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1965

## Liquid-liquid equilibria for a butyl acetate-wateracetic acid system

Martin Urrutia Hernando *Lehigh University*

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## LIQUID-LIQUID EQUILIBRIA FOR A BUTYL ACETATE-WATER-ACETIC ACID SYSTEM

By

MARTIN URRUTIA HERNANDO

## LIQUID-LIQUID EQUILIBRIA FOR

A BUTYL ACETATE-WATER-ACETIC ACID SYSTEM

by

Martin Urrutia Hernando

A Research Report Presented to the Graduate Faculty of Lehigh University in Candidacy for the Degree of

Master of Science

Lehigh University

**Bethlehea, Pennsylvania** 

1965

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Certificate of Approval

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This research report is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

 $(Date)$ 

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(Professor in Charge)

(Head of the Department)

### **Acknowledgeaent**

I **wish** to express ay thanks to my advisor, Professor Curtis **W.** Clump for his patience and advice, and to the Kennecott Copper **Company** for their fellowship, which made this work possible.

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#### Abstract

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## **Appendix**



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# $\begin{array}{ccc} \bullet & & \circ & & \circ \\ & & \bullet & & \bullet \end{array}$ 0 • and  $A_3$  absolute  $A_3$  absolute the same state  $A_3$ <sup>30</sup> saturation Locus at  $40^{\circ}$ °C and  $30$  $\ddot{\phantom{a}}$ •  $\begin{array}{|c|c|c|c|}\hline \begin{array}{c} \text{O} & \text{O} & \text{O} \end{array} & \text{Initial Compositions at } 20\text{\textdegree{}C} & \text{34} \ \hline \end{array} \end{array}$

 $\sim 10^7$ 

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 $\sim$ r $^{-1}$ 

#### **ABSTRACT**

mentally the equilibrium curves, tie-lines and conjugate curves at 20°C, 30°C, and 40°C for the ternary system Acetic acid - Water - Butyl acetate. The data are presented on equilateral tri-

angular graphs with composition in volume per cent.

 $\zeta^{(2)}$ 

 $\epsilon$ 

- The purpose of this work is to study experi-
	-
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#### INTRODUCTION

#### A) Acetic Acid

In the field of Organic Chemistry the acetic acid is by far the most important acid from the point of **view** of quantity used. Also, in this field, the importance of the acetic acid is comparable with the importance of the sulfuric acid in the heavy chemical industry.

Acetic acid is widely used, especially when a cheap organic acid is required. Some of these uses are: Cellulose derivatives (e.g., cellulose acetate and acetate plastics), acetic anhydride, ester solvents, metallic acetates, pigments (e.g., white lead), insecticides (e.g., Paris green), some pharmaceutical products (e.g., aspirins), vinegar, etc.

#### B) Concentration

There exists several methods of preparation of acetic acid. Most of them produce dilute aqueous solutions (except synthetic process). Also, when acetic acid is used like solvent, large amounts of diluent acid are produced and it is necessary to concentrate it in an economical **way.** 

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Distillation along is not practical for

recovering the acetic acid from the aqueous solution because the composition of the vapor is not different enough **froa** the composition of the liquid being necessary to build a very long column with a heavy reflux (4).

Hence, mixed methods of liquid-liquid extraction and distillation have been developed to recover the acetic acid in an economic way. This work studies the action of butyl acetate, as solvent, at certain temperatures that can have industrial interest. These three liquids form a threecomponent-system or a ternary system.

**Most** of the industries use ethyl acetate as solvent for the extraction of the acetic acid from aqueous solutions.

#### **TERNARY SYSTEM**

Liquid-liquid extraction principle is based on the different solubility of the solute (acetic acid) in the diluent and solvent phases. The mutual solubility of two liquids varies in presence of a third component. Hence, it is necessary to determine the properties of the new system experimentally.

The compositions of a ternary system is usually represented on an equilateral triangle. The different compositions can be expressed in per cent by volume, weight, or molar (1). In Figure 1 a three-component-system is presented in a general manner. Let us assume that point <sup>A</sup> is the solvent, point B the diluent, and point C the solute. Each of these vertices represents one hundred per cent of the respective component. The perpendicular from each vertex to the opposite side is divided into one hundred parts, then, from the geometrical point of view any point within the triangle represents a composition of a mixture in percentage.

**When** an intimate mixture of a three componen<sup>t</sup> system form<sub>5</sub> a turbid solution, it is said that the solution consists of two immiscible ternary solutions in equilibrium of A, B, and C (Figure 1). This mixture when plotted on the triangular **diagram** gives two points of the solubility

'I I

> curve, and the line joined both points is defined as <sup>a</sup> tie-line.

Any point outside the equilibrium curve represents a homogeneous solution (single phase); any point within this curve represents a mixture of two phases in equilibrium.

In general, for getting a good extraction of the solute (acetic acid from water), one pair of liquids must be as immiscible as possible (solute-diluent and solute-solvent). In this case, the solute will be distributed in both phases forming two equilibrium layers. When the solute is increased, the mutual solubility of the system will increase too (1).

In order to avoid interpolation between a complete set of equilibrium tie-lines the concept of a single conjugate curve was used (5).

 $\mathbf{r} = \mathbf{r} \mathbf{r}$  , where  $\mathbf{r}$  $\mathcal{A}^{\mathcal{A}}_{\mathcal{A}}$  ,  $\mathcal{A}^{\mathcal{A}}_{\mathcal{A}}$  $\label{eq:2} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{dx}{dx}dx = \frac{1}{2}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{dx}{dx}dx$  $\label{eq:1} \frac{1}{\sqrt{2\pi}\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{1/2}$ 

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THE PHASE RULE

In this work the temperature and the pressure **were** kept constant for each equilibrium curve determined. The pressure was high enough (1 atm.) to condensate the vapor phase.

Let us define:

v: Number of degrees of freedom or total number

Then, the total number of independent variables

of independent variables

p: Number of phases

If each phase of the equilibrium system has C components, its composition is determined by (C-1) concentrations. Hence, there are (C-1) independent variables for each phase, and the total variables in the equilibrium system will be p  $(C-1)$ . In this case the temperature and the pressure are not variables.

There are (p-1) equilibrium relationships for each component. Hence, the total number of equations

**between** the variables will be C (p-1).

or **variance,v,** will be:

 $\mathbb{R}^2$ 

 $v - p$  **(C-1)** – C **(p-1)** 

 $\mathbf{v} - \mathbf{C} - \mathbf{p}$ 

 $\ddot{\phantom{a}}$ in Li  $\mathcal{L}_{\mathbf{z}}$  and  $\mathcal{L}_{\mathbf{z}}$ 

 $\sim 10$  $\sim 10^{-1}$  $\mathcal{A}^{\text{max}}$  $\Delta \mathbf{q} = \left( \begin{array}{cc} 1 & 0 \\ 0 & 0 \end{array} \right) \in \mathcal{A} \times \mathcal{A} \times \mathcal{A}$  $\langle \tau_{\rm eff} \rangle = 100$  In this case (ternary system)  $C = 3$ , then

 $\mathbf{v} = 3 - \mathbf{P}$ 

**a) Within** the Equilibrium Curve

**briua** curve, so that

 $v - 1$ 

There is one phase  $(p - 1)$  outside the equilibrium curve, so that

 $v - 2$ 

Hence, it is enough to determine the precentage of one **coaponent** in one of the two phases for describing the **systea.** 

## b) Outside the Equilibrium Curve

In this region of the graph it is necessary to **determine** the percentage of two components in order to describe the **system.** 

There are  $two$  phases  $(p - 2)$  within the equili-

## CHOICE OF SOLVENT AND TEMPERATURES

**There are** many factors to consider in the selection of **a** solvent for a ternary **system.** They are (1) selectivity, cost and availability, inflammability, toxicity, chemical reactivity, freezing point, viscosity, density and interfacial tension, **vapor** pressure, mutual solubility, and solvent recovery. Some of these factors **were** considered in the present work. Selectivity is one of the **most** important tech-

nical factors to be considered in tlre selection of **a** solvent. A solvent is selective if the concentration of the solute, C, is higher in the solvent phase, S, than the diluent phase, D. In this work, the diluent is water, B, and the solute is acetic acid, C.

## Let us define:  $X_{CS}$  = concentration of acetic acid in the solvent phase  $X_{BS}$  = concentration of water in the solvent phase  $X_{CD}$  = concentration of acetic acid in the diluent phase **XBW** • concentration of water in the diluent phase

Selectivity is defined as (1):

$$
B = \frac{X_{\text{CS}}}{X_{\text{BS}}} / \frac{X_{\text{CD}}}{X_{\text{BD}}}
$$

 $\mathcal{L}^{\text{max}}$ 

 $\langle \hat{\mathbf{t}}_i \rangle$  .  $\hat{\mathbf{t}}_i$  $\langle \cdot \rangle$ 

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 $\frac{1}{2}\sum_{i=1}^{n} \frac{1}{\sqrt{2}} \sum_{i=1}^{n} \frac{1$ 

 $^{\circ}$ CS  $\mathbf{x}_{\rm cn}$ •

The distribution coefficient for a specific component i is defined as

 $K_{K}$  – concentration of i in the S phase i concentration of i in the D phase

Then, the selectivity can be expressed as:

 $B = \frac{K_C}{K_D}$ 

 $\pmb{\prime}$ 

The equilibrium distribution of a component i between two phases at constant pressure and temperature is the equality of the fugacities in both phases.

S <sup>0</sup>  $a_i^S f_{iS}^O$   $f_{iS} - f_{iD}$ 

> $f^0$  - fugacity in the standard state - activity

 $\&$  = activity coefficient

The standard state will be chosen at the pressure and temperature of the system and the pure component in the liquid phase. Then,

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 $\Lambda$  $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2.$  $\label{eq:2.1} \frac{1}{\left(1-\frac{1}{2}\right)}\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2.$ 

 $\mathbb{R}^{n}$  $\frac{1}{2} \int_{\mathbb{R}^2} \frac{1}{\sqrt{2}} \, \frac{1}{\sqrt{2$  $\sim$  excel  $\label{eq:2.1} \frac{1}{\sqrt{2\pi}}\int_{0}^{\infty}\frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{2\alpha} \frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{\alpha} \frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{\alpha} \frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{\alpha} \frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{\alpha} \frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right$  $\label{eq:2} \frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{1/2}\frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{1/2}\frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{1/2}\frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{1/2}\frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{1/2}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}$ 

$$
f_{iS}^{o} - f_{iD}^{o}
$$
  

$$
a_{iS} - a_{iD}
$$
  

$$
\delta_{iS} X_{iS} - \delta_{iD}^{'} X_{iD}
$$

Therefore, the distribution coefficient can be expressed as:

 $K_i$  -  $\frac{X_{iS}}{X_{iD}}$  -  $\frac{\sqrt[3]{iD}}{\sqrt[3]{iS}}$ 

Then, the selectivity can be written in terms

A good selective solvent will be one that has  $K_C \gg 1$ . The magnitude of the activity coefficients,  $\delta_{\text{CS}}'$  and  $\delta_{\text{CD}}'$ , will be determined by the nature of the interactions of the solute (acetic acid) with water and the solvent. When  $\delta_{CS}^{\wedge} < 1$ , the solute has been saturated

of activity coefficients:

$$
B = \frac{\delta_{CD}^2 \cdot \delta_{BS}^2}{\delta_{CS}^2 \cdot \delta_{BD}^2}
$$
  
and  $K_C = \frac{\delta_{CD}^2}{\delta_{CS}^2}$ 

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**Ewell,** Harrison and Berg (2) classified liquids in five different groups based on their potentialities for forming hydrogen bonds. Water was classified in Class I, these liquids are capable of forming three dimensional networks of strong hydrogen bonds, and the acetic acid was classified in Class II, these liquids also form three **dimensional** networks of hydrogen bonds, but these bonds are much **weaker.** Acetic acid (Class II) and **water (Class** I) form a solution that has a positive deviation from Raoult's law.

by the solvent, and in most of the cases, ad additional attraction **between** solute and solvent molecules can occur if hydrogen bonds exist and the equilibrium will be dis<sup>p</sup>laced **towards** the solvent phase.

The ideal solvent must have a solvent phase with a negative deviation from Raoult's law,  $\beta_{\text{CS}}^{\prime} < 1$ . This is applied to the liquids of Class III, these liquids are composed of molecules containing donor atoms but not active hydrogen atoms. Esters, ethers, ketones and aldehydes are some liquids that belong to this group. The water and the solvent should be as im-

miscible as possible in order to increase the degree of separation.

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Difference in densities between water and solvent contribute to get better and faster separation of the two layers.

Butyl acetate was chosen as the solvent since it shows negative deviation from Raoult's **law,** *i'<* <sup>1</sup> (Class III). It is immiscible with water but miscible with acetic acid in all proportions. Its freezing point (4) is at  $-76.3^{\circ}$ C, and its density in comparison with the densities of the water and acetic acid (3) is:

Some other properties, such as, inflammability, toxicity, chemical reactivity, viscosity and solvent recovery, were considered qualitatively in this work. Temperatures with some industrial interest were chosen. They were at 20°C, 30°C, and 40°C. At 24°C it was found that the equilibrium curve





was determined by eleven points (6). In this article

the source of the original research is not mentioned.

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> $\Delta \sim 10^{11}$  M  $_{\odot}$  $\sim 10^6$  $\mathcal{A}^{\mathcal{A}}$

 $\sim 0.6$  $\mathbf{r}^{\mathrm{c}}$ 

**0**   $\sim 10$  $\sim 10^{-1}$ 

 $\mathcal{L}$  $\mathbf{r}$  $\ddot{\phantom{a}}$  $\ddot{\phantom{0}}$ 

 $\sim 10^{-11}$  $\frac{1}{\sqrt{2}}$  $\ddot{\phantom{1}}$  $\langle \rangle_{\rm{tot}}$  $\langle \bullet \rangle$ 

 $\begin{array}{c} \bullet \\ \bullet \\ \bullet \end{array} \qquad \begin{array}{c} \bullet \\ \bullet \\ \bullet \end{array}$ •  $\mathbf{r}$ •  $\frac{1}{2}$  ,  $\frac{1}{2}$  ,  $\frac{1}{2}$  $\label{eq:2.1} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \left(\frac{1}{\sqrt{2}}\right)^{2} \left(\$ 

 $\mathcal{L}^{\text{max}}$  $\mathcal{A}^{\mathcal{A}}$  $\mathcal{L}_{\text{max}}$  $\label{eq:2} \frac{1}{2} \int_{\mathbb{R}^3} \left| \frac{d\mathbf{r}}{d\mathbf{r}} \right|^2 \, d\mathbf{r} \, d\mathbf{r} \, d\mathbf{r}$ 

Since little work on the acetic acid, butyl acetate, and water was found, it was decided to measure phase equilibria and solubility locus at several temperatures.

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#### Equipment

The equipment used was almost the **saae** for the deteraination of the equilibrium curves and the tielines. Bach **saaple was** put in a flask of 125 c.c.

A) Temperature Control

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The 125 c.c. Erlenmeyer flask was in a thermo**stat** consisting of a large reservior of water heated by an electrical coil. The different temperatures were controlled with a variac and two thermometers (one in the water and the other one in the sample.)

B) Stirring

The temperature of the **water** bath was kept uni**fora with** an electrical stirrer and its speed was controlled **with a** variac. The sample of the ternary **system**  was kept homogeneous by means of a magnetic stirrer with its own speed control.

C) Additional Equipment

Four burettes, one for each liquid of the ternary system and another for the sodium hydroxide, were **used.** Also used were a Westphal balance, glasses, pipets, etc.

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sodium hydroxide was used. Phenolthalien was used as the indicator.

The components used for the work were: butyl acetate (Fisher Reagent), acetic acid (A.C.S. specifications), and distilled water.  $\mathcal{L}_{\text{max}}$ 

For analyzing the acetic acid (titration),

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## **Bxperiaental** Procedure

## A) Equilibrium Curve

 $\begin{array}{c} \begin{array}{ccc} \end{array} & \begin{array}{ccc} \end{array} & \end{array} \end{array}$ 

The Othmer method was used in the determination of the equilibrium. curve (6). This aethod is shown in Figure 1. The points A, B, and C represent the solvent, water, and solute respectively. Let us assume an initial solution at point Q, then, Bis added until turbidity results. This means that one point on the equilibrium curve has been obtained (Point R). Point Rison the straight line joining Q and B. A new amount of solute C is added to the rupture R and a clear solution results again (Point S). This procedure is repeated and several points of the left side of the equilibrium curve are obtained (Points T, V, and W). The right side of the curve is gotten by starting with a mixture with a greater amount of B, and the method for determinating this side of the curve is the saae as that used for the left side.

Into **a** 125 c.c. Erlenaeyer flask was put a solution of known volumes of water, acetic acid and butyl acetate forming a clear solution (one phase). Water was added, drop by drop, until turbidity was seen. At that

#### $\mathcal{L}_{\mathrm{L}}$  , where  $\mathcal{L}_{\mathrm{L}}$  is the contract of the  $\mathcal{L}_{\mathrm{L}}$  $\mathcal{L}^{\text{max}}$

 $\sim$   $\sim$  $\label{eq:2.1} \mathcal{L}(\mathcal{L}^{(1)}) = \mathcal{L}(\$  $\label{eq:2.1} \mathcal{L}_{\mathcal{A}}(\mathbf{x},\mathbf{y})=\mathcal{L}_{\mathcal{A}}(\mathbf{x},\mathbf{y})=\mathcal{L}_{\mathcal{A}}(\mathbf{x},\mathbf{y})=\mathcal{L}_{\mathcal{A}}(\mathbf{x},\mathbf{y})$  $\label{eq:2.1} \frac{1}{\lambda_{\rm{max}}}\sum_{i=1}^{N} \frac{1}{\lambda_{\rm{max}}}\left(\frac{1}{\lambda_{\rm{max}}}\right)^2 \left(\frac{1}{\lambda_{\rm{max}}}\right)^2 \left(\frac{1}{\lambda_{\rm{max}}}\right)^2 \left(\frac{1}{\lambda_{\rm{max}}}\right)^2.$ 

pressed in percentage and plotted. (1) B) Tie-Lines

Tie-lines represent the connection between two coexisting phases (equilibrium layers). Two of these tie-lines have been drawn in Figure 1, between Rand **M,** and T and N. Any point inside the equilibrium curve represents a solution of two phases in equilibrium. These points, inside the equilibrium curve, **have a** variance equal to one (phase rule) and it would be sufficient to determine the percentage of one of the components in one phase to determine the sys**tem.** In order to check the tie-lines both layers were analyzed for acetic acid.

<sup>A</sup>solution of 50 per cent of butyl acetate and 50 per cent of water was placed in a 125 c.c. **Erlenmeyer flask.** Different amounts of acetic acid **were** added in each observation in order to get a set of tie-lines. During four hours the mixture was kept homogeneous by means of a magnetic stirrer, at constant

17

point, an equilibrium point was gotten. Acetic acid was added in order to get a clear solution again and to deteraine another point. This aethod was repeated until the curve was completed. The volumes were ex-

 $\Delta$ 

 $\mathbf{L}$ 

 $\label{eq:3.1} \frac{1}{\sqrt{2}}\left(\frac{1}{2}\left(1-\frac{1}{2}\right)\right)\left(\frac{1}{2}\left(1-\frac{1}{2}\right)\right)=\frac{1}{2}\left(\frac{1}{2}\right)$ 

temperature. During an additional four hours, at the same temperature, the mixture was allowed to settle. After this procedure some samples were taken for analyzing the acetic acid (titrated with NaOH). Densities were measured by means of a Westphal balance.  $\mathcal{L}^{\mathbb{R}}$ 

#### **Results and** Errors

The results obtained are presented in the **appendix.** In **part** one (P-1) the **values** of the focus of **saturation,** and in part two (P-11) the values of the tie-lines can be found.

In part II, three tables (A, B, and C) are presented for each temperature. Table A contains the initial compositions of each run, and tables Band C the equilibrium points for each tie-line.

The different values of Part I and Part II were plotted in Figures 3, 4, and 5. In Figure 2 the three equilibrium curves at 20°C, 30°C, and 40°C can be **seen,** besides this, the curve cited by Othaer for the same ternary system at 24°C was drawn for comparison (6).

In part I-A the different values of the saturation curve for each temperature are presented in four **colwans.** The first one shows the nwaber of the run, and the other three the concentration of Butyl acetate, Acetic acid, and water. These values **were** ordered with respect to butyl acetate (from high to low concentration). In part 1-B the initial concentration of each run is represented.

## $\label{eq:2.1} \mathcal{L}_{\mathcal{A}}(\mathcal{A},\mathcal{A})=\mathcal{L}_{\mathcal{A}}(\mathcal{A},\mathcal{A})=\mathcal{L}_{\mathcal{A}}(\mathcal{A},\mathcal{A})$

 $\sim$  $\mathbf{r}$ 

 $\epsilon$   $\tau$  $\begin{array}{ccc} & & & \circ & & \bullet \\ & & & \circ & & \circ \\ & & & & \circ & & \circ \end{array}$ 

•  $\label{eq:2} \frac{1}{\sqrt{2\pi}}\sum_{i=1}^N\frac{1}{\sqrt{2\pi}}\sum_{i=1}^N\frac{1}{\sqrt{2\pi}}\sum_{i=1}^N\frac{1}{\sqrt{2\pi}}\sum_{i=1}^N\frac{1}{\sqrt{2\pi}}\sum_{i=1}^N\frac{1}{\sqrt{2\pi}}\sum_{i=1}^N\frac{1}{\sqrt{2\pi}}\sum_{i=1}^N\frac{1}{\sqrt{2\pi}}\sum_{i=1}^N\frac{1}{\sqrt{2\pi}}\sum_{i=1}^N\frac{1}{\sqrt{2\pi}}\sum_{i=1}^N\frac{$ 

In Figures 3, 4, and 5 the solubility curves, several tie-lines, and its conjugate curve for each temperature **were** plotted.

obtained and theoretical data was not possible since

Since during the measurement the top of the flask had to be removed, a change of temperature of the system was noticed. This error is tabulated below.

A coaparison between the experimental data there are no complete theoretical data available. It is important to note that the determination of the solubility curve at high concentration of butyl acetate or water was not very precise, since it was very difficult to distinguish between the two phases solution and the clear solution.

A) Solubility Curve At 20°C  $30^{\circ}$ C  $40^{\circ}$ C B) Tie-lines At 20°C  $30^{\circ}$ C

40°c

Negl. 1.o•c 2.0°c 0.5°C (estimated) 2.0°c 4.0°C

 $\mathcal{A}=\mathcal{A}$ 

 $\alpha$  $\begin{array}{c} \bullet \\ \bullet \end{array}$ 

 $\bullet$  $\bullet$ 

curve, focus of the tie-lines, and deviation from initial composition were estimated to be approximately

At  $20^{\circ}$ C  $30^{\circ}$ C  $40^{\circ}$ C

The experimental error using solubility

- 
- - $0.5%$
	- $2.0%$
	- $5.0%$

 $\hat{\mathbf{v}}$ 

## APPENDIX

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Water Acetic Acid

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 $\sigma$ 

 $\mathbf{r}$ 

 $\sim$  $\ddot{\phantom{a}}$  $\sim$   $\sim$  $\sim 10$   $\mu$ 

23

**Water** 

Volume Per Cent





..

 $\mathcal{L}$ 

 $\frac{1}{2}$ 

24

 $\Pi$ 

/·



, I J

 $\mathbf{I}$ I I

I Ii

I,







I 11

 $\sim 10^7$ 

!,

**Water Acetic Acid** 

 $\mathbb{Z}^n$ 







-5  $\mathcal{A}$ 



# **B<sub>2</sub>**) Initial Composition

 $\mathbf{u}^{\prime}$  ,  $\mathbf{v}^{\prime}$  $\mathcal{L}^{\text{max}}_{\text{max}}$  , where  $\mathcal{L}^{\text{max}}_{\text{max}}$  $\mathcal{A}^{\pm}$  $\mathcal{L}_{\mathcal{A}}$  $\mathcal{O}(\frac{1}{\sqrt{2}})$  $\frac{1}{2}$  $\hat{\zeta}$  $\frac{1}{2}$  $\mathbf{r}$ 

 $\sim$ 

 $\ddot{\mathbf{v}}$ 

 $\sim 3\%$ 

Run. **No.** Butyl Acetate  $1$  20 c.c. 2 20 1 1.5  $3 \hspace{1.5cm} 21 \hspace{1.5cm} 3 \hspace{1.5cm} 6$ 

 $5$  0.5 19.0 3.5 6 0.5 30 2.5



i: i·



## $A_3$ ) Saturation Locus at  $40^{\circ}$ C







 $\hat{\mathcal{A}}$ 



 $\bullet$ 

 $\bullet$  $\overline{\Omega}$  $\mathbf{r} = \mathbf{r}$  $\mathbf{z} = \mathbf{z}$ 

 $\Delta$ 

 $\ddot{\phantom{a}}$ 

 $\mathbf{r}$  $\mathbf{r}$  $\mathbf{r}$  $\bullet$  $\ddot{\phantom{a}}$  $\Delta$ 

 $\frac{1}{2}$ 

 $32$ 

 $\omega_{\rm c}$  ,  $\omega_{\rm c}$ 



# $\langle \cdot \rangle$

 $\ddot{\phantom{a}}$  $\mathcal{L}^{\text{max}}_{\text{max}}$  and  $\mathcal{L}^{\text{max}}_{\text{max}}$  $\mathcal{L} = \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L}$  $\ddot{\phantom{a}}$  $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2.$  $\mathcal{L}^{\mathcal{L}}$  $\mathcal{A}$  $\mathcal{A}^{\mathcal{A}}$  $\mathcal{L}_{\mathcal{A}}$ 

 $\frac{1}{\sqrt{2}}$ 

 $\frac{1}{2}$ 

 $\bar{\mathbf{r}}$ 

 $\sim 10^6$ 

 $\sim 10^6$ 

 $B_3$ ) Initial Compositions



 $\sim$ 



 $\mathcal{A}^{\mathcal{A}}$ 

#### $\Delta \sim 10^{-10}$  km s  $^{-1}$  $\sim$   $\sim$

1) Equilibrium Tie Lines at  $20^{\circ}$ C

## $A_1$ ) Initial Compositions

Butyl Acetate Run No.  $45.0$  $\mathbf{1}$  $43.1$  $\overline{\mathbf{2}}$  $39.6$  $\overline{\mathbf{3}}$  $37.5$  $\overline{\mathbf{4}}$  $35.1$  $\overline{\mathbf{5}}$  $33.5$  $6\overline{6}$  $32.3$  $\overline{7}$  $32.0$  $\bf{8}$ 

 $\alpha$  , , , ,

 $34$ 

Water

Acetic Acid

 $\bar{\mathbf{v}}_1$ 



## $B_1$ ) Solvent Phase



 $\blacksquare$ 

 $\mathcal{A}$ 

 $\blacksquare$ 

 $\bullet$ 

 $\ddot{\phantom{a}}$  $\langle \cdot \rangle$  $\ddot{\phantom{a}}$ 

 $\ddot{\phantom{a}}$  $\sim$  $\mathcal{L}$ 

 $\sim$  .

 $\infty$ 

35

 $\sim 10^7$ 



 $\overline{I}$ 

 $\mathbf{A}^{\prime}$ 

:1 I I

 $\overline{\phantom{0}}$ 

8 12.1

7 10.8



 $\sim$   $\bullet$ 

 $\sim$   $\epsilon$ 

 $\Delta$ 

 $\ddot{\phantom{1}}$ 

 $\ddot{\phantom{a}}$ 



2) Equilibrium Tie Lines at  $30^{\circ}$ C





 $\mathcal{L}^{\pm}$  $\mathcal{L}$  $\mathcal{L}$  $\mathcal{L}$  $\mathbf{A}$  $\ddot{\phantom{a}}$  $\mathbf{A}$  $\sim$  $\ddot{\phantom{a}}$  $\langle \cdot \rangle$  $\mathcal{L}$  $\mathbf{v}^{\prime}$  $\mathbb{R}^2$  $\hat{\boldsymbol{\beta}}$ 

 $\langle \cdot \rangle$ 

 $\mathbf{r}$ 

 $\mathbf{A}$ 

 $\sim$ 

 $\sim$ 

 $\sim$ 

 $\mathcal{L}^{\pm}$ 

 $\sim$  $\bar{\mathcal{A}}$  $\ddot{\phantom{a}}$  $\ddot{\phantom{a}}$ 

 $\sim 10^7$  $\sim$ 

 $37$ 



 $\Box$ 

 $\mathbf{M}_{\mathrm{eff}}$ 



 $\hat{\mathbf{A}}$ 

•

 $\ddot{\phantom{a}}$ 

 $\ddot{\phantom{a}}$ 

 $\ddot{\phantom{a}}$ 

 $\sim$ 

 $\hat{\mathbf{r}}$  $\sim$ 

 $\ddot{\phantom{a}}$ 

 $\frac{1}{38}$ 

 $\sim$ 





 $\sim$ 

 $\sim$  $\mathcal{A}$ 

 $\cdot$ 

 $\Delta$ 

 $\ddot{\phantom{a}}$ 

 $\mathbf{r}$ 



 $\ddot{\phantom{a}}$  $\ddot{\phantom{a}}$ 

 $\ddot{\phantom{a}}$ 

 $\mathcal{L}$ 

 $\ddot{\phantom{a}}$ 

 $\ddot{\phantom{a}}$ 

 $\Delta$ 

4  $5.5$   $69.5$   $25.0$  $5 \hspace{1.5cm} 7.2 \hspace{1.5cm} 63.0 \hspace{1.5cm} 29.8$ 6 8.4 60.8 30.8  $7 \t 9.5 \t 58.5 \t 32.0$ 8 10.9 56.5 32.6 9 11.2 56.1 32.7



1,



 $\mathcal{L}$ 

Acid

 $\label{eq:2} \frac{\partial}{\partial t} \frac{\partial}{\partial t} \frac{\partial}{\partial x} \frac{\partial}{\partial y} = \frac{\partial}{\partial x} \frac{\partial}{\partial y} \frac{\partial}{\partial y} \frac{\partial}{\partial y}$ 

#### **B3)**  Solvent **Phase**

 $\int$ 

 $\sim 10^{-1}$ 



 $\mathcal{L}^{\mathcal{L}}$  $\ddot{\phantom{a}}$ 

 $\mathcal{L}^{\text{max}}_{\text{max}}$  $\mathcal{A}^{\mathcal{A}}$ 

 $\ddot{\phantom{a}}$ 

 $\mathbf{r}$ 

 $\ddot{\phantom{a}}$ 

 $\mathbf{r}$ 

 $\ddot{\phantom{a}}$ 

 $\mathbf{r}$ 

 $\frac{1}{2}$ 

 $\sim 10^{-1}$ 

41



 $\hat{A}$ 

 $\mathcal{L}$ 



 $\mathbf{A}^{\mathcal{A}}$  $\mathcal{L}_{\mathrm{H}}(\mathbf{r})$  $\ddot{\phantom{a}}$  $\mathcal{L}^{\mathcal{L}}$ 

 $\mathcal{L}_{\mathcal{A}}$ 

 $42$ 

 $\mathcal{L}^{\text{max}}_{\text{max}}$  , where  $\mathcal{L}^{\text{max}}_{\text{max}}$ 



 $\overline{a}$ 

 $\mathcal{A}^{\pm}$ 

 $\mathbf{f}$ 





 $F$ icure  $2$ Equilibrium Curves of the System at 20°C, 24°C, 30°C, and 40°C.









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 $\pmb{p}$ 

Vita

ks.

 $\mathcal{L}_{\mathcal{A}}$  $\mathcal{L}^{\text{max}}$ 

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