The UNIVERSITY OF JORDAN

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Section no. (1)

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Liquid - Liquid equilibrium

Full report

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1. Abstract

Liquid – Liquid equilibrium for ternary system involve (Water as solvent I – Acetone as solute – Toluene as solvent II) , this experiment's objective is to learn about mass transfer processes , and to plot the mutual solubility curve for the ternary system on an equilibrium triangle .

This experiment include transfer a material dissolved (Acetone) in one liquid phase (Water) to another solvent (Toluene) which must be insoluble or soluble to a limited extent only , in the solution to be extracted . The experiment has two layers, the layer which rich in the solvent and unrich in the solute is refered to as the extract. The other layer rich in the solute and unrich in the solvent is refered to as the raffinate.

The diagram was used to find out the concentration of solute in the two solvents and to know the point of transformation of the homogeneous mixture into two liquid layers.

Experiment shows that acetone is more soluble in toluene, due to the similarity in the chemical composition between acetone and toluene.

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2. Introduction

When two different liquids are placed in contact and allowed to come to thermal , mechanical , and transfer equilibrium . Liquid-phase equilibrium data of aqueous mixtures with organic solvents play an important role in the design and development of separation processes.

One of these application is the extraction process which is one of the separation technology used in industries to have a pure substances . In particular, liquid–liquid equilibria (LLE) investigations for ternary mixtures are important in the evaluation of industrial units for solvent extraction processes. Liquid-Liquid extraction is a process that separates component based on the chemical differences between two liquid phase. An operation which is used, for example, in the processing of coal tar liquids and in the production of fuels in the nuclear industry, and which has been applied exten-sively to the separation of hydrocarbons in the petroleum industry. The principle for this process is a mixture (solvent and solute) is contact with another liquid solvent which is insoluble or soluble to a limited extent only with the original mixture. In this operation the solute transfer between two layers that depend on the most preferred solvent to dissolve the solute. The layer which rich in the solvent is refered to as the extract . The other layer rich in the solute is refered to as the raffinate.

This process includes three stages:

(a) Bringing the feed mixture and the solvent into intimate contact.

(b) Separation of the resulting two phases.

(c) Removal and recovery of the solvent from each phase.

Important applications of liquid–liquid extraction include the separation of aromatics from kerosene-based fuel oils to improve their burning qualities and the separation of aromatics from paraffin and naphthenic compounds to improve the temperature-viscosity characteristics of lubricating oils. It is relatively used in the separation of materials with close volatility.

The measure of the affinity of the solute for two phases is distribution coefficient (K) which is the ratio at equilibrium of the solute concentration in extract and raffinate phases.

3. Theory

When two different liquids (one of them is a mixture) are placed in contact and allowed to come to transfer equilibrium, one of these application is the extraction process which include solute transfer from solvent to another solvent which must be insoluble or soluble to a limited extent only (the degree of solubility of the solvent , are important considerations in the selection of the solvent).

Liquid-liquid extraction offers prospects for substantial energy saving compared with distillation when a recovery of slight but highly dense component of the feed mixture is acquired , and the distillation process isn’t suitable for separating components of similar boiling point.

Liquid-liquid extraction consists basic steps :

1- Rapid mixing to insure perfect contact of the solvent with the solution to be treated , then transfer the solute from the solution to the solvent.
2- Stopping the mixing to ensure the sedimentation of the components and the formation of two phases, so that the less dense phase is at the top and the higher density phase is at the bottom, and between them there is an interphase line.
3- Separation of the liquid solution phase from the liquid solvent phase.

Liquid-liquid-extraction is widely used for the separation of the components of a solution, particularly when:

1. The components are relatively nonvolatile.

2. The components have substantially the same volatilities from the mixture (This means that they are in the same concentration in the two phases, which makes it difficult to separate them).

3. The components are sensitive to the temperatures required for the separation by distillation.

4. The desired less-volatile component is present in the solution only in relatively small amounts. In such a case, the less volatile component may be extracted solution from which it may be recovered more economically; or similar economics may be accomplished with a solvent less volatile than the desired component, even if the increase in concentration of the desired component is not particularly significant.

The solute is usually distributed between the two phases in different proportions, according to its solubility , the layer which rich in the solvent and containing the smaller concentration of the feed liquid is referred as the “extract” . The other layer which rich in the feed liquid and containing the smaller concentration of the solvent is referred as the “raffinate” layer.

- The majority of LLE data deals with ternary mixture (solvent I-Solute-Solvent II).
- Usually plotted on a ternary diagram.
- The ternary diagram are "a smart way" to escape from plotting three dimensional graphs.
- LLE data takes many shapes depending on the system under study.

Equations and mathematical models

- When a component "the solute" is distributed between two immiscible liquid phases we define the Distribution coefficient as :

$$K = \frac{Concentration\ of\ solute\ in\ phase\ I}{Concentration\ of\ solute\ in\ phase\ II} \ldots\ldots\ldots\ldots \text{(1)}$$

Where :

K: Distribution coefficient

- The Gibbs phase rule demonstrates that a mixture of three components that forms two liquid phases at equilibrium has three degrees of freedom. (Verify) If pressure (which in any case has little effect on liquid properties) and temperature are fixed, one degree of freedom remains. Specifying the mole fraction of one of the components in one of the phases is there fore sufficient to determine the compositions of both phases.

$$D = C + \pi - 2 \ \ldots\ldots\ldots\ldots \text{(2)}$$

Where :

C : the number of component

π : the number of phase

The number 2 refers to the state variables temperature T and pressure P .

The reliability of equilibrium data for any system may be tested by applying the Othmer-Tobias correlation. This correlation states that:

$$\log\frac{(1-a)}{a} = n\ log\frac{(1-b)}{b} + s \ \ldots\ldots\ldots\ldots\ldots\text{(3)}$$

where :

a: weight fraction of the solvent in the extract phase.

b: Weight fraction of the carrier liquid in the reffinate phase.

S : the intercept

n : slope

4. Apparatus

a. Mixer settler:

Consists of three cell, each cell has a central 100 ml of capacity, and has a side arm near the top to charging the feed.

Each glass vessel is surrounded by a glass jacket to maintain the cell contents at constant temperature. The cell is provided with a mixer to mix the component very well. It also contains a valve at the bottom of each cell to empty the contents.

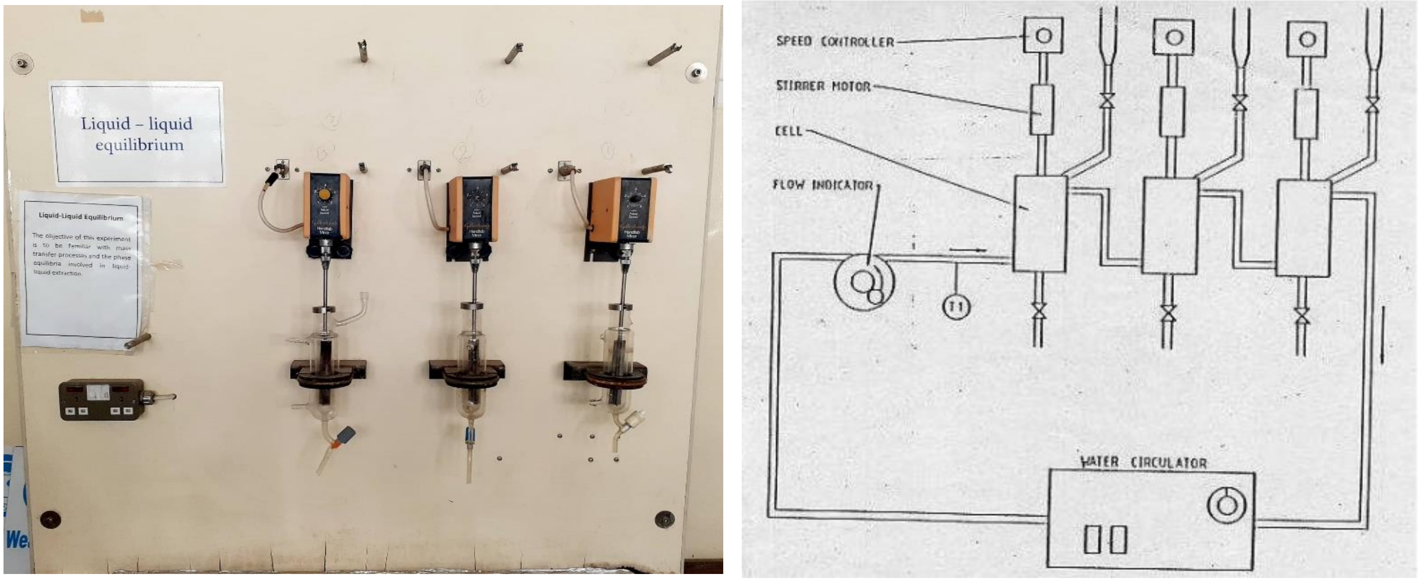

Figure (1): General Arrangement of liquid-liquid Equilibriua apparatus

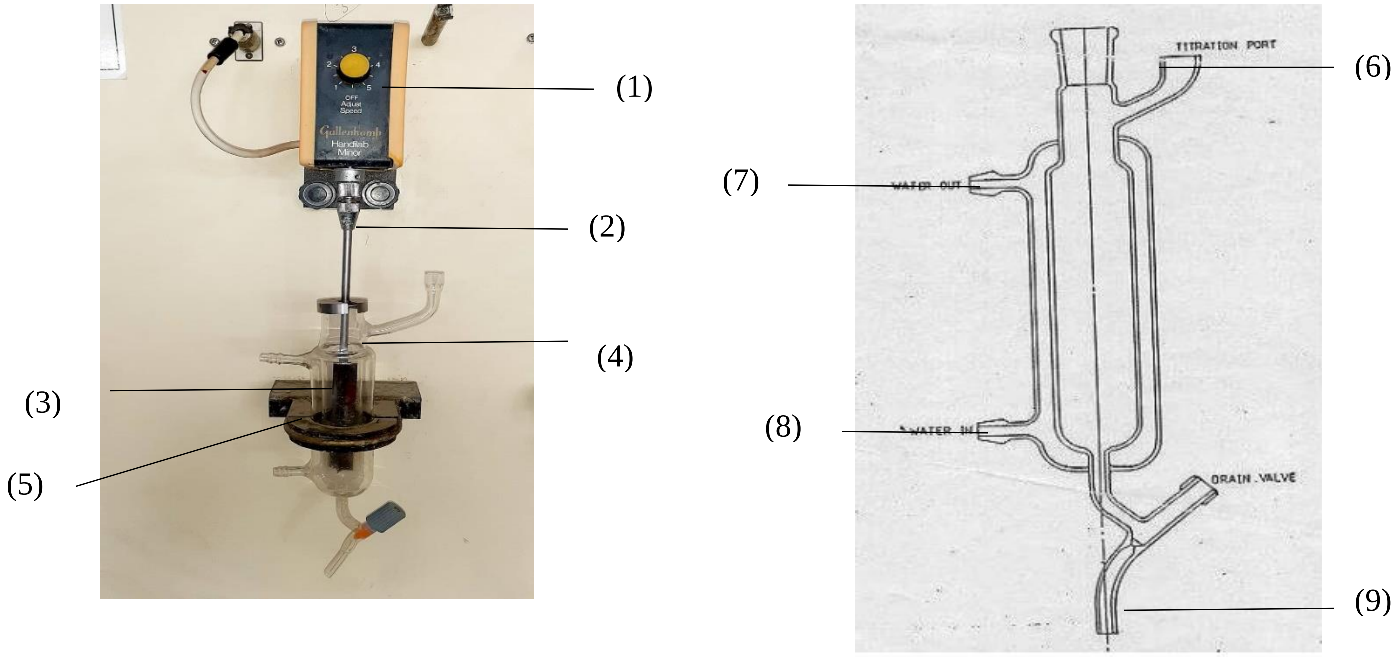

Figure (2) : Agitated glass cell for liquid-liquid equilibria determination

(1) Speed Controller: Rotation speed control
(2) Stirrer Motor: Transmit torque to the impeller
(3) Impeller: Mix the component
(4) Cell: Contain the mixture
(5) Glass jacket: maintain the cell contents at constant temperature
(6) Side Arm: for charging the liquids
(7) Water out
(8) Water in
(9) Valve: emptying

b. Refractometer:

The refractometer is a device used to measure the specific density of liquids and thus the ratio of solids to the sample.

The principle of the refractometer is based on the laws of natural refraction of light, since when a light ray passes from the center to another, it differs from it in light intensity, refraction occurs at the surface of the separation, and it shows the amount of refraction at a constant value under constant temperature and pressure, and it is expressed by the coefficient of refraction.

Refractive index = sin angle of fall / sin angle of refraction

Fig (3): Refractometer

5. Procedure

A. To determine the ternary mutual solubility curve :

a-For water rich phase

1- Put 20 mls of distilled water and 5 mls of solute (Aceton)in a beaker to prepare a mixture .
2- Slowly titrate the organic solvent (Toluene)into the mixture in the beaker until “Cloudness” appears.
3- Record the initial and final volume of organic solvent in a burette than take the difference which represent the volume of organic solvent in the mixture .
4- Add another 5 mls of the solute to the mixture and repeat the steps (2-3).
5- Repeat step (4).
6- Put 10 mls of distilled water and 10 mls of solute in a beaker .
7- Repeat the steps (2-3) .
8- Add another 10 mls of the solute (Acetone) to the mixture at each time as shown in the table .

Table (1) :Water rich phase

Volume of Acetone (ml)	Volume of Water (ml)
5	20
10	20
15	20
10	10
20	10
30	10

B. For the organic solvent rich phase

Repeat the same procedure in (a) , but using solute – organic solvent solution and titrating with water .

Use the following composition in the table .

Table (2) : Organic solvent rich

Volume of Acetone (ml)	Volume of Toluene (ml)
5	20
10	20
15	20
10	10
20	10
30	10

A- Tie line determination

1- Prepare heterogeneous mixture consisting of 18 mls of distilled water , 20 mls of Toluene and 13 mls of Acetone .
2- Fill the cell with a heterogeneous mixture through a side arm .
3- Agitate the mixture using the mid-point speed for 20 minutes at the desired temperature.
4- Stop the agitator and leave the mixture for about 20 minutes to settle into two layer based on density.
5- Withdraw a sample from bottom layer through a valve in a sample bottle.
6- Measure the refractive index of sample.
7- Withdraw the rest of the bottom layer.
8- Withdraw a sample from another layer and repeat step (6).
9- Using the calibration curves to determine the percentage of the solute in each phase.
10- Repeat all steps using the mixture in the following table.

Table (3): Tie-Lines determination

Volume of water (ml)	Volume of Toluene (ml)	Volume of Acetone (ml)
18	20	13
26	17	8
20	25	5

6. Results

Table (4): Densities at 20 °C in g/ml

Water density	Toluene density	Acetone density
0.9982	0.8669	0.7900

1-Ternary mutual solubility curve formation

A. For water rich phase

Table (5): Water rich phase results.

Acetone Volume (ml)	Water Volume (ml)	Toluene Volume (ml)	Acetone mass (g)	Water mass (g)	Toluene mass (g)	Total mass (g)	Acetone fraction (by mass)	Water Fraction (by mass)	Toluene Fraction (by mass)
5	20	0.2	3.95	19.96	0.1734	24.0834	0.1640	0.8288	0.0072
10	20	0.5	7.9	19.96	0.4335	28.2935	0.2792	0.7055	0.0153
15	20	0.3	11.85	19.96	0.2601	32.0701	0.3695	0.6224	0.0081
10	10	0.4	7.9	9.98	0.3468	18.2268	0.4334	0.5475	0.0190
20	10	1.9	15.8	9.98	1.6471	27.4271	0.5761	0.3639	0.0601
30	10	5.1	23.7	9.98	4.4212	38.1012	0.6220	0.2619	0.1160

B. For organic solvent rich phase

Table (6): Organic rich phase results.

Acetone volume (ml)	Toluene volume (ml)	Water Volume (ml)	Acetone mass (g)	toluene mass (g)	water mass (g)	total mass (g)	acetone fraction (by mass)	toluene fraction (by mass)	water fraction (by mass)
5	20	0.4	3.95	17.338	0.3993	21.6873	0.1821	0.7995	0.0184
10	20	1.1	7.9	17.338	1.0980	26.3360	0.3000	0.6583	0.0417
15	20	0.6	11.85	17.338	0.5989	29.7869	0.3978	0.5821	0.0201
10	10	0.3	7.9	8.669	0.2995	16.8685	0.4683	0.5139	0.0178
20	10	1.7	15.8	8.669	1.6969	26.1659	0.6038	0.3313	0.0649
30	10	3.8	23.7	8.669	3.7932	36.1622	0.6554	0.2397	0.1049

2-Tie Line determination:

Table (7): Tie-Line determination data.

sample no.	water volume (ml)	Toluene volume (ml)	Acetone volume (ml)	water mass (g)	Toluene mass (g)	Acetone mass (g)	Total mass (g)	water mass fraction	Toluene mass fraction	Acetone mass fraction
1	18	20	13	17.9676	17.338	10.27	45.576	0.3942	0.3804	0.2253
2	26	17	8	25.9532	14.7373	6.320	47.0105	0.5521	0.3135	0.1344
3	20	25	5	19.964	21.6725	3.95	45.5865	0.4379	0.4754	0.0866

Table (8): Tie-line composition and othmer-Tobias Correlation.

sample no.	RI of water layer	RI of toluene layer	Raffinate		Extract		othmer -Tobias correlation	
			Mass fraction of acetone in water layer	Mass fraction of water in water layer	Mass fraction of acetone in toluene layer	Mass fraction of toluene in toluene layer	log ((1-a)/a)	log ((1-b)/b)
1	1.35	1.4668	0.2277	0.7723	0.2422	0.7578	-0.5304	-0.4953
2	1.342	1.475	0.1046	0.8954	0.1815	0.8185	-0.9324	-0.6542
3	1.338	1.4799	0.0431	0.9569	0.1452	0.8548	-1.3466	-0.7699

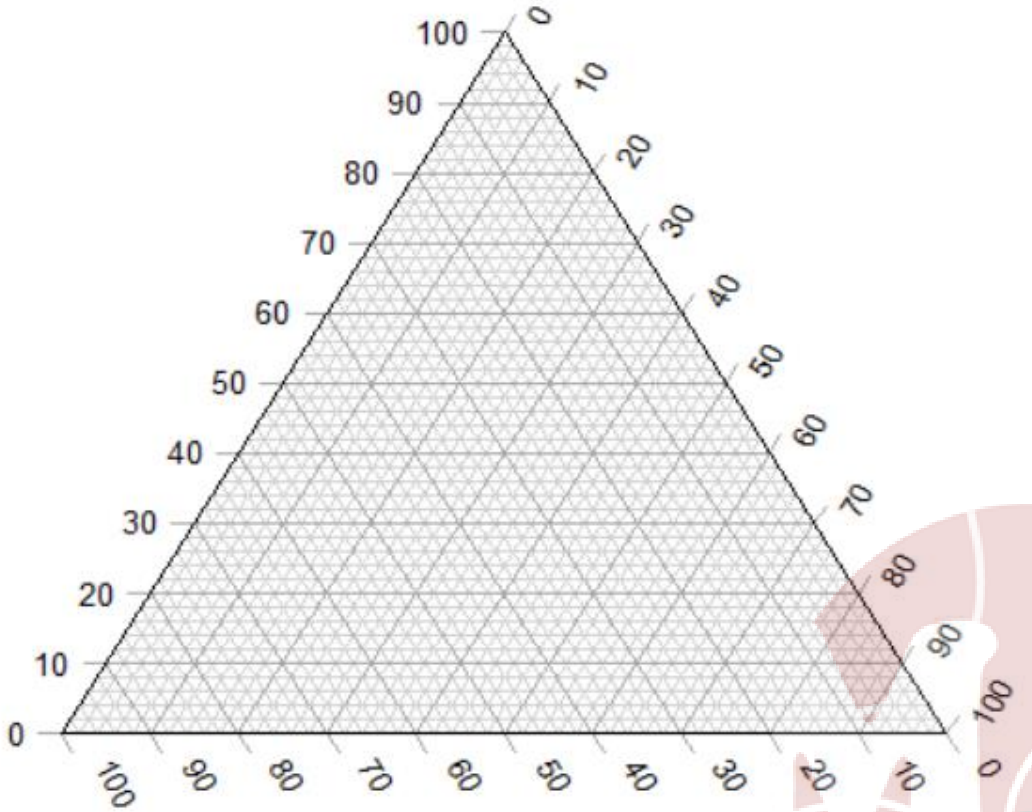

Figure (4): Mutual solubility curve for ternary system Represent Tie-line

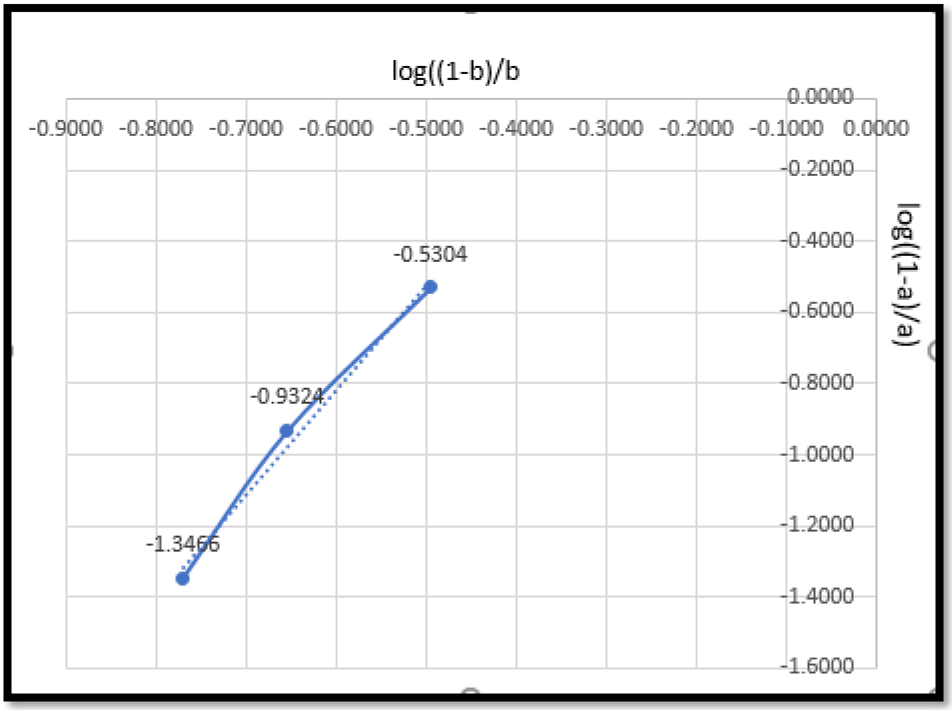

Figure (5): Othmer-Tobias Correlation.

7. Discussion

Liquid-liquid equilibrium is application of transfer solute from solution (liquid phase) to second phase, the solute is distributed between the two phases in different concentrations which are represented using an equilateral triangle. A ternary diagram is a graphical representation of the physical states of a substance under constant pressure and constant temperature, and is a smart way to escape from plotting three dimensional graphs.

In this experiment, the equilibrium curve is drawn using calibration by the cloud point (equivalence point), after this point, the solution moves from one liquid phase to two phases. Six samples were prepared with different concentrations of (Acetone, Distilled water and Toluene), where Acetone is the dissolved substance in the experiment and to be extracted. To draw the first part of the curve (rich in water), three samples of acetone and water of different sizes were prepared and a titrated with toluene by adding a limited amount of toluene until turbidity occurred, referring table (1).

The same previous steps were repeated to draw the second part of the curve (rich in toluene) using the the three samples remaining, which contain Acetone and Toluene, and titrated with distilled water to reach turbidity, referring table (2).

According to The results of the water-rich phase shown in the table (5), and another results of the Toluene rich phase shown in table (6), both data plotted on a ternary diagram to create the water rich side and solvent side of the solubility equilibrium curve.

For tie-line determination, three samples were prepared, containing heterogeneous mixtures of Acetone, Distilled water and Toluene, referring table (3), Then the mixture is stirred using the medium point speed for 20 minutes, then we leave the mixture for about 20 minutes until it settles in two layers. A sample was taken from each phase to determine the composition by using a reflectivity index (RI) meter. A calibration curve was used, to determine the percentage of solute in each phase. The result shown in Table (7) and plot it in Figure (4).

The reliability of equilibrium data for this system was tested by applying the Othmer-Tobias correlation as show in table(8) and plotted in figure (5).

There are several sources of error that can occur :

1. personal error while taking the readings
2. Inaccuracy in sample preparation

8. Conclusion

- Phase diagram is essentially for separation process, it links the physical states with the practical experience of separation and shows the composition of phase in ternery mixture depending on the temperature of the system at constant pressure
- The detector in the extraction process is the cloudness that represents the end point for each mixture
- The extract phase is richer in acetone than the raffinate phase.
- The tie line indicates the equilibrium of liquid and liquid mixture at the same temperature and pressure.
- The Othmer-Tobias correlation is used to test the reliability of equilibrium data for this system .
- If the concentrations of the three components are located outside the equilibrium curve, then they are located in the one phase liquid , but if they are located inside the curve, then they are located in the two phase liquid.

9. Reference

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1. Coulson, J.M.; and Richardson, J.F., "Chemical Engineering ", volume two. Pergamon Press Inc. third edition, 1978
2. . 2. Felder, R.M.; and Roussean R.W., "Elementary Principles of Chemical Processes". John Wily and Sons. second edition, 1986.
3. 3. McCabe, W.L.; and Smith, J.C., "Unit Operations of Chemical Engineering". McGraw-Hill, Inc. third edition, 1976.
4. Expanded from Chap. 8: Matsoukas, Themis. Fundamentals of chemical engineering thermodynamics. Pearson Education, 2013.
5. ¨Tylor & Francis online (2022). Separation Science and Technology, Volume 52, 2017 - Issue 16. Liquid–liquid equilibrium for the systems hydrocarbon–thiophene or pyridine–1-hexyl-3,5-dimethylpyridinium bis (trifluoromethyl sulfonyl) imide. Retrieved November 7,2022, from

https://www.tandfonline.com/doi/abs/10.1080/01496395.2017.1373674?journalCode=lsst20

10.Notation

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a : weight fraction of the solvent in the extract phase

b : weight fraction of the carrier liquid in the raffinate phase

Wt : weight fraction

R.I : Refractive Index

11.Appendices

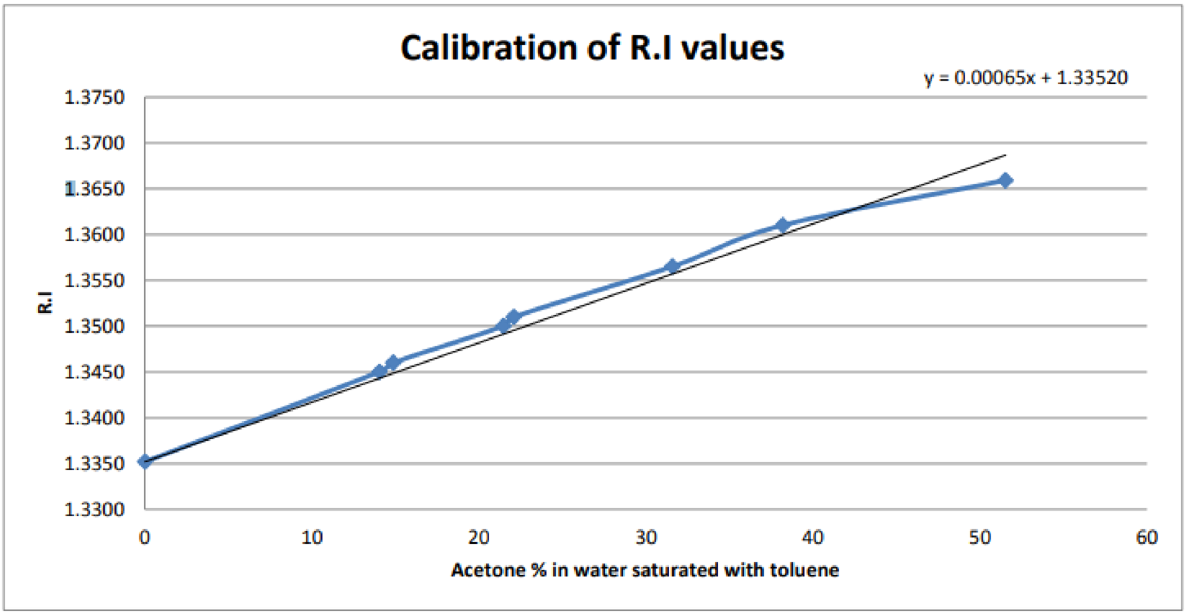


Figure (6): Wt % of Acetone in water saturated with Toluene Vs Refractive Index

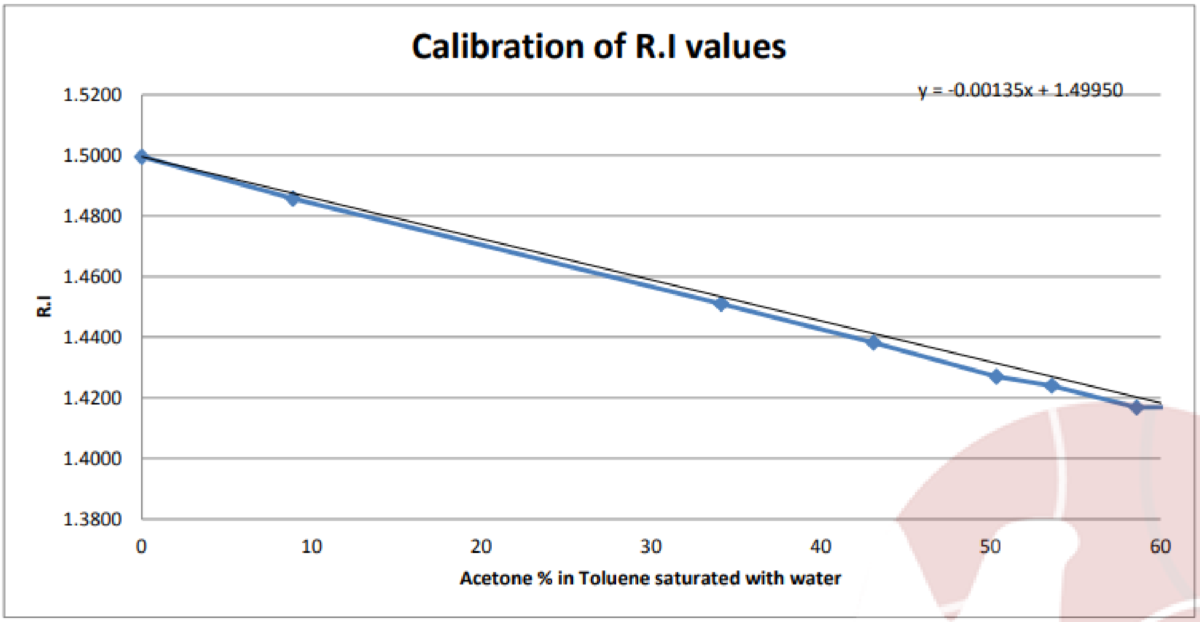


Figure (7): Wt % of Acetone in Toluene saturated with water Vs Refractive Index

a. Sample of calculation:

(The calculations for the first row of each table will be shown)

1.Ternary mutual solubility curve formation

1. For water rich phase (from table 2):

- Volume of Water: 20.00 ml.
    - Density of Water at 20 °C: 0.9982 g/ml.
        - Mass = Density * Volume
    - Mass of Water = 20.00 ml * 0.9982 $\frac{\text{g}}{\text{ml}}$ = 19.964 g.

- Volume of Acetone: 5.00 ml.
    - Density of Acetone at 20 °C: 0.7900 g/ml.
    - Mass of Acetone = 5.00 ml *0.7900 $\frac{\text{g}}{\text{ml}}$ = 3.95 g.

- Volume of Toluene: 0.20 ml.
    - Density of Toluene at 20 °C: 0.8669 g/ml.
    - Mass of Toluene = 0.20 ml * 0.8669 $\frac{\text{g}}{\text{ml}}$ = 0.17338g.
- Total mass = water mass + toluene mass +acetone mass
- Total mass = 19.964 g + 3.95 g + 0.17338g = 24.08338 g.
    - Mass fraction = $\frac{\text{mass of component}}{\text{total mass}}$
        - Water mass fraction = $\frac{19.964\ \text{g}}{24.08338\ \ \text{g}}$ = 0.828
        - Acetone mass fraction = $\frac{3.95\ \text{g}}{24.08338}$ = 0.164
        - Toluene mass fraction = $\frac{0.17338\text{g}\ \text{g}}{24.08338\ \text{g}}$ = 0.007

2. For Organic rich phase (from table 3):

- Volume of Water: 0.40 ml.
    - Density of Water at 20 °C: 0.9982 g/ml.
    - Mass of Water = 0.40 ml * 0.9982 $\frac{\text{g}}{\text{ml}}$ = 0.399g.

- Volume of Acetone: 5.00 ml.

  - Density of Acetone at 20 °C: 0.7900 g/ml.
  - Mass of Acetone = 5.00 ml *0.7900 $\frac{\mathrm{g}}{\mathrm{ml}}$ = 3.95 g.

- Volume of Toluene: 20.00 ml.
  - Density of Toluene at 20 °C: 0.8669 g/ml.
  - Mass of Toluene = 20.00 ml * 0.8669 $\frac{\mathrm{g}}{\mathrm{ml}}$ = 17.338 g.

  - <u>Total mass</u> = 0.399 g + 3.95 g + 17.338 g = 21.687 g.
  - Water mass fraction = $\frac{0.399\ \mathrm{g}}{21.687\ \mathrm{g}}$ = 0.018
    - Acetone mass fraction = $\frac{3.95\ \mathrm{g}}{21.687\ \mathrm{g}}$ = 0.182
    - Toluene mass fraction = $\frac{17.338\ \mathrm{g}}{21.687\ \mathrm{g}}$ = 0.799

2.Tie-line determination:

A. Tie-line determination (from table 4):

- Volume of Water: 18.00 ml.
  - Density of Water at 20 °C: 0.9982 g/ml.
  - Mass of Water = 18.00 ml * 0.9982 $\frac{\mathrm{g}}{\mathrm{ml}}$ = 17.968 g.

- Volume of Acetone: 13.00 ml.
  - Density of Acetone at 20 °C: 0.7900 g/ml.
  - Mass of Acetone = 13.00 ml *0.7900 $\frac{\mathrm{g}}{\mathrm{ml}}$ = 10.270 g.

- Volume of Toluene: 20.00 ml.
  - Density of Toluene at 20 °C: 0.8669 g/ml.
  - Mass of Toluene = 20.00 ml * 0.8669 $\frac{\mathrm{g}}{\mathrm{ml}}$ = 17.338 g.

- <u>Total mass</u> = 17.968 + 17.338 + 10.27 = 45.576 g.
- Water mass fraction = $\frac{17.968\ \mathrm{g}}{45.576\ \mathrm{g}}$ = 0.394

- Acetone mass fraction = $\frac{10.27\text{ g}}{45.576\text{ g}}$ = 0.225
- Toluene mass fraction = $\frac{17.338\text{ g}}{45.576\text{ g}}$ = 0.380

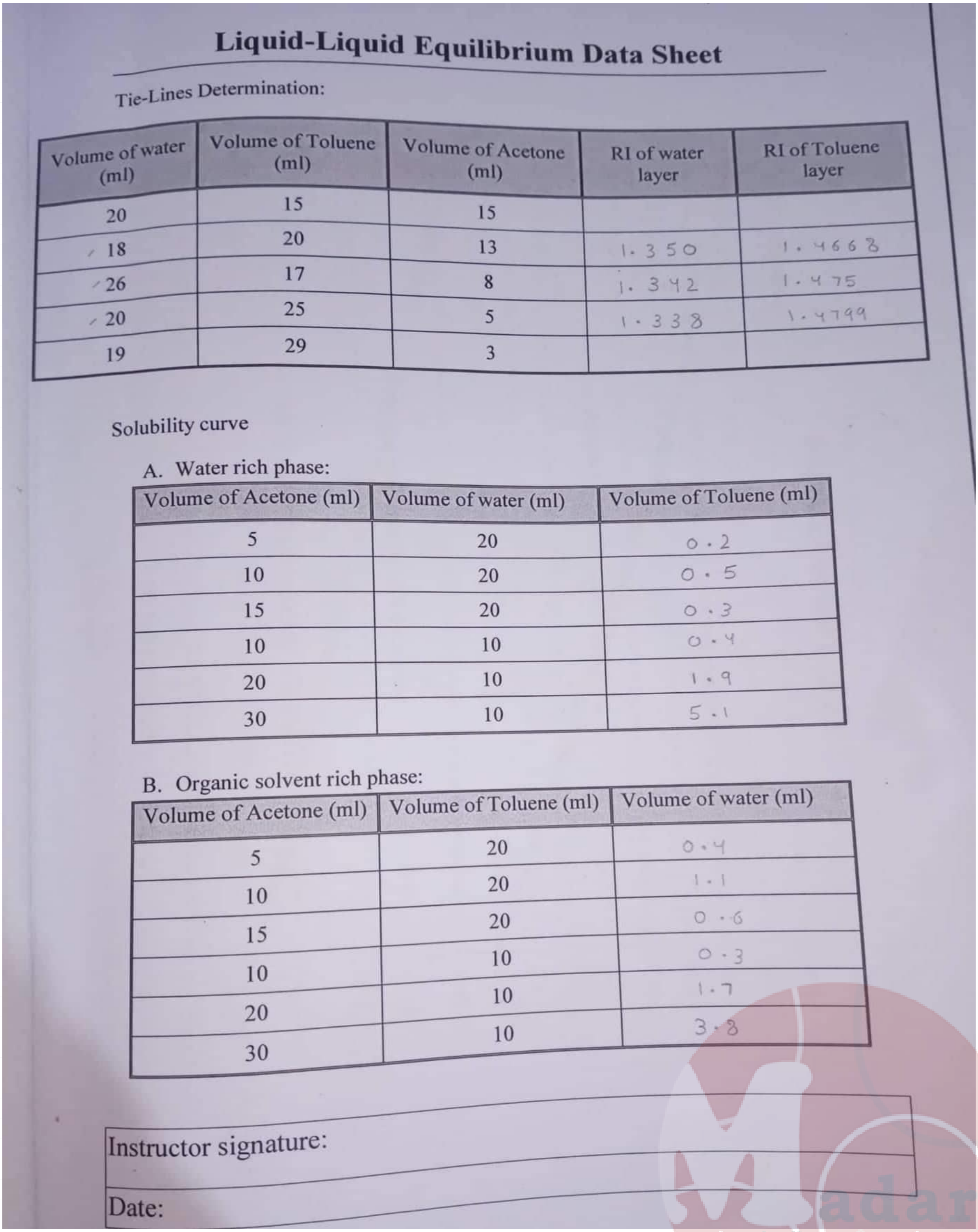
3.Tie-line determination:

- **RI of water layer =1.35**
  - From calibration curve of RI (figure (6)), the calibration equation
  - y = 0.00065x + 1.33520.
  - Mass fraction of acetone in water saturated with water $x = \frac{(y-1.3352)}{0.065}$
  - applying this: $x = \frac{(1.35-1.3352)}{0.065}$ x==0.2277
  - mass fraction of water = 1- mass fraction of acetone= 0.7723.

- **RI of toluene layer = 1.4668.**
  - From calibration curve of RI (figure (7)), the calibration equation
  - calibration equation y = -0.00135x + 1.49950.
  - Mass fraction of acetone in toluene layer $x = \frac{(y-1.49950)}{-0.135}$
  - applying this: $x = \frac{(1.4668-1.49950)}{-0.135}$ x==0.2422
  - mass fraction of toluene = 1- mass fraction of acetone= 0.7578.

- **Reliability Using the Othmer -Tobias Correlation**

  - The reliability of equilibrium data for any system may be tested by applying the Othmer-Tobias correlation. Which indicate that there is a linear relation between the value of (log$\frac{(1-a)}{a}$) and (log$\frac{(1-b)}{b}$) . where a represent water fraction in water layer ,while b represent toluene in toluene layer .
  - As sample of calculation x and f(x) can be found as below:
    - x= (log$\frac{(1-b)}{b}$) = (log$\frac{(1-0.7578)}{0.7578}$) = -0.4953
    - F(x)= (log$\frac{(1-a)}{a}$) = (log$\frac{(1-0.7723)}{0.7723}$) = -0.5304
  - The same calculation has been applied on the other points and plotted to find the linear expression for the resulting line.



Liquid-Liquid Equilibrium Data Sheet

Tie-Lines Determination:

Volume of water (ml)	Volume of Toluene (ml)	Volume of Acetone (ml)	RI of water layer	RI of Toluene layer
20	15	15		
18	20	13	1.350	1.4668
26	17	8	1.342	1.475
20	25	5	1.338	1.4799
19	29	3		

Solubility curve

A. Water rich phase:

Volume of Acetone (ml)	Volume of water (ml)	Volume of Toluene (ml)
5	20	0.2
10	20	0.5
15	20	0.3
10	10	0.4
20	10	1.9
30	10	5.1

B. Organic solvent rich phase:

Volume of Acetone (ml)	Volume of Toluene (ml)	Volume of water (ml)
5	20	0.4
10	20	1.1
15	20	0.6
10	10	0.3
20	10	1.7
30	10	3.8

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