strong base) is studied and compared with indicator based titration.

Basic concepts

When a strong acid like HCl is titrated against a strong alkali like NaOH (caustic soda), the H^+ ions are progressively replaced by the less mobile Na^+ ions, with no net change in the number of or charges of the ions, as shown in the equation:

$$H^+ + Cl^- \xrightarrow{+NaOH\ \ -H_2O} Na^+ + Cl^-$$

and the conductance of the solution falls linearly up to the end point. Beyond the end point it rises linearly due to the excess Na^+ and OH^- ions being added. The neutral point is thus marked by a minimum in a V-shaped titration curve.

Apparatus

Conductivity meter + cell, Beaker, Burette, Pipette, Volumetric flask, Conical flask, Funnel

Materials

0.1 N oxalic acid solution (standard), 0.5 N NaOH solution, 0.1 N HCl solution, phenolphthalein.

Experimental procedure

1. Prepare 100 mL ~ 0.1 N oxalic acid solution (the concentration should be known exactly, as this solution is used to standardise the other solutions).

2. Prepare about 250 mL of an ~ 0.5 N NaOH solution and standardise it against the oxalic acid solution using phenolphthalein as the indicator.
3. Prepare about 250 mL of an ~ 0.1 N HCl solution.
4. Rinse a clean burette with the NaOH solution and then fill it with the solution. Note the number of drops for 1 mL of NaOH falling from the burette and hence calculate the volume of a single drop.
5. Rinse the conductivity cell and the beaker with deionised water.
6. Pipette out 25 mL of the HCl solution into the conductivity cell and add water, if necessary, so that the electrodes are completely submerged within the solution. Measure the conductivity.
7. Add 3 – 5 drops of the NaOH solution from the burette, mildly shaking the beaker. Measure the conductivity. Repeat the process several times until at least five points are observed beyond the end point (where the conductivity is the lowest).
8. Plot the conductance against the number of drops of the NaOH solution added.
9. Titrate the HCl solution against the NaOH solution using phenolphthalein indicator.

Data and analysis

Preparation of ~ 0.1 N oxalic acid solution (Step 1)

Weight of empty container = __________ g

Weight of container + oxalic acid = __________ g

Weight of oxalic acid = __________ g

Concentration of oxalic acid solution prepared = __________ N

Standardization of the NaOH solution (Step 2)

Volume of the oxalic acid solution = __________ ml

Burette readings (ml)		**Volume of NaOH (ml)**	**Mean volume (ml)**
Initial	**Final**		

Concentration of the NaOH solution = __________ N

Volume of NaOH solution drop (Step 4)

Number of drops	**Volume of NaOH solution (ml)**	**Mean volume (ml)**

Conductometric titration of the HCl solution against the NaOH solution (Step 7)

Volume of the HCl solution taken = _________ ml

Number of drops of NaOH solution added	**Conductance (mho)**

From the plot (Step 8):

Number of drops of the NaOH solution at end point = _________

Volume of the NaOH solution added at end point = _________ ml

Concentration of the HCl solution = _________ N

Estimation of the HCl solution concentration by titration with the NaOH solution (Step 9)

Volume of HCl solution taken = _________ ml

Burette readings (ml)		**Volume of NaOH (ml)**	**Mean volume (ml)**
Initial	**Final**		

Concentration of the HCl solution = _________ N

Comparison of the HCl solution concentration estimated using the two methods

Method	**Concentration of HCl (N)**
Conductometric Titration	
Titration using indicator	

Experiment 7

Rate constant of the acid catalysed hydrolysis of ethyl acetate

Progress of a chemical reaction can be followed by monitoring the disappearance of a reactant or the formation of a product. In the acid catalysed hydrolysis of an ester, one of the products is an organic acid. Course of this reaction is monitored by determining the concentration of the organic acid formed as a function of time; this kinetic study provides the rate constant and order of the reaction.

Basic concepts

Hydrolysis of ethyl acetate, an extremely slow process in pure water, is catalyzed by H^+.

$$CH_3COOC_2H_5 + H_2O \overset{H^+}{\rightleftharpoons} CH_3COOH + C_2H_5OH$$

When water is present in large excess, the change in its concentration is negligible and the backward reaction is suppressed. Progress of the reaction can be monitored by withdrawing aliquots from the reaction mixture from time to time (t_1, t_2, … t_n) and at the end of the reaction, and titrating it against alkali. The amount of alkali required at any stage is equivalent to the sum of acetic acid produced during the course of the reaction and the acid catalyst, the latter remaining constant throughout the reaction. Let V_o and V_∞ be the volumes of alkali required initially and finally respectively, and V_n be the volume of alkali required at time t_n. Since the extent of hydrolysis is directly proportional to the amount of acetic acid formed, the initial concentration of the ester, $\boldsymbol{a}$, is proportional to $V_\infty - V_o$ and the concentration at time t_n, $(\boldsymbol{a - x_n})$ is proportional to $V_\infty - V_n$.

If the reaction follows first order kinetics, it follows the equation, $k = \frac{2.303}{t} log \frac{a}{a-x}$ where k is the rate constant. It can be written in terms of the volume of alkali as:

$$k = \frac{2.303}{t_n} log \frac{V_\infty - V_0}{V_\infty - V_n}$$

As the hydrolysis begins as soon as the ester is mixed with water, it is difficult to determine V_o. This problem can be eliminated using the difference equation:

$$\Delta t_n = t_n - t_1 = \frac{2.303}{k} log \frac{V_\infty - V_1}{V_\infty - V_n} \quad \text{for n = 2, 3, ….}$$

It is advisable to take t_1 value as soon as possible after starting the reaction. A plot of $log\frac{V_\infty - V_1}{V_\infty - V_n}$ against Δt_n for different n, provides a straight line passing through the origin; k is determined from the slope of this line.

Apparatus

Burette, Pipette, Bottle, Conical Flask, Glass trough, Stopwatch.

Materials

Ethyl acetate, HCl solution (0.5 N and 0.25 N), 0.05 N NaOH solution, Phenolphthalein

Experimental Procedure

1. Prepare 500 mL of an ~ 0.05 N NaOH solution.
2. Prepare 100 mL of an ~ 0.5 N HCl solution; take 50 mL of the solution and dilute to 100 mL to obtain ~ 0.25 N HCl solution.
3. Rinse the burette and fill it with the NaOH solution.
4. Take 25 mL of the 0.5 N HCl solution in a 250 mL dry conical flask and cover it with a watch glass.
5. Add 2 mL of pure (redistilled) ethyl acetate with a clean dry pipette constantly swirling the flask during addition and starting the stopwatch when the pipette is half empty. Shake the mixture quickly to for thorough mixing.
6. Immediately after the addition of ester, withdraw 2 mL of the reaction mixture and pour into a conical flask containing 25 - 30 mL of chilled water to quench any further hydrolysis of the ester, noting the time of half discharge (t_1). Titrate the reaction mixture as quickly as possible, against NaOH, using phenolphthalein as indicator; the titre value is V_1.
7. Repeat Step 6 several times, after ~ 5, 10, 15, 20, 30 and 40 min (i.e. at regular time intervals, t_n) after the initiation of the reaction, to determine the values of V_n.

8. Repeat Steps 4 – 7 with the 0.25 N HCl solution.
9. Heat both the reaction mixtures on water bath for 10 min (with watch glass cover) to drive the reactions to completion. Draw 2 mL of the reaction mixture and titrate against NaOH using phenolphthalein as indicator to determine the value of V_∞.
10. Plot $log\frac{V_\infty - V_1}{V_\infty - V_n}$ against Δt_n for each set (with 0.5 N and 0.25 N HCl) on the same graph; determine k_1 and k_2 from the slopes and find the ratio k_1/k_2.

Data and analysis

1. Note down the temperature of the reaction mixture before and after the experiment; determine the mean value.

2. Analyse the kinetics of ethyl acetate hydrolysis with 0.5 N HCl (Steps 4 - 7).

   V_∞ = ____________ mL

Time (min)	Δt (s)	Volume of NaOH (mL)	$V_\infty - V_n$ (mL)	$log\left(\frac{V_\infty - V_1}{V_\infty - V_n}\right)$
t_2	0	V_1		
t_2	$t_2 - t_1$	V_2		
t_3	$t_3 - t_1$	V_3		
…		…		
t_n	$t_n - t_1$	V_n		

3. Repeat the analysis of the kinetics with 0.25 N HCl (Step8).
4. Plot $log\frac{V_\infty - V_1}{V_\infty - V_n}$ against Δt_n for each set (with 0.5 N and 0.25 N HCl) on the same graph. Determine the slope of each line using least square fitting.
5. Determine k_1 and k_2 from the slopes and find the ratio k_1/k_2.

Experiment 8

Conductometric titration : silver nitrate with potassium chloride

The precipitation reaction between KCl and $AgNO_3$ is monitored by conductometric titration.

Basic concepts

A precipitation reaction such as,

$$KCl + AgNO_3 \rightarrow AKNO_3 + AgCl \downarrow$$

can be studied conductometrically. The net result up to the end point of this reaction is the replacement of Ag^+ by K^+ ions, without change in the number of or charges on the ions. As the mobility of K^+ ions is similar to that of Ag^+ ions, the conductance of the solution remains nearly the same up to the end point. Beyond the end point however, the conductance of the solution rises sharply due to the additional K^+ and Cl^- ions. The end point can be determined as a point of intersection, by plotting the conductance against volumes of KCl solution added.

Apparatus

Conductivity meter + cell, Beaker, Burette, Pipette, Volumetric flask, Funnel.

Materials

0.02 N $AgNO_3$ and HCl solutions, 0.1 N KCl solution.

Experimental Procedure

1. Prepare 100 mL of 0.02 N $AgNO_3$ solution and 100 mL of 0.1 N KCl solution (both standard solutions).
2. Rinse the conductivity cell and the beaker with deionised water.
3. Pipette 25 mL of $AgNO_3$ solution into the conductivity cell and add water, if necessary, so that both the electrodes are immersed fully in the solution. Connect the cell to the conductivity bridge and measure the conductivity.

4. Rinse a clean burette with the KCl solution and then fill it with the solution. Note the number of drops for 1 mL of KCl falling from the burette and hence calculate the volume of a single drop.
5. Add 3-5 drops of KCl solution into the $AgNO_3$ solution in the conductivity cell, while mildly shaking the beaker. Measure the conductance of the solution. Repeat the process several times until at least five points are observed beyond the end point (where the conductivity is the lowest).
6. Plot the conductance against the number of drops of the titrant, find the end point and calculate the concentration of the solution.
7. Compare the concentration of $AgNO_3$ determined above, with that obtained while preparing the solution in Step 1.

Data and analysis

Preparation of 0.1 N KCl solution (Step 1)

Weight of KCl required to make 100 mL 0.1 N solution: _________ g

Weight of empty container = _________ g

Weight of container + KCl = _________ g

Weight of KCl = _________ g

Concentration of KCl solution prepared = _________ N

Preparation of 0.02 N $AgNO_3$ solution (Step 1)

Weight of $AgNO_3$ required to make 100 mL 0.02 N solution: _________ g

Weight of empty container = _________ g

Weight of container + $AgNO_3$ = _________ g

Weight of $AgNO_3$ = _________ g

Concentration of $AgNO_3$ solution prepared = _________ N

Volume of KCl solution drop (Step 4)

Number of drops	**Volume of KCl solution (ml)**	**Mean volume (ml)**

Conductometric titration of the $AgNO_3$ solution against the KCl solution (Step 5)

Volume of the $AgNO_3$ solution taken = ___25 mL

Number of drops of KCl solution added	**Conductance (mho)**

From the plot (Step 6):

Number of drops of the KCl solution at end point = __________

Volume of the KCl solution added at end point = __________ mL

Concentration of the $AgNO_3$ solution = __________ N

Comparison of the $AgNO_3$ solution concentration from the two methods (Step 7)

Method	**Concentration of $AgNO_3$ (N)**
Conductometric Titration	
Standard solution preparation	

Experiment 9

Solubility product of potassium hydrogen tartrate and the common ion effect

Solubility product (K_{sp}) for potassium hydrogen tartrate in water is determined.

Basic concepts

Solubility product (K_{sp}) of a compound at a specified temperature is the equilibrium constant for its dissociation in a solvent at that temperature *ie.* product of the dissociated ion concentrations in the solvent, raised to the power of their stoichiometric coefficients. For a binary ionic compound, the equilibrium and the K_{sp} can be written as :

$$A_xB_y(s) \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq) \qquad \boldsymbol{K_{sp}} = [\boldsymbol{A}]^{\boldsymbol{x}}[\boldsymbol{B}]^{\boldsymbol{y}}$$

Unit of K_{sp} is concentration raised to the sum of the stoichiometric numbers of ions present at solution equilibrium. Smaller the solubility product of a substance, lower its solubility. For potassium hydrogen tartrate (KHTa) dissolved in a polar solvent like water, the dissolution can be described as :

$$KHTa(solid) \rightleftharpoons KHTa(solution) \rightleftharpoons K^{+}(aq) + HTa^{-}(aq)$$

HTa^- is a very weak acid; its dissociation in water can be neglected. As it is a monoprotic acid its concentration can be determined by titration with a strong alkali like NaOH.

Common ion effect

Solubility of a compound is reduced by the addition of another that has an ion common with it. This can be understood in terms of the Le Chatelier's principle: an equilibrium is shifted to the left by the increase in concentration of a component on the right. When the concentration of an ion formed from dissolution of a compound A is effectively increased by the introduction of the same ion by dissolution of a different compound B, the solution equilibrium of A is shifted to the left and hence its solubility and K_{sp} reduced.

Apparatus

Stoppered bottle, Volumetric flask, Pipette, Burette, Beaker, Conical flask, Funnel.

Materials

Potassium hydrogen tartrate, 0.03 N KCl solution, 0.1 N oxalic acid solution (standard), ~ 0.05 N NaOH solution, Phenolphthalein.

Experimental Procedure

1. Prepare 100 mL of 0.1 N oxalic acid solution and 0.03 N KCl solution (standard solutions) and ~ 0.05 N NaOH solution.
2. Standardize the NaOH solution by titrating against the oxalic acid solution.
3. Put 0.4 g each of KHTa in four bottles and label them I, II, III and IV. Add water and KCl solution to these bottles as shown in the table below:

Bottle	**Water (mL)**	**0.03 N KCl solution (mL)**
I	30	-
II	20	10
III	10	20
IV	-	30

4. Shake the bottles in a shaker for an hour and allow them to stand for about 20 min. Filter the contents of the bottles and collect the filtrates (after discarding the first 5 – 6 mL) in four dry beakers labeled I, II, III and IV.
5. Take 5 mL of filtrate I and titrate it against the standardized NaOH solution and calculate the concentration of HTa^- *ie.* KHTa. Repeat the titration for consistent results. Calculate the solubility product.
6. Repeat Step 5 for other three bottles and calculate the solubility product of KHTa in each case.

Data and analysis

Mean of the temperatures before and after the experiment = _________°C

Preparation of 0.1 N standard oxalic acid solution (Step 1)

Weight of oxalic required to make 100 mL 0.1 N solution: _________ g

Weight of empty container = _________ g

Weight of container + oxalic acid = _________ g

Weight of oxalic acid = _________ g

Concentration of oxalic solution prepared = _________ N

Standardization of NaOH solution (Step 2)

Volume of the oxalic acid solution = _________ mL

Burette readings (ml)		**Volume of NaOH (ml)**	**Mean volume (ml)**
Initial	**Final**		

Concentration of the NaOH solution = _________ N

Preparation of 0.03 N KCl solution (Step 1)

Weight of KCl required to make 100 mL 0.03 N solution: _________ g

Weight of empty container = _________ g

Weight of container + KCl = _________ g

Weight of KCl = _________ g

Concentration of KCl solution prepared = _________ N

Determination of the concentration of KHTa in bottle I (Step 5)

Volume of the KHTa solution = __________ mL

Burette readings (ml)		**Volume of NaOH (ml)**	**Mean volume (ml)**
Initial	**Final**		

Concentration of the KHTa solution = __________ N

Repeat for bottles II - IV

Calculation of the solubility and solubility product (Step 6)

Bottle	**$[HTa^-]$ = [KHTa] = solubility of KHTa = s (M)**	**[KCl] = $[Cl^-]$ = c (M)**	**$[K^+]$ = ($s+c$) (M)**	**K_{sp} of KHTa = $s\times(s+c)$ (M^2)**
I				
II				
III				
IV				

Experiment 10

Partition coefficient of benzoic acid between water and toluene

Partition coefficient or distribution coefficient of benzoic acid between the immiscible solvents, water and toluene, is calculated by determining its equilibrium concentrations in the two phases.

Basic concepts

Consider a solute, X soluble in two solvents A and B that are immiscible with each other. Ratio of the equilibrium concentrations of X in A and X in B is termed the partition coefficient or distribution coefficient (K_D). Purification of compounds by extraction into a solvent is a widely used technique in chemistry. Liquid-liquid extraction involves partitioning of a solute between two immiscible solvents present in a mixture. Distribution of the solute between the two immiscible solvents is the basis for this technique. Transfer of a solute from one solvent to another is achieved by shaking them together and reaching the equilibrium. Once equilibrium is reached, no further solute transfer can occur and the concentration of the solute in each solvent remains constant. Ratio of these concentrations is known as the partition coefficient. This value is dependent on the nature of solute, solvents and the temperature of the system. Measurement of partition coefficient provides an easy method to study the degree of association (or dissociation) of a solute in a solvent.

If the solute is in the same state of association (or dissociation) in both the solvents at a specified temperature, the ratio of concentrations of the solute in the two solvents remains constant independent of the total amount of substance taken.

$$\frac{C_A}{C_B} = K_D$$

where C_A and C_B are the concentrations of the solute in solvents A and B respectively and K_D is the partition or distribution coefficient. This may be explained on the basis that at equilibrium, the chemical potential of a solute in the two liquid phases become equal *ie.*

$$\mu(A) = \mu(B) \qquad \Rightarrow \qquad \mu_0(A) + RTln a_A = \mu_0(B) + RTln a_B$$

since $\mu_0(A)$ and $\mu_0(B)$ are constants, $\frac{a_A}{a_B} = \frac{C_A}{C_B} = constant$

{when the concentrations of the solutes in the two phases are small, the activities, a can be replaced by the concentrations}

If a solute exists as a monomer, X in solvent A, while it associates to give the dimer, X_2 or n-mer X_n such that the equilibrium, $nX \rightleftharpoons X_n$ is set up in the solvent B, then the ratio

$$\frac{C_A}{\sqrt[n]{(C_B)}} = K_D$$

where C_B is the total concentration of X in B. Benzoic acid generally exists as a dimer in toluene, whereas it exists as a monomer in water. The present experiment is to calculate the partition coefficient of benzoic acid between these nonpolar and polar solvents.

Apparatus

Stoppered bottle, Volumetric flask, Pipette, Burette, Beaker, Conical flask, Funnel.

Materials

0.1 N oxalic acid solution (standard), ~ 0.1 N NaOH solution, Benzoic acid, Toluene, Phenolphthalein.

Experimental Procedure

1. Prepare 100 mL of a saturated solution of benzoic acid: take ~ 1 g benzoic in ~ 90 mL water in a stoppered bottle, stir using a magnetic bar, filter and make up to 100 mL in a volumetric flask.
2. Take 50 mL of the saturated aqueous benzoic acid solution and 50 mL of toluene in a 250 mL bottle; mark it as I. In another 250 mL bottle (II), take 25 mL of the saturated aqueous benzoic acid solution and add 25 mL of water and 50 mL of toluene. Stopper the two bottles properly and shake in a mechanical shaker for half an hour and then allow to settle.

3. Prepare 100 mL of 0.1 N oxalic acid (standard). Prepare ~ 250 mL of ~ 0.1 N NaOH and standardize it against the oxalic acid using phenolphthalein as the indicator.
4. Take 20 mL of the aqueous layer from bottle I *[Note: Close the top end of the pipette with your finger, insert it carefully into the lower aqueous layer in the bottle, and withdraw the solution carefully]*. Titrate it against the NaOH solution using phenolphthalein as the indicator. Repeat for consistent readings.
5. Withdraw 10 mL of the upper toluene layer from bottle I, pour it in ~ 20 mL of water in a conical flask, shake to accelerate the passage of the benzoic acid across the interface into the water layer; titrate with NaOH. Repeat for consistent readings.
6. Repeat Steps 4 and 5 for bottle II.
7. Calculate the molar (M) concentrations of benzoic acid in the two layers and find the ratios $\frac{C_W}{C_T}$ and $\frac{C_W}{\sqrt{C_T}}$.

Data and analysis

Mean of the temperatures before and after the experiment = _________ °C

Preparation of 0.1 N standard oxalic acid solution (Step 3)

Weight of oxalic required to make 100 mL 0.1 N solution: _________ g

Weight of empty container = _________ g

Weight of container + oxalic acid = _________ g

Weight of oxalic acid = _________ g

Concentration of oxalic solution prepared = _________ N

Standardization of NaOH solution (Step 3)

Volume of the oxalic acid solution = _________ mL

Burette readings (ml)		**Volume of NaOH (ml)**	**Mean volume (ml)**
Initial	**Final**		

Concentration of the NaOH solution = _________ N

Composition of the sets in the two bottles (Step 2)

Bottle	**Volume (mL)**		
	Benzoic acid	**Water**	**Toluene**
I	50	0	50
II	25	25	50

Bottle I

Titration of aqueous layer (Step 4)

Volume of the aqueous solution = __________ mL

Burette readings (mL)		**Volume of NaOH (mL)**	**Mean volume (mL)**
Initial	**Final**		

Concentration of benzoic acid in the aqueous layer, C_W = __________ M

Titration of toluene layer (Step 5)

Volume of the toluene layer + water = __________ mL

Burette readings (mL)		**Volume of NaOH (mL)**	**Mean volume (mL)**
Initial	**Final**		

Concentration of benzoic acid in the toluene layer, C_T = __________ M

Bottle II

Titration of aqueous layer (Step 6)

Volume of the aqueous solution = __________ mL

Burette readings (mL)		**Volume of NaOH (mL)**	**Mean volume (mL)**
Initial	**Final**		

Concentration of benzoic acid in the aqueous layer, C_W = __________ M

Titration of toluene layer (Step 6)

Volume of the toluene layer + water = __________ mL

Burette readings (mL)		**Volume of NaOH (mL)**	**Mean volume (mL)**
Initial	**Final**		

Concentration of benzoic acid in the toluene layer, C_T = __________ M

Partition coefficient (Step 7)

Bottle	**C_W (M)**	**C_T (M)**	**C_W / C_T**	**$K_D = C_W / \sqrt{C_T}$**	**Mean value of K_D**
I					
II					