

- d) The lowest temperature at which any liquid mixture can exist is called _____ temperature.
- e) The smallest number of independently variable factors which must be specified in order to define the system completely is called _____.
2. What is phase rule equation?
3. What is a condensed system?

11.6 ANSWERS

Self-Assessment Questions

1. a) Three (two due to toluene and water liquids which are immiscible and, one due to their vapours).
- b) Two (one liquid and one vapour phase, since acetone and water are miscible).
2. a) $C = 1$ as per Eq. 11.1, since $S = 3$ and $R = 2$
- b) $C = 2$, since $S = 3$ and $R = 1$

Terminal Questions

1. a) Phase
- b) Components
- c) $F = C - P + 1$
- d) Eutectic
- e) Degrees of freedom
2. $F = C - P + 2$
3. Heterogeneous system in which the gas phase is absent, is called a condensed system.

UNIT 12 PHASE EQUILIBRIA - II

Structure

- 12.1 Introduction
 - Objectives
- 12.2 Critical Solution Temperature
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- 12.8 Summary
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12.1 INTRODUCTION

In Unit 11 of the CHE-04 course, you were introduced to critical solution temperature (CST) of two partially miscible liquids and the distribution law. In this unit, we will describe four experiments which are based upon these two concepts. You studied that the presence of small amounts of impurity produces a very large change in critical solution temperature and the change in CST values is usually a linear function of concentration of impurity. Thus, the amount of impurity can be determined by measuring the CST values.

The distribution law can be used to study the state of association or dissociation of a solute in one or both of the liquid phases. It also helps us in selection of a solvent for extraction of a compound.

After studying this unit and having performed the experiments described in it, you should be able to:

- define critical solution temperature and state the distribution law,
- describe the effect of impurity on critical solution temperature,
- determine the CST of partially miscible liquid pairs such as phenol and water,
- determine the concentration of NaCl in a solution by the CST method,
- determine the distribution coefficient of iodine between water and carbon tetrachloride, and
- determine the distribution coefficient of benzoic acid between water and toluene.

12.2 CRITICAL SOLUTION TEMPERATURE (CST)

You studied in Unit 11 of the CHE-04 course that some liquid pairs do not give homogeneous solutions at all compositions. Such liquid pairs are said to be partially miscible liquids. However, due to increased solubility with increase or decrease of temperature, these may become completely miscible. We can explain such a system of liquids using phenol and water. When a very small amount of phenol is added to water at room temperature, it dissolves completely to give a single liquid phase. However, when the addition of phenol is continued, a point is reached when phenol does not dissolve any more. At this point, two phases, i.e., two liquid layers are formed - one consisting of water saturated with phenol and the other containing phenol saturated with water. Further addition of phenol causes water to shift from water-rich layer to phenol-rich layer. If the addition of phenol is continued, a point is reached when phenol acts as a solvent for all the water present and the two phases merge with each other to form a single phase, i.e., solution of water in phenol. Thus, on shaking equal volumes of phenol and water, two layers are formed - one of phenol in water and the other of water in phenol.

It has been experimentally found that at constant temperature, the composition of the two layers, although different from each other, remains constant as long as the two phases are present. Such solutions of different compositions coexisting with each other are termed as conjugate solutions. The addition of small amounts of phenol or water changes the volume of the two layers and not their compositions. As the temperature is increased, the behaviour remains the same except that the mutual solubility of the two phases increases. When the temperature reaches 338.8 K, the composition of the two layers becomes identical and thereafter the two liquids are completely miscible. Thus, at and above 338.8 K, phenol and water dissolve in each other in all proportions and yield only a single liquid layer on mixing. The variation of mutual solubility of water and phenol with temperature is shown in Fig. 12.1.

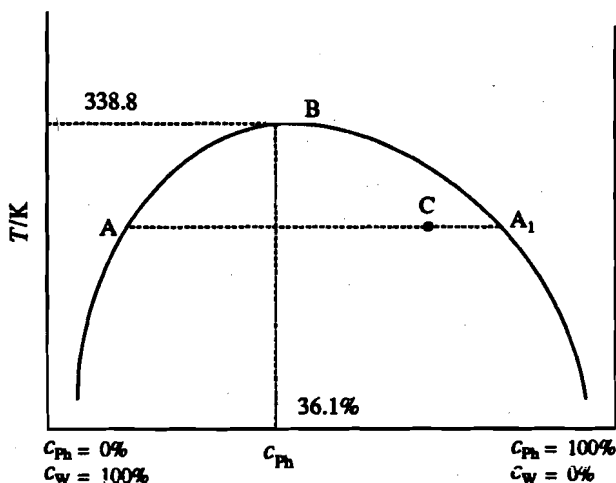


Fig. 12.1: Phenol-water system; c_{ph} stands for composition of phenol and c_w for composition of water.

At a particular temperature, say 325 K, point A represents the composition of water-rich layer and point A_1 represents the composition of phenol-rich layer in equilibrium with A. Between these compositions, all mixtures will yield two layers of compositions A and A_1 . Outside these compositions, the two liquids are soluble mutually at 325 K. Similar behaviour is seen at other temperatures below 338.8 K. We can conclude that the dome-shaped area represents the range of existence of two liquid phases and the area outside the dome represents a single liquid phase. The temperature corresponding to the point B, i.e., the temperature at which the solubility becomes complete is called the **critical solution temperature** or the **consolute temperature**. Since the mutual solubility of phenol and water increases with rise in temperature, the critical solution temperature (CST) lies well above the room temperature. Hence, such liquid systems are said to possess an upper critical solution temperature or consolute temperature. Thus, the critical solution temperature, for phenol-water system is 338.8 K. At and above 338.8 K, phenol and water are completely miscible with each other in all proportions. At this temperature, the composition of the solution is 36.1% phenol and 63.9% water. At any point C, the relative weights of the two separate layers are given by the relationship,

$$\frac{\text{Mass of water rich layer}}{\text{Mass of phenol rich layer}} = \frac{A_1 C}{AC} \quad \dots (12.1)$$

There are some liquid pairs (e.g., triethylamine-water) for which mutual solubilities decrease with rise in temperature. As the temperature is decreased, the mutual solubilities increase and below the consolute temperature, the two liquids become miscible in all proportions. Such systems possess lower consolute temperatures. The variation of mutual solubility of triethylamine and water with temperature is shown in Fig. 12.2. Above 291.5 K, on shaking triethylamine and water, two layers are formed; but below 291.5 K, triethylamine and water are completely miscible with each other in all proportions.

Some liquid pairs, e.g., nicotine and water, show both the upper and lower consolute temperatures. These liquid pairs are completely miscible above a certain temperature (upper consolute temperature) and below a certain temperature (lower consolute temperature). The variation of mutual solubilities of nicotine and water with temperature is shown in Fig. 12.3. Within the enclosed area, the liquids are only partially miscible, while

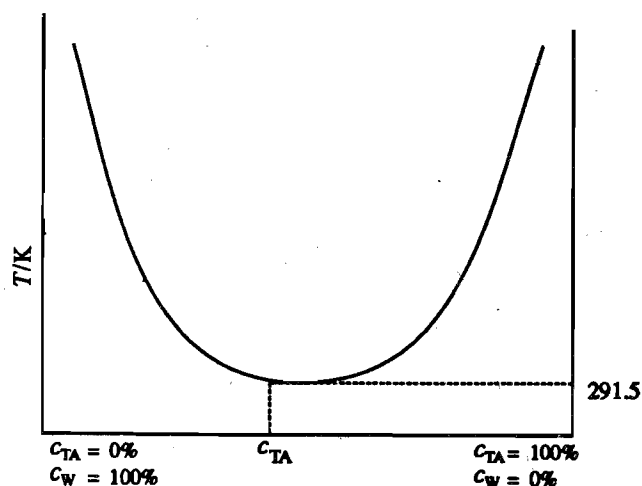


Fig. 12.2: Triethylamine-water system; c_{TA} stands for the composition of triethylamine.

outside the enclosed area, they are completely miscible. The composition corresponding to both the upper and the lower consolute temperatures is the same, i.e., 34% nicotine. Table 12.1 lists the consolute temperatures of some liquid pairs. The two components are denoted as A and B.

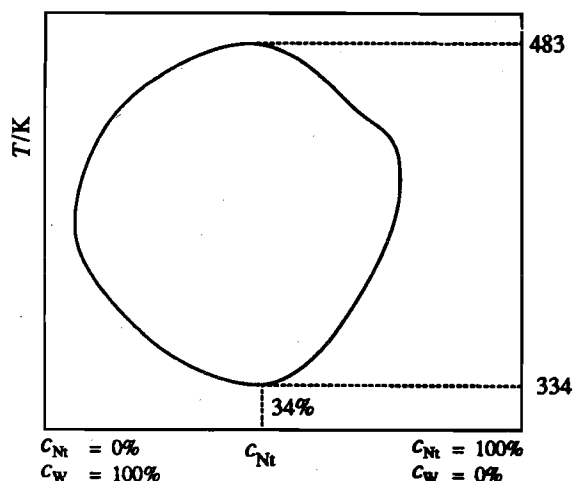


Fig. 12.3: Nicotine-water system; c_{Nt} stands for the composition of nicotine.

Effect of Impurities on CST Values

The presence of an impurity, dissolved in one or both of the phases, changes the CST values as well as the liquid phase composition at CST. Substances soluble in only one of the liquids raise the upper CST and lower the lower CST. For example, one percent solution of sodium chloride raises the upper CST of phenol-water system by 12° . About 0.12 molar solution of naphthalene (insoluble in water) in phenol raises the upper CST of phenol-water system by about 30° . Substances which are soluble in both the liquids tend to lower the upper CST and raise the lower CST. For example, sodium oleate is soluble in both water and phenol. Addition of 1% solution of sodium oleate to phenol-water system lowers the CST value by 45° .

Table 12.1: Consolute Temperatures of Some Liquid Pairs

Components		Consolute temperature/K	
A	B	Upper	Lower
Water	Phenol	338.8	-
Aniline	Hexane	333.6	-
Methanol	Carbon disulphide	323.5	-
Water	Diethylamine	-	316
Water	Triethylamine	-	291.5
Water	Nicotine	483	334
Glycerine	m-Toludine	393	280

As seen above, the presence of small amounts of impurities produces a very large change in the CST values. The change in CST values is usually a linear function of concentration of impurities. Traces of water present in alcohol are estimated by measuring the CST values for alcohol-cyclohexane system.

As mentioned above, a very small amount of sodium oleate lowers the CST value of phenol-water system considerably. Thus, by making phenol completely miscible with water (by adding appropriate amounts of sodium oleate), lysol-like disinfectants are made.

SAQ 1

Fill in the blanks with appropriate word:

- (i) The two liquid layers in equilibrium are known as _____ solutions.
- (ii) The temperature at which the two partially miscible _____ liquids first become miscible in all proportions is called temperature.
- (iii) The critical solution temperature is also called _____ temperature.
- (iv) A system having lower critical solution temperature is _____.
- (v) A system having both the upper and the lower critical solution temperatures is _____.

12.3 EXPERIMENT 12A : CST OF PHENOL-WATER SYSTEM

You know that phenol and water constitute a partially miscible liquid pair which has an upper CST. Objective of this experiment is to determine the CST of this system.

12.3.1 Principle

In this experiment miscibility temperatures of different mixtures of phenol and water are determined. A graph is plotted by taking percentage composition of mixture along x-axis and miscibility temperature along the y-axis. Temperature corresponding to the highest point on the dome shaped curve gives the CST of the system.

12.3.2 Requirements

Apparatus

- | | | |
|----|----------------------------|--------|
| 1. | Beaker 250 cm ³ | 1 No. |
| 2. | Boiling tube | 1 No. |
| 3. | Burettes | 2 Nos. |
| 4. | Burner | 1 No. |

**Applications of
Thermodynamics**

Stock solution can be prepared by adding 20 g of distilled water to every 80 g of phenol.

- | | |
|---|--------|
| 5. Corks | 1 No. |
| 6. Graduated pipette 10 cm ³ | 1 No. |
| 7. Test tubes | 5 Nos. |
| 8. Thermometer 100° | 1 No. |
| 9. Wire gauze | 1 No. |
| 10. Wire stirrer | 1 No. |

Stock Solution Provided

1. Phenol 80% (mass/mass)

12.3.3 Procedure

Phenol is a highly poisonous and strongly caustic substance. It produces painful burns on coming in contact with skin. Phenol should be handled with abundant care. In case of accidental contact with phenol or its solution, wash the affected part with plenty of water and then apply vaseline.

Set up two burettes, one for phenol solution and the other for distilled water. Take five test tubes and number them 1 to 5. Then prepare the following mixtures of phenol and water in test tubes:

Test tube no.	1	2	3	4	5
80% Phenol Soln. (cm ³)	10.0	9.0	8.0	7.0	6.0
Water (cm ³)	0.0	1.0	2.0	3.0	4.0
% Phenol (mass/mass)	80	72	64	56	48

Take solution no. 1 in the boiling tube. Fix the wire stirrer and thermometer in the boiling tube through the cork and place the boiling tube in the water bath. The bulb of the thermometer should dip in the phenol-water mixture. The level of water in the bath should be 1 cm above the level of mixture in the boiling tube (Fig. 12.4).

The phenol-water mixture in the tube may give rise to two layers. Stir the mixture with the wire stirrer. It will produce a cloudiness or turbidity in the tube. Raise the temperature of the bath slowly while stirring the mixture constantly. Note down the temperature (in Table 12.2) of the bath at which the last trace of cloudiness disappears. Remove the burner and allow the clear solution to cool slowly while keeping it stirred. Note down the temperature at which cloudiness just reappears. The average of the two temperatures, which should be nearly equal, is the miscibility temperature for the mixture. Transfer the mixture into test tube no. 1.

If the phenol-water mixture does not produce two layers, it means that the miscibility temperature of this mixture is below room temperature. Cool the mixture with ice-cold water. Keep on stirring the mixture. Note down the temperature at which cloudiness just appears in the mixture. Cool the mixture to 4-5° below this temperature and then remove the cold bath. Allow the mixture to warm naturally and note down the temperature at which cloudiness just disappears. Take average of the two temperatures, which would give the miscibility temperature of this mixture.

Find out the miscibility temperature for each mixture in the same manner and record the values in Table 12.2. Now dilute the mixtures 1-5 with an equal volume of water (i.e., 10 cm³). This will give five more mixtures (no. 6-10) having 40, 36, 32, 28 and 24% phenol, respectively. Find miscibility temperatures for these also and record the values in Table 12.2. After the experiment, transfer all the mixtures to a used phenol bottle kept in the laboratory for recovery of phenol by fractional distillation.

Plot a graph by taking percentage composition of mixture along the x-axis and the miscibility temperature along the y-axis. Draw a smooth curve through the points. Mark the maximum point on the curve. Read the temperature and the composition of the mixture at the maximum

point from the graph. The temperature for the maximum point on the graph is the critical solution temperature for the phenol-water system.

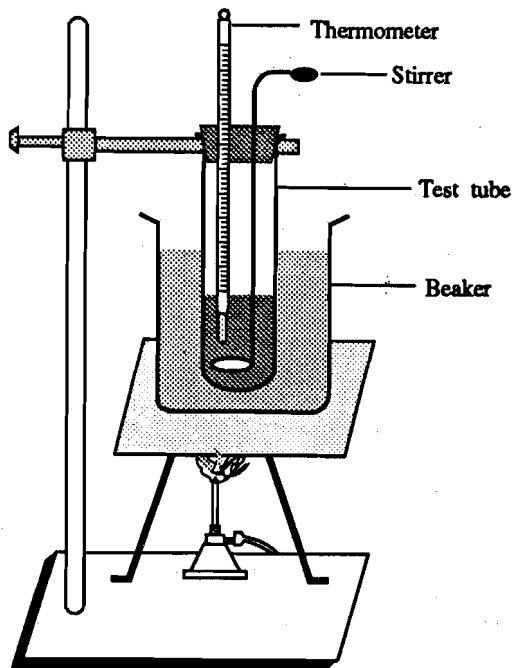


Fig. 12.4 : Determination of miscibility temperature.

12.3.4 Observations

Room temperature = °C

Table 12.2 : % Composition - Miscibility Temperature Data

Sl.No.	%Phenol	Miscibility temperature/°C		
		Turbidity disappears	Turbidity re-appears	Average
1	80			
2	72			
3	64			
4	56			
5	48			
6	40			
7	36			
8	32			
9	28			
10	24			

12.3.5 Result

The critical solution temperature (CST) of phenol-water system = °C.

12.4 EXPERIMENT 12B : EFFECT OF NaCl ON CST OF PHENOL-WATER SYSTEM

In this experiment, you will study the effect of an impurity (sodium chloride) on the CST of the phenol-water system. You will also determine the concentration of NaCl in an unknown solution by critical solution temperature method.

12.4.1 Principle

In Section 12.2, you studied that the impurities have a marked effect on the CST of a partially miscible liquid pair. Sodium chloride is soluble only in water and not in phenol. Therefore, it will raise the CST of phenol-water system.

In this experiment, the miscibility temperatures for various mixtures of phenol and aqueous solutions of sodium chloride are determined. A calibration curve (usually a straight line) is plotted between the concentration of NaCl and the miscibility temperature.

The miscibility temperature for a mixture of phenol and the unknown NaCl solution is also determined. From the calibration curve, the concentration of unknown NaCl solution is then obtained.

12.4.2 Requirements

Apparatus

1.	Beaker 250 cm ³	1 No.
2.	Boiling tube	1 No.
3.	Burettes	2 Nos.
4.	Burner	1 No.
5.	Cork	1 No.
6.	Graduated pipette	1 No.
7.	Test tubes	7 Nos.
8.	Thermometer 100°	1 No.
9.	Wire stirrer	1 No.
10.	Wire gauze	1 No.

Stock Solutions Provided

1.	Phenol	80% (mass/mass)
2.	Sodium chloride	1% (mass/volume)

Phenol solution can be prepared as described in Experiment 12A. Sodium chloride solution can be prepared by dissolving 1 g of NaCl in every 100 cm³ of solution.

12.4.3 Procedure

Take seven test tubes and number them from one to seven. Add 5 cm³ of 80% (m/m) phenol solution to each test tube with the help of a burette. From another burette add 1, 2, 3, 4 and 5 cm³ of 1% NaCl solution to test tubes numbered 2 to 6, respectively. Add 5 cm³ of unknown NaCl solution to the test tube numbered 7. Now add 5, 4, 3, 2 and 1 cm³ of distilled water to test tube numbered 1 to 5, respectively. This makes the volume of mixture 10 cm³ in each test tube.

Take each mixture in the boiling tube and find out its miscibility temperature as described in Experiment 12A. Record the data in Table 12.3.

Draw a graph between the percentage of sodium chloride (taken as x-axis) and the miscibility temperature (taken as y-axis). Find out the percentage of unknown sodium chloride solution (from the graph) corresponding to its miscibility temperature, using interpolation method discussed in Section 2.6 of Unit 2 of this course.

Table 12.3 : Composition - Miscibility Temperature Data

Test Tube No.	(Volume of phenol soln. taken)/cm ³	(Volume of 1% NaCl taken)/cm ³	(Volume of distilled water taken)/cm ³	% NaCl in aqueous solution	Miscibility temperature/°C		
					Turbidity dis-appears	Turbidity re-appears	Mean
1	5	0.0	5.0	0.0			
2	5	1.0	4.0	0.20			
3	5	2.0	3.0	0.40			
4	5	3.0	2.0	0.60			
5	5	4.0	1.0	0.80			
6	5	5.0	0.0	1.0			
7	5	5.0 (Unknown)	0.0	Unknown			

12.4.6 Result

Concentration of NaCl in unknown solution = %

12.5 DISTRIBUTION LAW

Distribution law was given by Nernst, that is why it is also known as the Nernst distribution law. According to this law, at a fixed temperature, a substance X distributes itself between the two immiscible solvents A and B in equilibrium with each other in such a way that the ratio of the concentrations of X in the two solvents is constant, provided that the solute X is in the same molecular state in both the solvents. Mathematically,

$$\frac{\text{Concentration of } X \text{ in solvent A}}{\text{Concentration of } X \text{ in solvent B}} = \frac{c_1}{c_2} = K \quad \dots (12.1)$$

The constant K is called the distribution or partition coefficient of the solute between the two liquids. It is independent of the total amount of the solute added or the amounts of solvents used or the units in which the concentration is expressed. Generally, it is the convention that the higher concentration is kept in the numerator, so that K is greater than 1.

The value of distribution coefficient depends upon

- nature of the solute
- nature of the solvent, and
- temperature

The distribution law can be derived by taking into account thermodynamic considerations. If you are interested, you can refer to Unit 11 of the CHE-04 course.

Nernst pointed out that the above statement of the distribution law is valid only when the solute undergoes no change such as dissociation or association in either of the solvents. If a solute dissociates into simple molecules or ions, or if it associates to form complex molecules, then the distribution law does not apply to the total concentration of the solute in each of the two phases. It is applicable only to the concentration of a particular species common to both

the layers. Let us look at the distribution law in brief in these cases, which we have discussed in detail in Section 11.4 of Unit 11 of the CHE-04 course.

When the Solute Undergoes Association

Suppose the solute X undergoes association in one of the liquids to form associated molecules, X_n , i.e.,



If the concentration of the solute in this liquid is c_1 before association and that in the other liquid is c_2 , then the distribution law would be

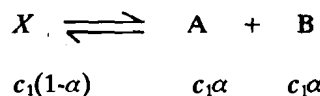
$$\frac{(c_1)^{1/n}}{c_2} = K = \text{constant}$$

In benzene and toluene solutions, benzoic acid exists as dimeric molecules (i.e., $n = 2$). In distribution of benzoic acid between benzene or toluene and water, the distribution law would be

$$\frac{(c_1)^{1/2}}{c_2} = \frac{\sqrt{c_1}}{c_2} = K = \text{constant} \quad \dots (12.2)$$

When the Solute Undergoes Dissociation

Let us suppose that the solute X undergoes dissociation into A and B in one of the liquids. If c_1 is the total concentration of the solute in this liquid before dissociation, and α is the degree of dissociation, then we can write



If the concentration of the solute in the other liquid, in which it remains undissociated, is c_2 , then the distribution coefficient is given by

$$\frac{c_1(1-\alpha)}{c_2} = K = \text{constant} \quad \dots (12.3)$$

SAQ 2

Fill in the blanks using appropriate words:

- i) The _____ law deals with the distribution of a solid between two immiscible liquids.
- ii) The ratio of the concentrations of the solute between two liquids is called _____ coefficient.
- iii) The distribution law is valid when the dissolved substance has the _____ molecular form in the two solvents.

12.6 EXPERIMENT 13 : DISTRIBUTION COEFFICIENT OF IODINE IN CARBON TETRACHLORIDE-WATER SYSTEM

Objective of this experiment is to determine the distribution coefficient of iodine in carbon tetrachloride-water system.

12.6.1 Principle

Carbon tetrachloride and water are practically immiscible with each other but iodine dissolves in both of them. When iodine is added to a mixture of CCl_4 and H_2O at a certain

temperature, iodine distributes itself between the two immiscible layers. At a particular temperature, let the concentration of iodine in CCl_4 and H_2O be c_1 and c_2 , respectively. In both CCl_4 and H_2O iodine exists in molecular form. Therefore, according to the distribution law, we have

$$\frac{c_1}{c_2} = K = \text{constant} \quad \dots (12.3)$$

Different amounts of iodine are added to a mixture of CCl_4 and H_2O . The concentration of iodine in two layers is estimated by titration against sodium thiosulphate solution. For dilute solutions, the ratio c_1/c_2 is found to be constant within experimental limits and gives the value of distribution coefficient, K .

12.6.2 Requirements

Apparatus

1. Burette	1 No.
2. Graduated pipette 10 cm ³	1 No.
3. Pipette 20 cm ³	1 No.
4. Pipette 5 cm ³	1 No.
5. Conical flask 100 cm ³	1 No.
6. Stoppered bottles 250 cm ³	3 Nos.
7. Thermometer 100	1 No.
8. Glass trough	1 No.

Chemicals

1. Carbon tetrachloride

Stock Solutions Provided

1. Iodine
2. Freshly prepared starch
3. 1.000×10^{-1} M and 1.000×10^{-2} M sodium thiosulphate

Details of preparation of stock solutions are given in Appendix-I.

12.6.3 Procedure

Take three 250 cm³ glass stoppered bottles and label them with numbers 1, 2 and 3. Using two separate burettes, take 20, 25 and 30 cm³ of saturated solution of iodine in CCl_4 and add 10, 5 and 0 cm³ of carbon tetrachloride, respectively to these bottles to make the total volume 30 cm³ in each bottle.

Now add to each bottle 100 cm³ of distilled water. Stopper the bottles, shake them vigorously and place them in a thermostat (or glass trough filled with water maintained at room temperature) for about half an hour. Shake the bottles 2-3 times. After the final shaking, wait till there is a complete separation of the two liquid layers. Since carbon tetrachloride is heavier than water, it will form the lower layer, while the upper layer will be the aqueous layer. Note down the temperature of water in the trough. Pipette out 20 cm³ of aqueous layer into a conical flask from bottle no. 1. Add 4-5 drops of freshly prepared starch solution. The solubility of iodine in water is very low. Titrate this solution with 1.000×10^{-2} M sodium thiosulphate (hypo) solution. The equivalence point is indicated by the disappearance of the blue colour. Repeat the titration to get two concordant readings and record them in Table 12.4. In the same manner take the samples of upper layer from bottle nos. 2 and 3. Perform titrations and record the titre values in the Table 12.4.

While pipetting one of the two layers, you should ensure that the other layer does not enter the pipette. You are advised to take the help of the Counsellor during this operation.

After finishing the titrations of the upper aqueous layer, separate the remaining upper layer by decantation or with the help of a separating funnel. Pipette out 5 cm³ of CCl_4 layer (of bottle 1) into a 100 cm³ conical flask. Add about 20 cm³ of distilled water into it. The addition of water helps in titration by gradually extracting iodine into water layer where the reaction with sodium thiosulphate occurs. By covering the CCl_4 layer with a water layer, loss of iodine

as vapour from the exposed solution is also prevented. Add 4-5 drops of freshly prepared starch solution. Titrate the solution with 1.000×10^{-1} M sodium thiosulphate solution. Disappearance of blue colour will indicate the equivalence point. Repeat the titration to get two concordant readings and record them in Table 12.5. In the same manner, take the samples of CCl_4 layer from bottle nos. 2 and 3, perform titrations and record the titre values in Table 12.5.

12.6.4 Observations

Temperature of water in trough = °C =

Table 12.4 : Titration of Aqueous layer

Sl. No.	Bottle No.	(Volume of aqueous layer)/ cm^3	Burette reading		(Volume of 1.000×10^{-2} M hypo consumed)/ cm^3
			Initial	Final	
1	1	20.0			
2	1	20.0			
3	1	20.0			
4	2	20.0			
5	2	20.0			
6	2	20.0			
7	3	20.0			
8	3	20.0			
9	3	20.0			

Table 12.5 : Titration of CCl_4 layer

Sl. No.	Bottle No.	(Volume of CCl_4 layer)/ cm^3	Burette reading		(Volume of 1.000×10^{-1} M hypo consumed)/ cm^3
			Initial	Final	
1	1	5.0			
2	1	5.0			
3	1	5.0			
4	2	5.0			
5	2	5.0			
6	2	5.0			
7	3	5.0			
8	3	5.0			
9	3	5.0			

12.6.5 Calculations

Sodium thiosulphate reacts with iodine as follows:



If V_a cm³ of $\text{Na}_2\text{S}_2\text{O}_3$ of molarity M_a react with V_b cm³ of I_2 of molarity M_b , then using Eq. 1.13 of Unit 1 of this course, we can write,

$$\frac{M_a V_a}{M_b V_b} = \frac{2}{1}$$

or $M_a V_a = 2 M_b V_b$

Using this equation, calculate the concentration of I_2 in terms of molarity in aqueous and in CCl_4 layers in each bottle. After that, find out the ratio of concentration of I_2 in CCl_4 layer (c_1) to that in the aqueous layer (c_2), which will give the value of distribution coefficient, K . Remember that the molarities of $\text{Na}_2\text{S}_2\text{O}_3$ used for the titration of aqueous and CCl_4 layers are 1.000×10^{-2} M and 1.000×10^{-1} M., respectively. Record the values in Table 12.6 and report the average value of K .

Table 12.6 : Values of Distribution Coefficient

Bottle	c_1/M	c_2/M	$K = \frac{c_1}{c_2}$	Average value of K
1				
2				
3				

12.6.6 Result

The distribution coefficient of iodine between carbon tetrachloride and water was found to be .

12.7 EXPERIMENT 14 : DISTRIBUTION COEFFICIENT OF BENZOIC ACID IN TOLUENE-WATER SYSTEM

Objective of this experiment is to determine the distribution coefficient of benzoic acid between toluene and water.

12.7.1 Principle

As you know toluene and water are practically immiscible with each other but benzoic acid dissolves in both of them. When benzoic acid is added to a mixture of toluene and water, it distributes itself between the two immiscible layers. In water, benzoic acid exists almost in monomeric form. No doubt benzoic acid is a weak acid. We assume that its dissociation in water is negligibly small to facilitate the calculations in this experiment. In toluene, it undergoes association to form dimers. By performing this experiment, we can verify the validity of these two assumptions.

At a particular temperature, let the concentration of benzoic acid in toluene and in water be c_1 and c_2 , respectively. Therefore, according to Eq. 12.2,

$$\frac{\sqrt{c_1}}{c_2} = K = \text{constant} \quad \dots (12.2)$$

Different amounts of benzoic acid are added to a mixture of toluene and water. The mixture is shaken vigorously and the layers are allowed to separate. The concentrations (c_1 and c_2) of benzoic acid in the two layers are estimated by titrating against standard NaOH solution and the value of K is calculated. The ratio $\sqrt{c_1/c_2}$ is calculated and is found to be constant within experimental limits thereby justifying the assumptions made above. Also, this gives the value of the distribution coefficient.

12.7.2 Requirements

Apparatus		Chemical
1.	Burette	1 No.
2.	Graduated pipette 10 cm ³	1 No.
3.	Pipette 10 cm ³	1 No.
4.	Pipette 5 cm ³	1 No.
5.	Conical flask	1 No.
6.	Stoppered bottles 250 cm ³	3 Nos.
7.	Thermometer 100°	1 No.
8.	Glass trough	1 No.
		1. Toluene

Details of preparation of stock solutions are given in Appendix-II.

Stock Solutions Provided

1. Benzoic acid
2. 5.000×10^{-2} and 1.000×10^{-1} M NaOH
3. Phenolphthalein

12.7.3 Procedure

Take three 250 cm³ capacity stoppered glass bottles and label them 1, 2 and 3. Place 20, 25 and 30 cm³ of benzoic acid solution and, 10, 5 and 0 cm³ of toluene to bottles 1, 2 and 3, respectively making the total volume of organic layer 30 cm³ in each bottle.

Add 100 cm³ of distilled water to each bottle. Stopper the bottles, shake them vigorously and place them in the trough of water for about half an hour. Allow the layers to separate. Toluene being lighter than water will form the upper layer. Note down the temperature of water in the trough.

Pipette out 5 cm³ of toluene layer from bottle 1 in a 100 cm³ conical flask. Add 25 cm³ of distilled water and 2 drops of phenolphthalein solution. Titrate the mixture with standard 1.000×10^{-1} M NaOH solution. The equivalence point is indicated by the appearance of a pink colour. Repeat the titration till you get two concordant readings. Similarly perform titration with toluene layer in bottles 2 and 3 separately and record the readings in Table 12.7.

After performing titrations of the upper toluene layer, separate the upper layer by decantation or with the help of a separating funnel. Pipette out 10 cm³ of lower aqueous layer from bottle 1 into a 100 cm³ conical flask and add 2 drops of phenolphthalein indicator. Titrate the solution with standard 5.000×10^{-2} M NaOH solution. The equivalence point is marked by the appearance of pink colour. Repeat the titration till you get two concordant readings. Similarly perform titration with aqueous layer in bottles 2 and 3. Record the readings in Table 12.8.

12.7.4 Observations

Temperature of water in trough = °C

While pipetting one of the two layers, you should ensure that the other layer does not enter the pipette. You are advised to take the help of the Counsellor during this operation.

Table 12.7 : Titration of Toluene layer

Sl No.	Bottle No.	(Volume of toluene layer)/cm ³	Burette reading		(Volume of 1.000 × 10 ⁻¹ M NaOH consumed)/cm ³
			Initial	Final	
1	1	5.0			
2	1	5.0			
3	1	5.0			
4	2	5.0			
5	2	5.0			
6	2	5.0			
7	3	5.0			
8	3	5.0			
9	3	5.0			

Table 12.8 : Titration of Aqueous layer

Sl. No	Bottle No.	(Volume of aqueous layer)/cm ³	Burette reading		(Volume of 5.000 × 10 ⁻² M NaOH consumed)/cm ³
			Initial	Final	
1	1	10.0			
2	1	10.0			
3	1	10.0			
4	2	10.0			
5	2	10.0			
6	2	10.0			
7	3	10.0			
8	3	10.0			
9	3	10.0			

12.7.5 Calculations

Benzoic acid reacts with sodium hydroxide as follows:



If V_a cm³ of benzoic acid of molarity M_a react with V_b cm³ of sodium hydroxide of molarity M_b , then using Eq. 1.13 of Unit 1 of this course,

$$\frac{M_a V_a}{M_b V_b} = 1$$

or $M_a V_a = M_b V_b$

Using the above equation, calculate the concentration of benzoic acid solution in terms of molarity in toluene layer (c_1) and in aqueous layer (c_2) in each bottle. After that calculate the ratio $\sqrt{c_1}/c_2$, which will give the value of distribution coefficient, K . Record the values of c_1 , c_2 and K in Table 12.9 and report the average value of K .

Table 12.9 : Values of Partition coefficient

Bottle No.	c_1/M	c_2/M	$K = \frac{\sqrt{c_1}}{c_2}$	Average value of K
1				
2				
3				

12.7.6 Result

The distribution coefficient of benzoic acid between toluene and water was found to be

The constant value for K brings out the validity of the assumption made regarding the monomeric nature of benzoic acid in water and the dimeric nature of benzoic acid in toluene.

12.8 SUMMARY

In this unit, you were introduced to the concepts of critical solution temperature and distribution coefficient. Two experiments based on critical solution temperature were discussed. Two experiments for determination of distribution coefficient of iodine between carbon tetrachloride and water, and of benzoic acid between toluene and water were also described.

12.9 TERMINAL QUESTIONS

1. What is CST?
2. What is the effect of impurity on CST?
3. Give the definition of the distribution coefficient.
4. State the form of distribution law when the solute associates in one of the two liquids.
5. State the form of distribution law when the solute dissociates in one of the two liquids.

12.10 ANSWERS

Answers to Self-Assessment Questions

1. i) conjugate
ii) critical solution or consolute
iii) consolute

- iv) triethylamine-water
 - v) nicotine-water
2. i) distribution
- ii) distribution or partition
 - iii) same

Answers to Terminal Questions

1. The temperature at which the two partially miscible liquids become miscible in all proportions is called critical solution temperature, CST.
2. Impurities have a marked effect on CST. If an impurity is soluble only in one of the two liquids, it will raise the upper CST, while the lower CST will be lowered. If on the otherhand, it is soluble in both the liquids, the upper CST will be lowered, while the lower CST will be raised.
3. If to a system of two immiscible liquids a substance, which is soluble in both the liquids, is added, the solute will distribute itself in such a way that the ratio of the molar concentrations of the solute in the two liquids is constant at a given temperature.
4. $\frac{(c_1)^{1/n}}{c_2} = K$, where n is the degree of association of the solute in one of the liquids.
5. $\frac{c_1(1-\alpha)}{c_2} = K$, where α is the degree of dissociation of the solute in one of the liquids.

FURTHER READING

1. Senior Practical Physical Chemistry, B.D. Khosla, A. Gulati and V.C. Garg, R. Chand & Co., New Delhi, 4th ed., 1985.
2. Practical Chemistry, S. Giri, D.N. Bajpai and O.P. Pandey, S. Chand & Company Ltd., New Delhi, 7th ed., 1993.

Iodine solution : Each student will need about 80 cm^3 of solution. Prepare a saturated solution of iodine by dissolving 25 g of iodine crystals in 500 cm^3 of CCl_4 . Filter the solution and store in a brown bottle.

Starch solution : Take 1 g of starch and make a fine paste of it in about 20 cm^3 of distilled water. Add 80 cm^3 of hot water and boil the mixture. Keep the mixture stirred during boiling. Since starch solutions degrade in short time, it is advised to test its suitability. For this, take a small portion of the solution in a test tube and to this, add a little of iodine solution. It should give an intense blue colour.

Sodium thiosulphate : $1.000 \times 10^{-1} \text{ M}$ and $1.000 \times 10^{-2} \text{ M}$: Prepare a stock solution of sodium thiosulphate of about 0.25 M concentration by dissolving 62.5 g crystals in distilled water and making up the volume to 1 dm^3 . Standardise this solution by titrating against a standard solution of potassium dichromate, as described in Appendix-I to Unit 15 of this course. Let the molarity of stock solution be $x \text{ mol dm}^{-3}$.

Prepare sodium thiosulphate solutions of $1.000 \times 10^{-1} \text{ M}$ and $1.000 \times 10^{-2} \text{ M}$ concentrations by diluting appropriate volumes of the stock solution with distilled water. Volume of stock solution required to prepare 1 dm^3 of $1.000 \times 10^{-1} \text{ M}$ and $1.000 \times 10^{-2} \text{ M}$ sodium thiosulphate solution can be calculated by using the formula,

$$M_1 V_1 = M_2 V_2$$

$$\text{or } V_1 = \frac{M_2 V_2}{M_1}$$

Thus, volume of stock solution (V_1) required to prepare 1 dm^3 of

$$\begin{aligned} 1.000 \times 10^{-1} \text{ M solution} &= \frac{1.000 \times 10^{-1} \text{ M} \times 1000 \text{ cm}^3}{x \text{ M}} \\ &= \frac{100}{x} \text{ cm}^3 \end{aligned}$$

Volume of stock solution (V_1) required to prepare 1 dm^3 of

$$\begin{aligned} 1.000 \times 10^{-2} \text{ M solution} &= \frac{1.000 \times 10^{-2} \text{ M} \times 1000 \text{ cm}^3}{x \text{ M}} \\ &= \frac{10}{x} \text{ cm}^3 \end{aligned}$$

where x is the molarity of the stock solution.

APPENDIX - II

Benzoic acid solution : Prepare a saturated solution of benzoic acid by dissolving about 40 g of acid in 500 cm³ of toluene. Filter the solution.

Phenolphthalein solution : Dissolve 0.1 g of phenolphthalein in 125 cm³ of ethanol and add 125 cm³ of distilled water with constant stirring. Filter the solution if there is any precipitate.

Sodium hydroxide : 1.000×10^{-1} M and 5.000×10^{-2} M : Prepare a solution of NaOH of about 0.1 M concentration by dissolving 4.4 g of NaOH in distilled water and making up the volume to 1 dm³. Standardise this solution by titrating against a standard solution of HCl using phenolphthalein as indicator. Preparation of standard solution of HCl has been described in Appendix-I to Unit 9 of this Block. Let the concentration of this solution be x M (which will be around 0.1 M).

Take 250 cm³ of the above solution and dilute to 500 cm³ in a volumetric flask using distilled water. Concentration of this solution will be $x/2$ M (which will be around 0.05 M).

UNIT 4 EXPERIMENT NO. 1

- i) You can make aqueous solutions of 3-4 common household detergents such as Surf, Wheel, Nirma, Key etc. for the determination of surface tension. You can make 0.5 to 1% aqueous solution of the above detergents by mass. For this, dissolve 1g detergent powder in 100 cm³ of distilled water by stirring gently. You can warm a little so that you get a clear solution. You should take care that no froth forms in the above process. If you have warmed the contents, then keep this solution for sometime to acquire room temperature.

Determine the surface tension of these solutions as given in Experiment 1 and compare the values so obtained.

- ii) For this experiment 1% (w/w) stock solution of a detergent can be made as given above. Dilute this stock solution to 80%, 60%, 40%, 20% and 10% and study the variation of γ with concentration.

UNIT 5 EXPERIMENT NO.2

30% Sucrose Solution: You can make 30% (w/w) aqueous solution of sucrose by dissolving 30g of sucrose in 70 cm³ of water. The values of viscosity co-efficient for this solution at various temperature are as given below:

Temp/°C	10 ³ η /Pa s
15	3.757
20	3.187
25	2.735

UNIT 6 EXPERIMENT NO.4

The following solutes could also be used for the determination of integral enthalpy of solution:

- i) Potassium nitrate (1:200)
- ii) BaCl₂ · 2H₂O (1:400)
- iii) K₂Cr₂O₇ (1:400)

UNIT 7 EXPERIMENT NO.5

0.50 Mol dm⁻³ HCl

Refer to Appendix of Unit 16 Point No.2

Make the stock solution of hydrochloric acid (A) as in NO.2.

To prepare 0.50 M HCl from hydrochloric acid (A), take $\frac{1000 \times 0.50}{20\rho} = \frac{25}{\rho}$ cm³ of hydrochloric acid (A) in a 1 dm³ standard flask and make the solution upto the mark with distilled water. You get the resultant solution as 0.50 M HCl.

0.50 M NaOH

First prepare approximately 1 M NaOH solution by dissolving 40 g NaOH in 1 dm³ of distilled water. Take 10 cm³ of this approx. 1 M solution and dilute it to 100 cm³. Titrate this solution of NaOH with 0.1 M HCl (prepared above) using phenolphthalein as the indicator. Calculate the exact strength of this solution. If the molarity of this solution is y, then the molarity of the initial (1 M NaOH) solution is 10y.

To get 0.50 M NaOH from the NaOH solution of molarity 10y, take $\frac{50}{y}$ cm³ of the above solution in 1 dm³ standard flask and dilute it with distilled water by making up the solution upto the mark. This will give 0.50 M NaOH.

Phenolphthalein solution - kindly see Appendix II of Unit 12.

EXPERIMENT NO.6

0.50 M CH₃COOH

Using a burette, transfer 60 cm³ of glacial acetic acid into a 1 dm³ volumetric flask containing 500 cm³ of distilled water and make the solution upto the mark. This solution (A) is approximately 1 M CH₃COOH. To find out the exact molarity of this solution take 20 cm³ of A and dilute it to 200 cm³. Let it be named as B. Titrate CH₃COOH (B) with the standard solution of 0.1 M NaOH (as prepared above) using phenolphthalein as the indicator. Find out the exact molarity of CH₃COOH (B). If the molarity of this solution is x, then the molarity of CH₃COOH (A) is 10x.

To get 0.50 M acetic acid from CH₃COOH (A), take $\frac{50}{x}$ cm³ of CH₃COOH (A) in a 1 dm³ volumetric flask and add distilled water to make the solution upto the mark. This will give you 0.50 M CH₃COOH.

NOTE