

# Liquid-Liquid Equilibrium for the Binary Mixtures of $\alpha$ -Pinene + Water and $\alpha$ -Terpineol + Water

Herti Utami, Sutijan, Roto, and Wahyudi Budi Sediawan

**Abstract**— $\alpha$ -Pinene is the main component of the most turpentine oils. The hydration of  $\alpha$ -pinene with acid catalysts leads to a complex mixture of monoterpenes. In order to obtain more valuable products, the  $\alpha$ -pinene in the turpentine can be hydrated in dilute mineral acid solutions to produce  $\alpha$ -terpineol. The design of separation processes requires information on phase equilibrium and related thermodynamic properties. This paper reports the results of study on liquid-liquid equilibrium (LLE) of system containing  $\alpha$ -pinene + water and  $\alpha$ -terpineol + water.

Binary LLE for  $\alpha$ -pinene + water system, and  $\alpha$ -terpineol + water systems were determined by experiment at 301K and atmospheric pressure. The two component mixture was stirred for about 30min, then the mixture was left for about 2h for complete phase separation. The composition of both phases was analyzed by using a Gas Chromatograph. The experimental data were correlated by considering both NRTL and UNIQUAC activity coefficient models. The LLE data for the system of  $\alpha$ -pinene + water and  $\alpha$ -terpineol + water were correlated successfully by the NRTL model. The experimental data were not satisfactorily fitted by the UNIQUAC model. The NRTL model ( $\alpha = 0.3$ ) correlates the LLE data for the system of  $\alpha$ -pinene + water at 301K with RMSD of 0.0404%. And the NRTL model ( $\alpha = 0.61$ ) at 301K with RMSD of 0.0058 %. The NRTL model ( $\alpha = 0.3$ ) correlates the LLE data for the system of  $\alpha$ -terpineol + water at 301K with RMSD of 0.1487% and the NRTL model ( $\alpha = 0.6$ ) at 301K with RMSD of 0.0032%, between the experimental and calculated mole fractions.

**Keywords**— $\alpha$ -Pinene,  $\alpha$ -Terpineol, Liquid-liquid Equilibrium, NRTL model, UNIQUAC model

## I. INTRODUCTION

**A**LPHA-PINENE, the major component of turpentine is important compound for fine chemical synthesis and important intermediate in pharmaceutical industry and perfumery [4]. The acid-catalyzed hydration and isomerization of  $\alpha$ -pinene yield a complex mixture of monoterpenes, alcohols, and hydrocarbons. The main products are  $\alpha$ -

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terpineol, limonene, and terpinolene [8]. By controlling the reaction variables it is possible to make the reaction highly selective towards the desired products.  $\alpha$ -Terpineol ( $C_{10}H_{18}O$ ) is the most important of the monocyclic monoterpene alcohols.

In the chemical process industries, fluid mixtures are often separated into their components by operations such as distillation and extraction. Design of such operations requires quantitative estimates of the partial equilibrium properties of fluid mixtures. Unfortunately, such data are often not available. In the literature, it has been found that several LLE systems containing  $\alpha$ -pinene and the other compounds such as the LLE data for ternary  $\alpha$ -pinene +  $\Delta^3$ -carene + polar compound systems [2], LLE for linalool + ethanol + water, water + ethanol + limonene, and limonene + linalool + water ternary systems at 298.15K [3], ternary and quaternary LLE for (water + ethanol +  $\alpha$ -pinene, +  $\beta$ -pinene, or + limonene) and (water + ethanol +  $\alpha$ -pinene + limonene) at the temperature 298.15K [6], and ternary liquid-liquid equilibrium for (water + terpene + 1-propanol or 1-butanol) systems at the temperature 298.15K [7].

This paper reports on the experimental data on LLE of binary mixtures of  $\alpha$ -pinene + water and  $\alpha$ -terpineol + water at the temperature of 301K. The experimental data have also been correlated using the NRTL [9] and UNIQUAC [1] activity coefficient models.

## II. EXPERIMENTAL

$\alpha$ -Pinene was supplied by Aldrich with content of  $\alpha$ -pinene of 99% w/w and  $\alpha$ -Terpineol is 90% w/w (technical grade), distilled water was purchased from General Lab, Yogyakarta, Indonesia.

Liquid-liquid equilibrium was determined at 301K and atmospheric pressure. The two component mixture was stirred for about 30min, then the mixture was left for about 2h for complete phase separation. The composition of both phases was analyzed. The concentration of each component was determined by using a Gas Chromatograph (GC). The analysis was performed with a Hewlett-Packard model 5890 gas chromatograph. The separation was performed using HP-5 capillary column and Flame Ionization Detector with helium as a carrier gas. The GC oven temperature was set at initial temperature of 80°C, held for 5min, increased at a rate of 5°C/min to 115°C and then increased to 280°C at a rate of 20°C/min. The injector and detector temperatures were set at 280°C respectively.

## III. RESULTS AND DISCUSSION

LLE for binary system of  $\alpha$ -pinene + water and  $\alpha$ -terpineol + water were measured at temperature of 301K and atmospheric pressure. The experimental and calculated results were reported in Tables I to IV. The data have been correlated with the NRTL and UNIQUAC models. The optimum NRTL and UNIQUAC binary interaction parameters between  $\alpha$ -pinene + water and  $\alpha$ -terpineol + water were determined by minimizing the differences between the experimental and calculated mole fractions for each of the components over all the tie lines. Comparison of the calculated and experimental

data is expressed in the terms of root mean square deviations (RMSD). The RMSD equation has been defined as follows:

$$\text{RMSD} = 100 \left[ \frac{\sum_{k=1}^M \sum_{j=1}^2 \sum_{i=1}^2 (x_{\text{calc}} - x_{\text{exp}})^2}{6M} \right]^{\frac{1}{2}} \quad (1)$$

where M is the number of tie lines,  $x_{\text{exp}}$  indicates the experimental mol fraction,  $x_{\text{calc}}$  the calculated mole fraction, and subscripts  $i, j$  and  $k$  denote, respectively, component, phase and tie line. It is expected that the RMSD can represent the goodness of fit.

TABLE I  
EXPERIMENTAL AND CALCULATED LLE DATA FOR THE BINARY OF ALPHA-PINENE (1) + WATER (2) SYSTEM AT 301 K

Aqueous phase				
(x <sub>1</sub> ) exp	(x <sub>1</sub> )calc NRTL (ALPHA=0.2)	(x <sub>1</sub> )calc NRTL (ALPHA=0.3)	(x <sub>1</sub> )calc NRTL (ALPHA=0.61)	(x <sub>1</sub> ) calc UNIQUAC
0.000014492	0.000000038	0.000000001	0.000051785	0.005204219
0.000111909	0.000000042	0.000000007	0.000098256	0.005163267
0.000298112	0.000000047	0.000000086	0.000265632	0.004699638
0.000346808	0.000000048	0.000000154	0.000335254	0.004607848
0.000452874	0.000000051	0.000000476	0.000524837	0.004292090
0.000469001	0.000000038	0.000000408	0.000408229	0.002638084
(x <sub>2</sub> ) exp	(x <sub>2</sub> )calc NRTL (ALPHA=0.2)	(x <sub>2</sub> )calc NRTL (ALPHA=0.3)	(x <sub>2</sub> )calc NRTL (ALPHA=0.61)	(x <sub>1</sub> ) calc UNIQUAC
0.999985508	0.999999962	0.999999999	0.999948215	0.994795781
0.999888091	0.999999958	0.999999993	0.999901744	0.994836733
0.999701888	0.999999953	0.999999914	0.999734368	0.995300362
0.999653192	0.999999952	0.999999846	0.999664746	0.995392152
0.999547126	0.999999949	0.999999524	0.999475163	0.995707910
0.999530999	0.999999962	0.999999592	0.999591771	0.997361916

TABLE II  
EXPERIMENTAL AND CALCULATED LLE DATA FOR THE BINARY OF ALPHA-PINENE (1) + WATER (2) SYSTEM AT 301K

Organic phase				
(x <sub>1</sub> ) exp	(x <sub>1</sub> )calc NRTL (ALPHA=0.2)	(x <sub>1</sub> )calc NRTL (ALPHA=0.3)	(x <sub>1</sub> )calc NRTL (ALPHA=0.61)	(x <sub>1</sub> ) calc UNIQUAC
0.703008812	0.690302595	0.702988402	0.702974820	0.745129803
0.700319819	0.689036618	0.700349682	0.700321045	0.366994075
0.654281431	0.650730366	0.654236485	0.654281226	0.591721065
0.645390460	0.643869079	0.645345964	0.645385824	0.652014059
0.613976758	0.617058688	0.613939939	0.613967360	0.755972947
0.444613146	0.457041243	0.444639064	0.444642049	0.478713128
(x <sub>2</sub> ) exp	(x <sub>2</sub> )calc NRTL (ALPHA=0.2)	(x <sub>2</sub> )calc NRTL (ALPHA=0.3)	(x <sub>2</sub> )calc NRTL (ALPHA=0.61)	(x <sub>1</sub> ) calc UNIQUAC
0.296991188	0.309697405	0.297011598	0.297025180	0.254870197
0.299680181	0.310963382	0.299650318	0.299678955	0.633005925
0.345718569	0.349269634	0.345763515	0.345718774	0.408278935
0.354609540	0.356130921	0.354654036	0.354614176	0.347985941
0.386023242	0.382941312	0.386060061	0.386032640	0.244027053
0.555386854	0.542958757	0.555360936	0.555357951	0.521286872

TABLE III  
EXPERIMENTAL AND CALCULATED LLE DATA FOR THE BINARY OF ALPHA-TERPINEOL (1) + WATER (2) SYSTEM AT 301K

Aqueous phase				
(x <sub>1</sub> ) exp	(x <sub>1</sub> )calc NRTL (ALPHA=0.2)	(x <sub>1</sub> )calc NRTL (ALPHA=0.3)	(x <sub>1</sub> )calc NRTL (ALPHA=0.6)	(x <sub>1</sub> ) calc UNIQUAC
0.000060053	0.075988881	0.000022525	0.000075592	0.017819894
0.000060865	0.075484361	0.000022255	0.000074990	0.017532644
0.000079222	0.075151992	0.000022253	0.000082626	0.017319046
0.000110107	0.074958436	0.000022453	0.000097784	0.017170614
0.000192846	0.074839525	0.000023234	0.000151496	0.017008580
0.000473016	0.071447000	0.000023699	0.000484802	0.014434744
(x <sub>2</sub> ) exp	(x <sub>2</sub> )calc NRTL (ALPHA=0.2)	(x <sub>2</sub> )calc NRTL (ALPHA=0.3)	(x <sub>2</sub> )calc NRTL (ALPHA=0.6)	(x <sub>2</sub> ) calc UNIQUAC
0.999939947	0.924011119	0.999977475	0.999924408	0.982180106
0.999939135	0.924515639	0.999977745	0.999925010	0.982467356
0.999920778	0.924848008	0.999977747	0.999917374	0.982680954

0.999889893	0.925041564	0.999977547	0.999902216	0.982829386
0.999807154	0.925160475	0.999976766	0.999848504	0.982991420
0.999526984	0.928553000	0.999976301	0.999515198	0.985565256

TABLE IV  
EXPERIMENTAL AND CALCULATED LLE DATA FOR THE BINARY OF ALPHA-TERPINEOL (1) + WATER (2) SYSTEM AT 301K

Organic phase				
(x <sub>1</sub> ) exp	(x <sub>1</sub> )calc NRTL (ALPHA=0.2)	(x <sub>1</sub> )calc NRTL (ALPHA=0.3)	(x <sub>1</sub> )calc NRTL (ALPHA=0.6)	(x <sub>1</sub> ) calc UNIQUAC
0.717401483	0.658237488	0.717253375	0.717378495	0.785992108
0.708333503	0.659435512	0.708577540	0.708312237	0.765648178
0.702047187	0.744039378	0.704409467	0.702037788	0.642906780
0.698117356	0.758504072	0.700000776	0.698123361	0.568382078
0.694981125	0.557419866	0.693803767	0.695002410	0.568952499
0.620884567	0.630676235	0.621028800	0.620880191	0.737680785
(x <sub>2</sub> ) exp	(x <sub>2</sub> )calc NRTL (ALPHA=0.2)	(x <sub>2</sub> )calc NRTL (ALPHA=0.3)	(x <sub>2</sub> )calc NRTL (ALPHA=0.6)	(x <sub>2</sub> ) calc UNIQUAC
0.282598517	0.341762512	0.282746625	0.282621505	0.214007892
0.291666497	0.340564488	0.291422460	0.291687763	0.234351822
0.297952813	0.255960622	0.295590533	0.297962212	0.357093220
0.301882644	0.241495928	0.299999224	0.301876639	0.431617922
0.305018875	0.442580134	0.306196233	0.304997590	0.431047501
0.379115433	0.369323765	0.378971200	0.379119809	0.262319215

In the UNIQUAC model, the values of volume and surface area parameter of pure component  $r_i$  and  $q_i$ , for water and  $\alpha$ -pinene have been taken from literature [6]. The volume and surface area of the  $\alpha$ -terpineol was estimated from the Bondi's method [5]. The pure-component molecular parameters,  $r_i$  and  $q_i$  were listed in Table V. In the NRTL model, for all binary pairs, the value of the non randomness parameter ( $\alpha$ ) was set as 0.2, 0.3 and obtained from fitting.

TABLE V  
THE VOLUME AND SURFACE AREA PARAMETERS FOR THE UNIQUAC MODEL

	$\alpha$ -Pinene	$\alpha$ -Terpineol	Water
$r$	6.056	7.0389	0.920
$q$	4.760	5.8800	1.400

For binary system,  $\alpha$ -pinene (1) + water (2), the result is shown in Fig. 1. The calculated points are relatively very close to the experimental ones for the NRTL model, so it proves that the model can well approximate the equilibrium data.

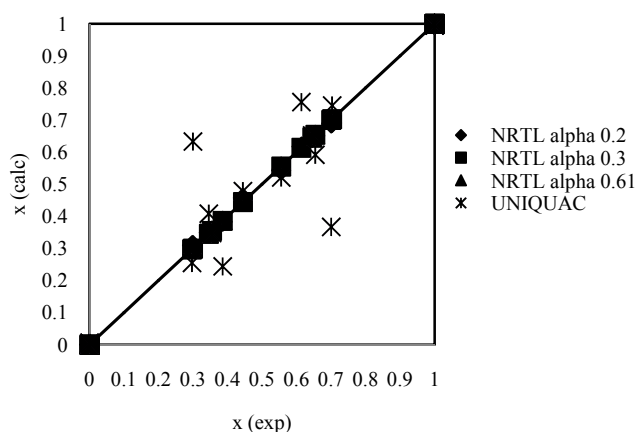


Fig. 1 Liquid – liquid equilibrium calculation and experimental data for the system  $\alpha$ -pinene (1) + water (2) at 301K

For binary system,  $\alpha$ -terpineol (1) + water (2), the result is shown in Fig. 2. The calculated values are in good agreement with experimental ones for the NRTL model, except the value of the non randomness parameter ( $\alpha$ ) = 0.2. The experimental data are not satisfactorily fitted by the UNIQUAC model.

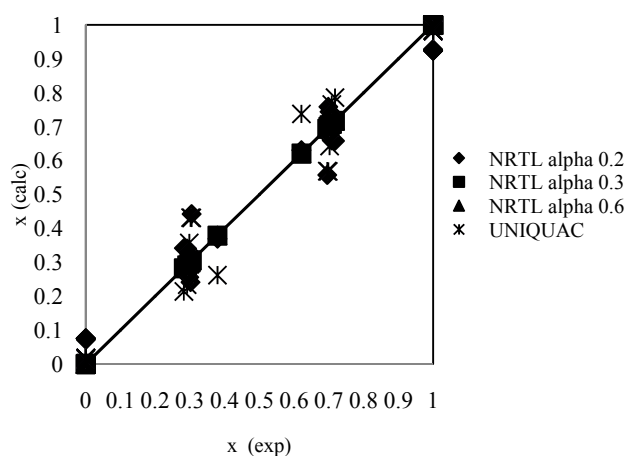


Fig. 2 Liquid – liquid equilibrium calculation and experimental data for the system  $\alpha$ -terpineol (1) + water (2) at 301 K

Tables VI, VII and VIII summarize the values of the binary parameters obtained fitting the models to the experimental binary LLE system. The deviation between experimental and calculated values expressed in terms of the root mean square deviations (RMSD) defined by using (1).

TABLE VI  
INTERACTION PARAMETERS OF THE NRTL MODEL FOR THE BINARY OF ALPHA-PINENE (1) + WATER (2) SYSTEM AT 301K

Parameters of NRTL				
$\alpha$ (alpha)	pairs	$b_{ij}$ (Jmol <sup>-1</sup> )	$b_{ji}$ (Jmol <sup>-1</sup> )	RMSD (%)
0.2	1-2	-8.127e-008	10015.5609	1.0528
0.3	1-2	-8.8127e-010	12165.3934	0.0404
0.61	1-2	-5.8505e-007	5752.8896	0.0058

TABLE VII  
INTERACTION PARAMETERS OF THE NRTL MODEL FOR THE BINARY OF  
ALPHA-TERPINEOL (1) + WATER (2) SYSTEM AT 301K

Parameters of NRTL				
$\alpha$ (alpha)	pairs	$b_{ij}$ (Jmol <sup>-1</sup> )	$b_{ji}$ (Jmol <sup>-1</sup> )	RMSD (%)
0.2	1-2	-36.8323	1483.9311	14.0594
0.3	1-2	-0.02847	6221.026	0.1487
0.6	1-2	-8.4082e-007	5693.1474	0.0032

TABLE VIII  
INTERACTION PARAMETERS OF THE UNIQUAC MODEL

Parameters of UNIQUAC				
System	pairs	$u_{ij}$ (Jmol <sup>-1</sup> )	$u_{ji}$ (Jmol <sup>-1</sup> )	RMSD (%)
$\alpha$ -Pinene+Water	1-2	-85.9232	361.0679	14.6751
$\alpha$ -Terpineol+Water	1-2	577.5684	-183.1829	14.9140

In fitting the models to the binary LLE data, it was satisfactorily fitted by the NRTL model. The NRTL model ( $\alpha=0.3$ ) correlates the LLE data for the system of  $\alpha$ -pinene (1) + water (2) at 301K with RMSD of 0.0404%. And the NRTL model ( $\alpha=0.61$ ) at 301K with RMSD of 0.0058%. The NRTL model ( $\alpha=0.3$ ) correlates the LLE data for the system of  $\alpha$ -terpineol (1) + water (2) at 301K with RMSD of 0.1487% and the NRTL model ( $\alpha=0.6$ ) at 301K with RMSD of 0.0032%, between the experimental and calculated mole fractions.

The UNIQUAC model correlates the LLE data for the binary system of  $\alpha$ -pinene (1) + water (2) at 301K with RMSD of 14.6751%, and the LLE data for the system of  $\alpha$ -terpineol (1) + water (2) at 301K with RMSD of 14.914%. In the UNIQUAC model, it was found high deviations between the experimental and correlated data.

#### IV. CONCLUSION

The experimental data on liquid-liquid equilibrium of binary mixtures of  $\alpha$ -pinene (1) + water (2) and  $\alpha$ -terpineol (1) + water (2) were obtained at the temperature of 301K and atmospheric pressure. The NRTL and UNIQUAC models were used to correlate the experimental LLE data. The optimum NRTL and UNIQUAC parameters were determined using the experimental liquid-liquid equilibrium data. It was found that the NRTL model fitted satisfactorily to the experimental data. In the UNIQUAC model, it was found high deviations between the experimental and correlated data. The experimental data were not satisfactorily fitted by the UNIQUAC model.

#### NOMENCLATURE

$b_{ij}$	interaction parameter in the NRTL equation
$u_{ij}$	interaction parameter in the UNIQUAC equation
LLE	liquid-liquid equilibrium
NRTL	non random two liquid
T	temperature (K)
UNIQUAC	universal quasi chemical equation
x	composition in mole fraction
$\alpha$ (alpha)	non randomness parameter in the NRTL equation

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