Liquid-Liquid Equilibrium for System Composed of α-Pinene, α-Terpineol and Water

Herti Utami, Sutijan, Roto, and Wahyudi Budi Sediawan

***Abstract*—The major component of turpentine is α-pinene and the main hydration product of α-pinene is α-terpineol. To obtain the optimal process design of α-terpineol production, some initial information regarding the principle of the thermodynamics and phase equilibrium are required. The aim of this paper is to present liquid-liquid equilibrium (LLE) of system containing α-pinene, α-terpineol and water. Ternary LLE for α-pinene, α-terpineol and water system was determined by experiment at the temperatures of 301, 327 and 353 K and atmospheric pressure. The three component mixture was stirred for about 30 min, then the mixture was left for about 2 h for complete phase separation. The composition of both phases was analyzed by using a Gas Chromatograph. The thermodynamic equilibrium models were proposed. LLE model in this study includes activity coefficient model based on NRTL and UNIQUAC models. The NRTL model (α = 0.2) correlates the LLE data for the system of α-pinene + α-terpineol + water at the temperatures 301, 327 and 353 K with RMSD of 0.5464%, 0.000169% and 0.0054%, respectively. The UNIQUAC model correlates the LLE data for the system of α-pinene + α-terpineol + water at the temperatures 301, 327 and 353 K with RMSD of 0.756%, 1.314% and 1.6615%, respectively. The LLE data for the system of α-pinene + α-terpineol + water were successfully correlated using the NRTL and UNIQUAC models at that temperatures.**

***Index Terms*—α-Pinene, α-terpineol, liquid-liquid equilibrium.**

I. Introduction

α-Pinene, one of the most widespread bicyclic monoterpenes, is a chiral compound obtained from turpentine. This compound which is used in the synthesis of a variety of chemicals, such as α-terpineol which is widely used as flavor in the cosmetic industry, as mineral flotation in the mineral benefit industry, and as antifungal and disinfectant in the pharmaceutical industry [1]. Therefore, the direct hydration of turpentine to synthesize α-terpineol has an important value in industrial application. During the process of α-terpineol production, some initial information regarding the principle of the thermodynamics and phase equilibrium are required.

The design of separation processes requires information on phase equilibrium and related thermodynamic properties. However, information related to LLE involving terpenes and water is relatively scarce in the literature. LLE information for α-pinene + Δ3 carene + polar compound (acetonitrile, nitromethane, and dimethylformamide) systems has been studied [2]. Hengde Li studied the ternary LLE for water + ethanol + α-pinene, + β-pinene, or + limonene and quaternary LLE for water + ethanol + α-pinene + limonene systems at the temperature of 298.15K [3]. The authors also report data for ternary LLE for water + terpene + 1-propanol or 1-butanol systems at the same temperature [4]. Xiaoli Li studied the ternary liquid-liquid equilibrium for water + acetone + α-pinene, + β-pinene, or + limonene mixtures [5] and Ghizellaoui studied the LLE of water + 1-propanol + 1-pentanol system at 298.15 and 323.15 K [6]. Gramajo studied the LLE of water + linalool + limonene ternary system [7] and Bilgin studied the LLE of water + propionic acid + oleyl alcohol ternary system at several temperatures [8].

This paper reports on the experimental data on liquid-liquid equilibrium of ternary mixtures of α-pinene + α-terpineol + water at the temperatures of 301, 327 and 353 K. It is generally believed that LLE are influenced by several factors including the nature of the components, concentrations in both phases, and temperature of the system [9]. To predict LLE in multi component system, it needs adequate equilibrium model. This paper also reports the theoretical studies on this system. NRTL [10] and UNIQUAC [11] models are used to correlate the phase equilibrium in the system using the interaction parameters determined from the experimental data.

II. Experimental

α-Pinene was purchased from Alfa Kimia, Yogyakarta, Indonesia. The content of α-pinene is 99% w/w (Aldrich) and α-Terpineol is 90% w/w, technical grade (Aldrich), distilled water was purchased from General Lab, Yogyakarta, Indonesia.

Liquid-liquid equilibrium was determined at 301 and 353 K temperatures. The three component mixture was stirred for about 30 min, then the mixture was left for about 2 h for complete phase separation. The composition of both phases was analyzed. 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 5 min, increased at a rate of 5°C/min to 115°C and then increased to 280°C at a rate of

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20°C/min. The injector and detector temperatures were set at 280°C respectively.

TABLE I: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 301 K

Aqueous phase

(x_1) exp	(x_1)calc NRTL (ALPHA=0.68)	(x_1) calc UNIQUAC
0.000002225	0.000192424	0.001011309
0.000004267	0.000157599	0.000802614
0.000019032	0.000158519	0.000767702
0.000033192	0.000144116	0.000655445
0.000036191	0.000134829	0.000601017
0.000104414	0.000157205	0.000572298

TABLE II: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 301 K

Aqueous phase

(x_2) exp	(x_2)calc NRTL (ALPHA=0.68)	(x_2) calc UNIQUAC
0.000010082	0.000044693	0.000283883
0.000024375	0.000054624	0.000301635
0.000021976	0.000055809	0.000312639
0.000040927	0.000071048	0.000342576
0.000052685	0.000077049	0.000337998
0.000126311	0.000116041	0.000329832

TABLE III: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 301 K

Aqueous phase

(x_3) exp	(x_3)calc NRTL (ALPHA=0.68)	(x_3) calc UNIQUAC
0.999987693	0.999762883	0.998704808
0.999971359	0.999787777	0.998895750
0.999958992	0.999785672	0.998919659
0.999925881	0.999784836	0.999001979
0.999911124	0.999788122	0.999060985
0.999769274	0.999726754	0.999097870

TABLE IV: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 301 K

Organic phase

(x_1) exp	(x_1)calc NRTL (ALPHA=0.68)	(x_1) calc UNIQUAC
0.564726685	0.564700622	0.557989595
0.451498317	0.451399494	0.453578837
0.432219468	0.432120367	0.433870732
0.370363017	0.370340900	0.371675496
0.341529596	0.341561288	0.345625693
0.328045769	0.328101275	0.334104587

TABLE V: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 301 K

Organic phase

(x_2) exp	(x_2)calc NRTL (ALPHA=0.68)	(x_2) calc UNIQUAC
0.318301276	0.318456456	0.311479336
0.345289912	0.345294882	0.343838283
0.358439524	0.358416912	0.356361307
0.395538159	0.395476427	0.392366941
0.394719656	0.394664687	0.395456963
0.390350616	0.390300587	0.394139561

TABLE VI: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 301 K

Organic phase

(x_3) exp	(x_3)calc NRTL (ALPHA=0.68)	(x_3) calc UNIQUAC
0.116972039	0.116842922	0.130531069
0.203211772	0.203305624	0.202582879
0.209341009	0.209462721	0.209767961
0.234098824	0.234182673	0.235957563
0.263750748	0.263774025	0.258917343
0.281603615	0.281598138	0.271755852

TABLE VII: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 327 K

Aqueous phase

(x_1) exp	(x_1)calc NRTL (ALPHA=0.65)	(x_1) calc UNIQUAC
0.000008650	0.000035108	0.000023123
0.000009954	0.000031517	0.000020449
0.000038964	0.000046471	0.000019896
0.000058617	0.000054768	0.000018412
0.000064382	0.000051434	0.000016498
0.000072607	0.000046076	0.000015096

TABLE VIII: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 327 K

Aqueous phase

(x_2) exp	(x_2)calc NRTL (ALPHA=0.65)	(x_2) calc UNIQUAC
0.000000000	0.000025821	0.000641272
0.000000000	0.000025915	0.000642158
0.000001112	0.000026189	0.000635522
0.000010255	0.000031225	0.000662790
0.000025561	0.000039070	0.000660995
0.000105242	0.000108801	0.000666428

TABLE IX: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 327 K

Aqueous phase

(x_3) exp	(x_3)calc NRTL (ALPHA=0.65)	(x_3) calc UNIQUAC
0.999991135	0.999939071	0.999335605
0.999990046	0.999942569	0.999337393
0.999959924	0.999927340	0.999344583
0.999931128	0.999914007	0.999318798
0.999910057	0.999909496	0.999322507
0.999822151	0.999845123	0.999318476

III. RESULTS AND DISCUSSION

Liquid-liquid equilibrium for ternary system of α-pinene, α-terpineol and water was measured at 301, 327 and 353 K and atmospheric pressure. The experimental and calculated results were shown on Tables I to XVIII. Six effective binary interaction parameters are required for ternary system. The optimum NRTL and UNIQUAC binary interaction parameters were determined by minimizing the differences between the experimental and calculated mole fractions for each of the components over all the tie lines. The Root Mean Square Deviations (RMSD) has been defined as follows:

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

where M is the number of tie lines, x_{exp} indicates the experimental mol fraction, x_{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 X: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 327 K

Organic phase

(x_1) exp	(x_1)calc NRTL (ALPHA=0.65)	(x_1) calc UNIQUAC
0.501655204	0.501662594	0.512785063
0.445442353	0.445431259	0.446315119
0.434455541	0.434443370	0.433110660
0.402987883	0.402978593	0.399372670
0.363334566	0.363337914	0.355119378
0.334778001	0.334798850	0.324655959

TABLE XI: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 327 K

Organic phase

(x_2) exp	(x_2)calc NRTL (ALPHA=0.65)	(x_2) calc UNIQUAC
0.360829708	0.360847055	0.372298428
0.365779133	0.365773277	0.369989707
0.363790691	0.363783360	0.366097753
0.381083792	0.381068561	0.381720314
0.384943674	0.384936712	0.380641529
0.392538688	0.392548579	0.385590983

TABLE XII: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 327 K

Organic phase

(x_3) exp	(x_3)calc NRTL (ALPHA=0.65)	(x_3) calc UNIQUAC
0.137515088	0.137490351	0.114916509
0.188778514	0.188795464	0.183695173
0.201753768	0.201773269	0.200791587
0.215928325	0.215952846	0.218907016
0.251721760	0.251725375	0.264239092
0.272683311	0.272652571	0.289753058

TABLE XIII: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 353 K

Aqueous phase

(x_1) exp	(x_1)calc NRTL (ALPHA=0.64)	(x_1) calc UNIQUAC
0.000002301	0.000010001	0.001324097
0.000019182	0.000017767	0.001257396
0.000027211	0.000023176	0.001249681
0.000068792	0.000068641	0.001102542
0.000082478	0.000092951	0.001071039
0.000078188	0.000062100	0.000786337

TABLE XIV:EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A -PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 353K

Aqueous phase

(x_2) exp	(x_2)calc NRTL (ALPHA=0.64)	(x_2) calc UNIQUAC
0.000000000	0.000000470	0.007237430
0.000000000	0.000000496	0.007621110
0.000000000	0.000000508	0.007826990
0.000000000	0.000000533	0.008123779
0.000013844	0.000009768	0.008634235
0.000020252	0.000027933	0.009387390

TABLE XV: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 353 K

Aqueous phase

(x_3) exp	(x_3)calc NRTL (ALPHA=0.64)	(x_3) calc UNIQUAC
0.999997699	0.999989528	0.991438473
0.999980818	0.999981738	0.991121494
0.999972789	0.999976316	0.990923330
0.999931208	0.999930826	0.990773679
0.999903678	0.999897281	0.990294727
0.999901560	0.999909967	0.989826272

TABLE XVI: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 353 K

Organic phase

(x_1) exp	(x_1)calc NRTL (ALPHA=0.64)	(x_1) calc UNIQUAC
0.451655204	0.451656189	0.455993227
0.429172353	0.429172818	0.430126648
0.426216241	0.426216366	0.421906815
0.377987883	0.377987829	0.382681678
0.366677111	0.366676270	0.361239026
0.271290444	0.271289167	0.276134517

TABLE XVII: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 353 K

Organic phase

(x_2) exp	(x_2)calc NRTL (ALPHA=0.64)	(x_2) calc UNIQUAC
0.338416677	0.338417471	0.340612301
0.356664246	0.356664699	0.355651610
0.365543443	0.365543787	0.359279289
0.383345147	0.383344968	0.386051510
0.405789459	0.405788978	0.395786865
0.448373084	0.448371495	0.452642847

TABLE XVIII: EXPERIMENTAL AND CALCULATED LLE DATA FOR THE TERNARY OF A-PINENE (1) + A-TERPINEOL (2) + WATER (3) SYSTEM AT 353 K

Organic phase

(x_3) exp	(x_3)calc NRTL (ALPHA=0.64)	(x_3) calc UNIQUAC
0.209928119	0.209926340	0.203394472
0.214163401	0.214162483	0.214221742
0.208240315	0.208239847	0.218813896
0.238666970	0.238667203	0.231266812
0.227533430	0.227534753	0.242974109
0.280336472	0.280339338	0.271222636

TABLE XIX: THE VOLUME AND SURFACE AREA PARAMETERS FOR THE UNIQUAC MODEL

	α-Pinene	α-Terpineol	Water
r	6.056	7.0389	0.920
q	4.760	5.8800	1.400

In the UNIQUAC model, the values of volume and surface area parameter of pure component r_i and q_i, for water and α-pinene have been taken from literature [3]. The volume and surface area of the α-terpineol was estimated from the Bondi's method [12]. The pure-component molecular parameters, r_i and q_i were listed in Table XIX. In the NRTL model, the values of the non randomness parameter (α) was set as 0.2 and obtained from fitting.

The values of interaction parameters for the NRTL and

UNIQUAC models at different temperatures are shown in Tables XX to XXIII. The deviation between experimental and calculated values, expressed in terms of the root mean square deviations (RMSD) defined by using (1).

TABLE XX: INTERACTION PARAMETERS OF THE NRTL MODEL FOR THE TERNARY OF ALPHA-PINENE (1) + ALPHA-TERPINEOL (2) + WATER (3) SYSTEM AT 301 K

Parameters of NRTL				
α(alpha)	pairs	bij ($Jmol^{-1}$)	bji ($Jmol^{-1}$)	RMSD (%)
0.2	1-2	4363.2449	-323.2558	0.5464
	1-3	7964.4715	7994.0665	
	2-3	-1952.7141	8490.8635	
0.68	1-2	-213.6191	662.6515	0.0233
	1-3	4777.8387	5141.9908	
	2-3	5306.6406	5878.5794	

TABLE XXI: INTERACTION PARAMETERS OF THE NRTL MODEL FOR THE TERNARY OF ALPHA -PINENE (1) + ALPHA -TERPINEOL (2) + WATER (3) SYSTEM AT 327 K

Parameters of NRTL				
α(alpha)	pairs	bij ($Jmol^{-1}$)	bji ($Jmol^{-1}$)	RMSD (%)
0.2	1-2	-45041.503	27272.681	0.000169
	1-3	48895.3203	31335.093	
	2-3	0.5576	-7563.4117	
0.65	1-2	488.5559	-309.3192	0.000049
	1-3	5652.4886	7305.7548	
	2-3	8197.413	7314.2554	

TABLE XXII: INTERACTION PARAMETERS OF THE NRTL MODEL FOR THE TERNARY OF ALPHA -PINENE (1) + ALPHA -TERPINEOL (2) + WATER (3) SYSTEM AT 353 K

Parameters of NRTL				
α(alpha)	pairs	bij ($Jmol^{-1}$)	bji ($Jmol^{-1}$)	RMSD (%)
0.2	1-2	-67.306	90877.4904	0.0054
	1-3	60890.8031	34522.7342	
	2-3	25926.1675	38171.0575	
0.64	1-2	6876.9054	4744.9432	0.0008
	1-3	16042.7182	8985.6788	
	2-3	43413.1749	10791.1033	

TABLE XXIII: INTERACTION PARAMETERS OF THE UNIQUAC MODEL FOR THE TERNARY OF ALPHA-PINENE (1) + ALPHA-TERPINEOL (2) + WATER (3) SYSTEM

Parameters of UNIQUAC				
Temperature, K	pairs	uij ($Jmol^{-1}$)	uji ($Jmol^{-1}$)	RMSD (%)
301	1-2	-885.2238	878.8773	0.7560
	1-3	4359.9185	498.7212	
	2-3	-1207.1664	6368.9558	
327	1-2	-318.9388	-528.671	1.3140
	1-3	6464.8237	90.6234	
	2-3	675.4101	-164.7618	
353	1-2	-1079.2635	267.9923	1.6615
	1-3	19890.7311	-469.4888	
	2-3	-223.578	90.5193	

The experimental tie lines data and the correlated results of the ternary LLE of the α-pinene, α-terpineol and water system at 301, 327 and 353 K in terms of NRTL and UNIQUAC models are shown in Fig. 1, 2 and 3.

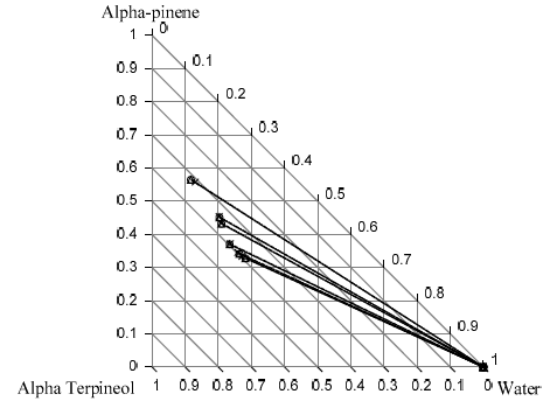

Fig. 1. Experimental and calculated LLE data of the α-pinene + α-terpineol + water system at T= 301 K. (O —— experiment; Δ – – – NRTL model; x – · – · – UNIQUAC model)

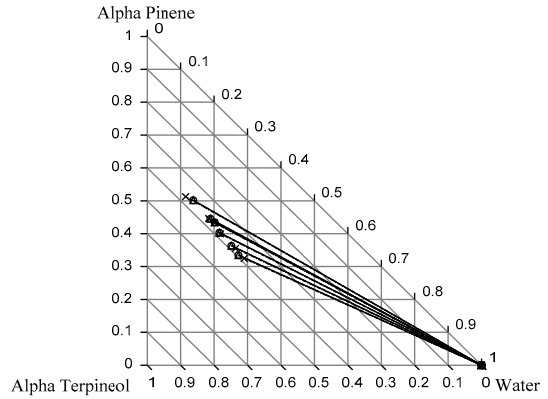

Fig. 2. Experimental and calculated LLE data of the α-pinene + α-terpineol + water system at T= 327 K. (O —— experiment; Δ – – – NRTL model; x – · – · – UNIQUAC model)

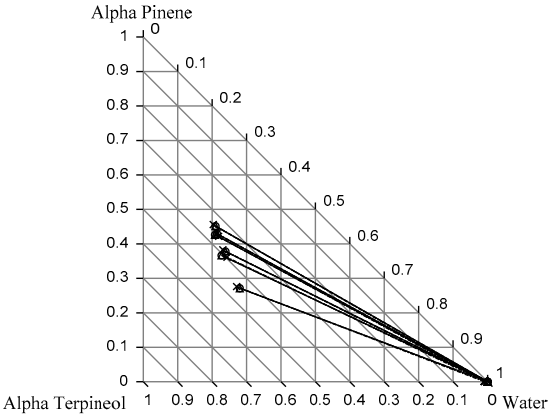

Fig. 3. Experimental and calculated LLE data of the α-pinene + α-terpineol + water system at T= 353 K. (O —— experiment; Δ – – – NRTL model; x – · – · – UNIQUAC model)

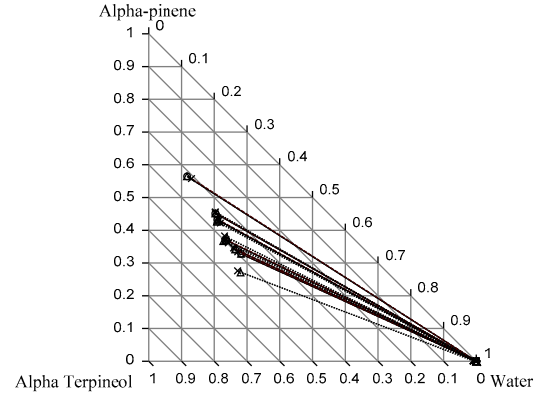

Fig. 4. Experimental and calculated LLE data of the α-pinene + α-terpineol + water system at T= 301, 327, and 353 K. (O —— experiment; Δ NRTL model ; x UNIQUAC model ; – – – 301 K; ····· 327 K; – · – 353 K)

In fitting the models to the ternary LLE data, the two models well represented the ternary system. The NRTL model (α = 0.2) correlates the LLE data for the system of α-pinene + α-terpineol + water at the temperatures 301, 327 and 353 K with RMSD of 0.5464%, 0.000169% and 0.0054%, respectively. And the NRTL model (α = 0.68) at the temperature 301 K with RSMD of 0.0233%, the NRTL model (α=0.65) at the temperature 327 K with RSMD of 0.000049% and the NRTL model (α=0.64) at the temperature 353 K with RSMD of 0.0008%, between the experimental and calculated mole fractions.

The UNIQUAC model correlates the LLE data for the system of α-pinene + α-terpineol + water at the temperatures 301, 327 and 353 K with RMSD of 0.756%, 1,314% and 1.6615%, respectively. The results show that the RMSD for the ternary systems are less than 2%. In Fig. 4 the slope of tie lines changes slightly with the different temperatures.

The calculated points are relatively very close to the experimental ones, so it proves that the models proposed can well approximate the equilibrium data.

IV. Conclusion

The experimental data on liquid-liquid equilibrium of ternary mixtures of α-pinene + α-terpineol + water were obtained at the temperatures of 301, 327 and 353 K. 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 data. It was found that both the NRTL and UNIQUAC methods fitted satisfactorily to the experimental data. The results show that the RMSD for the ternary systems are less than 2%.

Notification

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
α (alpha)	non randomness parameter in the NRTL equation

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