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Liquid−Liquid Equilibrium for the Water + Acetonitrile + Limonene System at Different Temperatures

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Isobaric liquid−liquid equilibrium (ELL) data (tie lines and miscibility gaps) for the ternary system water + acetonitrile + limonene were determined at atmospheric pressure and at temperatures ranging from (296.15 ± 0.5) K to (323.15 ± 0.5) K. The reliability of the experimental tie-line data was ascertained by using two overall concentrations for each tie line. The equilibrium data were correlated using NRTL and UNIQUAC equations. New and previously unavailable UNIQUAC and NRTL interaction parameters were obtained. Experimental data were also compared with those predicted by the UNIFAC group contribution method. At the studied temperatures, the UNIQUAC equation fit the experimental data better than NTRL, with a root-mean-square deviation value between 0.39 % and 0.99 %. The miscibility gap disappears for an acetonitrile mass fraction equal to about 81 % at 306.15 K.

Introduction

Citrus essential oils are widely used in the chemical and pharmaceutical industries, and in general terms, limonene is their largest component (>60 %).[1] Limonene is usually epoxidized to make fragrances, perfumes, and food additives. An effective catalytic system for limonene epoxidation is H_2O_2 + acetonitrile + PW-Amberlite, which gives conversions of over 80 % and epoxide selectivities higher than 90 %.[2] Limonene is completely soluble in acetonitrile but not completely soluble in water. Hence, acetonitrile is used to enhance the mutual solubility between water and limonene. The phase equilibrium study of the ternary system water + acetonitrile + limonene is essential for process design and control.

A precise description of the dependence on temperature, pressure, and composition of the water + acetonitrile + limonene system requires a reliable thermodynamic model that allows the calculation of its properties from available experimental data. The solubility of limonene in water at temperatures from 273.15 K to 293.15 K has been reported.[3,4] Liquid−liquid equilibrium (LLE) data of the limonene + linalool + 2-aminoethanol system at 298.15 K, 308.15 K, and 318.15 K[5] and the *d*-limonene + ethanol + water system at 293.15 K[4] and more recently from 293.15 K to 323.15 K have been determined.[6] However, no data of the LLE of the ternary system water + acetonitrile + limonene has yet been reported. To this end, we explored the behavior of acetonitrile aqueous solutions and limonene.

In this work, miscibility gaps and distribution coefficients for the ternary system water + acetonitrile + limonene are determined at atmospheric pressure and at (296.15 ± 0.5) K, (306.15 ± 0.5) K, (316.15 ± 0.5) K, and (323.15 ± 0.5) K. The LLE data have been compared with those predicted by the universal function-group activity coefficient method (UNIFAC)[7] and correlated with NRTL[8] and the universal quasi-chemical model (UNIQUAC).[9] New and previously unavailable UNIQUAC interaction parameters for the water + acetonitrile + limonene system have been determined.

Experimental Section.

Chemicals. All chemicals were used without further treatment. Limonene with a mass fraction purity of 97 % (Aldrich), acetonitrile with a mass fraction purity of 99.5 % (Fluka), and distilled water were used throughout all experiments.

Procedure. Limonene solubility in water was determined by weighing 500 g of water in a glass flask and adding limonene by means of an automated microburet (Dosimat) with an accuracy of ±0.005 mL until a small limonene drop did not dissolve. Isobaric ternary LLE data were determined for the water + acetonitrile + limonene system at (296.15 ± 0.5) K, (306.15 ± 0.5) K, (316.15 ± 0.5) K, and (323.15 ± 0.5) K. The equilibrium was established in an 8 mL glass flask equipped with a magnetic stirrer and immersed in a temperature-controlled oil bath. The binodal curve was obtained separately from the determination of tie lines. The binodal curve for the water + limonene + acetonitrile system was determined by the cloud-point method.[10] Using an electronic balance accurate to ±0.1 mg, known mixtures of water + limonene were prepared, and acetonitrile was added by means of a Dosimat. The end point of the titration was determined by the detection of the transition from a heterogeneous to a homogeneous mixture. All measurements were repeated four times for each mixture.

Tie lines were determined by analyzing samples taken from each layer of partially miscible ternary mixtures of known overall composition that were shaken for about 2 h to allow intimate contact between the phases. The mixtures were allowed to settle in a 10 mL graduated buret with 0.02 mL divisions until no volume changes of phase were observed, between 4 h and 24 h depending on the temperature. Then, samples of the two liquid phases were carefully taken and analyzed. The complete process was carried out at constant temperature using a thermostatic bath controlled to within ±0.5 K. To ascertain the reliability of the tie lines, ternary mixtures of known overall composition

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Table 1. Limonene Solubility (w_2) in Water at Different Temperatures

T/K	$10^{-6}(w_2 \pm \sigma)$	reference
296.15	20 ± 4	4
296.15, 306.15, 316.15	13 ± 1.6	this work
323.15	17 ± 1.6	this work

Table 2. Mass Fraction Solubility (w) for Water (1) + Limonene (2) + Acetonitrile (3)

$T = 296.15$ K		$T = 306.15$ K		$T = 316.15$ K		$T = 323.15$ K	
w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2
0.418	0.003	0.439	0.005	0.510	0.004	0.597	0.005
0.374	0.008	0.327	0.011	0.489	0.005	0.509	0.005
0.355	0.014	0.221	0.029	0.461	0.006	0.416	0.009
0.311	0.020	0.162	0.045	0.330	0.013	0.347	0.013
0.241	0.032	0.470	0.005	0.293	0.019	0.298	0.019
0.159	0.053	0.386	0.008	0.244	0.033	0.259	0.035
0.105	0.082	0.101	0.086	0.246	0.032	0.199	0.057
0.070	0.101	0.130	0.063	0.202	0.047	0.188	0.062
0.060	0.122	0.066	0.133	0.173	0.057	0.126	0.098
0.010	0.225	0.018	0.235	0.148	0.074	0.048	0.210
0.114	0.069	0.120	0.072	0.098	0.111	0.078	0.155
0.044	0.142	0.048	0.164	0.072	0.143	0.028	0.288
0.025	0.177	0.033	0.193	0.015	0.268	0.061	0.187
0.024	0.178	0.028	0.207	0.135	0.082	0.055	0.197
0.000	0.262	0.001	0.330	0.050	0.175	0.033	0.257
0.000	0.989	0.000	0.324	0.000	0.463	0.000	0.548

lying on the calculated tie lines were prepared, and the phase composition was determined.

Analyses. Liquid samples were analyzed using a gas chromatograph (Varian Star, 3400) equipped with a thermal conductivity detector (TCD) for the quantitative determination of water, limonene, and acetonitrile and a flame ionization detector (FID) for the determination of limonene and acetonitrile. A 30 m megabore DB-WAX capillary column was used; the column temperature was increased from 120 °C to 160 °C at a heating rate of 10 °C/min, and the injector temperature was 200 °C. The TCD temperature was 300 °C, and the FID temperature was 280 °C. Flowing nitrogen (7.7 cm^3/min) was used as the carrier gas. The injected sample volume was 1.0 μL. Each sample was analyzed three times. For quantification, calibration curves were prepared using solutions of known concentrations. Calibration solutions were gravimetrically prepared by means of an electronic balance accurate to ±0.1 mg. Calibration coefficients were obtained by fitting the calibration results for each composition range to a straight line. All measurements were performed in triplicate. The estimated uncertainties in the mass fraction determinations were ±0.00044 and ±0.007 for water and limonene, respectively, in the terpene-rich phase and ±0.0053 for water and limonene in the water-rich phase.

Results and Discussion

LLE Measurements. Table 1 gives the limonene solubility in water at different temperatures. Slight differences between experimental and reported data[4] are observed. No variation of limonene solubility in water was detected between 296.15 K and 316.15 K. The experimental binodal curves and tie-line data for water + acetonitrile + limonene at different temperatures are given in Tables 2 and 3. A typical plot at 306.15 K is shown in Figure 1a. Water + acetonitrile and acetonitrile + limonene are completely miscible, but limonene + water is a partially miscible liquid pair. Therefore, the ternary system behaves as a type-1 LLE. Under the conditions of this study, the temperature has a small effect on the area of the two-phase region. The immiscibility region slightly decreases by increasing the temperature from 296.15 K to 323.15 K.

Table 3. Experimental Tie Lines for Water (1) + Limonene (2) + Acetonitrile (3)

terpene-rich phase				water-rich phase			
w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2
$T = 296.15$ K							
0.0011	0.9970	0.0008	0.9959	0.5346	0.0068	0.2362	0.0294
0.0010	0.9968	0.0007	0.9956	0.3876	0.0045	0.2205	0.0329
0.0010	0.9964	0.0006	0.9954	0.3417	0.0159	0.1902	0.0417
0.0009	0.9961			0.3123	0.0223		
$T = 306.15$ K							
0.0141	0.9847	0.0120	0.9860	0.5403	0.0001	0.2424	0.0195
0.0138	0.9848	0.0116	0.9859	0.3880	0.0052	0.2191	0.0315
0.0132	0.9852	0.0111	0.9862	0.3390	0.0118	0.1969	0.0319
0.0126	0.9856			0.2950	0.0150		
$T = 316.15$ K							
0.0059	0.9875	0.0056	0.9890	0.5435	0.0005	0.2400	0.0355
0.0058	0.9879	0.0056	0.9893	0.3983	0.0045	0.2200	0.0346
0.0057	0.9883	0.0055	0.9897	0.3570	0.0060	0.1850	0.0496
0.0057	0.9886			0.3000	0.0210		
$T = 323.15$ K							
0.0121	0.9699	0.0121	0.9740	0.5381	0.0002	0.2576	0.0260
0.0121	0.9709	0.0120	0.9750	0.4019	0.0050	0.2210	0.0440
0.0121	0.9716	0.0120	0.9760	0.3583	0.0070	0.1900	0.0525
0.0121	0.9729			0.3143	0.0110		

Correlation of Experimental Data. The NRTL[8] and UNIQUAC[9] models were used to correlate the experimental data for the ternary system water + limonene + acetonitrile, and UNIQUAC structural parameters r, q, and q' of pure components were taken from previous reports.[11,12] The nonrandomness parameter of the NRTL equation, α_{ij}, was taken to be 0.388 for all binary systems of this study because they are aqueous−organic systems.[13]

The activity coefficients at infinite dilution γ_i^∞ for the miscible binary systems water + acetonitrile and limonene + acetonitrile were determined on the basis of the UNIFAC model at temperatures of 296.15 K, 306.15 K, 316.15 K, and 323.15 K. For the water + limonene binary system, we determined mutual solubility as reported by Prausnitz.[14] The activity coefficients at infinite dilution γ_i^∞ and the binary parameters τ_{ij} used in NRTL calculations are listed in Table 4.

The values of interaction parameters in the UNIQUAC equation (a_{ij} and a_{ji}) of water, limonene, and acetonitrile (Table 5) were determined by minimizing the differences between the experimental and calculated distribution coefficients for each component over all tie lines at different temperatures. A MATLAB 6.1 computer program and an effective optimization algorithm (Levenberg−Marquardt) and the optimization toolbox (fminsearch) were used. As can be observed in Table 5, there is no relationship between the parameters determined at each temperature. The objective function (OF) is presented in eq 1:

$$\mathrm{OF} = \sum_k \frac{[\sum_i (K_{i,\mathrm{exptl}} - K_{i,\mathrm{calcd}})/K_{i,\mathrm{exptl}}]^2}{n} \tag{1}$$

where i = water, limonene, or acetonitrile; k = 1, 2, ... n tie lines; $K_{i,\mathrm{exptl}}$ is the experimental distribution coefficient of component i; and $K_{i,\mathrm{calcd}}$ is the calculated distribution coefficient of component i .

Experimental and correlated data by NRTL and UNIQUAC equations at 306.15 K are compared in parts a and b of Figure 1, respectively. The quality of correlation was estimated by means of the root-mean-square deviations (rmsd's) obtained from the difference between the experimental and calculated mass fractions using UNIQUAC and

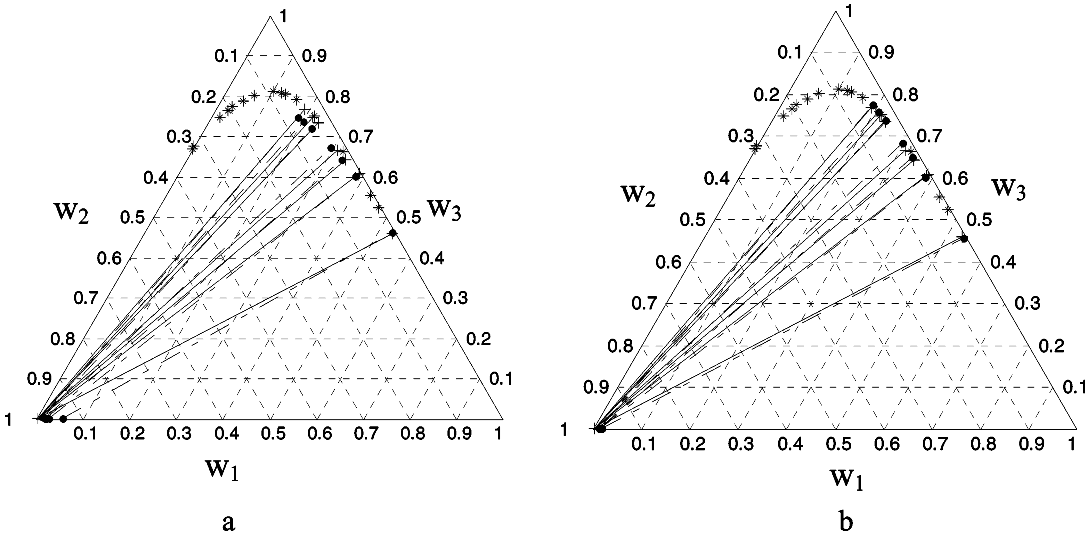

Figure 1. Ternary liquid−liquid equilibrium of water (1) + limonene (2) + acetonitrile (3) at 306.15 K: *, experimental binodal curve −+, experimental tie lines; - -●, correlated data from (a) NRTL and (b) UNIQUAC.

Table 4. Activity Coefficients at Infinite Dilution γ_i^∞ and Binary Parameters τ_{ij} Used in NRTL Calculations

system	*T*/K	γ_1^∞	γ_2^∞	τ_{12}	τ_{21}
	296.15	4.623	11.616	1.9685	0.6140
water + acetonitrile 1−2	306.15	4.506	11.077	1.9342	0.5922
	316.15	4.398	10.594	1.9023	0.5718
	323.15	4.327	10.286	1.8813	0.5581
	296.15	1540.18	802699.4	13.1616	7.2600
water + limonene 1−2	306.15	1238.88	662133.9	12.9444	7.0367
	316.15	1009.74	552160.4	12.7387	6.8266
	323.15	881.389	489119.8	12.6001	6.6866
	296.15	46.346	61.858	3.1840	2.9105
acetonitrile + limonene 1−2	306.15	40.391	58.699	3.1268	2.7691
	316.15	35.509	55.737	3.0728	2.6371
	323.15	32.601	53.774	3.0367	2.5496

Table 5. Optimized UNIQUAC Binary Interaction Parameters a_{ij}/K for the System Water (1) + Limonene (2) + Acetonitrile (3) at Different Temperatures

T/K	components *i*−*j*	a_{ij}	a_{ji}
	1−2	179.6	1285.4
296.15	1−3	−290.1	328.5
	2−3	783	12.1
	1−2	11 737	396
306.15	1−3	9963	−240
	2−3	995	−33
	1−2	11 329	867
316.15	1−3	9068	124
	2−3	888	−44
	1−2	10 715	678
323.15	1−3	12 159	177
	2−3	741	−23

NRTL equations at each temperature (eq 2).

$$\mathrm{rmsd} = \left(\sum_k^n \left[\frac{\sum_i^3 \sum_j^2 (w_{ijk,\mathrm{exptl}} - w_{ijk,\mathrm{calcd}})^2}{6n} \right] \right)^{1/2} \qquad (2)$$

where *i* represents index components (water, limonene, or acetonitrile); *j* represents the water- or terpene-rich phase; and *k* = 1, 2, ..., *n* (tie lines). The rmsd values for the NRTL and UNIQUAC models are listed in Table 6. The overall magnitude of the rmsd values suggests that both the UNIQUAC and NRTL models provide an adequate representation of the phase behavior of the ternary water + limonene + acetonitrile system in the temperature range studied. Notwithstanding, the UNIQUAC model provides a much better correlation of the experimental tie lines than the NRTL model, particularly at low temperatures. Complete miscibility for the water + acetonitrile + limonene system at (306.15 ± 0.5) K is observed for an acetonitrile mass fraction greater than about 81 %.

Table 6. Root-Mean-Square Deviations

T/K	UNIFAC	NRTL	UNIQUAC
296.15	0.0096	0.0321	0.0047
306.15	0.0107	0.0185	0.0039
316.16	0.0089	0.0133	0.0062
323.15	0.0123	0.0164	0.0099

Prediction. Experimental values were compared with those predicted by the UNIFAC (functional-group activity coefficients) method developed by Fredenslund et al.[7] In this work the equilibrium data for the ternary mixture were predicted using the software UNIFAC.BAS[15] modified with the LLE parameters reported by Magnussen et al.[16] The quality of the predictions was evaluated by calculating the rmsd (Table 6). Predicted and experimental tie lines at 306.15 K are compared in Figure 2. In the temperature range studie. A good prediction of the LLE of the water + acetonitrile + limonene system is obtained by UNIFAC.

Conclusions

LLE data for the water + limonene + acetonitrile ternary system were obtained at 296.15 K, 306.15 K, 316.15 K, and 323.15 K. Equilibrium data were correlated using the

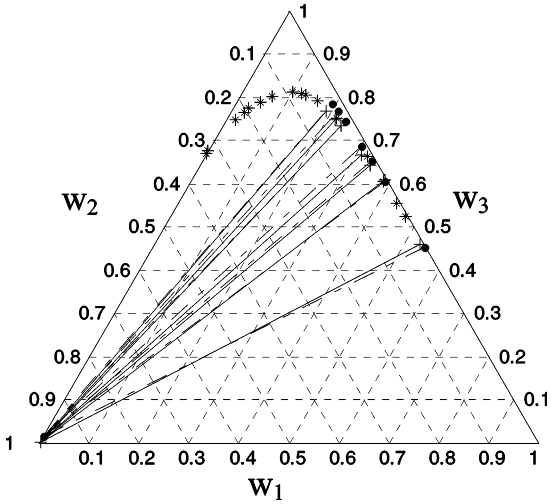

Figure 2. Ternary liquid−liquid equilibrium of water (1) + limonene (2) + acetonitrile (3) at 306.15 K: *, experimental binodal curve; −+, experimental tie lines; - -●, predicted data from UNIFAC.

NRTL and UNIQUAC methods and predicted by UNIFAC. New UNIQUAC and NRTL interaction binary parameters for the water + limonene + acetonitrile system are reported. It was found that the UNIQUAC equation gives the best fit. The LLE data predicted with UNIFAC are in good agreement with experimental data.

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