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Solid-Liquid Equilibrium Study of Binary System Saturated Fatty Acid in Short Chain Alcohols

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ABSTRACT. Unsaturated fatty acids can potentially be used to prevent degenerative diseases and develop brain function in babies. The urea complexation fractionation method efficiently separates unsaturated fatty acids from saturated fatty acids. It is considered to be the simplest, most efficient, and lowest-cost method. This study aimed to optimize urea complexation for increasing PUFA concentrations by determining solid-liquid equilibrium data of saturated fatty acids in short-chain alcohols. In this study, there were two types of short-chain alcohol, methanol and ethanol, in various concentrations (99.7%; 95%; 88%; 76% w/w) towards the solubility of saturated fatty acids, palmitic and stearic acid (PA and SA). PA and SA dissolved in various concentrations of methanol and ethanol to get homogeneous solutions. When solid SFA disappeared by heating the solution or was first formed by cooling the solution, the temperature was determined as the solid-liquid equilibrium temperature. The best composition of solvent that provided the highest solubilities are 95% ethanol and 99.7% methanol to both palmitic and stearic acid.

1. INTRODUCTION

Fatty acids are generally derived from triglycerides and phospholipids. Most natural fatty acids have unbranched chains of 4-28 carbon atoms [1]. Fatty acids are categorized based on carbon bonds into saturated fatty acids (SFA) and unsaturated fatty acids (UFA). Saturated fatty acids have no double bonds, while unsaturated fatty acids have single, double bonds or more [2]. Polyunsaturated fatty acids (PUFAs) are essential neutraceuticals and should be consumed through foods [3]. PUFAs which are contained in vegetable and animal oils have great potential to support growth and normal function in the body system [4]. Meanwhile, SFAs are utilized for non-consumable needs, such as alternative fuels, the coating industry and many oleochemical raw materials [3].

The benefits of PUFA for health has encouraged researchers to conduct an optimization study of PUFA separation from vegetable and animal oils. There are fatty acid separation methods that have been investigated, such as crystallization at low temperatures [5], distillation, adsorption [6], chromatography [7], membrane separation [8], and fractionation of urea complexation [9]. The principle of urea complexation fractionation is separation based on the diameter of fatty acid molecules. Urea complexation is also considered an SFA adsorption phenomenon in urea crystals [3].

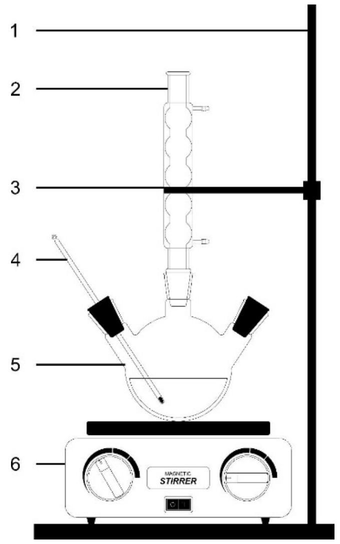
Urea complexation is commonly used in the separation of fatty acid mixtures resulting from hydrolysis. Urea crystal acts as “host molecule” while linear aliphatic compounds adsorbed in it as a “guest molecule”, called urea inclusion compounds (UIC) [10]. This method was chosen as the separation process for fatty acids due to the simple, efficient, inexpensive and easily controlled operating conditions compared to other PUFA separation methods. Separation and optimization can be viewed from the solid-liquid equilibrium profile to produce PUFA in high purity [11]. In addition to the fundamentals of solid-liquid equilibrium and thermodynamic models, solubility in solvents is also a concern for researchers to develop theories [12].

Palmitic acid (PA) and stearic acid (SA) were dissolved in various solvents which behave as wetting agent. It encourages crystal formation and increase yield [13]. Regarding sustainable development goals (SDGs), solvents, such as organic solvent, should have a favorable environmental and social impact [14]. Organic solvents are categorized into aliphatic hydrocarbons, aromatics, esters, aldehydes and alcohols [15]. Alcohol is widely used for fatty acid extraction and separation through urea complexation. Previous research showed that urea was more soluble in water than alcohol, due to their polarities [3]. However, fatty acids mostly insoluble in water. Short-chain alcohols (methanol and ethanol) are solvents with lower polarity than water, but they can dilute urea and fatty acids at certain solubilities.

This research studied the solid-liquid equilibrium of SFA in binary systems with alcohols: SA-ethanol, PA-ethanol, SA-methanol and PA-methanol in various solvent concentrations). The purpose of this study was to obtain solid-liquid equilibrium (SLE) data of SFA (palmitic and stearic acid) and short-chain alcohols (methanol and ethanol). The SLE is presented in the temperature vs composition (T-X) diagram to determine the fitting model. This is useful to optimize the urea complexation process condition.

2. MATERIALS AND METHODS

This study used pure and artificial fatty acids, instead of fatty acids from vegetable oil or animal fat to obtain more accurate solid-liquid phase equilibrium data. High purities of 98% palmitic acid p.a (Merck), 98% stearic acid p.a (Merck) were used as artificial SFA. Additional materials were 95% technical-grade ethanol, 98% methanol p.a (Riedel-de Haen), and distilled water. The apparatus used to determine solubility temperature is shown in **Figure 1**.



Keterangan:
1. Clamp stand
2. Bulb condenser
3. Clamp
4. Thermometer
5. Three neck flask
6. Heater equipped by *magnetic stirrer*

Figure 1. Fatty Acid Solubility Apparatus Scheme

This experiment studied the solid-liquid equilibrium between saturated fatty acid (PA and SA) and short-chain alcohol (methanol and ethanol). The equilibrium data presented in temperature (T) versus composition (X) diagram, which is known as T-X diagram.

Solubility of saturated fatty acids (PA/SA) in alcohol was carried out by mixing SFA (various mole fractions) in 100 mL of ethanol or 129.2 mL of methanol into 250 mL erlenmeyer. The solution was stired using a magnetic stirrer until homogeneous at room temperature. The variables used in this study can be seen in **Table 1.** If the crystals dissolve, cooling down with an icebath is necessary. Meanwhile, the crystals are not dissolved, it is necessary to heat up using a three-neck flask.

Table 1. Fixed and Free Variables in the Solubility Process

No	Fixed Variables	Independent Variables
1	Volume of SFA-etanol solution at 100 mL	Ethanol composition (95%; 88%; 76% w/w)
2	Volume of SFA-metanol solution at 129.2 mL	Methanol composition (99.7%; 88%; 76% w/w)
3	Stirring speed at 300 rpm	

Observation of the temperature when SFA was dissolved in solvents (solid→liquid) or the first solid SFA appeared in solution (liquid→solid) are recorded as solid-liquid equilibrium data. The phase change was characterized by the appearance of SFA crystals and/or the dissolution of SFA solids. Observations must be clear and precise in order to obtain accurate data.

Solubility data that has been obtained is interpreted to determine the solubility of SFA in short-chain alcohols. Comparison of these data with similar studies then have been carried out. The results of the solubility graph produce a relationship between mol fraction of SFA and solubility temperature for each variable.

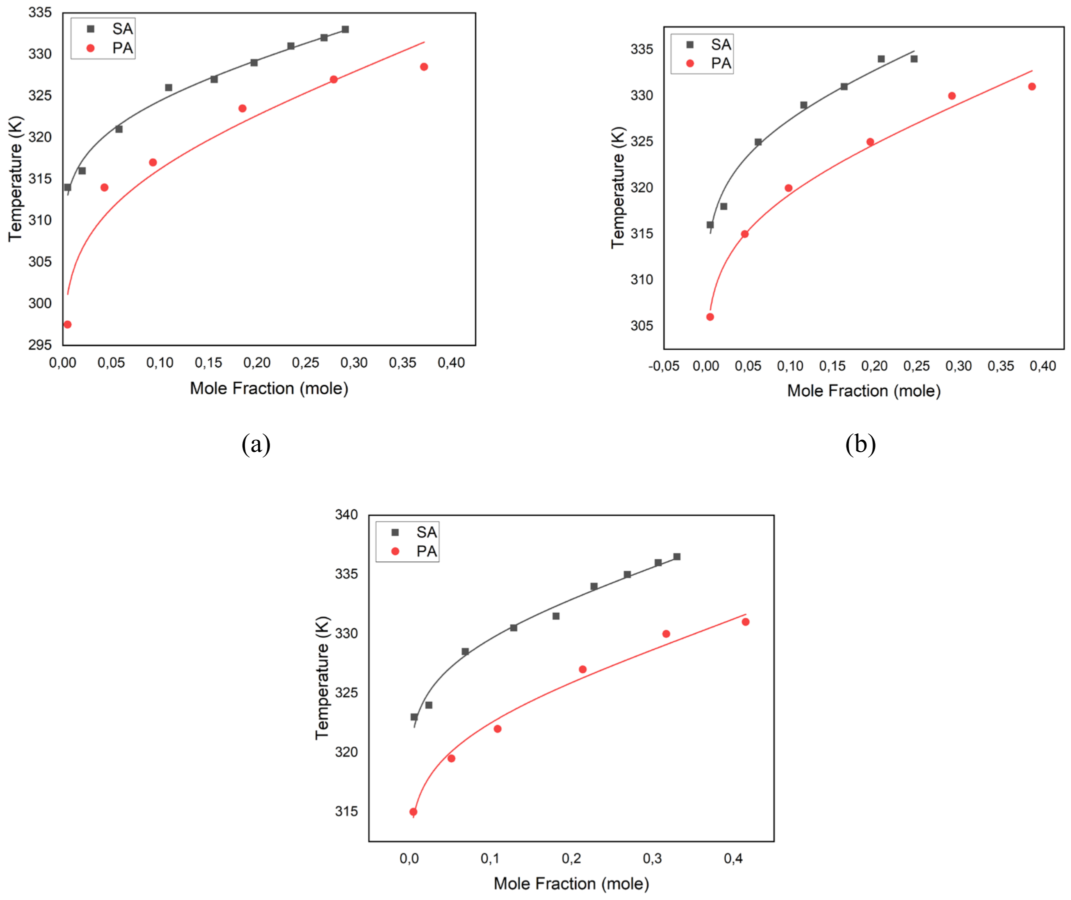
3. RESULTS AND DISCUSSION

SA/PA solid-liquid equilibrium in ethanol/methanol solvents at various concentrations (w/w) resulted in solubility data, which are presented in **Table 2** and **Table 4**.

Table 2. Fatty Acids Solubility in Ethanol

Ethanol Concentration (w/w)	Stearic Acid		Palmitic Acid	
	Mole fraction (X_{SA})	Temperature (K)	Mole Fraction (X_{PA})	Temperature (K)
95%	0.005	314	0.005	297.5
	0.020	316	0.043	314
	0.058	321	0.093	317
	0.109	326	0.185	323.5
	0.156	327	0.279	327
	0.197	329	0.372	328.5
	0.235	331		
	0.269	332		
	0.291	333		
88%	0.005	316	0.005	306
	0.021	318	0.046	315
	0.062	325	0.098	320
	0.116	329	0.195	325
	0.164	331	0.292	330
	0.208	334	0.387	331
	0.247	334		
76%	0.006	323	0.005	315
	0.024	324	0.052	319.5
	0.069	328.5	0.109	322
	0.129	330.5	0.214	327
	0.181	331.5	0.317	330
	0.228	334	0.415	331
	0.269	335		
	0.307	336		
	0.330	336.5		

Based on the solubility data, fatty acid solubility in ethanol at various concentrations (w/w) generated T-X diagram of fatty acid mole fractions against solubility temperature as shown on **Figure 2**. The fitting models are presented in **Table 3**.



(a)

(b)

(c)

Figure 2. Solubility of Stearic Acid and Palmitic Acid in: (a) 95% Ethanol, (b) 88% Ethanol, (c) 76% Ethanol

Table 3. Fitting model of the FA-ethanol solubility diagrams

Binary solid-liquid equilibrium	Fitting model	R^2
SA - 95% ethanol	T = 4.8948 ln X + 337.26	0.9394
SA - 88% ethanol	T = 5.003 ln X + 339.99	0.9364
SA - 76% ethanol	T = 3.534 ln X + 338.99	0.9200
PA - 95% ethanol	T = 7.0318 ln X + 335.34	0.9946
PA - 88% ethanol	T = 5.7989 ln X + 335.22	0.9614
PA - 76% ethanol	T = 3.7458 ln X + 332.8	0.9062

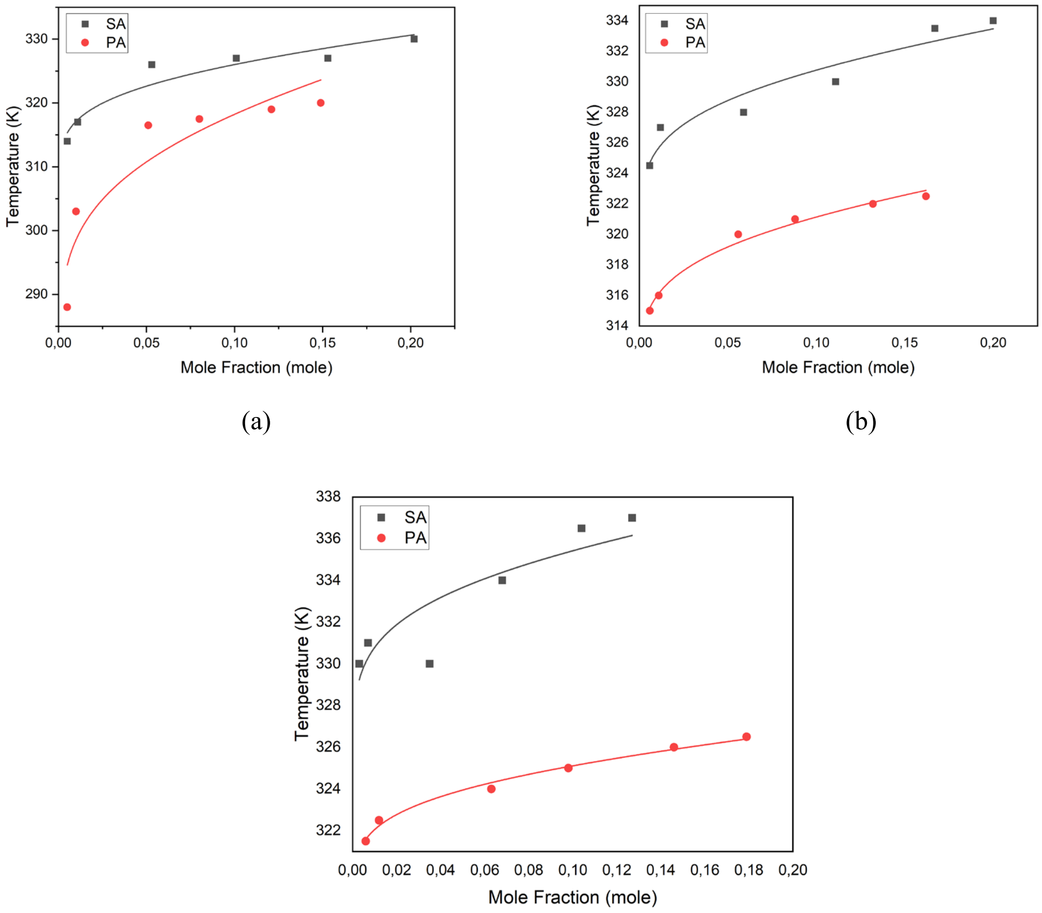
Table 4 shows the fatty acid solubility in methanol at various concentrations (w/w) which generated T-X diagram of fatty acid mole fractions against solubility temperature, as shown on **Figure 3**. The fitting models are presented in **Table 5**.

Table 4. Solubility of Fatty Acids in Methanol

Methanol Concentration (w/w)	Stearic Acid		Palmitic Acid	
	Mole fraction (X_{SA})	Temperature (K)	Mole fraction (X_{PA})	Temperature (K)
99.7%	0.005	314	0.005	288
	0.011	317	0.010	303
	0.053	326	0.051	316.5
	0.101	327	0.080	317.5
	0.153	327	0.121	319
	0.202	330	0.149	320
88%	0.006	324.5	0.006	315
	0.012	327	0.011	316
	0.059	328	0.056	320
	0.111	330	0.088	321
	0.167	333.5	0.132	322
	0.200	334	0.162	322.5
76%	0.003	330	0.006	321.5
	0.007	331	0.012	322.5
	0.035	330	0.063	324
	0.068	334	0.098	325
	0.104	336.5	0.146	326
	0.127	337	0.179	326.5

Table 5. Fitting model of the FA-methanol solubility diagrams

Binary solid-liquid equilibrium	Fitting model	R^2
SA - 99.7% methanol	$T = 4.2216 \ln X + 336.51$	0.9691
SA - 88% methanol	$T = 2.378 \ln X + 336.64$	0.8717
SA - 76% methanol	$T = 1.7721 \ln X + 339.3$	0.6914
PA - 99.7% methanol	$T = 8.7459 \ln X + 338.99$	0.9248
PA - 88% methanol	$T = 2.2703 \ln X + 326.55$	0.9967
PA - 76% methanol	$T = 1.3945 \ln X + 328.48$	0.9641



(a)

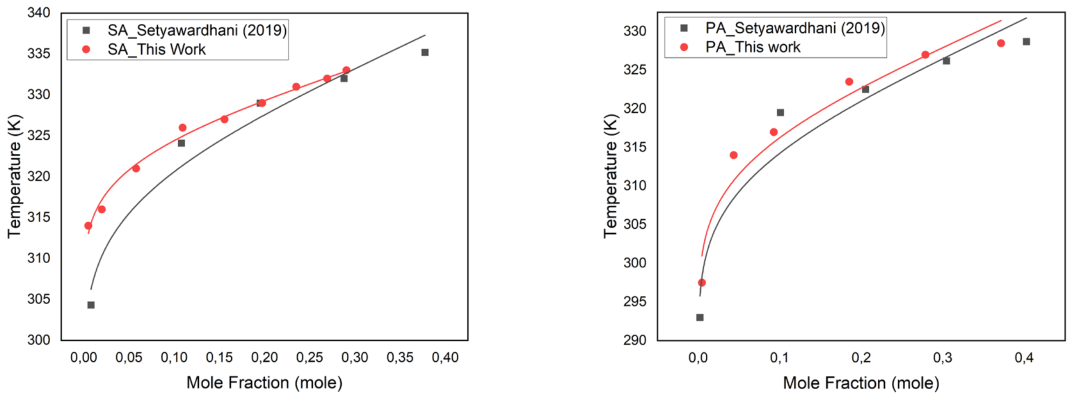
(b)

(c)

Figure 3. Solubility of Stearic and Palmitic Acid in: (a) 99.7% Methanol, (b) 88% Methanol, (c) 76% Methanol

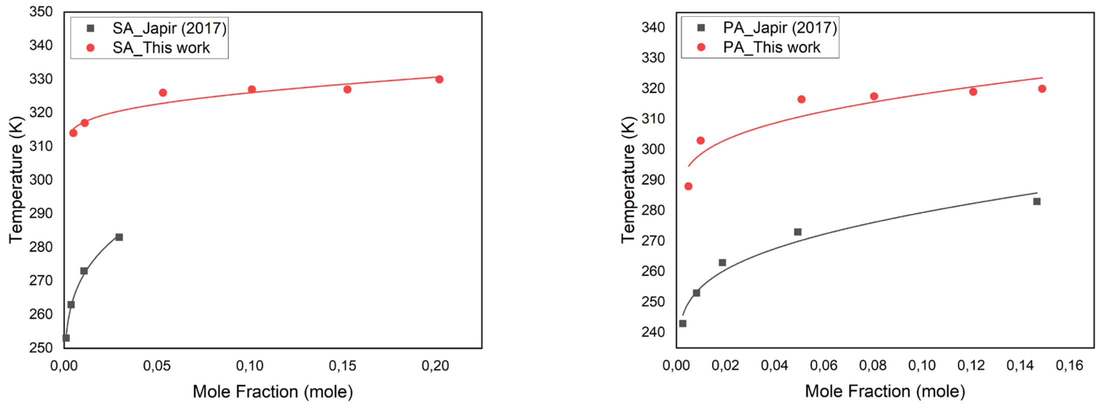
The T-X diagrams showed that palmitic acid was more soluble in ethanol and methanol than stearic acid. Palmitic acid was soluble at room temperature (300 K) in methanol 99.7% (w/w) and a mole fraction of less than 0.01 mole PA/mole solution. In contrast, stearic acid was soluble at temperatures above room temperature. The solubility of palmitic acid reached 288 K in absolute methanol. Palmitic acid has two shorter carbon chains than stearic acid, which caused higher polarity and higher solubility to ethanol and methanol. The shorter the carbon chain in the fatty acid molecular structure, the higher the solubility in polar solvents.

The experimental data from this study showed a tendency for fatty acids to reach the highest solubility in 95% ethanol (w/w). **Figure 4** compares the solubility data of fatty acids in 95% ethanol (w/w) from this study with the research conducted by Setyawardhani, et al [3]. This research studied wider range of fatty acid mole fractions to complete the data from previous research. Nevertheless, both T-X diagrams showed similar tendencies. **Figure 5** shows the experimental data conducted in this study (95% methanol) compared with data from Japir, et al [16] (99.7% methanol). This research obtained higher solubilities of SA and PA in methanol. For SA solubility, they studied only in very low concentration.



(a) (b)

Figure 4. Solubility of Fatty Acids in 95% Ethanol: (a) Stearic Acid, (b) Palmitic Acid Comparation with previous researches



(a) (b)

Figure 5. Solubility of Fatty Acids in 99,7% Methanol and 95% Methanol: (a) Stearic Acid, (b) Palmitic Acid. Comparation with previous researches.

The organic solvents used in this study are methanol (CH_3OH) and ethanol (C_2H_5OH). They have hydroxyl groups attached to carbon atoms and hydrogen atoms. These two solvents have been widely used for urea complexation due to the economically consideration. Although pure water is cheaper, it is a highly polar solvent which can not dissolve non polar fatty acids such as PA and SA. The fatty acids solubility experiments in methanol and ethanol generate T-X diagrams of fatty acid mole fractions against solubility temperature. **Figure 6.** and **Figure 7** show SA/PA solubility comparative between 2 different solvents.

The solubility of two components depend on their polarity. Ethanol has a better ability to dissolve towards stearic acid and palmitic acid compared to methanol. Both PA and SA indicate higher solubility in ethanol than methanol, due to the lower polarity of ethanol. This is affected by the length of carbon chain in ethanol, which is longer than the carbon chain in methanol. The length of the carbon chains affect the polarity of a compound. Longer carbon chain tends to lower polarity. Meanwhile, long chain fatty acids such as PA and SA are non-polar compounds that are difficult to dissolve in polar solvents like water. They have lower polarity than short chain ones (2 to 5 carbon chain) such as propionic and butiric acid which are found in animal fat. Therefore, PA and SA are mole soluble in ethanol than methanol.

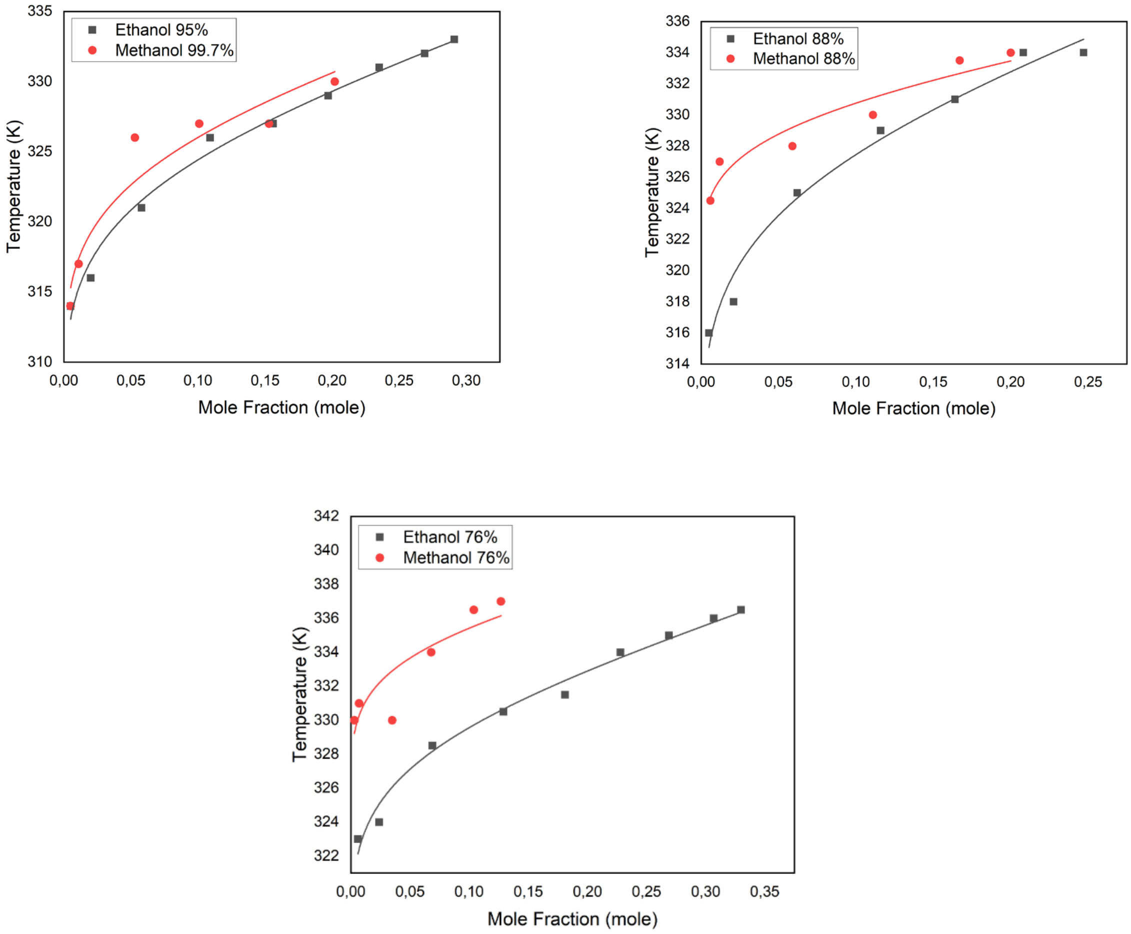
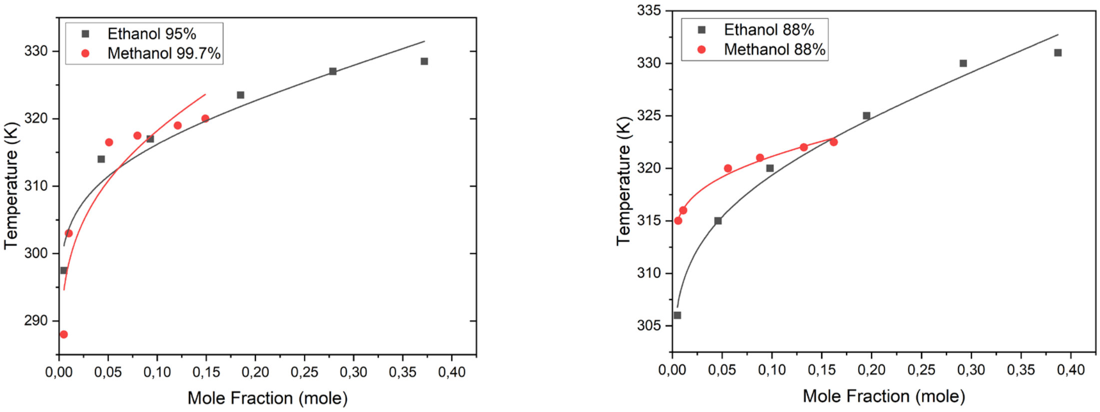


Figure 6. Solubility of Stearic Acid in Ethanol and Methanol



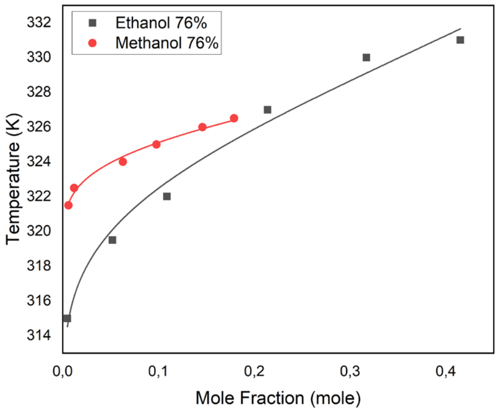


Figure 7. Solubility of Palmitic Acid in Ethanol and Methanol

Fatty acid solubilities were studied in various concentration of ethanol and methanol in water (95%, 88%, 76% w/w). Varied ethanol concentrations were made with a fixed volume solution (100 mL), then 95% ethanol is defined as 95% by weight of ethanol and 5% by weight of water. While the varieties in methanol concentration was made with a fixed solution volume (129.2 mL), then 88% methanol is defined as 88% by weight of methanol with 12% by weight of water. This experiment obtained T-X diagrams of fatty acids' mole fraction data against solubility temperature, as shown in Figures 8 **and 9.**

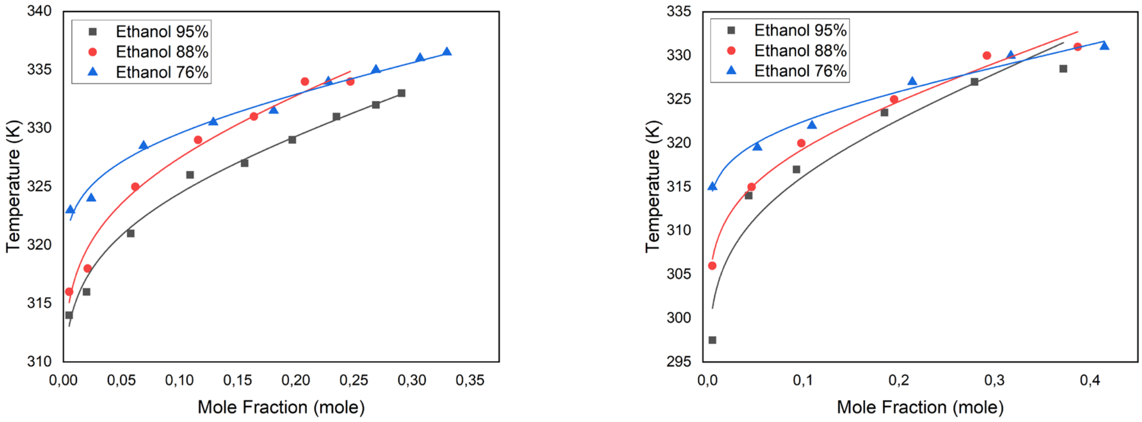


Figure 8. Solubility of Stearic Acid and Palmitic Acid in Ethanol 95%; 88%; 76% (w/w)

The experiment results show that palmitic acid and stearic acid can dissolve better in 95% ethanol compared to 88% and 76% ethanol concentrations. In addition, palmitic acid is able to dissolve under room temperature when dissolved in 95% ethanol. 95% ethanol solution means that the solution contains 95% by weight of ethanol and 5% by weight of water. The presence of water (impurity) which has a high polarity can cause difficulty to dissolve. This is because long fatty acids are non-polar, making them difficult to dissolve in polar solvents.

This experiment also used methanol solvent at various concentrations of 99.75%, 88%, 76% (w/w) to obtain data on the solubility of fatty acids in methanol solution. The results of the experimental data are presented in the **Figure 9**.

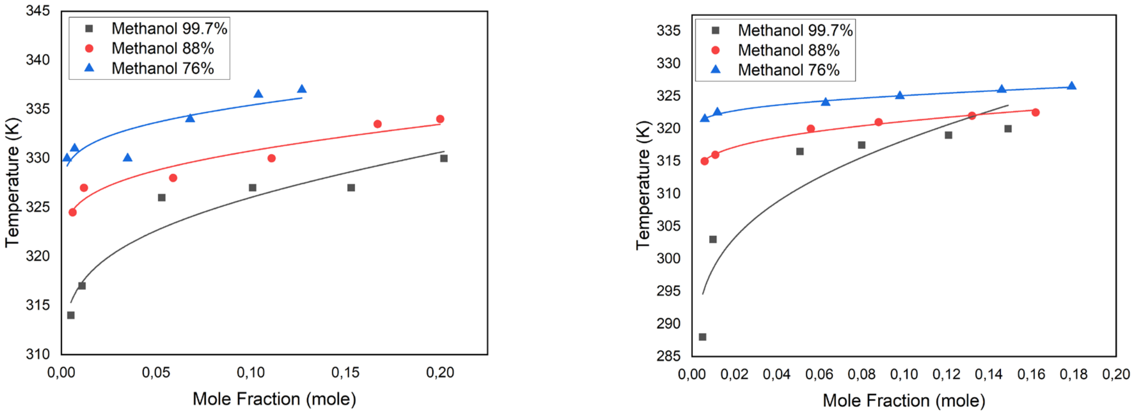


Figure 9. Solubility of Stearic Acid and Palmitic Acid in Methanol 99,7%; 88%; 76% (w/w)

The T-X diagrams show that stearic acid and palmitic acid have the best solubility in 99.7% methanol solution with a very small amount of impurities. From **Figure 7, Figure 8,** and **Figure 9,** it can be seen that the presence of water can reduce the solubility of fatty acids.

4. CONCLUSION

Solid-liquid equilibrium data of SFA in short chain alcohol is important for determining the optimum condition of fatty acid fractionation using urea complexation. PA and SA provide good solubilities in ethanol and methanol in lower concentration. Higher alcohol concentration represented higher long-chain fatty acids' solubility. The best composition of solvent that provided the highest solubilities are 95% ethanol and 99.7% methanol to both palmitic and stearic acid.

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