

Experiment (11)

Phase diagram for a Binary system (phenol + Water)

Theory

The phase diagram for a two- component system is the plot of temperatures and compositions, in which they exist (solid and liquid) in equilibrium, defined by solids and liquids curves.

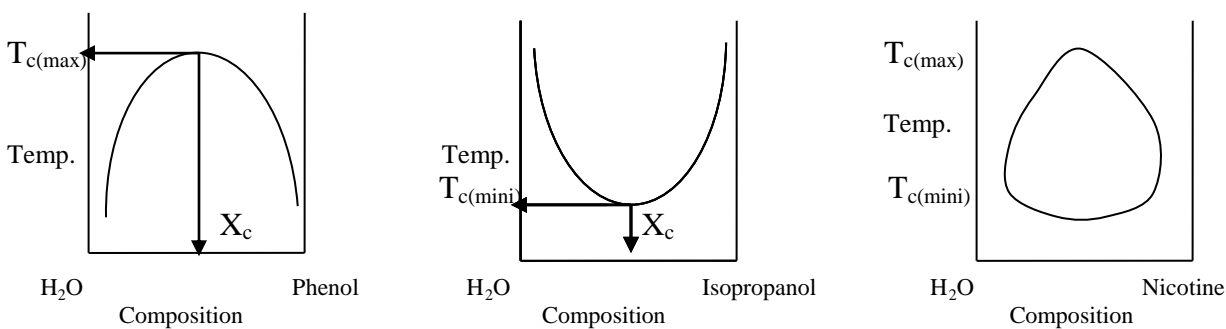
There are three type of solution:

1-Miscible solutions: These solutions are completely miscible at any temperature, such as a solution of water and CH_3COOH .

2-Immiscible solutions: These are solutions which are not miscible with each other and not affected by temperature or any other factors, such as a solution of water and CCl_4 .

3-Partially miscible solutions: These solutions are miscible at a definite temperature (they are affected by temperature), such as a solution of water and phenol.

These are different phase diagram of binary system



Where T_c is the critical temperature in which the two components are miscible, X_c is the critical composition in which the two components are miscible with each other.

Apparatus and Chemicals

Thermostat bath, conical flask, Sensitive balance, thermometer, phenol, distilled water.

Procedure

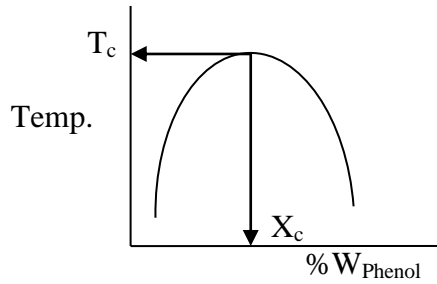
- 1- Place 3g of phenol in a conical flask.
- 2- 1.5ml of water is added to the phenol, then placed in a thermostat bath and gently warmed until the solution become one phase at this time read the temperature (T_a), then cool the solution and with appearing the turbidity read the temperature (T_b).
- 3- Take the mean of temperature, and let it will be (T_1).
- 4- Repeat the steps (2 and 3) by adding another four 1.5ml of water and let the temperature will be T_2, T_3, T_4, T_5 and the total added water will be 7.5ml.
- 5- Add 0.5ml of water and repeat steps 2 and 3, look if the temperature decreased add another 1.5ml of water five times, otherwise; if the temperature not decreased you must add another 0.5ml of water until the temperature decreasing, all temperatures must be recorded.

Calculation

1-After taking the mean of temperatures, find % W_{phenol} at each addition like this:

$$\% W_{Phenol} = \frac{W_{Phenol}}{W_{Phenol} + W_{H_2O}} \times 100$$

2-Plot a diagram between the temperature and % W_{Phenol}, then find the critical temperature and critical composition of the solution.



Experiment (12)

The radius of molecule from viscosity measurements

Theory

The ratio of the viscosity η of a solution of large spherical particles to the viscosity of a pure solvent η_o is related to the fraction ϕ of the total volume of spheres per milliliter of solution by the expression, derived by Einstein,

$$\frac{\eta}{\eta_o} = 1 + 2.5 \phi$$

This equation may be rewritten:

$$\frac{\eta}{\eta_o} = 1 + 6.3 \times 10^{21} r^3 C$$

Where r is the radius of the particle and (C) is the concentration of the particles in moles/L. Hence if η / η_o is plotted against (C) a straight line is obtained and r may be determined from the slope.

The relative viscosity η / η_o may be determined using the relationship.

$$\frac{\eta}{\eta_o} = \frac{t d}{t_o d_o}$$

In this equation t and t_o refer to the time of flow through the capillary of a given volume of the solution and pure solvent, respectively and d and d_o are the densities of the solution and pure solvent respectively.

Apparatus and Chemicals

Viscometer, stop watch, water, glycerol.

Procedure

- 1- The time of flow(t_o) of 50ml of water is determined by using the viscometer.
- 2- Prepare 100ml of 1M glycerol.
- 3- Dilute the glycerol solution to (0.2 , 0.4 , 0.6 , 0.8 M) and measure the time of flow(t) for each dilution using the same volume as before, beginning from 0.2M solution.

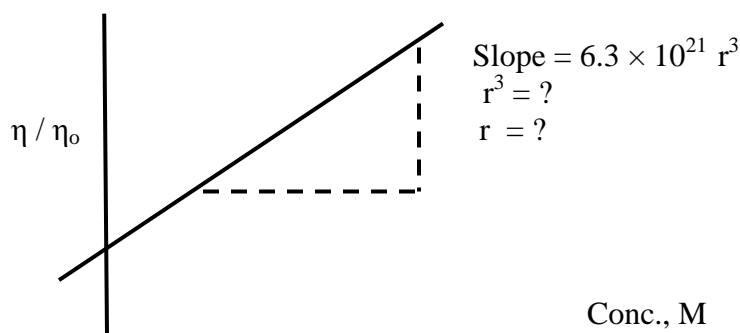
Calculation

- 1- Results are recorded in such a table:

Conc. of glycerol soln., M	t, sec	t _o ,sec	$\frac{t}{t_o}$	$\frac{d}{d_o}$	$\frac{\eta}{\eta_o}$
0.2					
0.4					
0.6					
0.8					
1.0					

- 2- Find $\frac{d}{d_o}$ by $\frac{d}{d_o} = 1 + 0.021 C$

- 3- Plot a graph between η / η_o Vs. concentration



Experiment (13)

Determination of molecular association degree of benzoic acid in benzene

Theory

The addition of a solute to a solvent, in general, lowers the freezing point of the solvent. In this experiment the molecular weight of benzoic acid can be determined in benzene; this method is named cryoscopic method. Always the detected value (measured value) of molecular weight by this method is differ from that of the true value (actual value), due to the association of molecules, it means that two or more molecules were joined to form a big molecules.

When the solute is dissociated to ions, each ion has it's effect on increasing ΔT , and by this the measured molecular weight is decreased, thus dissociation degree can be found by

$$\alpha = \frac{M_0 - M_r}{M_r(n-1)} \text{ ----- (1)}$$

Where α is the dissociation degree

M_0 : true molecular weight of benzoic acid

M_r : measured molecular weight of benzoic acid

n : number of dissociate ion of benzoic acid

While if the solute associated in solvent, the value of ΔT is decreased and the measured molecular weight is increased

$$\bar{\alpha} = \frac{M_r - M_0}{M_r(1 - \frac{1}{n})}$$

Where $\bar{\alpha}$ is the association degree.

M_0 : true molecular weight of benzoic acid

M_r : measured molecular weight of benzoic acid

n : mole numbers of solute ($n = \frac{Wt}{M.wt}$)

Apparatus and Chemicals

Freezing point apparatus, Beckman thermometer, benzene, benzoic acid, ice

Procedure

1- Add a known volume of benzene (10ml) is add to the center of the tube.

2-The tube is cooled by slightly immersion in the ice bath and stirred continuously until the

benzene starts to freeze, then read the temperature of the thermometer (T_0).

3- Add 0.05g of benzoic acid and then record the freezing point of the solution (T_1).

4-Repeat step (3) three times, by adding 0.05g at each case to the same solution, then record

the freezing point of each solution (T_2, T_3, T_4) respectively.

Calculation

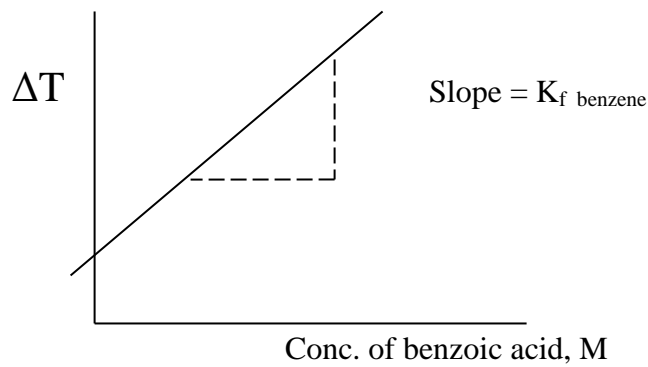
1- Find ΔT in each case ($\Delta T_1, \Delta T_2, \Delta T_3, \Delta T_4$) by

$$\Delta T_1 = T_0 - T_1$$

2- Calculate the concentration of each solution of benzoic acid in benzene.

3- (Note: $W_1 = 0.05g$, $W_2 = 0.1g$, $W_3 = 0.15$, $W_4 = 0.2$)

4- Plot a graph between the depression of the freezing point and concentration of the substance.



5- Calculate the molecular weight (M_A) for each solution

$$6- M_A = \frac{K_f \times W_A \times 1000}{\Delta T_f \times W_B}$$

7- Find α and $\bar{\alpha}$

Experiment (14) Phase Diagram of three components System

Theory

According to the phase rule of Gibbs, the variance F (number of degree of freedom) of a system at equilibrium is equal to the number of components c minus the number of phases p plus 2, provided that the equilibrium is influenced only by temperature, pressure and concentration.

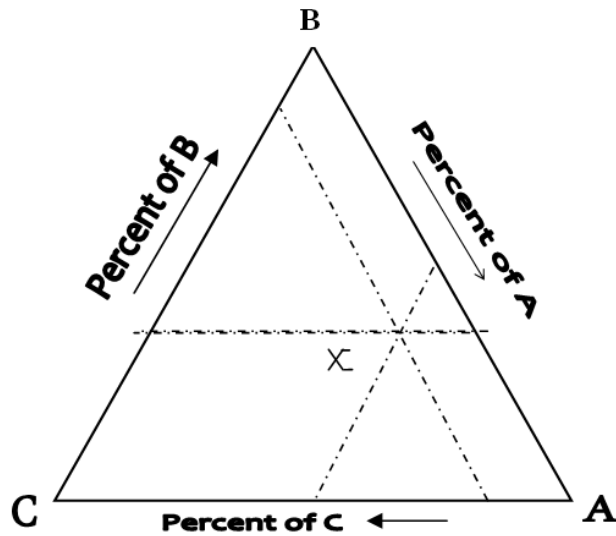
$$F = c - p + 2$$

The variation F is smallest number of independent variables required to completely fix the state of the system. This experiment is carried out at a constant temperature and pressure so that these are not variables. Thus eq. (1) becomes

$$F = c - p$$

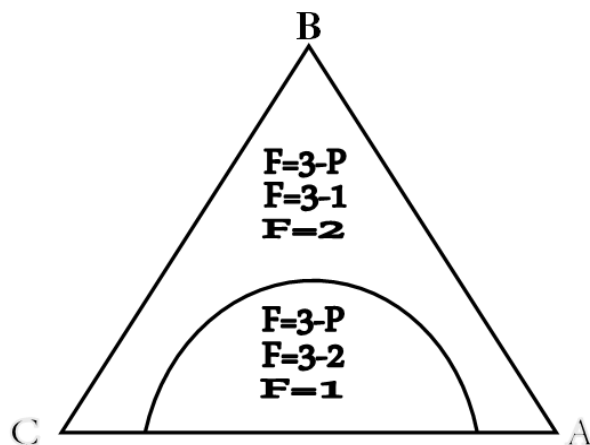
And for a three – component system $F = 3 - p$. Thus in a three – component system if only one liquid phase is present, $F = 2$ and the concentration of two of the chemical substances must be specified in order to describe the system completely. If two immiscible liquid phase are present in equilibrium, $F = 1$ and the concentration of only one component

needs to be specified. It is convenient to represent a three component system on a triangular diagram such as that illustrated in fig (1)



In an equilateral triangle, the sum of the perpendiculars from a given point to the three sides is a constant. The perpendicular distance from each apex, representing a pure compound, to the opposite side is divided to 100 equal parts, corresponding to percent, and labeled along the side at the right of the perpendicular. Thus point (X) corresponding to a composition of 25 percent B, 25 percent C and 50 percent A.

The components benzene and water are essentially immiscible hence two layers will be obtained on mixing. The third component (ethanol), is soluble in each layer and on addition to a mixture of benzene and water distributes itself between these layers. The composition of the layers changes as more ethanol is added. Under these conditions, P equals 2, and the system is completely defined by the composition. Thus if the points corresponding to these compositions are plotted, a smooth curve may be drawn indicating the limits of miscibility of water – benzene mixtures in ethanol as in fig.2.



Apparatus and Chemicals

Five conical flask (25 ml) , benzene , water , ethanol , 5ml pipette , burette .

Procedure

1- Prepare the following mixtures

No. of Conical Flask	Vol.of water added(ml)	Vol.of Benzene(ml)
1	1	5
2	2	4
3	3	3
4	4	2
5	5	1

2- For conical number one , add ethanol slowly until the mixture converts from a turbid to a clear solution by vigorously shaking the mixture . The volume of ethanol which has been added is then recorded .

3- Repeat step 2 for each conical and record the volume of ethanol added.

Calculation

1. By knowing the density of water, benzene and ethanol, calculate the weight of each component in the conical flask.

$$d_{\text{water}} = 1.00 \text{ g/ml}$$

$$d_{\text{Benzene}} = 0.87 \text{ g/ml}$$

$$d_{\text{Ethanol}} = 0.79 \text{ g/ml}$$

$$\text{wt} = d \times v$$

2. Calculate the %wt of each component in the conical flask.

$$\%wt_{\text{water}} = \frac{W_{\text{water}}}{W_{\text{water}} + W_{\text{benzene}} + W_{\text{ethanol}}} \times 100$$

$$\%wt_{\text{benzene}} = \frac{W_{\text{benzene}}}{W_{\text{water}} + W_{\text{benzene}} + W_{\text{ethanol}}} \times 100$$

$$\%wt_{\text{ethanol}} = \frac{W_{\text{ethanol}}}{W_{\text{water}} + W_{\text{benzene}} + W_{\text{ethanol}}} \times 100$$

3. Plot an equilateral triangle, each side equal to 10 cm.

4. Put the data's on the diagram, and find the degree of freedom at miscible region and immiscible region.

Experiment (15)

Determination of the molecular weight of a polymer from viscosity measurements

Theory

Measurements of viscosities of high – polymer solutions offer an indirect method for determining molecular weight. The theoretical background for this method starts with Einstein's derivation ,

$$\lim_{\phi \rightarrow 0} \left[\frac{(\eta / \eta_0) - 1}{\phi} \right] = \frac{\eta_{sp}}{\phi} = \frac{5}{2} \text{ -----(1)}$$

Where η is the viscosity of solution , η_0 is the viscosity of the solvent. The quantity (η / η_0) is of frequent – occurrence in the theory of viscosity and is known as the specific viscosity , η_{sp} .

Because of the difficulty of knowing the fraction of the volume occupied by high – polymer molecules in solution and the fact that the reduced viscosity η_{sp} / c , is not independent of concentration , it is necessary to utilize the limiting viscosity number { η } defined by

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{C} \text{ -----(2)}$$

Where C is the concentration of the high – polymer in grams per ml . The limiting viscosity number is obtained by plotting the ratio of specific viscosity to the concentration against concentration for series solution and extra polting to zero concentration.

For a series of samples of the same polymer in a given solvent and at a constant temperature the following empirical relation is obeyed quite well

$$[\eta] = KM^\alpha \text{ ----- (3)}$$

Here K and α are constants which may be determined by measuring the intrinsic viscosities of a series of samples of a polymer for which the molecular weight have been measured by another method.

Apparatus and chemicals

Viscometer , stop watch , 25ml volumetric flasks , 25ml conical flasks , poly styrene , toluene .

Procedure

- 1- Solutions of poly styrene sample of unknown molecular weight (0.1gm , 0.2 gm , 0,3 gm , 0.4 gm , 0,5 gm) are prepared in pure toluene .
- 2- The flow time in the viscometer is determined for toluene (t_0)
- 3- The flow time for the solutions of polystyrene in toluene is determined (t_i)

Calculation

1. To calculate η / η_0 , the bellow equation must be used

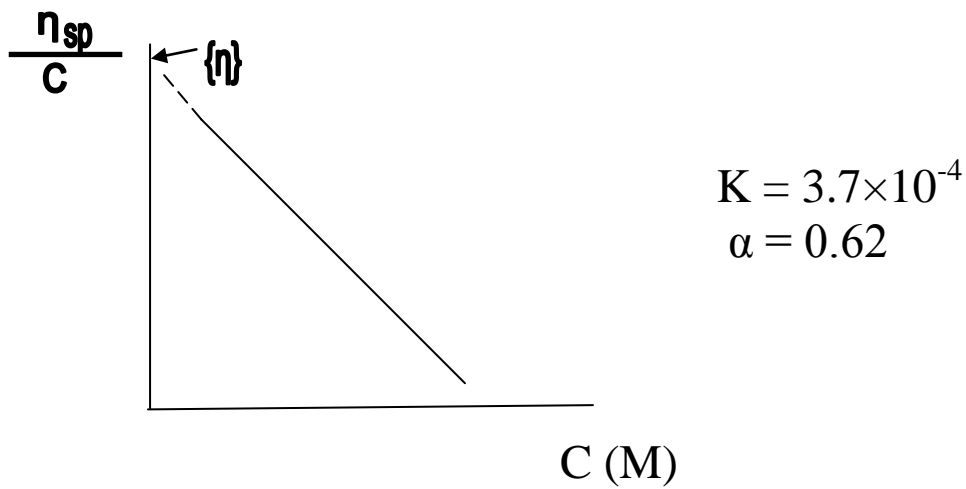
$$\frac{\eta}{\eta_0} = \frac{td}{t_0d_0}$$

Let $d/d_0 = 1$ for easing

$$\therefore \frac{\eta}{\eta_0} = \frac{t}{t_0}$$

wt (g)	Conc. (M)	η/η_o	$\eta_{sp} = (\eta/\eta_o) - 1$	η_{sp}/C
0.1				
0.2				
0.3				
0.4				
0.5				

2- Plot a graph between η_{sp} / C and C



3-Find M by

$$[\eta] = KM^\alpha$$

Experiment (16)

Calculation of the degree of dissociation of KCl in water, and van't Hoff factor.

To represent the colligative properties of electrolytes by means of the same relations as for nonelectrolytes, van't Hoff (1880) suggested the use of a factor i . This is now known as van't Hoff factor and is defined as: the ratio of the colligative effect produced by an electrolyte solution to the corresponding effect for the same concentration of a nonelectrolyte solution. Applying this definition of i to the freezing-point depression, we have

$$i = \frac{\Delta T_f}{[\Delta T_f]_o} \dots \dots \dots (1)$$

Where ΔT_f is the freezing-point depression for the electrolyte measured experimentally and $[\Delta T_f]_o$ is the corresponding value calculated for a nonelectrolyte of the equal concentration.

Relation Between van't Hoff Factor and Degree of Dissociation.

$$\alpha = \frac{i - 1}{\nu - 1} \dots \dots \dots (2)$$

α = Degree of dissociation.

ν = Number of ions on complete dissociation.

For KCl ($\nu = 2$).

As a result of dissociation, the total number of particles increases; hence the depression of freezing point will also increase. Therefore, the molecular weights of those substances which dissociate will be lower than their normal molecular weights.

$$\Delta T_f = m \times k_f \dots \dots \dots (3)$$

m = molality of the KCl in water

k_f = molal freezing point depression constant

For an electrolyte

$$\Delta T_f = i \times m \times k_f \dots \dots \dots (4)$$

$$m = \frac{w_{solute} \times 1000}{M.wt_{solute} \times W_{solvent}} \dots \dots \dots (5)$$

Apparatus and chemicals

Beaker, test tube, Beckman thermometer, Water, sample (solute), ice.

Procedure

- 1- A known weight of water (about 10g) is added to the center of the test tube.
- 2- The thermometer is immersed in the tube, then cooled by direct immersion in the Snowy salt bath with continuous stirring until the water starts to freeze, read the thermometer T_o .
- 3- Remove the tube from the Snowy salt bath and melt the water with gentle warming.
- 4- Then add 0.5g weight of KCl to the water.
- 5- Repeat the same procedure to determine the freezing point of the solution T_f .
- 6- Repeat step 4 and 5 for another 0.5g of KCl.

Calculation:

- 1- Calculate the average ΔT_f .
- 2- Calculate i and α .