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Liquid−Liquid Equilibria of Methanol, Ethanol, and Propan-2-ol with Water and Dodecane

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ABSTRACT: Ternary liquid−liquid equilibrium (LLE) data were measured and their binodal curves and tie-lines correlated at atmospheric pressure for the systems methanol + water + dodecane at $T = (298.14 \text{ and } 313.14)$ K, ethanol + water + dodecane at $T = (298.14, 313.14, 323.15, \text{ and } 333.15)$ K, and propan-2-ol + water + dodecane at $T = (328.15 \text{ and } 333.15)$ K. The LLE data were measured using the direct analytical technique with a double-walled glass cell. It was found that no plait point could be observed for the ternary system consisting of methanol + water + dodecane; however the miscibility in the system was greatly increased by increasing the carbon chain-length of the alcohol, as well as increasing the equilibrium temperature of the system. The trends observed were consistent with those observed for similar systems in literature. The binodal curves were correlated using the Hlavatý equation, a β function equation, and a log γ equation. It was found that the log γ equation provided the best fit to the experimental data for all of the systems measured. The tie-line data were correlated using both the nonrandom two-liquid (NRTL) and universal quasichemical (UNIQUAC) Gibbs excess models. It was found that the best fit was obtained with the NRTL equation.

INTRODUCTION

To remove light alcohols from water in certain petrochemical streams, solvent extraction can be used with dodecane serving as a potential solvent. After removal of the light alcohols from the water, it would be fairly simple to separate the alcohols from the solvent (i.e., the dodecane) by distillation due to the large differences in boiling points between the two chemicals. In such a process, it is clear that the dodecane and water will necessarily come into physical contact. Due to the fact that water and dodecane are highly immiscible, it will result in the formation of two liquid phases: an aqueous (water-rich) phase and an organic phase (dodecane-rich). Hence, it is important to accurately measure phase equilibrium data for the systems concerned. To this end, liquid−liquid equilibrium (LLE) measurements were undertaken in this study for methanol, ethanol, and propan-2-ol with water and dodecane which form ternary mixtures at various temperatures and atmospheric pressure. Pressure variation was unnecessary as liquids are largely unaffected by pressure changes, and additionally, any Gibbs excess parameters which are regressed from such LLE data are independent of pressure.

EXPERIMENTAL SECTION

Materials. The dodecane and alcohols were obtained from Merck Ltd., as well as Capital Laboratory Suppliers. The distilled water was produced on site in the laboratories. The purities of the various chemicals were determined by analyzing both the refractive index and the density. Gas chromatography analysis using a thermal conductivity detector revealed no significant impurities, and the measured refractive indices and densities agreed closely with the literature. The results of the purity analysis are presented in Table 1.

Equipment. The apparatus used for the measurements is illustrated in Figure 1 and is the same as that used by Narasigadu et al.[1] The experimental setup consisted of the following pieces of equipment: a double-walled glass LLE cell, a stirrer with motor, a Labotec water bath with a Grant GD 120 temperature controller, and pump containing an aqueous ethylene glycol solution for thermoregulation, two Pt-100 temperature probes with displays, and a Julabo FT 200 coldfinger. For phase sample analysis, a Shimadzu 2010 gas chromatograph (GC) equipped with a thermal conductivity detector was used to analyze the systems containing methanol and ethanol at (298.14 and 313.14) K. The GC was operated with a CWAX 20 M bonded column of 30 m length with an internal diameter of 0.53 mm. A Hewlett-Packard 5890 Series II gas chromatograph was used to analyze the remaining systems. This GC was also operated with a thermal conductivity detector and had a 2.5 m long stainless steel column with a 2.2 mm diameter, which was packed with 80/100 mesh Chromosorb P. Helium was used as the carrier gas in both gas chromatographs.

A detailed description of the equilibrium cell and experimental apparatus can be found in the work of Ndlovu,[2] and the experimental procedure is described by Narasigadu et al.[1] The uncertainty in the composition analysis was within 0.007 mole fraction, and the uncertainty in the temperature measurement was within 0.02 K. The procedure for calibrating the GC was the area ratio method as discussed by Raal and Mühlbauer.[3]

DATA CORRELATION

The data measured in this study were correlated along the binodal curves, as well as for tie-line data sets between the two liquid phases in equilibrium. Three different empirical equations were used for the binodal curve correlation, and two Gibbs excess models were used for the tie-line correlation.

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Table 1. Purity Analysis

			measured $\rho^{a,d}$	$\rho^{a,d,19}$				
species	measured $n_D{}^{a,c}$	$n_D{}^{a,c,19}$	$kg \cdot m^{-3}$	$kg \cdot m^{-3}$	GC area fraction	GC area fraction^b	volume fraction purity^b	mass fraction purity^b
methanol	1.32862	1.3288	791.46	791.4	1.000	≥ 0.999		
ethanol	1.36162	1.3611	792.05	789.3	0.999		≥0.998	
propan-2-ol	1.37709	1.375	785.46	785.5	0.999			≥0.995
dodecane	1.42155	1.4216	749.6	748.7	1.000	≥ 0.990		
water	1.33303	1.33299	998.1	998.23	1.000			

[a] At T = 293.15 K. [b] According to the suppliers, Merck Ltd. and Capital Laboratory Suppliers. [c] n_D is the refractive index. [d] ρ is the density.

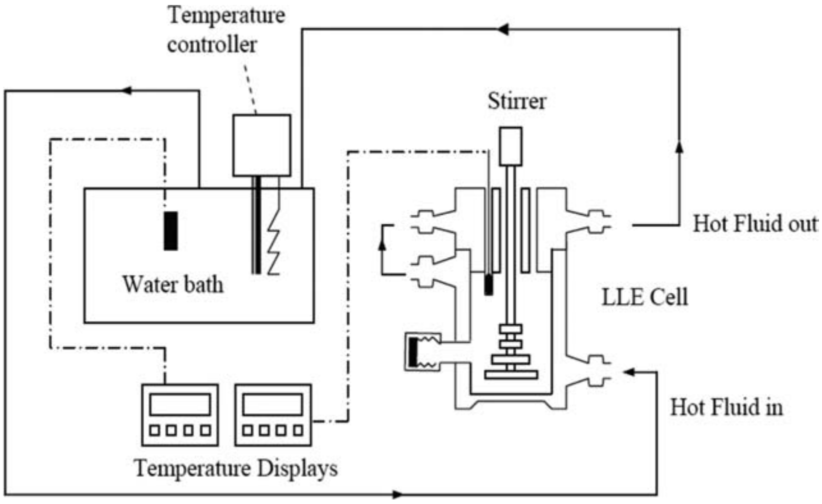

Figure 1. Schematic diagram of the experimental setup.[2]

Table 2. UNIQUAC Volume Parameters, r, and Surface Area Parameters, q[11]

compound	r	q
methanol	1.9011	2.048
ethanol	2.5755	2.588
propan-2-ol	3.2491	3.124
dodecane	8.5462	7.096
water	0.9200	1.400

Binodal Curves. The binodal curves of each of the ternary systems measured in this work was correlated using three different equations. These equations have been discussed previously in the literature.[4] Such empirical equations may be used to smooth the binodal curve data for the instance of one immiscible pair in a ternary system.[4−6] In all of the equations, x_1 refers to the mole fraction of dodecane, and x_2 refers to the mole fraction of the alcohol. The parameters which are determined by fitting the equations to the experimental measurements are A_i, B_i, and C_i, from eqs 1, 2, and 3, respectively. The values x_A and x_B are defined in eqs 4 and 5, respectively. The values $x_{11}{}^0$ and $x_1{}^0$ are the values of x_1 at the points where x_2 is equal to zero. These equations are listed as follows:

(1) The Hlavatý equation:[7]

$$x_2 = A_1 x_A \ln(x_A) + A_2 x_B \ln(x_B) + A_3 x_A x_B \qquad (1)$$

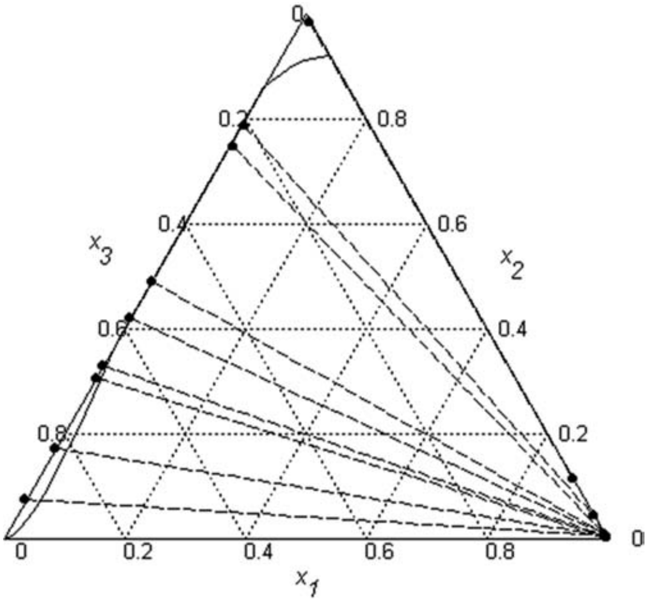

Figure 2. LLE data for dodecane (1) + methanol (2) + water (3) at 298.14 K and 101.3 kPa: ●, experimental; —, binodal model; - - -, tie lines.

(2) The β function equation:[8]

$$x_2 = B_1(1 - x_A)^{B2} x_A{}^{B3} \qquad (2)$$

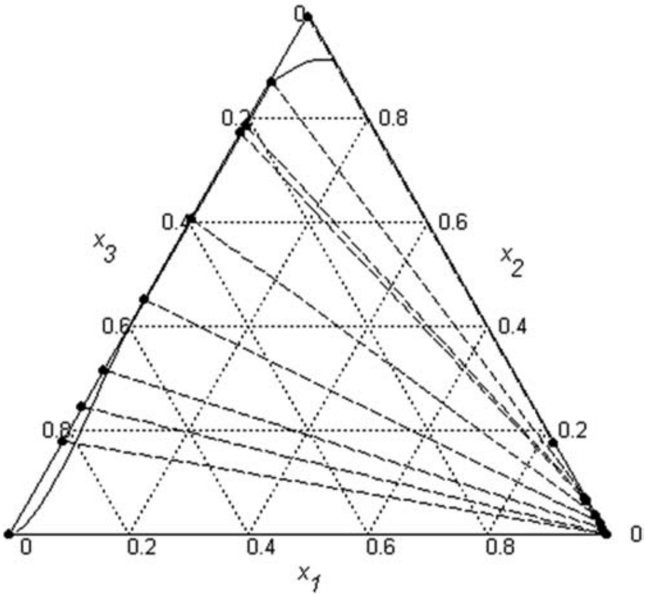

Figure 3. LLE data for dodecane (1) + methanol (2) + water (3) at 313.14 K and 101.3 kPa: ●, experimental; —, binodal model; - - -, tie lines.

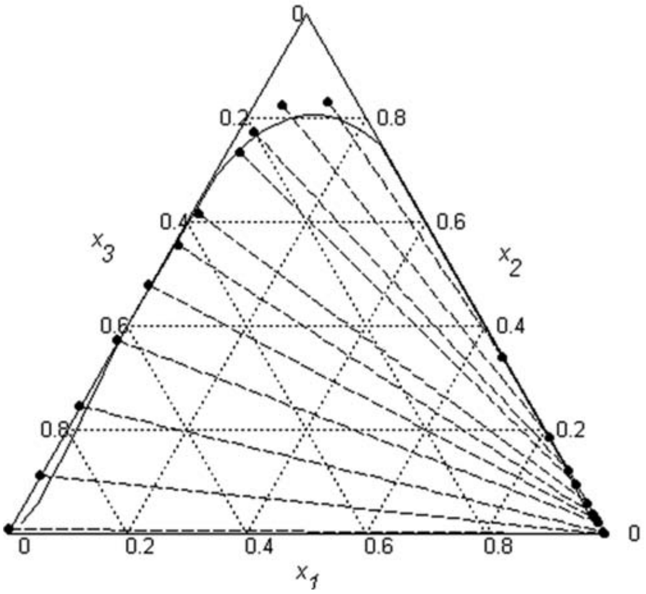

Figure 4. LLE data for dodecane (1) + ethanol (2) + water (3) at 298.14 K and 101.3 kPa: ●, experimental; —, binodal model; - - -, tie lines.

(3) The log γ equation:[9]

$$x_2 = C_1(-\ln[x_A])^{C2} x_A{}^{C3} \tag{3}$$

where:

$$x_A = (x_1 + 0.5x_2 - x_1^0)/(x_{11}^0 - x_1^0) \tag{4}$$

$$x_B = (x_{11}^0 - x_1 - 0.5x_2)/(x_{11}^0 - x_1^0) \tag{5}$$

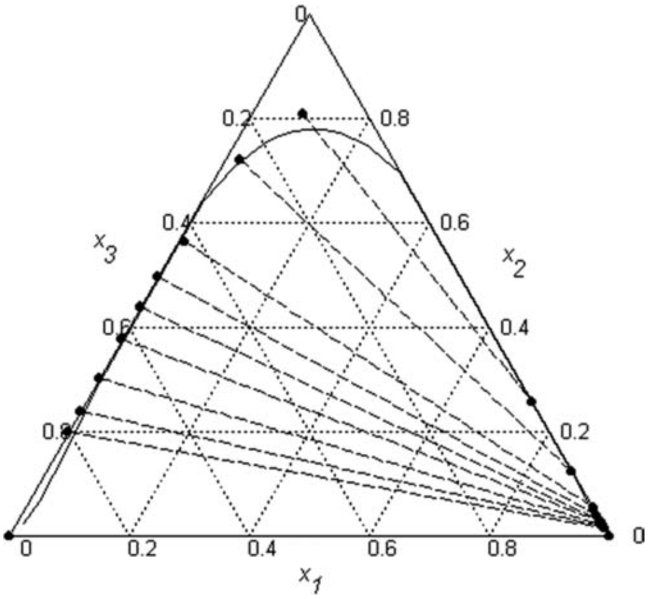

Figure 5. LLE data for dodecane (1) + ethanol (2) + water (3) at 313.14 K and 101.3 kPa: ●, experimental; —, binodal model; - - -, tie lines.

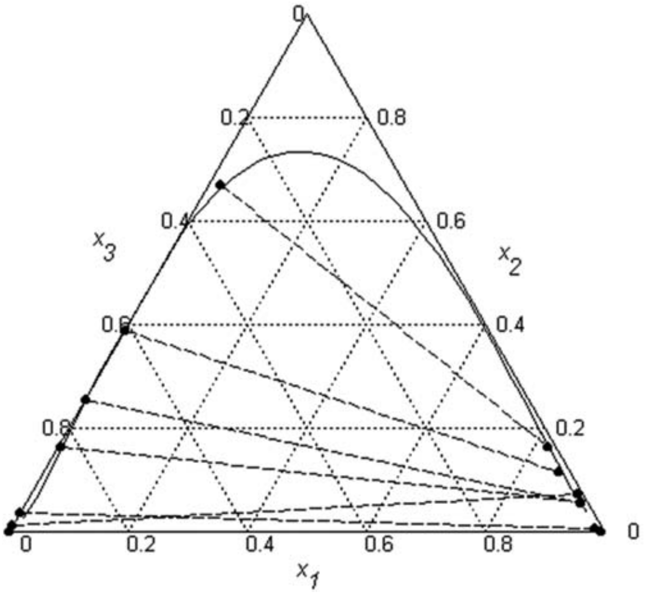

Figure 6. LLE data for dodecane (1) + ethanol (2) + water (3) at 323.15 K and 101.3 kPa: ●, experimental; —, binodal model; - - -, tie lines.

The choice of independent variables for both the β function equation and the log γ equation avoids the problem arising out of variables being highly intercorrelated. These equations were regressed by means of minimizing the standard deviation of the correlation which was taken as:

$$\sigma = \{[(x_2^{\text{calculated}} - x_2^{\text{measured}})^2/(n-3)]\}^{0.5} \tag{6}$$

where, in the denominator, n refers to the number of data points in the data set, and 3 refers to the number of coefficients, according to the work of Sen and Srivastava.[10]

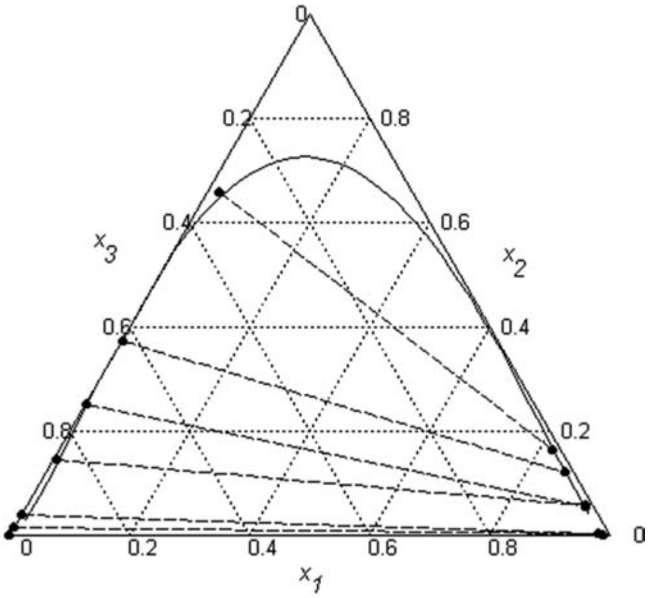

Figure 7. LLE data for dodecane (1) + ethanol (2) + water (3) at 333.15 K and 101.3 kPa: ●, experimental; —, binodal model; - - -, tie lines.

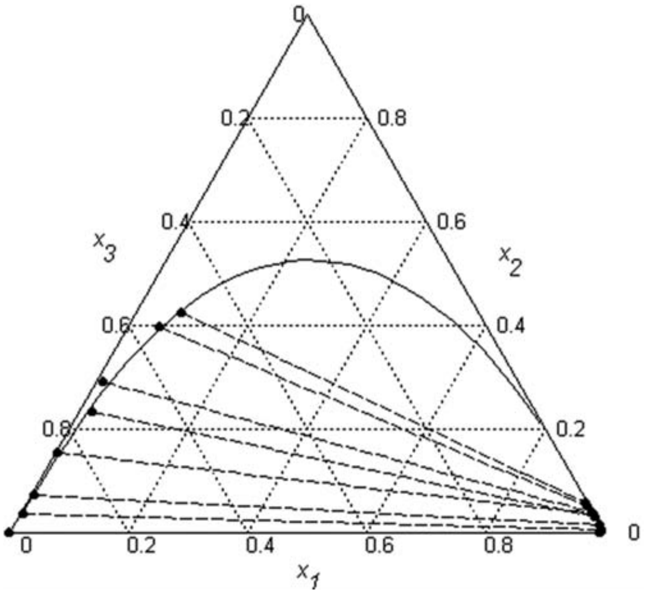

Figure 8. LLE data for dodecane (1) + propan-2-ol (2) + water (3) at 328.15 K and 101.3 kPa: ●, experimental; —, binodal model; - - -, tie lines.

Tie-Line Correlation. The thermodynamic criterion used for LLE, which is analogous to equality of fugacities in the general case,[11,12] is:

$$(x_i\gamma_i)_{\text{organic}} = (x_i\gamma_i)_{\text{aqueous}} \tag{7}$$

where x refers to the mole fraction of species i in a liquid phase, γ represents the activity coefficient of species i in a liquid phase, and the two phases concerned are an aqueous-rich one and an organic-rich one.

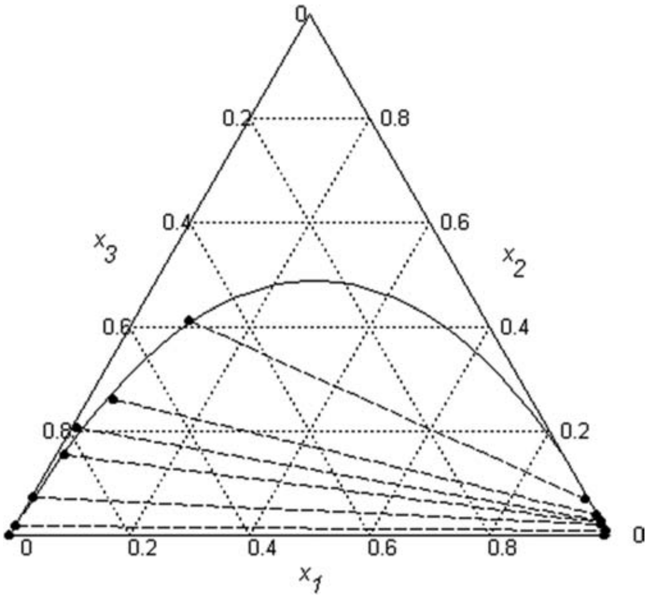

Figure 9. LLE data for dodecane (1) + propan-2-ol (2) + water (3) at 333.15 K and 101.3 kPa: ●, experimental; —, binodal model; - - -, tie lines.

Table 3. Tie-Line Data for the Dodecane (1) + Methanol (2) + Water (3) System at 101.3 kPa

organic phase (I)[a]			aqueous phase (II)[a]		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
		T/K = 298.14 ± 0.02			
0.998	0.002	0.000	0.000	0.305	0.695
0.997	0.003	0.000	0.000	0.172	0.828
0.997	0.003	0.000	0.000	0.074	0.926
0.995	0.006	0.000	0.000	0.329	0.671
0.994	0.006	0.000	0.000	0.490	0.510
0.993	0.007	0.000	0.000	0.421	0.579
0.993	0.007	0.000	0.006	0.748	0.246
0.957	0.043	0.000	0.003	0.790	0.207
0.887	0.113	0.000	0.013	0.987	0.000
		T/K = 313.14 ± 0.02			
1.000	0.000	0.000	0.000	0.000	1.000
1.000	0.000	0.000	0.001	0.178	0.821
1.000	0.000	0.000	0.001	0.244	0.756
0.989	0.011	0.000	0.001	0.315	0.684
0.981	0.019	0.000	0.002	0.453	0.546
0.965	0.035	0.000	0.002	0.607	0.391
0.936	0.064	0.000	0.003	0.773	0.224
0.935	0.065	0.000	0.004	0.872	0.124
0.931	0.069	0.000	0.005	0.786	0.209
0.824	0.176	0.000	0.005	0.996	0.000

[a] All compositions have an uncertainty of 0.007 mole fraction.

The tie lines, representing the compositions of each of the phases in equilibrium, were correlated using the nonrandom two-liquid (NRTL) model of Renon and Prausnitz[13] and the UNIQUAC model of Abrams and Prausnitz[14] to calculate the

Table 4. Tie-Line Data for the Dodecane (1) + Ethanol (2) + Water (3) System at 101.3 kPa

organic phase (I)[a]			aqueous phase (II)[a]		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
		T/K = 298.14 ± 0.02			
1.000	0.000	0.000	0.000	0.007	0.993
1.000	0.000	0.000	0.000	0.111	0.889
0.997	0.003	0.000	0.000	0.244	0.756
0.981	0.019	0.000	0.000	0.374	0.627
0.975	0.025	0.000	0.000	0.478	0.522
0.965	0.036	0.000	0.010	0.555	0.435
0.945	0.055	0.000	0.015	0.617	0.369
0.907	0.093	0.000	0.026	0.733	0.242
0.881	0.119	0.000	0.029	0.773	0.199
0.817	0.183	0.000	0.049	0.825	0.126
0.663	0.337	0.000	0.123	0.833	0.044
		T/K = 313.14 ± 0.02			
1.000	0.000	0.000	0.000	0.000	1.000
0.986	0.014	0.000	0.000	0.196	0.788
0.984	0.016	0.000	0.000	0.234	0.751
0.979	0.021	0.000	0.000	0.298	0.687
0.974	0.026	0.000	0.000	0.373	0.614
0.970	0.030	0.000	0.000	0.434	0.554
0.961	0.039	0.000	0.000	0.498	0.502
0.948	0.052	0.000	0.013	0.563	0.425
0.876	0.124	0.000	0.026	0.721	0.253
0.742	0.258	0.000	0.085	0.810	0.105
		T/K = 323.15 ± 0.02			
0.996	0.000	0.004	0.000	0.000	1.000
0.921	0.071	0.008	0.001	0.011	0.988
0.984	0.005	0.011	0.002	0.034	0.964
0.932	0.057	0.011	0.006	0.162	0.832
0.934	0.054	0.012	0.003	0.255	0.742
0.867	0.114	0.019	0.003	0.387	0.610
0.826	0.163	0.011	0.021	0.671	0.308
		T/K = 333.15 ± 0.02			
0.992	0.000	0.008	0.002	0.000	0.998
0.982	0.003	0.016	0.002	0.013	0.985
0.983	0.001	0.015	0.003	0.037	0.960
0.932	0.057	0.011	0.008	0.143	0.849
0.934	0.054	0.012	0.004	0.252	0.744
0.867	0.120	0.013	0.004	0.372	0.624
0.826	0.161	0.013	0.024	0.657	0.319

[a] All compositions have an uncertainty of 0.007 mole fraction.

Table 5. Tie-Line Data for the Dodecane (1) + Propan-2-ol (2) + Water (3) System at 101.3 kPa

organic phase (I)[a]			aqueous phase (II)[a]		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
		T/K = 328.15 ± 0.02			
0.993	0.000	0.007	0.001	0.000	0.999
0.993	0.006	0.001	0.007	0.035	0.959
0.987	0.012	0.001	0.006	0.073	0.921
0.964	0.036	0.000	0.008	0.152	0.840
0.971	0.029	0.001	0.026	0.231	0.743
0.962	0.037	0.001	0.014	0.291	0.695
0.949	0.049	0.002	0.056	0.397	0.547
0.942	0.056	0.002	0.078	0.425	0.497
		T/K = 333.15 ± 0.02			
0.993	0.000	0.007	0.001	0.000	1.000
0.990	0.009	0.001	0.005	0.017	0.979
0.978	0.020	0.003	0.004	0.072	0.924
0.976	0.024	0.000	0.016	0.154	0.831
0.975	0.024	0.001	0.012	0.206	0.782
0.930	0.067	0.003	0.094	0.413	0.494
0.963	0.037	0.000	0.046	0.259	0.695

[a] All compositions have an uncertainty of 0.007 mole fraction.

Table 6. Parameters and Model Deviations for the Binodal Curve Data of the Dodecane (1) + Methanol (2) + Water (3) System at 101.3 kPa

Hlavatý[7]		β[8]		$\log \gamma$[9]	
		T/K = 298.14			
A_1	1.7240	B_1	6.6850	C_1	5.9718
A_2	0.7753	B_2	1.3021	C_2	1.2581
A_3	7.0070	B_3	1.5629	C_3	2.0441
σ^a	0.0394	σ^a	0.0290	σ^a	0.0010
		T/K = 313.14			
A_1	1.9043	B_1	7.3015	C_1	6.4758
A_2	1.0748	B_2	1.3855	C_2	1.3399
A_3	7.6833	B_3	1.6136	C_3	2.1258
σ^a	0.0391	σ^a	0.0315	σ^a	0.0011

[a] σ is the closeness of the fit to the experimental data and is described in eq 6.

activity coefficients. To regress the data, one of the forms of objective function for LLE data as discussed by Walas[15] was used, which essentially determines the best fit based upon the total sum of the squared errors.

The nonrandomness parameter in the NRTL equation, α_{ij}, was varied according to the recommendations of Walas,[13] such that the same values were used in each system for each of the three binary pairs, for fixed values, namely, 0.20, 0.25, 0.30, 0.35, and 0.40. The value for this parameter which resulted in the best fit was then presented together with the associated interaction parameters.

The parameters used in the UNIQUAC equation for the volume and surface area parameters[16] (r and q), respectively, are presented in Table 2.

■ RESULTS AND DISCUSSION

LLE measurements were performed for the following systems at atmospheric pressure: methanol + water + dodecane at T = (298.14 and 313.14) K, ethanol + water + dodecane at T = (298.14, 313.14, 323.15 and 333.15) K, and propan-2-ol + water + dodecane at T = (328.15 and 333.15) K. The experimental data are presented in Figures 2 to 9, and also in Tables 3 to 5.

Table 7. Parameters and Model Deviations for the Binodal Curve Data of the Dodecane (1) + Ethanol (2) + Water (3) System at 101.3 kPa

Hlavatý[7]		β[8]		log γ[9]	
		T/K = 298.14			
A_1	1.3512	B_1	5.9280	C_1	5.2722
A_2	1.0065	B_2	1.3913	C_2	1.3425
A_3	6.4433	B_3	1.4814	C_3	1.9992
σ^a	0.0273	σ^a	0.0206	σ^a	0.0005
		T/K = 31314			
A_1	1.1806	B_1	5.1798	C_1	4.5730
A_2	0.8352	B_2	1.3237	C_2	1.2736
A_3	5.8835	B_3	1.3981	C_3	1.8787
σ^a	0.0194	σ^a	0.0147	σ^a	0.0003
		T/K = 323.15			
A_1	0.9456	B_1	4.9058	C_1	4.2274
A_2	0.8987	B_2	1.3533	C_2	1.3018
A_3	5.4776	B_3	1.3611	C_3	1.8360
σ^a	0.0130	σ^a	0.0084	σ^a	0.0001
		T/K = 333.15			
A_1	0.8683	B_1	4.5804	C_1	3.9585
A_2	0.7767	B_2	1.3025	C_2	1.2522
A_3	5.1690	B_3	1.3293	C_3	1.7842
σ^a	0.0112	σ^a	0.0074	σ^a	0.0001

[a] σ is the closeness of the fit to the experimental data and is described in eq 6.

Table 8. Parameters and Model Deviations for the Binodal Curve Data of the Dodecane (1) + Propan-2-ol (2) + Water (3) System at 101.3 kPa

Hlavatý[7]		σ^a		log σ^a	
		T/K = 328.15			
A_1	0.1109	B_1	2.1486	C_1	1.8746
A_2	−0.1671	B_2	0.9470	C_2	0.9132
A_3	2.0836	B_3	1.0380	C_3	1.3508
σ^a	0.0087	σ^a	0.0088	σ^a	0.0001
		T/K = 333.15			
A_1	0.0411	B_1	1.9053	C_1	1.6766
A_2	−0.2473	B_2	0.9141	C_2	0.8804
A_3	1.7114	B_3	1.0127	C_3	1.3163
σ^a	0.0085	σ^a	0.0085	σ^a	0.0001

[a] σ is the closeness of the fit to the experimental data and is described in eq 6.

Table 9. NRTL and UNIQUAC Model Parameters and Sum of Squared Errors for the Dodecane (1) + Methanol (2) + Water (3) System at 101.3 kPa

	NRTL[13]				UNIQUAC[14]		
	$(g_{ij} - g_{jj})$	$(g_{ji} - g_{ii})$			$(u_{ij} - u_{jj})$	$(u_{ji} - u_{ii})$	
i j	J·mol^{-1}	J·mol^{-1}	α_{ij}	S^a	J·mol^{-1}	J·mol^{-1}	S^a
			T/K = 298.14				
1 2	−2811000	−1069000			−530000	−1074000	
1 3	421600	90210			−848000	−18440	
2 3	−1075000	49170	0.2	0^b	−1123000	293100	0^b
			T/K = 313.14				
1 2	−9126000	−4110000			−537100	−1344000	
1 3	−94350	297000			−1152000	52090	
2 3	−5093000	31450	0.2	0^b	396900	383800	0^b

[a] $S = \Sigma([x_i\gamma_i]_{\text{organic}} - [x_i\gamma_i]_{\text{aqueous}})^2$. [b] This value was obtained as it was lower than the minimum precision of the MATLAB regression.

It was found that the two liquid phases were almost entirely immiscible at low alcohol concentrations, as evidenced by the data for all systems concerned. Increasing the temperature resulted in an increase in the mutual miscibility of the two liquid phases, although it should be noted that the water was essentially totally immiscible in dodecane in almost all cases. Increasing the carbon chain-length of the alcohol from C_1 (methanol) to C_2 and C_3 (ethanol and propan-2-ol, respectively) greatly increased the miscibility of the systems, such that methanol was the only case where a plait point was not observed at the temperatures concerned. Similar trends as observed in this work, particularly the exceedingly low mutual solubility of the water + dodecane pair can also be found in the work of Mohsen-Nia et al.[12] and Mohammad Doulabi et al.[16] Additionally, it was also found that an increase in the carbon chain-length of the alcohol, as well as an increase in the temperature increased the overall solubility of the systems studied in the two aforementioned works, which was also observed in this work. The work of Backlund et al.,[17] which used octane instead of dodecane, also exhibited similar trends with regard to the low mutual solubility of the water + alkane pair and the increasing solubility resulting from an increase in the carbon chain-length of the alcohol. Hu et al.[18] also provide further data regarding the low mutual solubility of water with dodecane.

With regard to the binodal curve correlation, it was found that the log γ equation of Letcher et al.[9] produced the lowest standard deviation and, thus, the best fit for all of the systems measured in this work. It should be noted that the standard deviation as a result of the log γ equation was generally approximately 1 order of magnitude less than the standard deviations produced by the two other correlating equations, thus indicating that the log γ equation is significantly superior to the Hlavatý and β function equations in representing the systems studied in this work. It was found that the largest deviations from the experimental data were unanimously afforded by the Hlavatý equation. It should be noted that the binodal curves shown in the ternary phase diagrams are merely the correlated representations and do not comply with the physical measurements in most instances across certain composition ranges.

In using the NRTL and UNIQUAC equations to regress along the tie-lines, it was found that both equations resulted in very good fits to the experimental data, with the largest sum of squared errors being of the order of 10^{-10}, and the lowest value being zero (see Tables 6 to 11). Overall, the best fit was obtained with the NRTL equation as in all cases it provided either an equally good or even better fit than the UNIQUAC equation. However, the fact that both models generated such close correlation with the experimental data suggests that either could be used in modeling or simulating the systems studied in this work.

Table 10. NRTL and UNIQUAC Model Parameters and Sum of Squared Errors for the Dodecane (1) + Ethanol (2) + Water (3) System at 101.3 kPa

		NRTL[13]				UNIQUAC[14]		
		$(g_{ij} - g_{jj})$	$(g_{ji} - g_{ii})$			$(u_{ij} - u_{jj})$	$(u_{ji} - u_{ii})$	
i	j	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	α_{ij}	S^a	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	S^a
$T/K = 298.14$								
1	2	−2649000	−969700			−388200	−627900	
1	3	880900	24740			−84280	40840	
2	3	−1164000	−694	0.2	0^b	−808800	219100	0^b
$T/K = 313.14$								
1	2	−5907000	−2242000			−643100	−765800	
1	3	−206100	88310			−798300	41300	
2	3	−2235000	−1818000	0.3	0^b	−1708000	−53150	0^b
$T/K = 323.15$								
1	2	−695500	−169500			3203	−42600	
1	3	302000	21070			10330	1853	
2	3	−380900	128500	0.2	$2.958 \cdot 10^{-30}$	−37940	−6999	$5.791 \cdot 10^{-10}$
$T/K = 333.15$								
1	2	−7184000	−1049000			2252	−28920	
1	3	−926800	328800			9536	1304	
2	3	−1107000	−893100	0.2	0^b	−51900	−3815	$1.293 \cdot 10^{-10}$

[a] $S = \Sigma([x_i\gamma_i]_{\text{organic}} - [x_i\gamma_i]_{\text{aqueous}})^2$. [b] This value was obtained as it was lower than the minimum precision of the MATLAB regression.

Table 11. NRTL and UNIQUAC Model Parameters and Sum of Squared Errors for the Dodecane (1) + Propan-2-ol (2) + Water (3) System at 101.3 kPa

		NRTL[13]				UNIQUAC[14]		
		$(g_{ij} - g_{jj})$	$(g_{ji} - g_{ii})$			$(u_{ij} - u_{jj})$	$(u_{ji} - u_{ii})$	
i	j	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	α_{ij}	S^a	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	S^a
$T/K = 328.15$								
1	2	−426500	−121300			6551	−27230	
1	3	89850	19340			9638	1589	
2	3	−158200	−1980	0.35	$7.934 \cdot 10^{-24}$	−52230	−3129	$4.072 \cdot 10^{-18}$
$T/K = 333.15$								
1	2	−790700	−151300			10730	−24110	
1	3	198300	21710			9750	1829	
2	3	−160300	−300300	0.35	$5.291 \cdot 10^{-24}$	−58750	5264	$2.791 \cdot 10^{-13}$

[a] $S = \Sigma([x_i\gamma_i]_{\text{organic}} - [x_i\gamma_i]_{\text{aqueous}})^2$.

CONCLUSIONS

Increasing the amount of alcohol in the overall composition increased the mutual miscibility of the aqueous and dodecane phases. It was also determined that increasing the temperature resulted in an increase in the mutual miscibility of both phases, as did increasing the carbon chain-length of the alcohol. The binodal curves were correlated using three equations with the best fit in all cases being obtained with the log γ equation. The greatest deviation from experimental data in all cases was obtained with the Hlavatý equation. The tie-lines were correlated using the NRTL and UNIQUAC equations. The NRTL model provided an equivalent or better fit to the experimental data than the UNIQUAC equation, although there was not much to distinguish between both models.

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