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Liquid−Liquid Equilibria of the (Water + Ethanol + Linalyl Acetate) Ternary System at Different Temperatures

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ABSTRACT: Liquid−liquid equilibrium (LLE) data of the solubility curves and tie-line compositions were examined of the (water + ethanol + linalyl acetate) system at T = (298.2, 308.2, and 318.2) K and P = 101.325 kPa. The relative mutual solubility of ethanol is higher in the water phase than in the linalyl acetate phase. The consistency of the experimental tie lines was determined through the Bachman correlation equation. The experimental LLE data were satisfactorily correlated with the nonrandom two-liquid model (NRTL), and the binary interaction parameters so obtained are reported. The best results were obtained with the NRTL method, using nonrandomness parameter (α = 0.3) for the correlation. Distribution coefficients (D) and separation factors (S) were evaluated over the immiscibility region. The influence of temperature on the LLE characteristics was found to be significant at the temperatures studied.

INTRODUCTION

Citrus oils contain not only volatile components such as monoterpenes and sesquiterpenes and oxygenated compounds (alcohols, esters, aldehydes, ketones, etc.) but also nonvolatile compounds (methoxylated flavones, carotenoids, etc.). Citrus oils separate industrially by cold-press or steam-distillation methods. The oxygenated compounds of the citrus oils are more valuable than hydrocarbons. The oxygenated compounds can be separate from terpenes economically by the liquid−liquid extraction method. The volatile components of the citrus oil are completely soluble in ethanol but not completely soluble in water. The citrus oil, which contained ethanol, are mainly demanded by commercial companies for the following three reasons: (a) The ethanol-contained citrus oil is fairly soluble in aqueous solutions. Therefore, this mixture can be used to formulate drinks and fragrances. (b) Oxidation reactions are decreased in the existence of the alcohol. (c) Ethanol increases the aromatic strength of the mixture.[1]

Bergamot peel oil has a large importance in perfumery and food applications. The main component of the bergamot oil is linalyl acetate (3,7-dimethyl-1,6-octadien-3-yl-acetate; Figure 1). Linalyl acetate is an oxygenated component which involves over 35 % of the bergamot peel oil constituents. Linalyl acetate is used as an intermediate substance and is found in cleaning products, cosmetics, soft drinks, and chewing gum.[2,3]

The liquid−liquid equilibrium (LLE) studies supply necessary information for the design and optimization of separation processes. Nevertheless, the solvent extraction technique is limited by the lack of LLE data for systems containing citrus oil components, water, and ethanol at some temperatures.[4] A number of investigations have been carried out in recent years on the LLE measurements by the some researchers.[5−11]

The aim of this study is examined on the phase behavior of LLE for the (water + ethanol+ linalyl acetate) system. For this system, three different temperatures, T = (298.2, 308.2, and 318.2) K, were chosen to study to observe the change of the equilibrium characteristics.

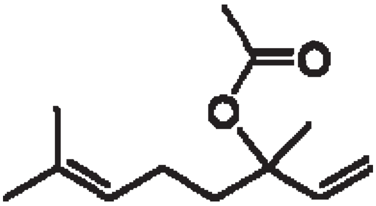

Figure 1. Linalyl acetate structure.

Table 1. Experimental and Literature[12] Properties of the Pure Components at T = 293.2 K and P = 101.325 kPa[a]

	$\rho/(\mathrm{kg \cdot m^{-3}})$		n_D		T_b/K	
compound	expt.	lit.	expt.	lit.	expt.	lit.
linalyl acetate	895.06	895.1	1.45445[b]	1.4544[b]	493.2	493.2
ethanol	789.26	789.3	1.36115	1.3611	351.4	351.4
water	998.24	998.23	1.33304	1.3330	373.3	373.3

[a] Density (ρ); refractive indices (n_D); boiling point (T_b/K). [b] 294 K.

EXPERIMENTAL SECTION

Materials. All chemicals used were chromatography-grade products supplied by Merck Co. with nominal purities of w < 0.99 for ethanol and w < 0.95 for linalyl acetate. NANO pure water was used throughout all of the experiments. These purities were verified by gas chromatography, and the chemicals were used without further purification.

Apparatus and Procedure. Refractive indices and densities were measured with an Anton Paar refractometer (RXA 170 model) and Anton Paar densimeter (DMA 4500 model), respectively. The estimated uncertainties in the refractive indices and density measurements were $\pm 5 \cdot 10^{-5}$ and $\pm 1 \cdot 10^{-2}$ $\mathrm{kg \cdot m^{-3}}$,

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Table 2. Experimental Solubility Curve Data of the (Water (1) + Ethanol (2) + Linalyl Acetate (3)) System at T = (298.2, 308.2, and 318.2) K

W_1 (mass fraction)	W_2 (mass fraction)	W_3 (mass fraction)
	T/K = 298.2	
0.9986	0.0000	0.0014
0.8481	0.1311	0.0208
0.7038	0.2736	0.0226
0.6070	0.3640	0.0290
0.3018	0.4919	0.2063
0.2407	0.4571	0.3022
0.1773	0.4117	0.4110
0.1115	0.3350	0.5535
0.0622	0.2423	0.6955
0.0294	0.1222	0.8484
0.0089	0.0000	0.9911
	T/K = 308.2	
0.9988	0.0000	0.0012
0.7965	0.2006	0.0029
0.5962	0.3996	0.0042
0.5117	0.4675	0.0208
0.3565	0.5390	0.1045
0.3207	0.5368	0.1425
0.2122	0.4780	0.3098
0.1584	0.4208	0.4208
0.1066	0.3606	0.5328
0.0837	0.3268	0.5895
0.0488	0.2161	0.7351
0.0047	0.0000	0.9953
	T/K = 318.2	
0.0033	0.0000	0.9967
0.0369	0.1931	0.7700
0.1084	0.3628	0.5288
0.1578	0.4205	0.4217
0.2111	0.4775	0.3114
0.3285	0.5339	0.1376
0.3581	0.5337	0.1082
0.4943	0.4805	0.0252
0.5827	0.3995	0.0178
0.7875	0.2066	0.0059
0.9986	0.0000	0.0014

Table 3. Experimental Tie-Line Data of (Water (1) + Ethanol (2) + Linalyl Acetate (3)) Systems at T= (298.2, 308.2, and 318.2) K

water-rich phase (mass fraction)			linalyl acetate-rich phase (mass fraction)		
W_{11}	W_{21}	W_{31}	W_{13}	W_{23}	W_{33}
			T/K = 298.2		
0.8826	0.1004	0.0170	0.0521	0.1983	0.7496
0.7965	0.1853	0.0182	0.0419	0.1595	0.7986
0.7100	0.2687	0.0213	0.0333	0.1271	0.8396
0.6510	0.3257	0.0233	0.0268	0.0986	0.8746
0.5735	0.3929	0.0336	0.0152	0.0440	0.9408
0.5111	0.4398	0.0491	0.0077	0.0135	0.9788
			T/K = 308.2		
0.8928	0.0992	0.0080	0.0388	0.2018	0.7594
0.7751	0.2157	0.0092	0.0330	0.1292	0.8378
0.7004	0.2901	0.0095	0.0217	0.0867	0.8916
0.6308	0.3592	0.0100	0.0203	0.0571	0.9226
0.5543	0.4296	0.0161	0.0088	0.0298	0.9614
			T/K = 318.2		
0.8390	0.1523	0.0087	0.0297	0.1649	0.8054
0.7615	0.2288	0.0097	0.0221	0.1265	0.8514
0.7130	0.2769	0.0101	0.0168	0.0902	0.8930
0.6467	0.3350	0.0183	0.0137	0.0600	0.9263

respectively. Boiling point measurements were obtained by using a Fischer boiling point apparatus; its stated accuracy is ± 0.1 K. All mixtures were prepared by weighing by means of a Sartorious CP224S balance with an exactness of $\pm 1 \cdot 10^{-7}$ kg. The measured and literature physical properties data are listed in Table 1.[12]

The solubility curves were determined by the cloud point method in an equilibrium glass cell. The temperature in the cell was kept constant by circulating water from a water bath (NUVE, BS 302 model), which was equipped with a temperature controller capable of maintaining the temperature within ± 0.1 K.

Mutual solubility values of the binary mixture (water + linalyl acetate) were measured using the method based on the detection of the cloud point. The transition point between the one-phase and the two-phase region was determined visually. The reliability of the method depends on the precision of the Metrohm micro buret, with an accuracy of $\pm 3 \cdot 10^{-9}$ m^3, and is limited by the visual inspection of the transition across the apparatus.

End-point determinations of the tie lines were carried out by the independent analysis of the coupled phases that were considered as being in equilibrium. Mixtures of known masses of water, ethanol, and linalyl acetate lying within the two-phase regions were introduced into the extraction cell and were stirred strongly for at least 4 h and then left to settle 6 h for phase separation. After separation, samples of water-rich phase and linalyl acetate-rich phase were analyzed to determine their compositions.

Analysis. The liquid samples were analyzed by a gas chromatograph (HP 6890 model), equipped with flame ionization detector (FID). A HP-19091A-015 methyl siloxane capillary column (50.0 m × 320 μm × 0.17 μm) for FID were utilized to separate components of samples at programmed oven programs suitable for each ternary system. The detector temperature was kept at T = 473.2 K, while the injection port temperature was held at T = 523.2 K. Injections were performed on the split 70:1 mode. Nitrogen was used as a carrier gas with a flow rate of 2.4 cm$^3 \cdot$min^{-1}. Injection volumes of the liquid samples were 0.3 μL. The greatest errors in the determination of mole fraction composition using the calibration curves were ± 0.002 in the aqueous-rich and solvent-rich phases.

RESULTS AND DISCUSSION

Experimental LLE Data. The mass fraction of the (water (1) + ethanol (2) + linalyl acetate (3)) system on the binodal curve, as well as the mutual binary solubility of water and linalyl acetate at T = (298.2, 303.2, and 318.2) K, was given in Table 2, in which W_i denotes the mass fraction of the ith (i = 1, 2, and 3) component. Table 3 shows the mass fraction experimental tie lines of the equilibrium phases, for which W_{i1} and W_{i3} refer to the mass fractions of the ith component in the water-rich phase and linalyl acetate-rich

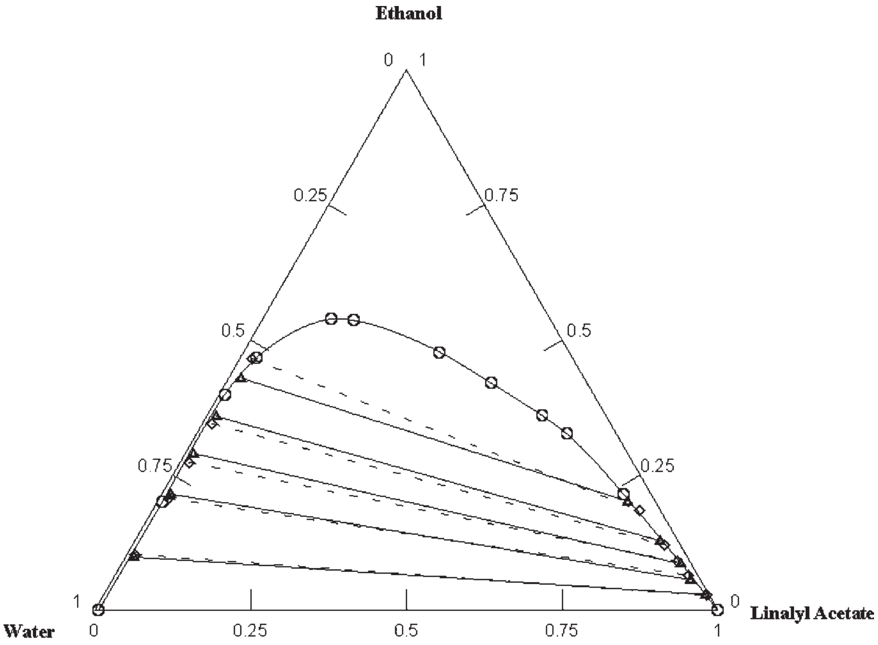

Figure 2. Ternary diagram for LLE of the {water (1) + ethanol (2) + linalyl acetate (3)} system at $T = 298.2$ K; —○—, experimental solubility curve; —△—, experimental tie lines; --◇--, calculated (NRTL) tie lines; (all concentrations are in mass fraction).

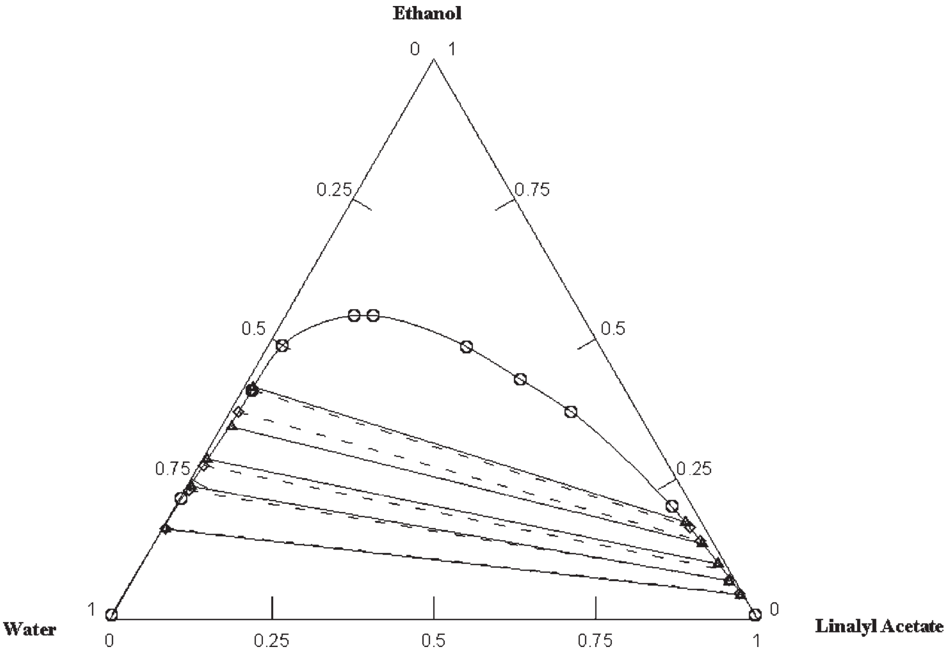

Figure 3. Ternary diagram for LLE of {water (1) + ethanol (2) + linalyl acetate (3)} at $T = 308.2$ K; —○—, experimental solubility curve; —△—, experimental tie lines; --◇--, calculated (NRTL) tie lines; (all concentrations are in mass fraction).

phase, respectively. The mass fraction binodal curves and tie lines of the ternary system are plotted from Figures 2 to 4. The slopes of the tie lines obtained in this study show that ethanol is more soluble in the water than in the linalyl acetate.

Because (ethanol + water) and (ethanol + linalyl acetate) are two liquid pairs that are completely soluble, the only liquid pair (water + linalyl acetate) is partially soluble; this ternary system behaves as a type 1 LLE. The area of the two-phase region obviously depends on the mutual solubility of water and the linalyl acetate. In general, temperature and the variety of solvent are the most important factors which influence the equilibrium characteristics and the solubility region of the ternary system.[13]

Distribution Coefficient and Separation Factor. The distribution coefficient, D_i, for water ($i = 1$) and ethanol ($i = 2$), and separation factor, S, are calculated as follows:

$$D_i = W_{i3}/W_{i1} \tag{1}$$

$$S = (W_{23}/W_{21})/(W_{13}/W_{11}) \tag{2}$$

The calculated distribution coefficients and separation factors of the ternary system are given in Table 4. The separation factor is

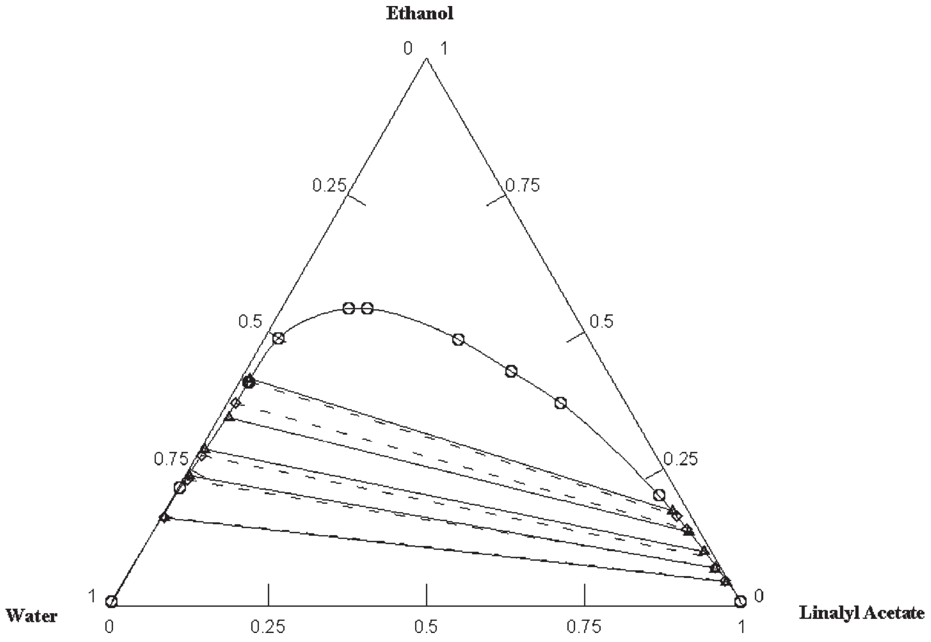

Figure 4. Ternary diagram for LLE of {water (1) + ethanol (2) + linalyl acetate (3)} at T = 318.2 K; −○−, experimental solubility curve; −△−, experimental tie lines; --◇--, calculated (NRTL) tie lines; (all concentrations are in mass fraction).

Table 4. Distribution Coefficients for Water (D_1) and Ethanol (D_2) and Separation Factors (S) for the (Water (1) + Ethanol (2) + Linalyl Acetate (3)) System at T = (298.2, 308.2, and 318.2) K

D_1	D_2	S
	T/K = 298.2 K	
0.059	1.975	33
0.053	0.861	16
0.047	0.473	10
0.041	0.303	7
0.027	0.112	4
0.015	0.031	2
	T/K = 308.2 K	
0.043	2.034	47
0.043	0.599	14
0.031	0.299	10
0.032	0.159	5
0.016	0.069	4
	T/K = 318.2 K	
0.035	1.083	31
0.029	0.553	19
0.024	0.326	14
0.021	0.179	8

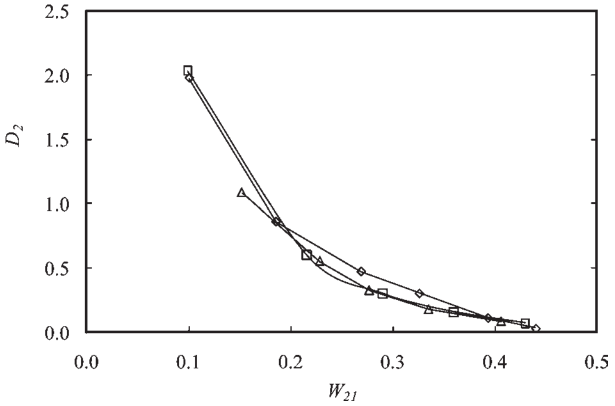

Figure 5. Distribution coefficient of ethanol (D_2) plotted against the mass fraction of ethanol in water phase (W_{21}); −◇−, 298.2 K; −□−, 308.2 K; −△−, 318.2 K.

found to be bigger than 1 (separation factors varying between 2 and 47) for the system reported here, which means that extraction of ethanol by the linalyl acetate is possible with highly efficiency for this system. The separation factors and distribution coefficients are not constant over the completely two-phase region at T = (298.2, 308.2, and 318.2) K. The extracting power of the linalyl acetate is shown in Figures 5 and 6.

Consistency of Tie-Line Data. The reliability of experimentally measured tie-lines data can be determined by using the Bachman correlation[14] for each temperature as follows:

$$W_{23} = A + B\left(\frac{W_{23}}{W_{11}}\right) \qquad (3)$$

where A and B are the constant and slope of eq 3. The correlations are given in Table 5. The correlation factor (R^2) being approximately unity and the linearity of the plots indicate the degree of consistency of the measured LLE data in this study (Figure 7).

Temperature Effect. Since it can be examined from Figures 2 to 4, temperature has little effect on the LLE of this system. In Figure 8, the temperature effects on the distribution of ethanol between the water-rich phase and the linalyl acetate-rich phase were plotted. The solubility of ethanol in linalyl acetate-rich phase decreases to a larger extend than the solubility in the water-rich phase.

Thermodynamic Modeling (NRTL) and Parameter Estimation. The nonrandom two-liquid (NRTL) model is based on

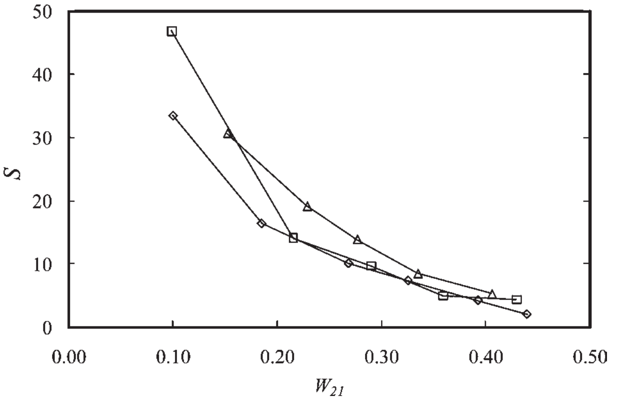

Figure 6. Separation factor (S) plotted against the mass fraction of ethanol in the water phase, (W_{21}); −◇−, 298.2 K; −□−, 308.2 K; −△−, 318.2 K.

Table 5. Bachman Correlations of the (Water (1) + Ethanol (2) + Linalyl Acetate (3)) System at T = (298.2, 308.2, and 318.2) K[a]

T/K	A	B	R^2
298.2	−0.0211	0.8938	0.9643
308.2	−0.0313	1.0006	0.9901
318.2	−0.0264	0.9469	0.9933

[a] A: constant; B: slope; R^2: regression coefficient.

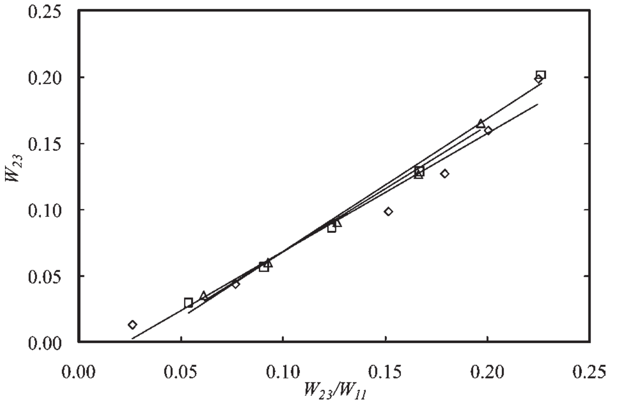

Figure 7. Bachman plots of the {water (1) + ethanol (2) + linalyl acetate (3)} system at different temperatures; −◇−, 298.2 K; −□−, 308.2 K; −△−, 318.2 K; (all concentrations are in mass fraction).

local composition and is applicable to partially miscible systems. This model has three adjustable parameters for each binary pair (a_{ij}, a_{ji}, and α). The parameters a_{ij} and a_{ji} are related to the characteristic energy of interaction between the molecules of type i and j. The parameter α is related to the nonrandomness of the mixture. The experimental LLE data were used to calculate the optimum NRTL interaction parameters among water, ethanol, and linalyl acetate. The NRTL[15] model was fitted to experimental data using an iterative computer program with the objective functions developed by Sørensen.[16]

The nonrandomness parameter α was taken as 0.3 in this study. The correlated results together with the experimental data of the (water (1) + ethanol (2) + linalyl acetate (3)) system were plotted at each temperature from Figures 2 to 4.

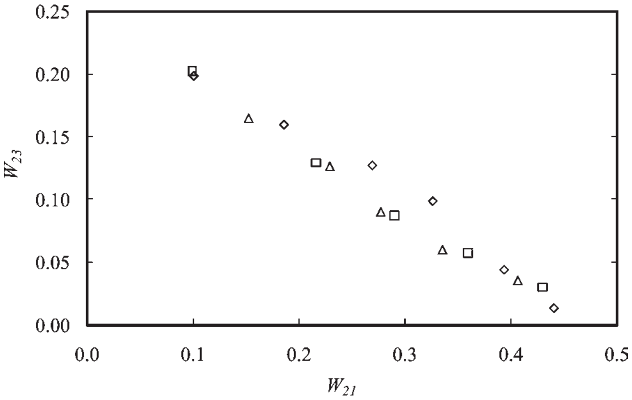

Figure 8. Influence of temperature on the distribution of ethanol between the water-rich phase (W_{21}) and the linaly acetate-rich phase (W_{23}) in the system {water (1) + ethanol (2) + linalyl acetate (3)}; −◇−, 298.2 K; −□−, 308.2 K; −△−, 318.2 K; (all concentrations are in mass fraction).

Table 6. NRTL Binary Interaction Parameters (a_{ij} and a_{ji}) Optimized for the {Water (1) + Ethanol (2) + Linalyl Acetate (3)} System at T = (298.2, 308.2, and 318.2) K

component	NRTL (J·mol^{-1})	
i−j	a_{ij} (K)	a_{ji} (K)
	T/K = 298.2	
1−2 2−1	−1689.5637	−282.1098
1−3 3−1	1682.1424	786.5521
2−3 3−2	1213.4191	−2360.8068
	T/K = 308.2	
1−2 2−1	−606.6696	−213.544
1−3 3−1	1904.285	925.3745
2−3 3−2	1665.1035	−1353.203
	T/K = 318.2	
1−2 2−1	−2778.3467	−55.1214
1−3 3−1	2106.5626	935.5462
2−3 3−2	1125.9123	−3323.6022

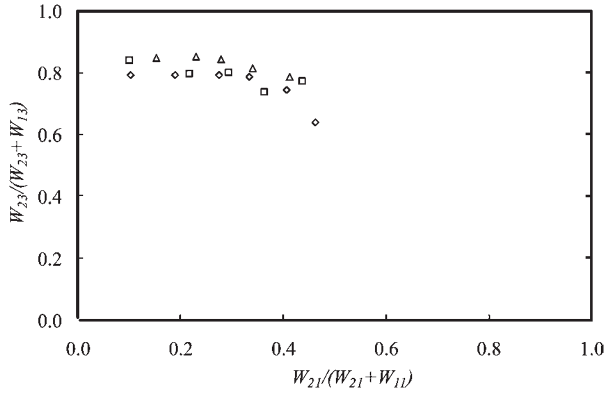

Figure 9. Selectivity diagram of the {water (1) + ethanol (2) + linalyl acetate (3)} ternary system at different temperatures; −◇−, 298.2 K; −□−, 308.2 K; −△−, 318.2 K; (all concentrations are in mass fraction).

The excellence of correlation is evaluated with the residual function (F). It is calculated from the difference between the experimental data and the correlations of the NRTL model for the ternary system according to the following equation:

$$F = \{\sum_{k} \min[\sum_{i} \sum_{j} (W_{i,\,\mathrm{exp}} - W_{i,\,\mathrm{calc}})^2]/6n\}^{1/2} \qquad (4)$$

where n is the number of tie lines; $W_{i,\mathrm{exp}}$ is the experimental mass fraction, $W_{i,\mathrm{calc}}$ is the calculated mass fraction of component i, j indexes refer to phases, and $k = 1, 2, 3, 4, ..., n$ (tie lines). The NRTL model has correlated the experimental data of this system at T = (298.2, 308.2, and 318.2) K with F values of 0.0110, 0.0211, and 0.0086, respectively. Therefore, the experimental data were used to determine the optimum NRTL model (a_{ij}, a_{ji}) binary interaction energy parameters between an $i-j$ pair of substances. Six effective binary interaction energy parameters were calculated for this system and given in Table 6.

Selectivity of the Ternary Systems. Selectivity diagrams on a solvent-free basis were obtained by plotting $W_{23}/(W_{23} + W_{13})$ versus $W_{21}/(W_{21} + W_{11})$ for each temperature in Figure 9. The selectivity plots of the ternary system at each temperature were found to be similar.

■ CONCLUSION

The LLE data were obtained for the (water (1) + ethanol (2) + linalyl acetate (3)) system at T = (298.2, 308.2, and 318.2) K. The NRTL model results were qualitatively and quantitatively fitted to the experimental data. Furthermore, the corresponding optimized binary interaction energy parameters were calculated.

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