

A
Thesis
On
**Liquid-Liquid Equilibrium Studies on Extraction of
Commercially Significant Carboxylic Acids**

Submitted by

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CERTIFICATE

This is to certify that the thesis entitled, “**Liquid-Liquid Equilibrium Studies on Extraction of Commercially Significant Carboxylic Acids**” submitted as an end semester report by **Chitra Das (710CH1151)** submitted by Chitra Das in fulfilment for the requirements for the award of Master of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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LIST OF FIGURES

Figure No.	Figure Caption	Page No.
1.3	Liquid Liquid Extraction Principle	14
2.1	Experimental Setup for determination of binodal curve and equilibrium tie-line phase compositions of the ternary systems	21
3.2	Water + Acetic acid + Hexanol at $T = 308\text{ K}$: ternary Phase diagram	29
3.3	water + Caproic acid + MIBK at $T = 308\text{ K}$: ternary Phase diagram	31

LIST OF TABLES

Table No.	Table Name	Page No.
3.1	Composition Of Aqueous And Organic Phase Of Sample 1: water +acetic acid + hexanol	25
3.2	Water + Acetic Acid + 1-Hexanol, experimental LLE data	28
3.3	Distribution Coefficients for Water and Acetic Acid and their Separation Factors	28
3.4	Composition Of Aqueous And Organic Phase Of Sample 1: water + Caproic Acid + mibk	29
3.5	Water + Caproic Acid + Methyl Isobutyl Ketone, experimental LLE data	29
3.6	Distribution Coefficients for Water and Caproic Acid and their Separation Factors	30

Contents

certificate.....	2
Acknowledgement	3
List Of Figures	4
List Of Table	5
Contents	6
Nomenclature	8
Abstract	9
Chapter 1. Introduction	11
1.1 carboxylic acid and their uses	11
1.2 phase equilibria	11
1.3 Liquid-Liquid Extraction.....	11
1.4 Uses Of Liquid Liquid Extraction.....	11
1.5 Useful Properties Of Solvents	11
1.6 ternary phase equilibrium.....	16
1.7 Experimental Techniques.....	11
1.8 Research Objectives.....	17
1.9 Project scope.....	18
1.10 organization of thesis.....	18
Chapter 2. Experimental work	
2.1 experimental Set up:.....	21
2.2 Experimental work:	22
2.2.1 chemicals.....	22
2.2.2 Apparatus and Procedure	22
Chapter 3 Results And Discussions	25
3.1 water + acetic acid + hexanol.....	25
3.2 water+caproicacid+MIBK.....	28
Chapter 4 Conclusion.....	32

Appendix.....	35
References.....	38

NOMENCLATURE

ω : selectivity

D: distribution coefficient

F: no. of degrees of freedom

P: no. of phases

UCST: upper critical solution temperature

MIBK: methyl isobutyl ketone

S: separation factor

x: mole fraction

ABSTRACT

Carboxylic acids are commercially very important organic acids and their extraction from fermentation broth can be one of the sources of recycling back these important organic acids. Here, we have worked on two systems: experimental tie-line results and solubility (binodal) curves were obtained for the ternary systems of water + acetic acid + hexanol and water + caproic acid + methyl isobutyl ketone at temperature of 308K and at atmospheric pressure. The concentrations of the components in the equilibrium phases were measured using gas chromatography for hexanol and methyl isobutyl ketone and acid concentration in each phase was determined by titration against NaOH solution. The water concentration was determined using mass balance. Using the equilibrium tie line phase compositions graph was plotted for the ternary systems. Solubility or binodal curves were obtained by joining these tie line phase compositions. The two phase and the one phase region were then determined for the ternary systems. Distribution coefficients and separation factors were calculated for the ternary systems to determine whether the solvents used were suitable for extraction of those specific organic acids from their aqueous phases.

Key words: Organic Acids, binodal curve, ternary systems, equilibrium, tie lines, solvents, distribution coefficients, separation factors

CHAPTER 1

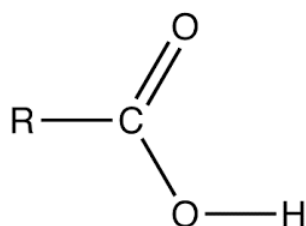
INTRODUCTION AND LITERATURE SURVEY

INTRODUCTION AND LITERATURE SURVEY

There has been a renewed interest in the production of chemicals via fermentation because of the rising concerns over use of fossil resources. Organic acids are a particularly attractive target because their functionality enables downstream catalytic upgrading to a variety of compounds. Carboxylic acids are commercially very important organic acids and they include acids like acetic, pyruvic, lactic, butyric, caproic and many others. One of the major sources of extraction of these organic acids is from the fermentation broth using solvents and taking the help of certain diluents like Tertiary alkylamines.

1.1 CARBOXYLIC ACIDS AND THEIR USES

Carboxylic acids are the compounds with a hydrocarbon group R and a functional group of carboxyl and its general formula is $R-C(O)OH$. Where R varies from a small to a possibly large molecule.



Some of the important uses of Carboxylic Acids are:-

- ✓ Organic acid compounds are used in the manufacture of soaps.
- ✓ Extensively used in foods, cold drinks. Vinegar has acetic acid in it. Organic acid sodium salts are used as preservatives.
- ✓ Many drugs like aspirin, phenacetin has organic acids as the main ingredient.
- ✓ Acetic acid is used as coagulant in the manufacture of rubber.
- ✓ Acetic acid is also used in the manufacture of various dye stuffs, perfumes and rayon.

1.2 PHASE EQUILIBRIUM

When there is transfer of substances from one phase to another then phase separation is involved. There is exchange of constituents from each phase into the other when phases are

brought into contact, this happens until the composition of each phase attains a constant value and this state of the phases is called macroscopic equilibrium. The phases in contact may be vapour-liquid, liquid-liquid. The equilibrium composition of two phases are usually different from one another and this difference makes it possible to separate mixtures by distillation, extraction and other phase contacting processes.

Temperature, pressure, chemical nature and concentrations of the substances in the mixture determine the equilibrium phase composition.

1.3 LIQUID-LIQUID EXTRACTION

In liquid liquid extraction two components in solution are separated by their distribution between the two immiscible phases with the addition of a third component. Solvent or the entrainer is the liquid added to the solution for the extraction process. This solvent takes up part of the components of the original solution and forms an immiscible layer with the remaining solution. Extract is the solvent layer and the other layer composed of the remaining original solution plus the solvent left is called the raffinate. Petroleum industry extensively uses the liquid liquid extraction process in separating hydrocarbons. The knowledge of liquid-liquid equilibrium (LLE) is necessary for design and optimization of a new separation process.

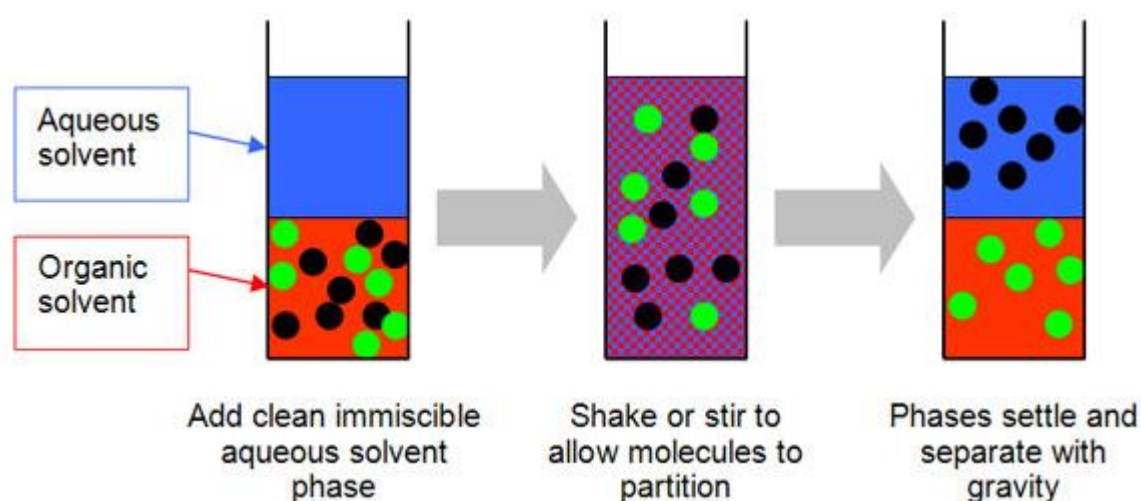


Figure 1.3 liquid-liquid extraction principle

1.4 USES OF LIQUID-LIQUID EXTRACTION

Liquid-liquid extraction is an easy method which is generally preferred over other methods. Some of the reasons why liquid-liquid extraction is preferred are as follows:-

- This method is used for heat sensitive materials or when components to be separated have very close boiling points.
- When there are expensive disposal problems for by products then this method can be used as a substitute. This method has less chemical consumption and also less formation of by products.
- This method is cost effective unlike other methods of separation in which capital is required for setting up various incentives.

1.5 USEFUL PROPERTIES OF SOLVENTS

1.5.1 Selectivity

Selectivity or relative separation, ω , is the capability of a solvent to separate a component from its unwanted phase. It is also defined as the ratio of the mole fraction of two components in one phase, divided by the ratio of the mole fractions of the same two components in the other phase, and is given by:

$$\omega = \frac{\frac{x_2}{x_3}(\text{phase 1})}{\frac{x_2}{x_3}(\text{phase 2})} \quad (1)$$

Where x_2 and x_3 refer to the mole fractions of the components to be separated.

1.5.2 Distribution Coefficient

Distribution coefficient is defined as the mole fraction of solute in the extract phase divided by the mole fraction of the same solute in the raffinate phase, at equilibrium (3 stands for extract phase and 1 is the raffinate phase).

$$K = \frac{x_{23}}{x_{21}} \quad (2)$$

1.5.3 Recoverability

The solvent used for extraction should be recoverable and can be re used if possible.

1.5.4 Solvent

A low solubility of the extraction solvent in one of the components is desirable. A low solubility of feed solvent in the extract leads to a high relative separation and generally to low

solute recovery costs. A ternary phase diagram with a large two phase region implies a high mutual insolubility of the three components in the ternary mixture.

1.5.5 Density

The differences in densities between two liquid phases in equilibrium affects the rates that can be achieved in extraction equipment as well as the coalescence rates. There should be a large difference in the densities of the liquid phases to ensure a rapid disengagement of phase.

1.5.6 Toxicity

Low toxicity from solvent vapour inhalation or skin contact is essential as with modern industrial processes where workplace conditions must conform to high standards.

1.5.7 Chemical Characteristics

Extraction solvents should have the following characteristics: high boiling point, low melting point, density range from 1.0 to 1.3 g/cm³, high thermal and chemical stability. It should be non-corrosive, low latent heat and specific heat.

1.5.8 Availability and Cost

A good solvent must be easily available and if not commercially available, it may represent a large initial cost for charging the system and a heavy continuing expense for replacing inevitable losses.

1.6 TERNARY PHASE EQUILIBRIA

Phase Rule

This involves a three component system. According to Gibbs, the phase rule is a general relation between the variance F (no. of degrees of freedom), the number of components C , and the number of phases P at equilibrium.

$$F = C - P + 2 \quad (3)$$

For a three component system at constant temperature and pressure the phase rule becomes,

$$F = 5 - P \quad (4)$$

where F is the number of degrees of freedom i.e. the smallest number of independent variables required to completely describe the state of the system.

1.7 EXPERIMENTAL TECHNIQUES

1.7.1 Introduction

The measurements of phase equilibria involves the experimental determination of pressure, temperature, phase compositions and phase amounts. It is not simple to obtain the experimental data of high accuracy. Care must be taken to assure that equilibrium really exists.

Determination of binodal curve in a ternary system

The binodal curve defines the heterogeneous region and can be used to determine the composition of the conjugate phases when other properties of the system studied are known. The usual or classical method of determining the tie-lines and the binodal curve is to make a lot of mixtures of unlimited miscibility, let them reach equilibrium, analyse each of the layers by gas liquid chromatography (GLC) and then mark the concentrations of the liquids in equilibrium. Joining all the experimental points relating to a system in equilibrium gives the tie-lines and joining all the points gives the binodal curve on a ternary graph. If the determination of components in the mixture is difficult by gas liquid chromatography then we can go for titrations with NaOH for measuring the concentration of organic acids.

1.8 Research Objectives

A lot of solvents have been examined for extraction of organic acids like acetic acid, butyric acid, caproic acid. Many investigators have published the liquid-liquid equilibria (LLE) of ternary systems like water-acetic acid-butyl acetate system were studied at temperatures of 298.15 ± 0.20 , 303.15 ± 0.20 and 308.15 ± 0.20 K (E. Ince, et al., 2010); liquid liquid equilibrium of the ternary system water + acetic acid + toluene was investigated at temperatures of (288.2, 298.2, and 313.2) K under atmospheric pressure (javad saien, et. al., 2013), MIBK + water + acetic acid, MIBK + lactic acid + water at temperature of 294.15K and atmospheric pressure (D. Laiadi, et. al., 2012), ternary system liquid-liquid equilibrium for water + toluene + benzaldehyde at temperature of 303.2–343.2 K (Hui Wang, et. al., 2013), Liquid-liquid equilibria for ternary system ethyl acetate + acetic acid + water (F H Garner, et. al., 2013).

The objective of this project work is to determine whether extraction of certain organic acids like acetic and caproic from their dilute aqueous solution is feasible using solvents. The solvents used in many such works usually belong to alcohol, benzene and some members of

the ketone family. The successful extraction of organic acids by solvents can be predicted by the distribution coefficient and the separation factor values obtained for that system. For successful designing of extraction and separation process, equilibrium tie line phase data for that system is very important. So, we have worked on two ternary systems and determined their equilibrium tie line phase data along with their distribution coefficients and separation factors.

1.9 Project Scope

The two systems that we have worked on are

1. Water + Acetic acid + Hexanol
2. Water + Caproic acid + MIBK

1.10 Organization of Thesis

1. The introduction and literature survey section explains why liquid liquid extraction is important, where it is used, the principle behind liquid liquid extraction and how liquid liquid equilibrium data is used for designing the extraction system.
2. The literature survey outlines some of the papers and works referred before working on the two ternary systems. Some of the important papers referred were work on ternary systems of water + Acetic acid + MIBK, water + acetic Acid + Hexanol and Water+ Lactic acid + MIBK and many other ternary systems.
3. Experimental section tells about the chemicals used, the procedure involved in determining binodal curve values and the equilibrium tie line data. Ternary graphs were plotted and the bimodal curve was determined.
4. Results and discussions section outlines the nature of the binodal curve obtained, the two phase region, determining the distribution coefficients and separation factors for the two ternary systems.
5. Conclusion section helps in deciding the better solvent out of the two used with reasons based on their distribution coefficients and separation factors.

CHAPTER 2

EXPERIMENTAL WORK

2.1 EXPERIMENTAL SET-UP:

The set up consists of an extraction test tube cell which holds different compositions of ternary systems: water + acetic acid + hexanol and water + caproic acid + MIBK as shown in figure 2.1. Magnetic stirrers are kept inside the extraction test tube cell for agitation of the ternary system undergoing equilibrium at a specified temperature. The PID temperature controller controls the temperature in the beaker with the hot water as the heating medium. The temperature controller probe helps in measuring the temperature inside the beaker and in controlling the temperature of the heating medium. The temperature of the beaker with the water as the heating medium is maintained by the magnetic stirrer hot plate. A thermometer is immersed in the beaker for accurate temperature readings.

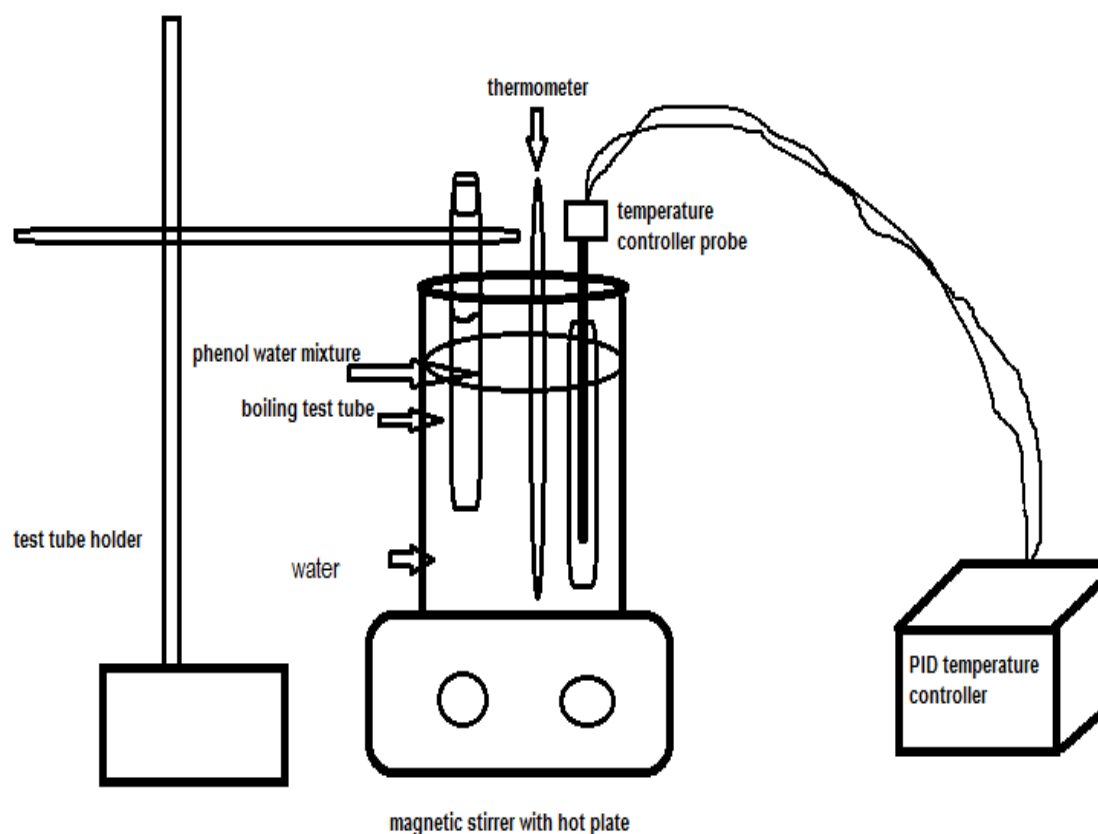


Figure 2.1: Experimental Setup for determination of binodal curve and equilibrium tie-line phase compositions of the ternary systems

2.2 EXPERIMENTAL WORK:

Liquid-liquid equilibria of the following ternary systems:

Water + Acetic Acid + 1-Hexanol and Water + Caproic Acid + Methyl isobutyl Ketone

2.3.1 Chemicals

Acetic acid, 1-hexanol were supplied by Research Scientific and methyl isobutyl ketone and Caproic acid were supplied by Loba Chemi with a purity of (98+)% . Water was distilled and demineralized before being used.

2.3.2 Apparatus and Procedure

Determination of binodal curve

Cloud point method was used for determination of binodal curve values. A glass test tube cell with magnetic stirrers was used for measuring the values. The cell was kept in a temperature controller bath and the temperature of the bath and the cell were controlled using a PID temperature controller. Initially, homogenous and transparent known composition of water + acetic acid and water + caproic acid was taken in the test tube at the specified temperature of 308 K. Using a micro burette MIBK and hexanol were added into their respective test tubes. The mixture turbidity was indicated as it turned from a homogenous to a heterogeneous mixture which marked the cloud point. The schematic diagram of experimental setup is shown in figure 2.1.

Determination of equilibrium tie phase compositions

- The samples were taken in 55 ml glass test tube cell which was surrounded by a water jacket. The water jacket was connected to a PID temperature controller which maintained the temperature of the jacket at 308 K. The mixture in the glass test tube was stirred for not less than 30 minutes and was allowed to settle for not less than 4 hours.
- Gas chromatography was used for measuring the concentrations of 1-hexanol and methyl isobutyl ketone in each phase. Agilent J&W DB-5 nonpolar, low bleed column gas chromatograph was used for analysing hexanol and methyl isobutyl ketone in each phase. The detector temperature was held at 573 K, and the injection port temperature was held at 553 K. The temperature program for hexanol + water + acetic

acid system was ramped at 20°C/min starting at 60°C up to 160°C with no hold. The total run time was 5 minutes. The temperature program for methyl isobutyl ketone + water + caproic acid system was ramped at 20°C/min starting at 150°C up to 210°C. The total run time was 3 minutes. The carrier gas used was Nitrogen with a column flow rate of 0.9868ml/min. The pressure in the column was maintained at 11.603 psi.

- The concentration of acetic acid and caproic acid in each phase was measured by titration with NaOH solution. Acetic acid system was titrated against 1.575(M) and caproic acid system was titrated against 0.126 (M) NaOH solution.
- The volume of each phase after equilibrium was measured and the volume of each component before equilibrium is known. Using material balance the volume of water was determined in aqueous and organic phase.

CHAPTER 3

RESULTS AND DISCUSSIONS

RESULT:

3.1 Water (1) + Acetic Acid (2) + 1-Hexanol (3)

Calculation

Sample 1:

Water: 16.4 ml

Acetic acid: 0.7 ml

Hexanol: 10 ml

Molarity of acetic acid in water before equilibrium = 0.7163 moles/ litre

Molarity of acetic acid after equilibrium determined by titration with 1.575 M NaOH= 0.343 moles/litre

Moles of hexanol in aqueous phase as determined by GC analysis = 0.0241 moles

After equilibrium quantities of aqueous and organic phases

Aqueous phase: 16.8 ml

Organic phase: 10.3 ml

Composition of aqueous phase after equilibrium is attained:

Volume of acetic acid in aqueous phase= $(60 \times 0.343 \times 16.818) / (1000 \times 1.05) = 0.33$ ml

Volume of hexanol in aqueous phase = $(102.17 \times 0.0241) / 0.8136 = 3.027$ ml

Volume of water in aqueous phase = $16.8 - (0.33 + 3.027) = 13.45$ ml

Composition of organic phase after equilibrium is attained:

Volume of water in organic phase = $16.4 - 13.45 = 2.93$ ml

Volume of acetic acid in organic phase = $0.7 - 0.33 = 0.37$ ml

Volume of hexanol in organic phase = $10 - 3.027 = 6.98$ ml

Table 3.1: composition of aqueous and organic phases of sample 1: water + acetic acid + hexanol

	Aqueous phase(ml)	% by volume	Organic phase(ml)	% by volume
Water	13.45	80.17	2.93	28.50
Acetic acid	0.33	1.96	0.37	3.59
Hexanol	3.027	18.01	6.98	67.89
Total	16.8	100	10.28	100

Table 3.2: Liquid liquid equilibrium data for the Ternary System of Water (1) + Acetic Acid (2) + 1-Hexanol (3)

Aqueous Phase			Organic Phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.80	0.02	0.18	0.28	0.04	0.68
0.76	0.04	0.21	0.32	0.06	0.62
0.72	0.06	0.22	0.30	0.08	0.61
0.79	0.03	0.18	0.29	0.05	0.66

Table 3.3: Distribution Coefficients for Water (D₁) and Acetic Acid (D₂) and Separation Factors (S)

D ₁	D ₂	S
0.35	2	5.71
0.42	1.5	3.57
0.41	1.33	3.25
0.36	1.66	4.62

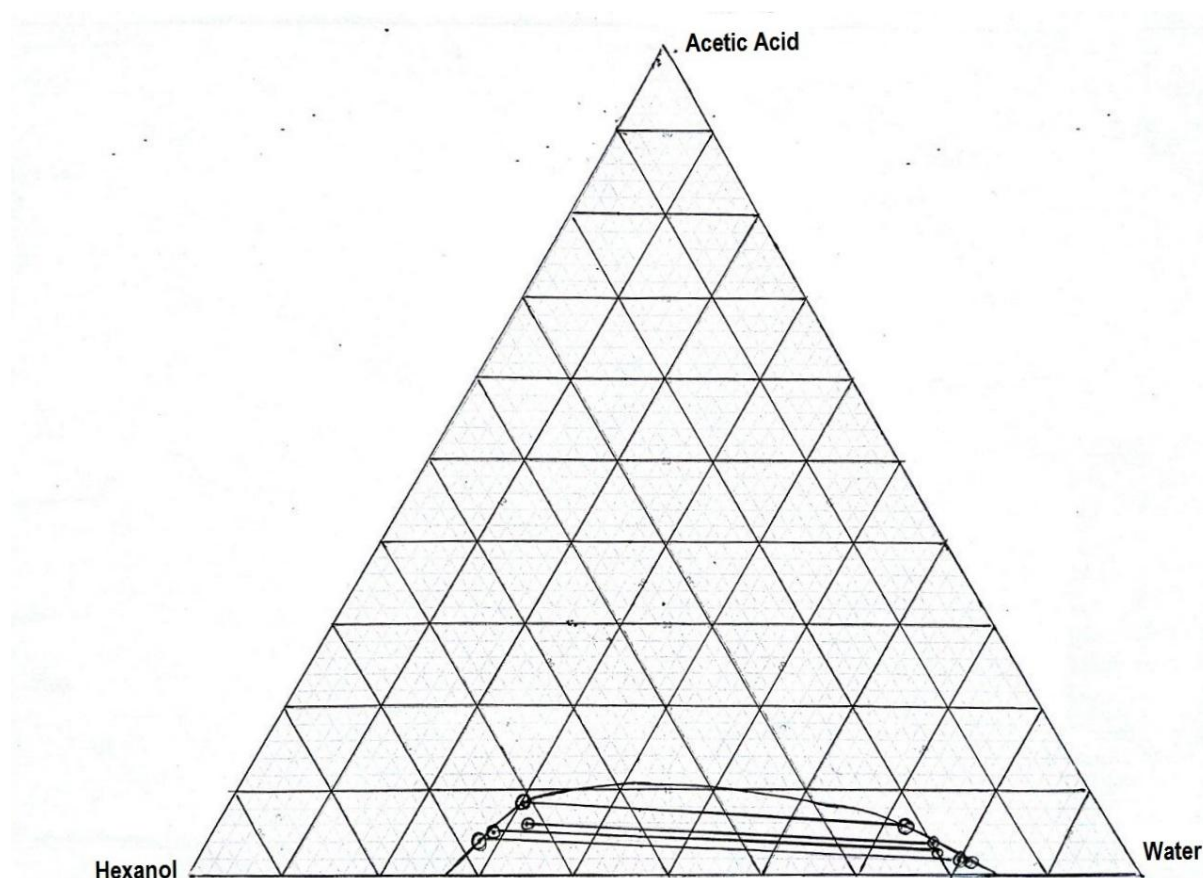


Fig 3.1: Ternary diagram for LLE of {water (1) + Acetic acid (2) + Hexanol (3)} at T = 308 K

Discussion: tie line compositions of the equilibrium phases of water + acetic acid + hexanol are shown in Table 3.2 where x_i denotes the mole fraction of the component i. The binodal curve for the Water + Acetic Acid + Hexanol system is also obtained by joining the tie line phase compositions. Figure 3.2 shows the binodal curve obtained by joining the equilibrium tie line compositions. The two phase region where the components of the system separate into aqueous and organic phase with acetic acid distributed among them lies below the binodal curve while the one phase region where all components are miscible lies above the curve. The distribution coefficients for water and acetic acid are shown in table 3.3 with their separation factors for Water+ Acetic Acid+ 1- Hexanol system. The separation factor is not constant for the ternary system and varies over an interval. The distribution coefficients were calculated using the formula:

$$D_1 = \frac{x_1(\text{solventphase})}{x_1(\text{aqueousphase})} \quad (7)$$

Where D_1 is the distribution coefficient for water and x_1 is the mole fraction of water.

Similary, for acetic acid

$$D_2 = \frac{x_2(\text{solventphase})}{x_2(\text{aqueousphase})} \quad (8)$$

Where, D_2 is the distribution coefficient for acetic acid and x_2 is the mole fraction of acetic acid

$$S = \frac{D_2}{D_1} \quad (9)$$

Where, S is the separation factor and D_1 and D_2 are the distribution coefficients for water and acetic acid.

3.2 Water (1) + Caproic Acid (2) + Methyl Isobutyl Ketone (3)

Calculation

Sample 1:

Water: 11.9 ml

Caproic acid: 0.8 ml

MIBK: 9.3 ml

Molarity of caproic acid in water before equilibrium = 0.5043 moles/ litre

Molarity of caproic acid after equilibrium determined by titration with 0.126 M NaOH = 0.2398 moles/litre

Moles of MIBK in aqueous phase as determined by GC analysis = 0.01657 moles

After equilibrium quantities of aqueous and organic phases

Aqueous phase: 13.82 ml

Organic phase: 8.17 ml

Composition of aqueous phase after equilibrium is attained:

Volume of caproic acid in aqueous phase = $(116.15 \times 0.2398 \times 13.82) / (1000 \times 0.93) = 0.414$ ml

Volume of MIBK in aqueous phase = $(100.16 \times 0.01657) / 0.802 = 2.07$ ml

Volume of water in aqueous phase = $13.82 - (0.414 + 2.07) = 11.33$ ml

Composition of organic phase after equilibrium is attained:

Volume of water in organic phase = $11.9 - 11.33 = 0.57$ ml

Volume of caproic acid in organic phase = $0.8 - 0.414 = 0.408$ ml

Volume of MIBK in organic phase = $9.3 - 2.07 = 7.2$ ml

Table 3.4: composition of aqueous and organic phases

	Aqueous phase(ml)	% by volume	Organic phase(ml)	% by volume
Water	11.33	81.98	0.57	6.97
caproic acid	0.414	2.99	0.408	4.99
MIBK	2.07	14.97	7.2	88.12
Total	13.82	100	8.17	100

Table 3.5: Experimental LLE Data for the Ternary System Water (1) + Caproic Acid (2) + Methyl Isobutyl Ketone (3)

Aqueous phase			Organic phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.82	0.03	0.15	0.07	0.05	0.88
0.74	0.04	0.22	0.08	0.07	0.85
0.72	0.05	0.23	0.10	0.12	0.78
0.80	0.02	0.18	0.07	0.04	0.89

Table 3.6: Distribution Coefficients for Water (D₁) and Caproic Acid (D₂) and Separation Factors (S)

D ₁	D ₂	S
0.085	1.66	19.60
0.108	1.75	16.20
0.138	2.4	17.39
0.087	2	22.98

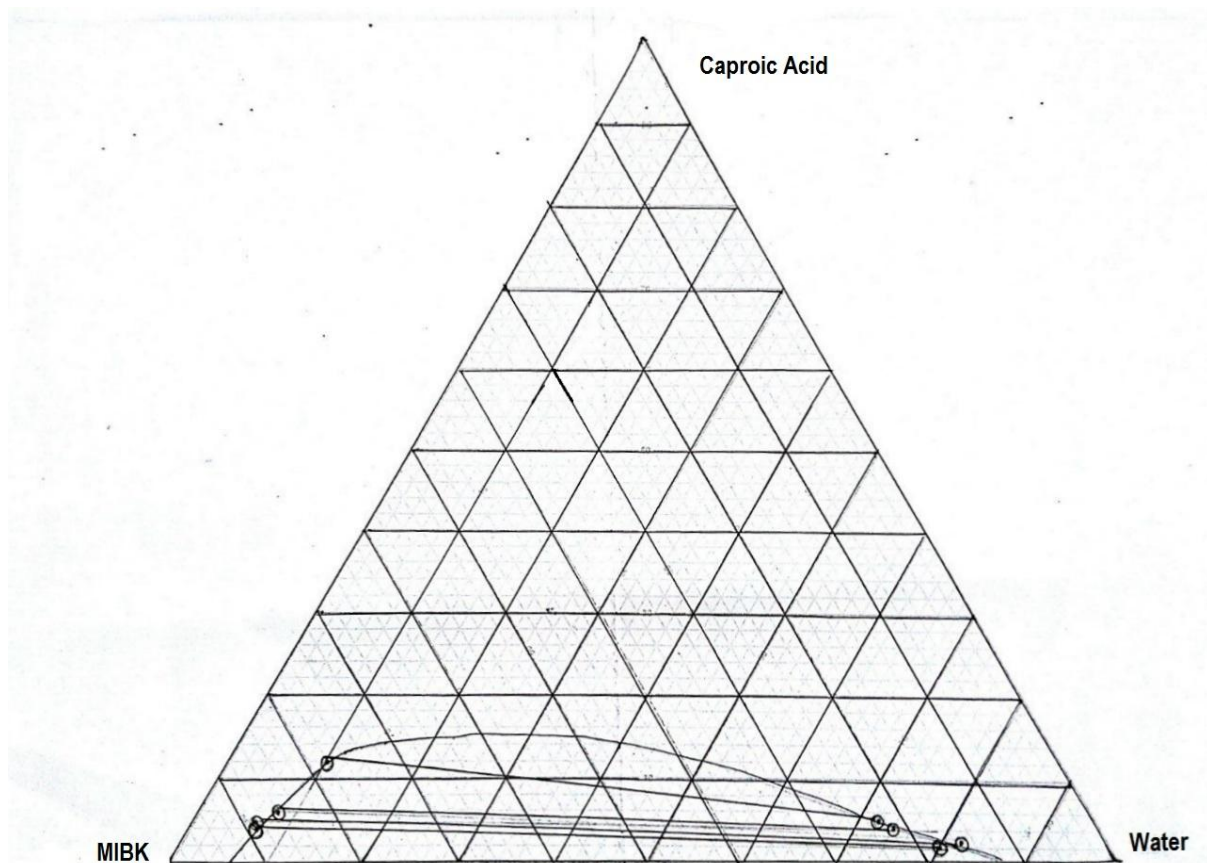


Figure3.2: Ternary diagram for LLE of {water (1) + Caproic acid (2) + MIBK (3)} at T = 308 K

Discussion: Similarly, tie line equilibrium phase compositions of water + caproic acid + MIBK is shown in Table 3.5 where x_i denotes the mole fraction of the component i . The binodal curve shown in figure 3.2, where the two phase region lies below the curve and the one phase region where all the components of the system are miscible lies above it. Table 3.5 shows the distribution coefficients for the components water and caproic acid and also gives the separation factors for the water + Caproic acid + MIBK system. The separation factor is not constant for the ternary system and varies over an interval.

The distribution coefficients were calculated using the formula :

$$D_1 = \frac{x_1(\text{solventphase})}{x_1(\text{aqueousphase})} \quad (10)$$

Where D_1 is the distribution coefficient for water and x_1 is the mole fraction of water

Similarly, for caproic acid

$$D_2 = \frac{x_2(\text{solventphase})}{x_2(\text{aqueousphase})} \quad (11)$$

Where, D_2 is the distribution coefficient for caproic acid and x_2 is the mole fraction of caproic acid

$$S = \frac{D_2}{D_1} \quad (12)$$

Where, S is the separation factor and D_1 and D_2 are the distribution coefficients for water and caproic acid

CHAPTER 4
CONCLUSION

4. Conclusion

We see that both the systems exhibit separation factor greater than one. It is evident from the values of separation factors and experimental tie-lines that MIBK and hexanol are found to be preferable solvent for separation of acetic and caproic acid from their aqueous solutions respectively. We also see that MIBK exhibits really high separation factor ranging from 19 to 25 compared to hexanol which has values ranging from 3 to 7. Therefore, it makes MIBK a better solvent for extraction of organic acids from aqueous solutions.

The two phase region for Water + Caproic acid + MIBK is comparatively more than that for Water + Acetic acid + Hexanol, which exhibits the fact that MIBK system has greater area of immiscibility than the hexanol system. We could have taken the same organic acid like acetic or caproic but with two different solvents and observed the change in their tie line composition and binodal curve. Similarly, we could have kept the solvent same like hexanol or MIBK and changed the organic acid to be extracted.

We could have also worked on totally new ternary system with an organic acid and solvent having no previous work.

CHAPTER 5

APPENDIX

5. Appendix

5.1 Water + Acetic acid + Hexanol

Acetic acid density = 1.05 g/cm^3

Hexanol density = 0.8136 g/cm^3

Molecular weight of acetic acid = 60 g/mol

Molecular weight of hexanol = 102.17 g/mol

Molarity of NaOH used = 1.575 M

- Calculation of molarity of acetic acid (M) by titration

$$N_1 V_1 = N_2 V_2 \quad (13)$$

N_1 : normality of NaOH used

V_1 : Volume of NaOH

N_2 : Normality of Acetic acid

V_2 : Volume of Acetic acid

	Aqueous Phase	Organic Phase
1.	0.343	0.3733
2.	0.699	0.707
3.	1.037	1.183
4.	0.525	1.025

- Calculation of moles of hexanol (M) by gas chromatography

	Aqueous Phase	Organic Phase
1.	0.0241	0.07133
2.	0.021793	0.053797
3.	0.02797	0.05953
4.	0.01992	0.051684

5.2 Water + Caproic acid + MIBK

MIBK density = 0.802 g/cm^3

Caproic acid density = 0.93 gm/cm^3

molecular weight of MIBK = 100.16 g/mol

molecular weight of caproic acid = 116.15 g/mol

- calculation of molarity of Caproic acid(M) by titration

$$N_1 V_1 = N_2 V_2 \quad (14)$$

N_1 : normality of NaOH used

V_1 : Volume of NaOH

N_2 : Normality of Caproic acid

V_2 : Volume of Caproic acid

	Aqueous phase	Organic phase
1.	0.0126	0.6024
2.	0.0164	1.0275
3.	0.0126	0.4664
4.	0.018	0.4034
5.	0.0063	1.1647

- calculation of moles of MIBK by gas chromatography

	Aqueous phase	Organic phase
1.	0.01657	0.0565
2.	0.0236	0.0404
3.	0.028	0.0528
4.	0.0156	0.05636
5.	0.0210	0.0430

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