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Ternary liquid-liquid equilibria for β -caryophyllene(1) + 1-propanol(2) + water(3) system at temperatures 303.15, 313.15, and 323.15 K

K Kuswandi*, G Wibawa, I Hidayatulloh, C Mahardhikawati and A D Pratiwi

Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia

*E-mail: kuswandi@chem-eng.its.ac.id

Abstract. The experimental liquid-liquid equilibrium data of the system β -caryophyllene(1) + 1-propanol(2) + water(3) at temperatures 303.15, 313.15, and 323.15 K are presented. The mixtures of β -caryophyllene + 1-propanol + water were stirred for 4 hours and settled for at least 20 hours at constant temperature. The samples taken from both phases were analyzed by a gas chromatography (GC). The experimental equilibrium data were correlated by NRTL and UNIQUAC models. The compatibility of the models is based on the value of root mean square deviation (RMSD). The liquid-liquid phase diagram of the system shows type I phase behavior, where two binary subsystems are miscible and only one binary subsystem is partially miscible. The temperature effect of this system on immiscible zone is very small. Based on the experiment and the calculation results, the ternary equilibrium data have been successfully represented using both the NRTL and the UNIQUAC models.

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1. Introduction

Indonesia is a potential country as a source of essential oils. Indonesia produces 40 of 70 types of essential oils that were traded on the world market. From that amount 15 types have been traded on the world market, one of which is clove oil. About 60% of the clove oil produced in Indonesia is exported to many countries in the world.

Clove oil (*Syzygium aromaticum*) consists of hydrocarbon compounds such as terpene, sesquiterpene, etc; oxygenated hydrocarbon compounds such as alcohol, ester, ether, ketone, lactone, phenol, phenol ether, etc; and a small amount of non-volatile residue such as paraffin. Eugenol, one of the oxygenated hydrocarbon compounds, is a main compound of clove oil with a content of 78-98%. There are three types of clove oil produced from leaves, stems and flower-buds of *S. Aromaticum* that contain eugenol



82-88%, 90-95% and 60-90% respectively [1]. Eugenol is a colorless liquid, aromatic, and spicy that can be used in many fragrance, flavor, and pharmacy industry [2,3]. Oxygenated hydrocarbon compound (non-terpene) is a main cause of aromatic in the clove oil, while terpene and sesquiterpene are easily oxidized under the effect of light and air or on poor storage conditions that affect the fragrance and decrease the solubility of the oil in alcohol. Therefore, the removal of terpenes will increase the quality of clove oil. One of the terpene compounds is β -caryophyllene with a content of 10% in the clove oil [2].

According to the USP (United States Pharmacopeia), to be traded in the world market, eugenol should have a purity more than 98%. The purity of eugenol determines the selling price of clove oil. The clove oil with eugenol content of more than 98% is traded at prices 6-8 times higher than clove oil with eugenol content of less than 90%.

To satisfy these standards, it is necessary to process the separation of β -caryophyllene from oil. The separation process is called deterpenation which is the process to remove a part or all of terpene hydrocarbon compounds to reduce concentrations of terpenes which affect flavor and fragrance, increase solubility in alcohols and fragrance oils [4]. In the deterpenation process, the characteristic of a solvent should be considered such as polar, non-polar, volatility, and toxicity. The use of alcohol as a solvent has several advantages [4,5]: (1) They have a high solubility in aqueous solutions; (2) They increase the aromatic strength of the mixture; (3) Since the presence of the alcohol, oxidation reactions can be reduced; (4) They are non-toxic; (5) An aqueous alcohol is selective to dissolve eugenol, but cannot dissolve terpenes.

The knowledge of phase equilibrium properties of the fluid mixture is an important issue in various separation processes in the industry [6], but the availability of data is inadequate, both for the type of fluid system and operating range. In the previous studies, the equilibrium data of clove oil have been presented using various solvents [5,7-9]. In this work, liquid-liquid equilibrium data were investigated for the system β -caryophyllene + 1-propanol + water at temperatures 303.15, 313.15, and 323.15 K. The experimental data obtained were correlated by the NRTL [10] and the UNIQUAC [11] equations.

2. Experimental

2.1. Chemicals

β -caryophyllene 99.9 % was supplied by PT. Indesso Niagatama. 1-Propanol 99.8 % was supplied by MERCK and bi-distilled water was supplied by PT. Ika Pharmindo Putramas. The purity of chemicals was checked by gas chromatography.

2.2. Procedure

The LLE measurements were conducted for the β -caryophyllene + 1-propanol + water system at 303.15, 313.15, and 323.15 K. About 30 cm³ of the mixture were stirred intensely in a thermostat equilibrium cell. The equilibrium cell was equipped by a magnetic stirrer and a water-jacket to circulate water as a heater to maintain a constant temperature. Thermocouple Anly AT-502 and Tianshi XMT-7000 with accuracy $\pm 0.1^\circ\text{C}$ was used. The mixtures were stirred by the magnetic stirrer for 4 hours and settled for at least 20 hours at constant temperature to ensure that the equilibrium is going to be reached. After phase equilibrium has been reached, samples of two layers were analyzed by gas chromatography (GC) Shimadzu 2010 plus.

2.3. Analysis

The composition of the sampled liquid phase was determined using gas chromatography Shimadzu 2010 plus with Thermal Conductivity Detector (TCD) and 30 m, 0.32 mm ID, 0.25 μm RTX-5 column. The carrier gas (helium) flowrate was maintained at 3 cm³/min, purge flow at 3 cm³/min, column flow at 0.59 cm³/min, and split ratio 50:1. The temperatures of detector and injector were set at 573.15 K. The oven temperature was set at 343.15 K hold time 5 min and increased to 473.15 K at a rate of 40 K/min, hold time 5 min. About 1 μL sample was injected to gas chromatography with

maximum capacity and accuracy of Microliter Syringe Shimadzu were 10 μL and $\pm 0.1 \mu\text{L}$. The peak areas of components were calibrated with gravimetrically prepared mixtures and converted to mole fraction. The results in area fraction were substituted by binary calibration equation (water + 1-propanol) and (1-propanol + β -caryophyllene) to get mole fraction each components.

3. Results and discussion

3.1. Experimental data

The experimental data of the LLE for ternary system β -caryophyllene + 1-propanol + water are presented in table 1. All concentrations are expressed in mole fractions. The ternary diagram of the experimental results can be seen in figures 1-3 for all temperatures studied.

Table 1. Experimental liquid-liquid equilibrium data of β -caryophyllene (1) + 1-propanol (2) + water (3) system at 303.15, 313.15, and 323.15 K.

Temperature (K)	Organic phase			Aqueous phase		
	X ₁	X ₂	X ₃	X ₁	X ₂	X ₃
303.15	0.4683	0.4046	0.1271	0.0890	0.5712	0.3397
	0.6018	0.2956	0.1026	0.0266	0.5188	0.4546
	0.5514	0.3429	0.1057	0.0437	0.5294	0.4269
	0.6758	0.2291	0.0951	0.0157	0.4260	0.5583
	0.7071	0.2006	0.0923	0.0034	0.4108	0.5857
	0.7502	0.1711	0.0788	0.0054	0.2846	0.7100
	0.7554	0.1713	0.0733	0.0043	0.1821	0.8136
	0.8111	0.1220	0.0669	0.0040	0.1399	0.8561
313.15	0.4850	0.4088	0.1063	0.0950	0.5467	0.3583
	0.5962	0.2894	0.1145	0.0268	0.5033	0.4699
	0.5591	0.3308	0.1100	0.0391	0.5258	0.4351
	0.6243	0.2639	0.1118	0.0078	0.4329	0.5594
	0.6843	0.2124	0.1033	0.0063	0.3870	0.6066
	0.7402	0.1689	0.0909	0.0073	0.2591	0.7336
	0.8238	0.0997	0.0765	0.0034	0.1446	0.8519
	0.7709	0.1457	0.0834	0.0066	0.1721	0.8213
323.15	0.4226	0.4276	0.1498	0.1273	0.5334	0.3393
	0.5988	0.2929	0.1083	0.0359	0.4982	0.4660
	0.5557	0.3229	0.1214	0.0572	0.5156	0.4272
	0.6175	0.2702	0.1124	0.0222	0.4173	0.5606
	0.7006	0.2019	0.0975	0.0145	0.3725	0.6130
	0.7423	0.1711	0.0866	0.0041	0.2591	0.7368
	0.8215	0.1059	0.0726	0.0095	0.1110	0.8795
	0.7512	0.1633	0.0855	0.0032	0.1477	0.8491

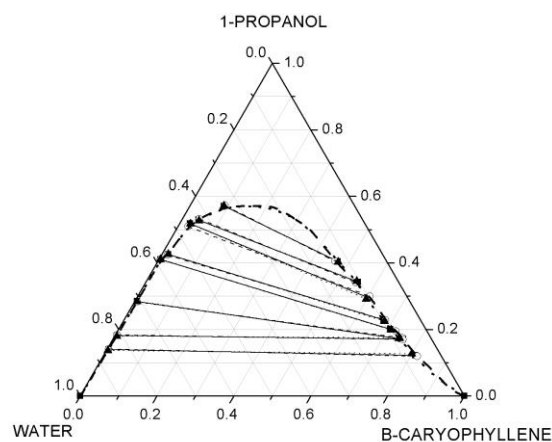


Figure 1. LLE of β -caryophyllene + 1-propanol + water system at 303.15 K; (■) experimental data; (○) correlated by NRTL; (▲) correlated by UNIQUAC; (—) experimental tie lines; (---) NRTL tie lines; (····) UNIQUAC tie lines; binodal curve calculated using: (---) NRTL Model; (····) UNIQUAC Model.

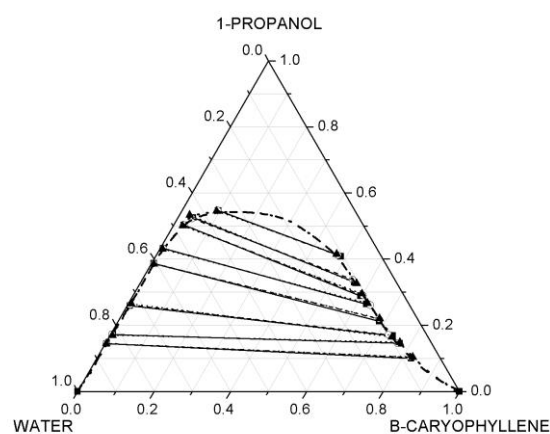


Figure 2. LLE of β -caryophyllene + 1-propanol + water system at 313.15 K; (■) experimental data; (○) correlated by NRTL; (▲) correlated by UNIQUAC; (—) experimental tie lines; (---) NRTL tie lines; (····) UNIQUAC tie lines; binodal curve calculated using: (---) NRTL Model; (····) UNIQUAC Model.

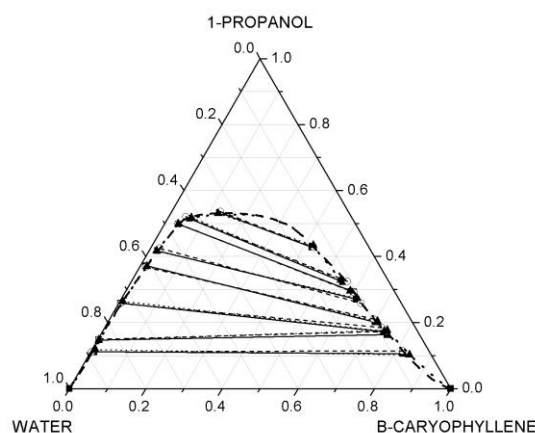


Figure 3. LLE of β -caryophyllene + 1-propanol + water system at 323.15 K; (■) experimental data; (○) correlated by NRTL; (▲) correlated by UNIQUAC; (—) experimental tie lines; (---) NRTL tie lines; (····) UNIQUAC tie lines; binodal curve calculated using: (---) NRTL Model; (····) UNIQUAC Model.

As can be observed on these figures, liquid-liquid equilibria of the ternary mixtures exhibit type I [12] that has one pair of partially miscible components (water + β -caryophyllene) and two pairs of miscible components (β -caryophyllene + 1-propanol and 1-propanol + water). The organic phase is dominated by β -caryophyllene meanwhile water is dominating in aqueous phase. 1-Propanol is more distributed in aqueous phase. It can also be observed that the temperature effect for this system is not significant with a relatively small change in the tie lines for all temperatures.

3.2. Data correlation

The experimental data for all temperatures were correlated using the NRTL and the UNIQUAC equations to obtain binary interaction parameters of the models. These parameters were important for the calculation data. In the NRTL correlation, the non-randomness (α) was set to 0.2 based on chemical characteristic group [10, 13]. This value was used for all binary pairs. For the UNIQUAC model, the structural parameters of the pure components (r_i and q_i) were calculated using the group contribution method and presented in table 2. The correlation results for the binary parameters using the NRTL and the UNIQUAC models are shown in table 3. Figures 1-3 show the equilibrium diagrams for the correlation data along with the experimental data at temperatures 303.15, 313.15, and 323.15 K.

Table 2. Structural parameters r_i and q_i used in UNIQUAC correlation.

Components	r_i	q_i
β -caryophyllene	9.1945	7.364
1-propanol	3.2499	3.128
water	0.92	1.40

Table 3. Binary interaction parameters of NRTL and UNIQUAC models for β -caryophyllene(1) + 1-propanol(2) + water(3) system.

T (K)	Comp (ij)	NRTL parameters			RMSD (%)	UNIQUAC parameters		RMSD (%)
		α	a_{ij} (J/mol)	a_{ji} (J/mol)		a_{ij} (J/mol)	a_{ji} (J/mol)	
303.15	1-2	0.2	1450.19	1475.98	0.48	368.19	-65.79	0.36
	1-3		1606.29	-852.31		640.85	13.49	
	2-3		1338.72	413.23		3389.02	-53.79	
313.15	1-2	0.2	1279.97	1522.86	0.46	-13.33	152.54	0.48
	1-3		1663.61	-888.46		881.40	-68.54	
	2-3		1340.58	296.18		124.86	-96.38	
323.15	1-2	0.2	437.37	1176.78	0.68	119.87	22.28	0.61
	1-3		1718.97	-1028.39		881.48	-49.50	
	2-3		1149.59	-73.24		176.95	-35.47	

The binary parameters for each component were determined by minimizing the differences between the experimental and calculated mole fractions for each component over all the tie lines. The objective function (OF) used as equation (1):

$$OF = \sum_{k=1}^M \sum_{j=1}^2 \sum_{i=1}^3 [x_{ijk} - x_{ijk}^{cal}]^2 \quad (1)$$

where M is the number of tie lines, x indicates the experimental mole fraction, x^{cal} is the calculated mole fraction, and subscripts i, j, k denote component, phase, and tie line respectively. Optimization of the parameters can be evaluated based on the root mean square deviation (RMSD) for both phases. The RMSD between experimental and calculated data are based on equation (2).

$$RMSD = 100 \times \left(\sum_{k=1}^M \sum_{j=1}^2 \sum_{i=1}^3 \frac{[x_{ijk} - x_{ijk}^{cal}]^2}{6M} \right)^{\frac{1}{2}} \quad (2)$$

The calculation of the binary interaction parameters a_{ij} and a_{ji} along with RMSD values given in table 3 was performed separately at each temperature. It can be seen that the UNIQUAC model provides a slightly better correlation than the NRTL model. Based on the RMSD values, both the NRTL and the UNIQUAC models give a good representation for the system β -caryophyllene + 1-propanol + water at all temperatures. The average values of the RMSD calculated by the NRTL and the UNIQUAC models are 0.54 and 0.48 % respectively.

4. Conclusions

Liquid-liquid equilibrium data of β -caryophyllene + 1-propanol + water system at temperatures 303.15, 313.15, and 323.15 K have been measured. The temperature effect of this system is very small. Correlation data using the NRTL and the UNIQUAC models fit the experimental data satisfactorily with the RMSD values are 0.54 and 0.48 % respectively. The UNIQUAC model gives slightly better results than the NRTL model for this system.

Acknowledgments

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