JFAChE
Journal of Fundamentals and Applications
of Chemical Engineering

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Liquid-Liquid Equilibrium of Propionic Acid + H_2O + 1-Pentanol and Propionic Acid + H_2O + 1-Hexanol at Temperatures of 303.15 and 323.15 K

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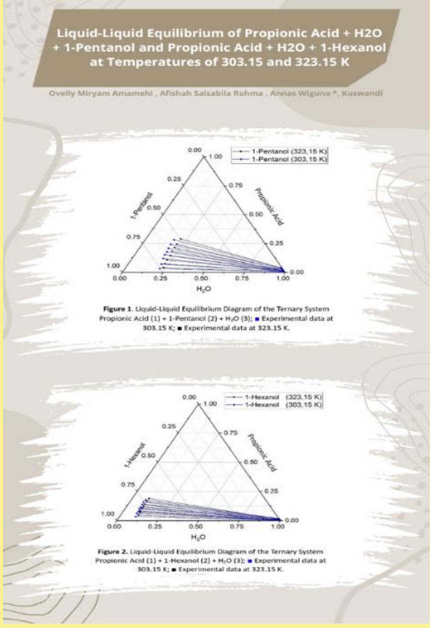
Received October 04, 2023; Revised July 26, 2024; Accepted August 14, 2024; Available online October 30, 2024
DOI: 10.12962/j2964710X.v5i1.19035

Abstract**—** This is a digest of the paper describing in brief the background, problems, methods, findings, and conclusion. Written in English with approximately 200 words. This study aims to measure the liquid-liquid equilibrium of the ternary system of propionic acid + H_2O + 1-pentanol and propionic acid + H_2O + 1-hexanol at temperatures of 303.15 and 323.15 K at atmospheric pressure. The primary equipment used in this study is an equilibrium cell with a heating jacket. The experiment lasted for 24 hours with time weighting, which included 4 hours of stirring using a magnetic stirrer. The remaining 20 hours were allotted for the solution to settle until perfect equilibrium occurred. Gas Chromatography with an FID-type detector was used to analyse the experimental results for composition. Other variables were tested by conducting experiments and the results were plotted on a ternary diagram with 8 tie lines for each system. The ternary diagram indicates that both systems adhere to the Treybal type I. The NRTL and UNIQUAC equations were used to correlate the research data from each system, resulting in a Root Mean Square Deviation (RMSD) of 3.20% of the equilibrium composition for each system.



Keywords**—** Liquid-Liquid Equilibrium, Propionic Acid, NRTL, UNIQUAC

I. INTRODUCTION

Carboxylic acid is the most significant pollutant found in the effluents of coal and the fermentation industry, as these compounds can negatively impact the environment and human health. The acidity of water and soil can be increased due to carboxylic acids, leading to a disturbance in the pH balance and adversely affecting the organisms that reside in them. Furthermore, carboxylic acids can generate harmful gases like hydrogen sulphide gas (H_2S), posing a significant risk to human health. Carboxylic acids are frequently present in the waste generated by coal and fermentation industry operations due to their by-product formation during these processes. Common examples of carboxylic acid compounds found in coal and fermentation industry waste consist of acetic acid, formic acid, propionic acid, and lactic acid [1].

Propionic acid ($C_3H_6O_2$) is a carboxylic acid with the molecular formula CH_3CH_2COOH. Propionic acid is frequently used across various industries due to its antimicrobial and preservative characteristics. Propionic acid serves as an industrial raw material with various uses. In the food and beverage industry, it functions as a preservative in products like bread, cheese, and soft drinks as stated in [1]; in the waste treatment industry, propionic acid acts as a substrate in the organic waste treatment process as indicated in [2]; while in the pharmaceutical industry, propionic acid works as a raw material in drug production and functions as an antifungal in topical and injectable drugs [1, 2].

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Presently, the primary means of producing propionic acid is chemical processes. However, it can also be produced through the processing of liquid waste such as waste from the pulp industry. Effluents in the liquid form generated by the wood pulp industry are often disposed of or incinerated, leading to the loss of organic matter and additional costs for waste treatment. The recycling of effluent through fermentation using anaerobic Propionibacterium bacteria, at a temperature of between 28-34°C for 8-14 days, can produce propionic acid, acetic acid, and butyrate. This process helps prevent the loss of organic matter in the effluent while converting it into commercially valuable products, such as propionic acid, thus reducing environmental impact and influencing positively the cost of effluent treatment [2].

Raw sulphite waste liquor from wood pulp mills typically contains sugar. The analysis of the latter usually shows that it comprises dextrose, mannose, galactose, and pentose, including xylose and arabinose. Industries such as the textile industry, olive oil industry and others, can produce waste that can be processed by fermentation and result in propionic acid [3]. Propionibacterium spp. bacteria, which are anaerobic gram-positive, form propionic acid ($C_3H_6O_2$) through glucose fermentation and the ratio of propionic acid to acetic acid in this reaction is 2:1, as shown in equation below:

$$3C_6H_{12}O_6 \rightarrow 4C_2H_5COOH + 2CH_3.COOH + 2CO_2 + 2H_2O \qquad (1)$$

Thermodynamics and behaviour of liquids are essential in modern methods of process design and control from an industrial point of view. To design an efficient process for propionic acid extraction and find a suitable solvent, it is essential to acquire liquid-liquid equilibrium data. Studies have been conducted to search for solvents for carboxylic acids including propionic acid + water + ether [4], propionic acid + water + ketone [5] and alkanes [4]. However, these solvents have drawbacks, such as low boiling points, limiting operating conditions and densities close to water, which slows the separation process.

To the best our knowledge, no research has been carried out on the liquid-liquid equilibrium of the ternary system of propionic acid + H_2O + 1-pentanol and propionic acid + H_2O + 1-hexanol at atmospheric pressure and temperatures of 303.15 K and 323.15 K,. To overcome this limitation, efforts are made to obtain data experimentally by correlating the NRTL and UNIQUAC equations so that equilibrium data are obtained [6, 7].

The temperatures 303.15K and 323.15K were selected to explore the equilibrium between two liquid phases in the system, while maintaining consistency with prior research. At these temperatures, the system exhibits relevant behavior for understanding liquid-liquid equilibrium, and the choice aligns with previous studies, facilitating comparative analysis of results across studies.

II. METHOD

A. Experiment Scheme

The research was carried out by conducting experiments to obtain samples of liquid-liquid equilibrium in the organic and aqueous phases. The experiment began with precise weighing of materials using an analytical balance, followed by heating water in a water bath to the specified temperature. The weighed materials were introduced into the equilibrium cell, and the pump was activated to circulate water to the cell while the magnetic stirrer was initiated. The experiment lasted for 4 hours, after which the magnetic stirrer was turned off. The system stood undisturbed for 20 hours to achieve liquid-liquid equilibrium samples in both the organic and aqueous phases. Subsequently, the organic and aqueous phase samples from the experiments were analysed using gas chromatography (GC) to determine the composition of their phase equilibrium. The following step entails predicting the equilibrium based on the correlation between the NRTL and UNIQUAC equations.

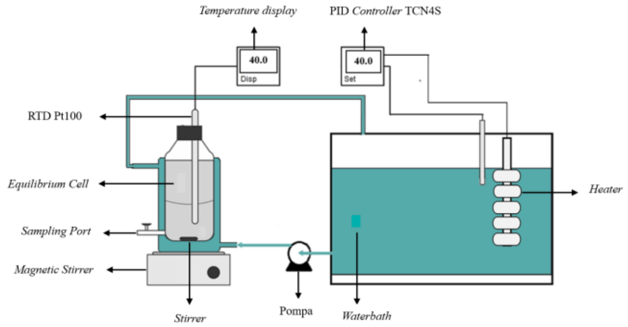

Figure 1. Experiental Equipment Setup [8, 9]

The experiment utilizes an equilibrium cell that features a heating jacket to maintain a constant temperature and a magnetic stirrer to stir the solution effectively. Figure 1 depicts that the equilibrium cell is furnished with a PID controller and Pt100 RTD to regulate the temperature of the circulating water.

In this research, a thorough examination of equipment uncertainty was carried out, involving the use of an analytical balance and a water bath with a heater to ensure the reliability of experimental data. Equipment uncertainty was calculated based on manufacturer specifications, particularly for the analytical balance and its sensitivity to loads. Regarding temperature measurements, uncertainty considered factors such as temperature measurement, heating, and readings, while also accounting for variations in operational conditions. Standard uncertainties are u(T) = 0.1 K; u(x_i) = 0.0003; and u(P) = 1 kPa where x_i is in mole fraction.

The GC type utilized was the GC Hewlett Packard 6890 series, equipped with an HP 19095P-Q04 column (HP-PLOT Q) - (Divinylbenzene/Styrene Polymer), FID detector, and Helium as the mobile phase.

The flowchart of research methodology, parameter fitting with NRTL equation, parameter fitting with UNIQUAC Equation and equilibrium composition calculation are shown by Figures 2 to 5.

B. Flowcharts

The flowchart of research methodology, parameter fitting with NRTL equation, parameter fitting with UNIQUAC Equation and equilibrium composition calculation are shown by Figures 2 to 5.

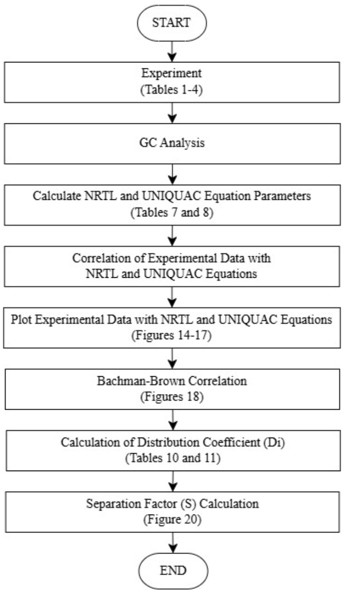

Figure 2. Research Flowchart

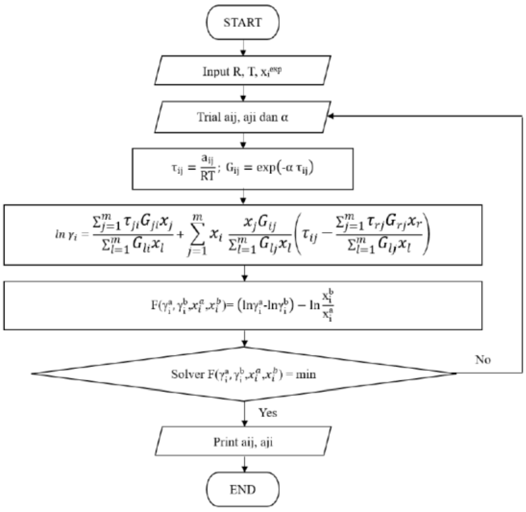

Figure 3. Flowchart of Parameter Fitting with NRTL Equation

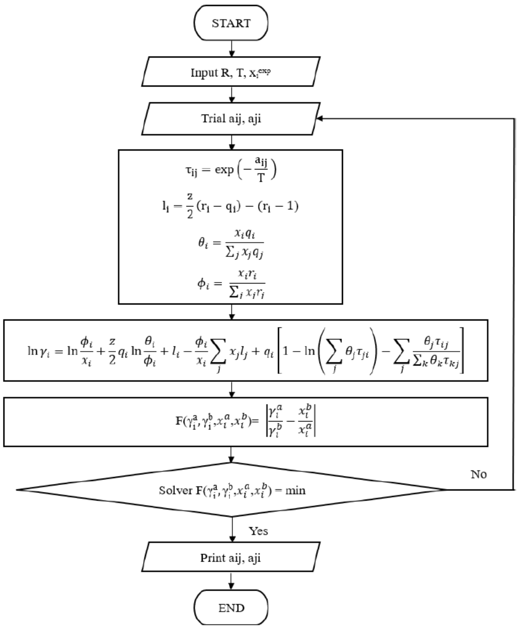

Figure 4. Flowchart of Parameter Fitting with UNIQUAC Equation

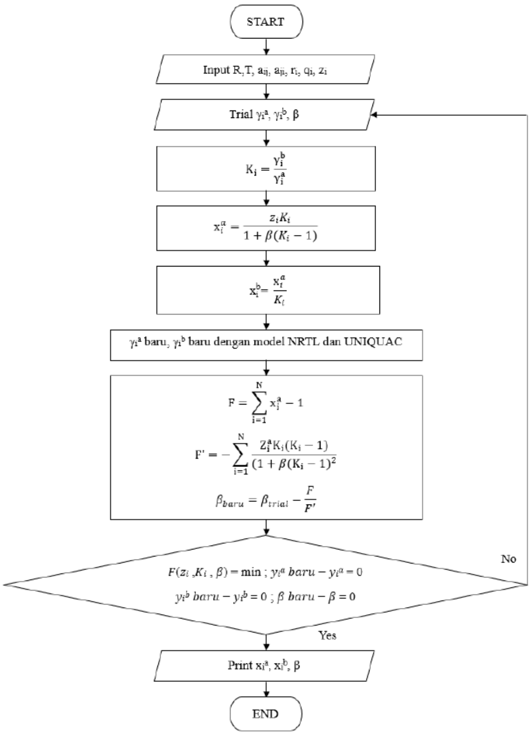

Figure 5. Flowchart of Equilibrium Composition Calculation

III. RESULTS AND DISCUSSION

A. *Experiment Scheme*

This research measured liquid-liquid phase equilibrium for four ternary systems containing Propionic Acid (1), Pentanol (2), and H_2O (3) as well as Propionic Acid (1), Hexanol (2), and H_2O (3), respectively.

TABLE 1.

LIQUID-LIQUID EQUILIBRIUM DATA OF THE TERNARY SYSTEM PROPIONIC ACID (1) + PENTANOL (2) + H_2O (3) AT TEMPERATURE 303.15 K

No	Temp (K)	Mol Fraction					
		x_1^a	x_2^a	x_3^a	x_1^b	x_2^b	x_3^b
1	303.15	0.0333	0.7531	0.2136	0.0060	0.0061	0.9879
2		0.0720	0.7237	0.2044	0.0067	0.0066	0.9867
3		0.1209	0.6881	0.1910	0.0098	0.0062	0.9840
4		0.1530	0.6626	0.1844	0.0113	0.0059	0.9828
5		0.1778	0.6371	0.1851	0.0146	0.0057	0.9798
6		0.2086	0.6117	0.1798	0.0214	0.0064	0.9722
7		0.2428	0.5814	0.1759	0.0276	0.0065	0.9658
8		0.2826	0.5413	0.1761	0.0367	0.0067	0.9566

TABLE 2.

LIQUID-LIQUID EQUILIBRIUM DATA OF THE TERNARY SYSTEM PROPIONIC ACID (1) + PENTANOL (2) + H_2O (3) AT A TEMPERATURE OF 323.15 K

No	Temp (K)	Mol Fraction					
		x_1^a	x_2^a	x_3^a	x_1^b	x_2^b	x_3^b
1	323.15	0.0422	0.7263	0.2315	0.0043	0.0061	0.9896
2		0.0742	0.6995	0.2263	0.0046	0.0052	0.9902
3		0.1080	0.6709	0.2211	0.0091	0.0060	0.9849
4		0.1443	0.6319	0.2238	0.0100	0.0065	0.9835
5		0.1826	0.6019	0.2155	0.0158	0.0061	0.9781
6		0.2141	0.5722	0.2137	0.0159	0.0059	0.9782
7		0.2443	0.5421	0.2135	0.0284	0.0070	0.9646
8		0.2895	0.4956	0.2149	0.0391	0.0075	0.9534

The measurements were taken at atmospheric pressure (101.3 kPa) and at temperatures of 303.15 K and 323.15 K. Tables 1 and 2 show experimental data on the liquid-

liquid equilibrium of the ternary system containing Propionic Acid (1), Pentanol (2), and H_2O (3) at temperatures of 303.15 K and 323.15 K. The superscripts of “a” and “b” indicate the mole fraction of components in the aqueous phase and organic phase. It is known that "a" is the organic phase and "b" is the aqueous phase.

TABLE 3.

LIQUID-LIQUID EQUILIBRIUM DATA OF THE TERNARY SYSTEM PROPIONIC ACID (1) + HEXANOL (2) + H_2O (3) AT TEMPERATURE 303.15 K

No	Temp (K)	Mol Fraction					
		x_1^a	x_2^a	x_3^a	x_1^b	x_2^b	x_3^b
1	303.15	0.0343	0.8666	0.0991	0.0021	0.0008	0.9972
2		0.0629	0.8449	0.0921	0.0026	0.0008	0.9966
3		0.0794	0.8266	0.0940	0.0043	0.0008	0.9949
4		0.1003	0.8109	0.0887	0.0118	0.0009	0.9873
5		0.1154	0.7960	0.0885	0.0097	0.0009	0.9894
6		0.1375	0.7745	0.0880	0.0169	0.0009	0.9822
7		0.1582	0.7571	0.0846	0.0163	0.0010	0.9827
8		0.1778	0.7339	0.0883	0.0181	0.0009	0.9810

TABLE 4.

LIQUID-LIQUID EQUILIBRIUM DATA OF THE TERNARY SYSTEM PROPIONIC ACID (1) + HEXANOL (2) + H_2O (3) AT A TEMPERATURE OF 323.15 K

No	Temp (K)	Mol Fraction					
		x_1^a	x_2^a	x_3^a	x_1^b	x_2^b	x_3^b
1	323.15	0.0467	0.8434	0.1099	0.0017	0.0008	0.9975
2		0.0707	0.8216	0.1077	0.0020	0.0007	0.9973
3		0.0839	0.8133	0.1028	0.0046	0.0009	0.9945
4		0.1042	0.7922	0.1036	0.0050	0.0007	0.9943
5		0.1213	0.7750	0.1037	0.0075	0.0009	0.9917
6		0.1397	0.7591	0.1012	0.0088	0.0008	0.9903
7		0.1650	0.7338	0.1012	0.0142	0.0009	0.9849
8		0.1900	0.7079	0.1021	0.0131	0.0008	0.9861

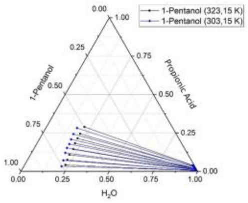

Figure 6. Liquid-Liquid Equilibrium Diagram of the Ternary System Propionic Acid (1) + Pentanol (2) + H_2O (3); ■ Experimental data at 303.15 K; ■ Experimental data at 323.15 K.

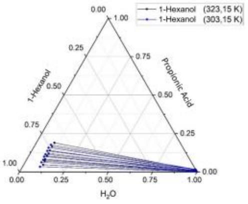

Figure 7. Liquid-Liquid Equilibrium Diagram of the Ternary System Propionic Acid (1) + Hexanol (2) + H_2O (3); ■ Experimental data at 303.15 K; ■ Experimental data at 323.15 K.

The Figures 6 and 7 indicate that the equilibrium systems of Propionic Acid (1) + Pentanol (2) + H_2O (3) and Propionic Acid (1) + Hexanol (2) + H_2O (3) have the same configuration, which is Treyball type I. The organic phase of the Propionic Acid (1) + Pentanol (2) + H_2O (3) and Propionic Acid (1) + Hexanol (2) + H_2O (3) systems is primarily controlled by pentanol/hexanol but still includes a moderate amount of water (with pentanol solvent) to some extent (with hexanol solvent), while the aqueous phase is dominated by water with an average mole fraction ≥ 0.95. This is attributable to the fact that the solvent (pentanol/hexanol) only partially dissolves in H_2O. This fact is supported by the GC analysis results of the propionic acid, 1-pentanol, 1-hexanol, and H_2O system at various concentrations and temperatures, which are then depicted in a ternary diagram. Additionally, both 1-pentanol and 1-hexanol have OH groups capable of forming hydrogen bonds with H_2O. However, simultaneously, they also possess long carbon chains, making them nonpolar and difficult to dissolve in H_2O.

As shown in Figures 6 and 7, the Propionic Acid (1) + Hexanol (2) + H_2O (3) system has a broader immiscible region (two-phase area) than the Propionic Acid (1) + Pentanol (2) + H_2O (3) system. This difference is due to the longer carbon chain in hexanol, which affects its solubility to propionic acid and water. Figures 6 and 7 depict the same system at different temperatures. It can be observed that at 323.15 K, the two-phase area is smaller because of the rising solubility of water and propionic acid in pentanol and hexanol. The increase in solubility with increasing temperature is attributed to the higher kinetic energy of the solvent molecules causing them to be more active and collide more frequently. Changes in solvent density also contribute to the variation in solubility with temperature, in addition to the increased kinetic energy. In several instances, raising the temperature causes the solvent to expand, leading to a decrease in its density. Due to the expression of solubility as mass per unit volume, a decrease in solvent density can escalate the void volume for propionic acid dissolved in the solvent (pentanol/hexanol).

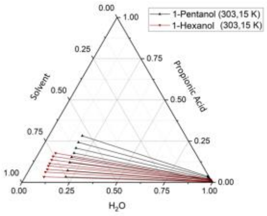

Figure 8. Liquid-Liquid Equilibrium Diagrams of the Ternary Systems Propionic Acid (1) + Hexanol (2) + H_2O (3) and Propionic Acid (1) + Pentanol (2) + H_2O (3) at 303.15 K; (▲) Pentanol Experimental Data; (—) Tie Line of Pentanol Experiment; (▼) Hexanol Experimental Data; (—) Tie Line of Hexanol Experiment.

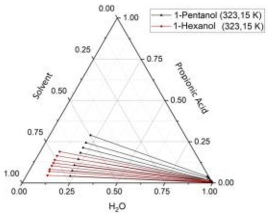

Figure 9. Liquid-Liquid Equilibrium Diagrams of the Ternary Systems Propionic Acid (1) + Hexanol (2) + H_2O (3) and Propionic Acid (1) + Pentanol (2) + H_2O (3) at 323.15 K; (▲) Pentanol Experimental Data; (—) Tie Line of Pentanol Experiment; (▼) Hexanol Experimental Data; (—) Tie Line of Hexanol Experiment.

B. Binary Parameter Correlation

The experimental LLE data (in mole fractions) was correlated using the NRTL and UNIQUAC activity coefficient models. The NRTL model's non-randomness parameter (α; 0.2 - 0.47) was established based on the lowest generated OF value. Consequently, in the Propionic Acid (1) + Pentanol (2) + H_2O (3) system α values of 0.39 and the Propionic Acid (1) + Hexanol (2) + H_2O (3) system α values of 0.38 & 0.43 were obtained at temperatures 303.15 and 323.15 K, respectively. The UNIQUAC model borrowed should R (volume parameter) and Q (surface area parameter) from B. Poling. By reducing the objective function (OF) value, the NRTL or UNIQUAC models obtained the binary interaction parameters (a_{ij} - a_{ji}).

Root-mean-square-deviation (RMSD) is a suitable criterion for determining correlation accuracy. In all systems, the average RMSD of the UNIQUAC model is lower than NRTL. Therefore, the UNIQUAC model has a higher accuracy in correlating Liquid-Liquid Equilibrium

(LLE) data for this system. The average RMSD from this study is less than 2.5%. Furthermore, the calculated tie line is almost identical to the experimental tie line. These results suggest that the NRTL and UNIQUAC models precisely characterize the phase behaviour of the ternary systems Propionic Acid (1) + Pentanol (2) + H_2O (3) and Propionic Acid (1) + Hexanol (2) + H_2O (3). Additionally, these models can be applied to simulate the extraction of propionic acid from water using pentanol or hexanol.

Table 5 shows the data used for the cluster volume (R) and cluster surface area (Q). Table 6 identifies the computed volume and molecular area parameters (r_i and q_i), while Tables 7 and 8 lists the calculated binary interaction parameters of the NRTL and UNIQUAC equations.

TABLE 5.
UNIQUAC CLUSTER SPECIFICATIONS

Molecule (i)	Name	Cluster Number		$V^{(i)}$	Molar Volume (R)	Surface Area (Q)
		Primary	Secondary			
Propionic Acid	CH_3	1	1	1	0.901	0.848
	CH_2	1	2	1	0.674	0.540
	COOH	20	42	1	1.301	1.224
Pentanol	CH_3	1	1	1	0.901	0.848
	CH_2	1	2	4	0.674	0.540
	OH	5	14	1	1.000	1.200
H_2O	H_2O	7	16	1	0.920	1.400
Hexanol	CH_3	1	1	1	0.901	0.848
	CH_2	1	2	5	0.674	0.540
	OH	5	14	1	1.000	1.200

TABLE 6.
UNIQUAC MOLECULAR STRUCTURAL PARAMETERS

Molecule	r_i	q_i	l_i
Propionic Acid	2.87680	2.61200	-0.55280
Pentanol	4.59870	4.20800	-1.64520
H_2O	0.92000	1.40000	-2.32000
Hexanol	5.27310	4.74800	-1.64760

Tables 7 and 8 present the calculated data results obtained from the flowchart (Figure 3 - 5).

TABLE 7.
INTERACTION PARAMETERS OF THE NRTL MODEL FOR THE TERNARY SYSTEM PROPIONIC ACID (1) + PENTANOL (2) + H_2O (3) AT 303.15 & 323.15 K

Temp (K)	Parameter	Component		α	a_{ij}	a_{ji}	RMSD
		i	J				
303.15	UNIQUAC	1	2	-	11.2	16.6	1.4%
		1	3		594.6	0.9	
		2	3		347.9	114.4	
	NRTL	1	2	0.39	3163.0	1459.7	2.6%
		1	3		14472.4	3055.4	
		2	3		1557.7	2640.5	
323.15	UNIQUAC	1	2	-	84.8	25.5	1.7%
		1	3		597.4	14.7	
		2	3		470.1	19.6	
	NRTL	1	2	0.39	2555.4	959.5	2.8%
		1	3		7023.4	3091.6	
		2	3		1572.0	2818.2	

Using the NRTL and UNIQUAC models, the equilibrium composition data of the ternary systems - Propionic Acid (1) + Pentanol (2) + H_2O (3) and Propionic Acid (1) + Hexanol (2) + H_2O (3) - were determined based on parameters obtained from Table 7 and Table 8. Furthermore, the liquid-liquid equilibrium diagrams of these ternary systems, depicted in Figure 8 - Figure 17, were also considered.

TABLE 8.
INTERACTION PARAMETERS OF THE NRTL MODEL FOR THE TERNARY SYSTEM PROPIONIC ACID (1) + HEXANOL (2) + H_2O (3) AT 303.15 & 323.15 K

Temp (K)	Parameter	Component		α	a_{ij}	a_{ji}	RMSD
		i	j				
303.15	UNIQUAC	1	2	-	18.4	29.9	3.2%
		1	3		1011.7	0.9	
		2	3		544.2	66.8	
	NRTL	1	2	0.38	2051.1	1289.6	2.8%
		1	3		38459.5	3410.2	
		2	3		2305.4	3864.8	
323.15	UNIQUAC	1	2	-	87.9	25.3	2.6%
		1	3		875.8	12.6	
		2	3		607.5	27.9	
	NRTL	1	2	0.43	1974.9	37787.5	2.9%
		1	3		34122.5	2673.4	
		2	3		2055.3	4130.4	

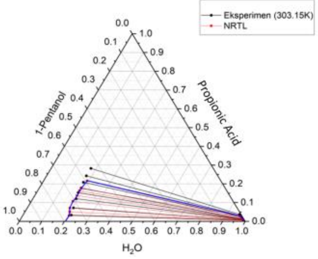

Figure 10. Liquid-Liquid Equilibrium Diagram of the Ternary System Propionic Acid (1) + Pentanol (2) + H_2O (3) at 303.15 K; (●) Experimental Data; (—) Experimental Tie Line; (■) Data with NRTL Equation; (---) Tie Line with NRTL Equation; (—) Binodal NRTL Equation

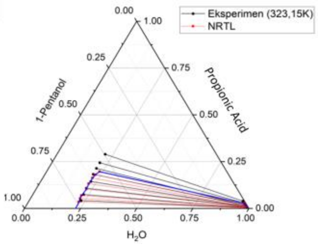

Figure 11. Liquid-Liquid Equilibrium Diagram of the Ternary System Propionic Acid (1) + Pentanol (2) + H_2O (3) at 323.15 K; (●) Experimental Data; (—) Experimental Tie Line; (■) Data with NRTL Equation; (---) Tie Line with NRTL Equation; (—) Binodal NRTL Equation

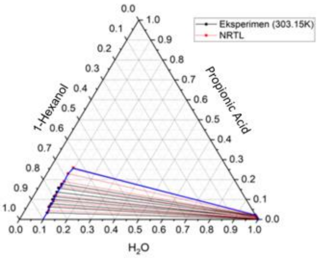

Figure 12. Liquid-Liquid Equilibrium Diagram of the Ternary System Propionic Acid (1) + Hexanol (2) + H_2O (3) at 303.15 K; (●) Experimental Data; (—) Experimental Tie Line; (■) Data with NRTL Equation; (---) Tie Line with NRTL Equation; (—) Binodal NRTL Equation.

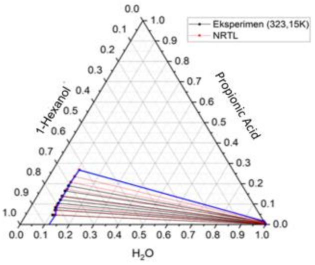

Figure 13. Liquid-Liquid Equilibrium Diagram of the Ternary System Propionic Acid (1) + Hexanol (2) + H_2O (3) at 323.15 K; (●) Experimental Data; (—) Experimental Tie Line; (■) Data with NRTL Equation; (---) Tie Line with NRTL Equation; (—) Binodal NRTL Equation.

The Figures 10 to 17 shows the tie line of the experimental outcomes with the dome of correlation results, which denotes the upper limit of the two-phase area (layer) and can be used as a reference to set the initial composition for separation. The establishment of the dome is based on the compositional relation of organic and aqueous phase correlation results for each sample. The diagram above indicates the difference between the experimental results and the equilibrium composition of the correlation models used. The equilibrium composition of the UNIQUAC equation model is closer to the experimental results than the NRTL equation. Deviations usually tend to be higher in the Propionic Acid (1) + Hexanol (2) + H_2O (3) system compared to the Propionic Acid (1) + Pentanol (2) + H_2O (3) system.

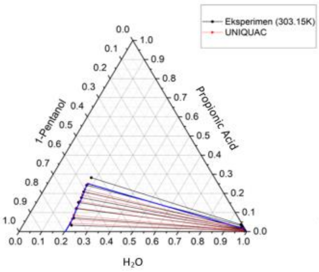

Figure 14. Liquid-Liquid Equilibrium Diagram of the Ternary System Propionic Acid (1) + Pentanol (2) + H_2O (3) at 303.15 K; (●) Experimental Data; (─) Experimental Tie Line; (▲) Data with UNIQUAC Equation; (---) Tie Line with UNIQUAC Equation; (─) Binodal UNIQUAC Equation

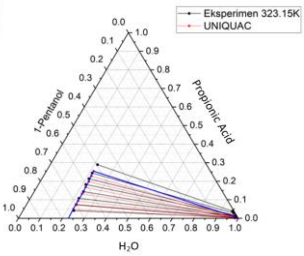

Figure 15. Liquid-Liquid Equilibrium Diagram of the Ternary System Propionic Acid (1) + Pentanol (2) + H_2O (3) at 323.15 K; (●) Experimental Data; (─) Experimental Tie Line; (▲) Data with UNIQUAC Equation; (---) Tie Line with UNIQUAC Equation; (─) Binodal UNIQUAC Equation

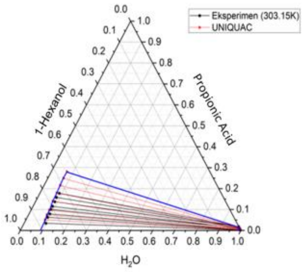

Figure 16. Liquid-Liquid Equilibrium Diagram of the Ternary System Propionic Acid (1) + Hexanol (2) + H_2O (3) at 303.15 K; (●) Experimental Data; (─) Experimental Tie Line; (▲) Data with UNIQUAC Equation; (---) Tie Line with UNIQUAC Equation; (─) Binodal UNIQUAC Equation

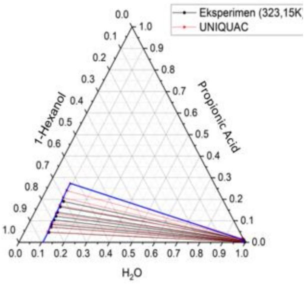

Figure 17. Liquid-Liquid Equilibrium Diagram of the Ternary System Propionic Acid (1) + Hexanol (2) + H_2O (3) at 323.15 K; (●) Experimental Data; (─) Experimental Tie Line; (▲) Data with UNIQUAC Equation; (---) Tie Line with UNIQUAC Equation; (─) Binodal UNIQUAC Equation

The Figures 10 to 17 shows the tie line of the experimental outcomes with the dome of correlation results, which denotes the upper limit of the two-phase area (layer) and can be used as a reference to set the initial composition for separation. The establishment of the dome is based on the compositional relation of organic and aqueous phase correlation results for each sample. The diagram above indicates the difference between the experimental results and the equilibrium composition of the correlation models used. The equilibrium composition of the UNIQUAC equation model is closer to the experimental results than the NRTL equation. Deviations usually tend to be higher in the Propionic Acid (1) + Hexanol (2) + H_2O (3) system compared to the Propionic Acid (1) + Pentanol (2) + H_2O (3) system.

C. *Distribution Coefficient, Separation Factor and Consistency of Experimental Data*

The experimental data was also correlated with the Bachman-Brown equation, which ensures the reliability of the data. The correlation shows the consistency of the experimental data for the ternary systems Propionic Acid (1) + Pentanol (2) + H_2O (3) and Propionic Acid (1) + Hexanol (2) + H_2O (3). Figures 18 and 19 illustrate the Bachman-Brown correlations for both systems at temperatures of 303.15 K and 323.15 K above atmospheric pressure (101.3 kPa). Table 9 lists the parameter values of the Bachman-Brown correlations with standard deviations (R2). Table 9 and Figures 18 and 19 show that the standard deviation of propionic acid is close to one or more than 0.9, indicating that the liquid-liquid equilibrium experimental data of the studied systems are highly consistent.

TABLE 9.
BACHMAN-BROWN CORRELATION RESULTS FOR ALL SYSTEMS

Correla-tion	Parameter	Pentanol		Hexanol	
		303.15 K	325.15 K	303.15 K	325.15 K
Bachman-Brown	A	0.9309	0.9301	0.8957	0.9302
	B	0.0596	0.0564	0.0923	0.0606
	R^2	0.9977	0.9991	0.998	0.9994

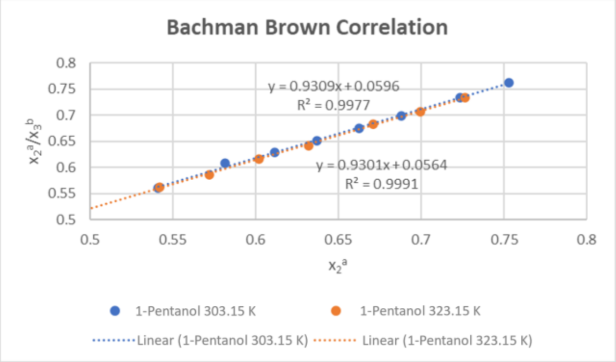

Figure 18. Bachman-Brown Plots for Systems: (♦) Propionic Acid (1) + 1-Pentanol (2) + H_2O (3) 303.15 K ; (■) Propionic Acid (1) + 1-Pentanol (2) + H_2O (3) 323.15 K

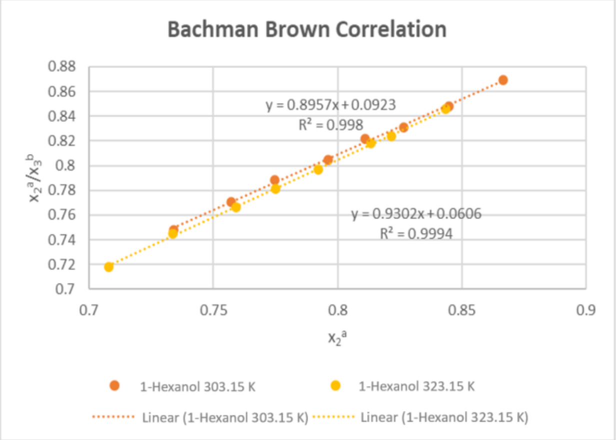

Figure 19. Bachman-Brown Plots for Systems: (♦) Propionic Acid (1) + 1-Hexanol (2) + H_2O (3) 303.15 K ; (■) Propionic Acid (1) + 1-Hexanol (2) + H_2O (3) 323.15 K

The distribution coefficient (D_i) and separation factor (S) are important parameters in liquid-liquid extraction and can indicate the ability of a solvent to extract propionic acid from its diluent. To achieve effective separation, the separation factor should be higher than the other solvents.

TABLE 10.
DISTRIBUTION COEFFICIENT (DI) AND SEPARATION FACTOR (S) FOR THE SYSTEM PROPIONIC ACID (1) + PENTANOL (2) + H_2O (3)

System	T (K)	D_1	D_3	S
		x_1^a/x_1^b	x_3^a/x_3^b	
Propionic Acid (1) + Pentanol (2) + H_2O (3)	303.15	5.549	0.216	25.669
		10.716	0.207	51.736
		12.307	0.194	63.410
		13.596	0.187	72.470
		12.220	0.188	64.676
		9.738	0.184	52.669
		6.613	0.183	35.972
		10.225	0.182	56.089
	323.15	9.777	0.233	41.795
		16.077	0.228	70.342
		10.750	0.224	47.805
		15.794	0.227	69.499
		11.499	0.220	52.198
		13.543	0.218	61.993
		8.609	0.221	38.897
		7.396	0.225	32.814

TABLE 11.
DISTRIBUTION COEFFICIENT (D_1) AND (D_3), AND SEPARATION FACTOR (S) FOR THE SYSTEM PROPIONIC ACID (1) + HEXANOL (2) + H2O (3)

System	T	D_1	D_3	S
		x_1^a/x_1^b	x_3^a/x_3^b	
Propionic Acid (1) + Hexanol (2) + H_2O (3)	303.15	16.590	0.099	167.020
		23.846	0.092	257.933
		18.424	0.094	195.058
		8.485	0.089	94.414
		11.861	0.089	132.543
		8.1146	0.089	90.583
		9.709	0.086	112.747
		9.845	0.090	109.376
	323.15	27.697	0.110	251.383
		35.963	0.107	333.014
		18.351	0.103	177.629
		21.001	0.104	201.590
		16.275	0.104	155.607
		15.803	0.102	154.603
		11.589	0.102	112.765
		14.521	0.103	140.246

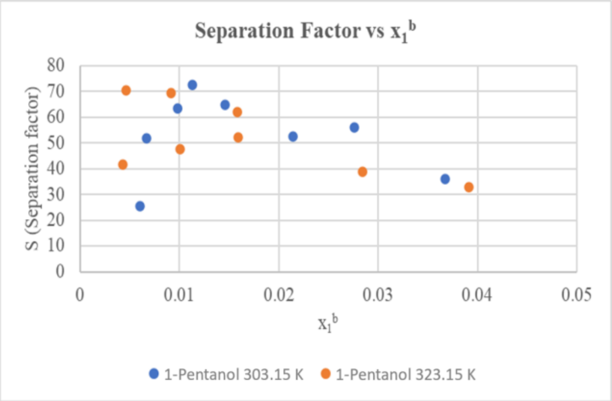

Figure 20. Plot of Separation Factor (S) versus Mole Fraction of Propionic Acid in aqueous phase for System: (♦) Propionic Acid (1) + 1-Pentanol (2) + H_2O (3) 303.15 K; (■) Propionic Acid (1) + 1-Pentanol (2) + H_2O (3) 323.15 K.

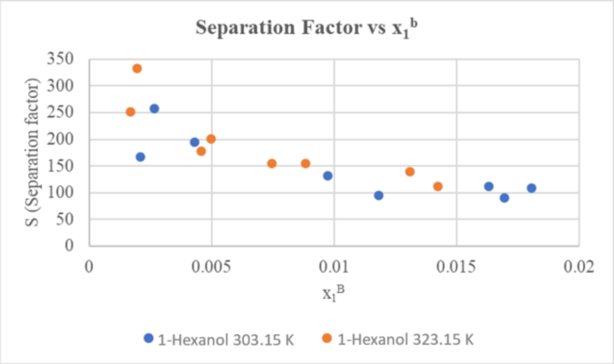

Figure 21. Plot of Separation Factor (S) versus Mole Fraction of Propionic Acid in aqueous phase for System: (♦) Propionic Acid (1) + 1-Hexanol (2) + H_2O (3) 303.15 K; (■) Propionic Acid (1) + 1-Hexanol (2) + H_2O (3) 323.15 K.

As shown in Tables 10 and 11, the separation factor values in all systems are above 1, indicating that both solvents are efficient in extracting propionic acid from its diluent. At higher operating temperatures, it is noticeable that the selectivity values reduce slightly. The selectivity is influenced not only by temperature but also by the type of solvent. In the system using hexanol as a solvent, the resulting separation factor is considerably higher, which implies that hexanol's ability to extract propionic acid from its aqueous phase is much greater.

IV. CONCLUSION

1. Liquid-liquid equilibrium data were obtained from the experimental results of the ternary system Propionic Acid + 1-Pentanol + H_2O and Propionic Acid + 1-Hexanol + H_2O at 303.15 K and 323.15 K at atmospheric pressure.
2. The correlation calculation of the NRTL and UNIQUAC models for this system are quite good, with the highest RMSD of 3.2%, the lowest RMSD of 1.4% and the average RMSD of 2.5%.
3. The two-phase region possessed by hexanol is larger, thus facilitating the extraction process. The boiling point of hexanol (155°C) is higher compared to pentanol (137.5°C), enabling the expansion of extraction operational conditions. The distribution coefficient and separation factor values for propionic acid using hexanol as a solvent are high, with an average of 16.7 for the distribution coefficient and 167 for the separation factor. Several of these parameters serve as evidence that hexanol has a better capability to extract propionic acid from its aqueous phase.

V. ACKNOWLEDGEMENT

The authors thank to the support from Department of Chemical Engineering, Faculty of Industrial Technology and Systems Engineering, Institut Teknologi Sepuluh Nopember that funded this research according to contract number: 1335/PKS/ITS/2023.

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