

Laboratory Manual – Part I
Physical Chemistry Laboratory I
CY29001

SPECIFIC INSTRUCTIONS:

1. Please wear a laboratory coat and covered shoes
2. Please manage your time judiciously – work out the requirements and protocol of how you intend to proceed prior to starting your experiment.
3. Complete the experiment within the stipulated time and try to finish your report as much as possible.
4. The discussion should be written on your own. Please do not copy from your partner.

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EXPERIMENT 1

Critical Solution Temperature of the Phenol Water System

Theory :

If two liquids not reacting chemically are mixed, three types of miscibility behavior are possible:

- (a) The liquid may be immiscible (for example, mercury and water).
- (b) The liquids may be miscible in all proportions (for example, ethanol and water).
- (c) The liquids may be partially miscible (for example, phenol and water).

In case (c), solubility varies with temperature and solubility (or miscibility) curve can be constructed. Above a certain temperature, however, the two components become completely miscible in all proportions. This temperature is called the critical solution temperature or consolute temperature. For the phenol-water system the critical solution temperature is 65.85 °C, the composition at this critical temperature is 34.5 percent by weight of phenol. Critical solution temperatures are very sensitive to the presence of impurities. Commercial phenol gives a higher value than a sample of purified phenol.

Materials :

Phenol, Distilled water, Ice.

Procedure :

Weigh 4 gm of phenol in a 500 mL beaker (**CAUTION: Phenol is corrosive**). Place the beaker on a tripod and fix a burette containing distilled water. Add 2ml. of water to the phenol. Stir the mixture and heat **slowly**. Note down the temperature at which the system becomes **homogeneous (clear solution)**. Allow the beaker to cool down and note the temperature at which the mixture becomes opalescent (**milky-white**) due to the separation of two liquid layers. The mean of the two temperatures is the miscibility temperature of the particular mixture used.

Repeat the procedure with further additions of water (2ml. in the initial stages to be followed by 3ml. and 5ml. of water in each addition). If the miscibility temperature goes down below room temperature, use ice-water mixture to cool down the temperature of the beaker.

Repeat the procedure with a 2% solution of the salt provided.

Results and calculations:

Density of water = 1gm. / ml.

Weight of phenol = 4gm. (say)

Serial no of observation	Wt. of water (x gm).	Percentage by wt. phenol $\frac{4}{4+x} \times 100$	Miscibility temperature		
			Opalescence disappears $^{\circ}\text{C}$	Opalescence Reappears $^{\circ}\text{C}$	Average $^{\circ}\text{C}$

GRAPHS AND CALCULATIONS

1. Plot the data for both the systems on the same graph. Report the concentration as mass fractions.
2. Label the diagram to show the phases present, the equilibria involved and the number of degrees of freedom in each region.
3. Indicate the critical temperatures and compositions for the phenol-water system.
4. Comment on the type of impurity provided.

EXPERIMENT 2

Adsorption From Solution

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 der 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:

- (a) the Freundlich isotherm is given by $N = Kc^a$ where K and a are empirical constants, N is the number of moles adsorbed per gram of charcoal, and c is the solution concentration, and
- (b) the Langmuir isotherm, $c/N = C/N_m + 1/(k N_m)$ where N_m is the number of moles required to cover one gram of charcoal with a monolayer of adsorbate, and k is a function of temperature.

Procedure

Place approximately 1 g (weighed accurately to the nearest 0.001 g) of charcoal into each of seven dry Erlenmeyer flasks. Prepare solutions of 0.15, 0.12, 0.09, 0.06, 0.03 and 0.015 M acetic acid. Add 100 mL of a different acetic acid solution to each flask, with 100 mL of distilled water to the seventh. An eighth flask should contain 0.03 M acetic acid, but no charcoal. The flasks should be tightly stoppered, then shaken periodically for thirty minutes, and allowed to equilibrate at a constant temperature.

After equilibration, the samples are filtered (discard the first 10 mL of filtrate). Titrate a 25 mL aliquot of each sample with a standardized NaOH solution, using phenolphthalein as an indicator.

Calculations

Determine the final concentration of acetic acid in each sample, then calculate the number of moles of acid adsorbed onto the charcoal by subtracting the final concentration from the initial concentration, then multiplying by the solution volume.

Adjust this value, if necessary, if the charcoal is determined to have residual acidity (the seventh flask data should tell you this).

Plot isotherms (N vs. c), then determine whether a Freundlich ($\log N$ vs. $\log c$) or Langmuir (c/N vs. c) isotherm provides a better fit to the data.

Experiment 3

Determination of the Dissociation constant of a weak electrolyte

Determination of Cell Constant

Strong and weak electrolytes are distinguished on the basis of the extent of dissociation. The equivalent conductance (λ) of a strong uni-uni valent electrolyte in dilute aqueous solution is given by the Debye-Hückel-Onsager equation as $\lambda = \lambda_0 - (A + B\lambda_0)\sqrt{C}$

The equivalent conductance (λ) can be calculated from the specific conductance (κ) using the equation $\lambda = 1000\kappa/C$ where the concentration is expressed in gm equivalents per litre.

The conductivity cell consists of two identical parallel plates sealed in a glass tube. The ratio of the distance between the electrodes (l) to the cross sectional area (a) of the electrode is called the cell constant. The value depends on the resistance (R) offered by the cell to the current flowing through the electrolytes and the specific conductance (κ), which is the conductance of the electrolyte kept in a conductivity cell with 1cm length and 1cm² cross sectional area..

The relation is *Cell constant* = $R \times \kappa$

Prepare 0.1 N and 0.01N KCl solutions by accurately weighing the required quantity of salt and making up to 100 ml in a volumetric flask. Rinse the cell with the solution to be measured and measure the conductance (reciprocal of resistance) of the solution. Determine the cell constant by using the specific conductance (κ) values from standard tables.

Determination of Dissociation Constant

For weak electrolytes that are partially dissociated in solution the dissociation constant is given by $K = C\alpha^2/(1-\alpha)$ where C is the molar concentration and α is the degree of dissociation. The value of α is given as the ratio of the equivalent conductivity (Λ) of the electrolyte at a particular concentration to that at infinite dilution Λ_0 .

Kohlrausch's law of independent migration of ions for NaCl is given by:

$$\Lambda_0(\text{NaCl}) = \lambda_0(\text{Na}^+) + \lambda_0(\text{Cl}^-)$$

If the Λ_0 value for NaCl, HCl and CH₃COONa are determined then the Λ_0 for CH₃COOH may be calculated. Thus the dissociation constant K can be determined.

Prepare a series of dilutions for EXACT concentrations of NaCl, HCl and CH₃COONa and determine the conductance. It is necessary to titrate the HCl to determine its exact concentration with standard NaOH.

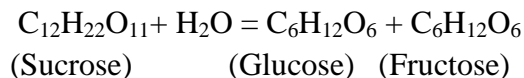
Plot the equivalent conductance vs \sqrt{C} to determine Λ_0 values. From the equations given above determine the dissociation constant (K) of acetic acid.

EXPERIMENT 4

Determination of the rate constant of inversion of cane sugar **in presence of an acid**

Theory:

The reaction for the inversion of sucrose (cane sugar) catalyzed by an acid is as follows



The rate of the reaction depends upon the concentrations of sucrose and water and also upon the concentration of H^+ , which acts as a catalyst. The concentration of water may be regarded as a constant since a large excess is normally present. Under a fixed H^+ concentration the reaction is thus 1st order with respect to sucrose.

Measuring the property of the solution of rotating the plane of polarized light, we can follow the rate of reaction. Cane sugar is dextrorotatory whereas invert sugar (mixture of glucose and fructose) is laevorotatory, so that, after the reaction, the sign of rotation changes from right to left. This can be followed with time.

Let A_0 = initial angle of rotation,

A_t = angle at any time t and

A_α = the angle after complete inversion occurred.

Thus the initial concentration of cane sugar (C_0) is proportional to the total range of change i.e., ($A_0 - A_\alpha$) and the concentration (C_t) at time t is proportional to the total range of change i.e., ($A_0 - A_t$).

For the 1st order reaction, $K = (2.303/t) \log(C_0/C_t)$

where C_0 = initial concentration

C = concentration at time t and

k = velocity constant

Hence a graph of $\log(A_0 - A_t)$ against t should give a straight line with a slope equal to, from which the rate constant can be calculated.

Materials

- a) 4N HCl (100 ml.)
- b) Sugar

Procedure

- i. Prepare 100 ml solution of 20% cane sugar (if the solution is hazy, then filter).
- ii. Place the sugar solution and HCl solution in separate flasks in the thermostat maintained at room temperature.
- iii. Set the polarimeter and determine the zero.
- iv. Dry the observation tube and replaced in the polarimeter.
- v. Add 25 ml of HCl solution into the sugar solution and pour the mixture into the observation tube (no air bubble in tube).
- vi. Preserve the remaining mixture for final reading

- vii. Determine quickly the angle of rotation and note the time at which the readings are taken. Take subsequent readings after 3, 6, 10, 15, 20, 30, 40, 60 minutes.
- viii. For final reading the mixture is heated at 70°C for few minutes. Cool down to room temperature and take the reading.

Results and calculations

Temperature

Time in minutes	Scale reading in degrees	Rotation in degrees (A)	(At- A _α)	log(At- A _α)

Slope= $k/2.303$ (from graph). Then calculate k (min^{-1})

EXPERIMENT 5

Measurement of the coefficient of viscosity of ethanol & ethanol-water system

When a liquid flows through a tube, the layer of liquid in contact with the wall of the tube is stationary whereas the liquid at the centre has the highest velocity, intermediate layers move with a gradation of velocities. The fluid may be regarded as composed of a number of concentric thin tubular layers, sliding past one another like the tubes of a telescope. Each layer exerts a drag on the next and work must be done to maintain the flow. The internal friction of viscosity would produce retarding force proportional to the velocity gradient (dv/dx) normal to the direction of flow and to the area of contact (A) between the moving sheets of liquid i.e., $F \propto A(dv/dx)$, or, $F = -\eta(A dv)/(dx)$ where η is a proportionality constant called the coefficient of viscosity, In C. G. S. unit it has the dimensions of g.cm^{-1} and the unit is called **poise**.

According to Poiseuille's equation for the streamlined flow of homogenous incompressible liquid through capillary tube (Newtonian flow),

$$\eta = \frac{P\pi r^4 t}{8Vl} \quad (1)$$

where V = Volume of fluid (viscous) passing through a tube of length l , radius r , in time t , when a pressure difference P is maintained between the ends of the tube.

In Ostwald viscometer, the force driving a liquid of viscosity η_1 , due to pressure difference, through the capillary depends on the difference in liquid level h the density d_1 and the acceleration due to gravity, g , and is given by hgd_1 . If exactly the same volume of a liquid of viscosity η_2 is introduced in the same tube the driving force is equal to hgd_2 where d_2 is the density of the second liquid.

By equation (1), viscosity η is equal to $(\pi r^4)/(8Vl) \cdot \Delta P \cdot t$. Therefore for a given apparatus and the same volume V of liquid, η is proportional to the driving force and to time of outflow.

Hence,

$$\frac{\eta_2}{\eta_1} = \frac{hd_2g}{hd_1g} \cdot \frac{t_2}{t_1} = \frac{d_2}{d_1} \cdot \frac{t_2}{t_1} \quad (2)$$

Materials:

1) Experimental liquid (Dehydrated Alcohol), 2) Distilled water, 3) Ostwald or Ubbelohde Viscometer, 4) Stop-watch, 5) Beaker, 6) pipette, 7) Burette-50ml & Burette-15ml, 8) conical flask (50 ml), 9) Dropper, 10) Unknown liquid.

Procedure:

The viscometer commonly used is the Ostwald viscometer. It consists of a fine capillary tube through which a definite volume of liquid is allowed to flow under gravity. The determination of η is performed as follows:

1. The viscometer is thoroughly cleaned (outside and inside the capillary) with distilled water.
2. The viscometer is clamped vertically and distilled water is introduced in such a way that the larger bulb is filled up to the mark (or, a fixed volume, say 10ml is introduced into the viscometer). The water or the solution is introduced into the viscometer by using the small burette.
3. Using the 'rubber bulb pipette', raise the water into the bulb above the capillary by sucking out the air until the meniscus is just above the upper mark.
4. Allow the water to flow down the capillary. Start a stopwatch as soon as the descending water level touches the upper mark and stop it when the level touches the lower mark. Record the time of flow between the marks. This procedure is repeated three times. Determine the mean time of flow.
5. Prepare 10%, 20%, 40% 50% 70% and 80% (vol./vol.) ethanol solution from the ethanol provided. Use two burettes for this purpose and prepare exactly 20ml solution.
6. Measure the time of flow for ethanol and all of the ethanol-water mixtures. Calculate the relative viscosities using equation (2)

Results

Samples	Time of flow			Mean time of flow (sec)	η (Poise)
	(i)	(ii)	(iii)		
Water					
10 % ethanol					
20%					
40 % ...					
Unknown					

Plot of η vs. percent composition of ethanol.

Describe the characteristic features of the plot and provide (molecular) interpretations.

Experiment 6

Determination of the partition coefficient of Iodine in water and carbon tetrachloride partition

Theory:

The partition law: The **partition law** (also called **distribution law**) states that at a given temperature, the ratio of the concentrations of a solute in two immiscible solvents is constant when dynamic equilibrium has been reached.

$$\text{Partition coefficient, } K_D = \frac{\text{Concentration of solute in solvent 1}}{\text{Concentration of solute in solvent 2}}$$

Apparatus:

- I. Reagent bottles; Separating funnel.
- II. Saturated solution of iodine in carbon tetrachloride
- III. Solid KI
- IV. Thiosulfate solution.(N/10, N/100)
- V. Starch indicator.

Procedure:

1. Prepare the mixtures as given in the table below in separate reagent bottles.
2. It is then allowed to stand till the layers separate out.
3. Drain the lower layer (water) in a clean beaker.
4. Titrate 50ml of the water solution against N/10 thiosulfate solution to get the concentration of Iodine in water.
5. End point is obtained with starch indicator.
6. Organic part is titrated by taking 5ml of solution and adding 25ml of water and 2g of solid KI, then titrated against N/100 thiosulfate solution.
7. Plot $[I_2]_{\text{org}}$ against $[I_2]_{\text{aq}}$ and obtain the value of K_D as the slope of the graph.

Results:

Vol of Iodine soln (ml)	Vol of water added (ml)	Titration for aq soln		Titration for org soln		
		Vol of thiosulfate(ml)	$[I_2]_{\text{aq}}$	Vol of thiosulfate(ml)	$[I_2]_{\text{org}}$	
10	100					
20	100					
30	100					

$K_D = \text{slope of graph } ([I_2]_{\text{org}} / [I_2]_{\text{aq}}) = \underline{\hspace{2cm}}$.