JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Liquid−Liquid and Vapor−Liquid−Liquid Equilibrium of the 2-Butanone + 2-Butanol + Water System

Estela Lladosa, Juan B. Montón,* Javier de la Torre, and Nelson F. Martínez

Departamento de Ingeniería Química, Escuela Técnica Superior de Ingeniería, Universitat de València, 46100 Burjassot, Valencia, Spain

ABSTRACT: Liquid−liquid phase equilibrium (LLE) data have been measured for the ternary system 2-butanone + 2-butanol + water at (293.25, 313.15, 323.15, and 333.15) K. Experimental results show the extreme phase sensitivity of this system to temperature. At (293.15 and 313.15) K the ternary system has two separate biphasic regions, while at (323.15 and 333.15) K the system has only one region of immiscibility. The nonrandom two-liquid (NRTL) and universal quasichemical activity coefficient (UNIQUAC) models were applied to correlate the ternary system at (323.15 and 333.15) K; the interaction parameters obtained from both models successfully correlated the equilibrium compositions. Moreover, isobaric vapor−liquid−liquid equilibrium (VLLE) is measured for this ternary mixture at 101.3 kPa. The experimental data were compared with the estimation from LLE binary interaction parameters using NRTL and UNIQUAC models and with the prediction of universal functional activity coefficient (UNIFAC) model.

INTRODUCTION

Separating the products obtained by chemical processes is necessary for an appropriate design of separation equipment and, therefore, experimental data of phase equilibrium (liquid−liquid and vapor−liquid data). Multicomponent multiphase equilibrium data are of fundamental importance in the design and/or in the optimal operation of chemical processes. Moreover, advancement of technology and refinement of process design requires high quality experimental data. However, because of the great number of systems and design conditions of potential practical interest, the amount of experimental data obtained will never amount to more than a small fraction of that required. Therefore, techniques for prediction of mixture properties have become essential parts of industrial computer simulators. To efficiently utilize this procedure, it is necessary to make predictions from a minimum amount of experimental data.

Specifically, in the case of partially miscible ternary mixtures it would be highly desirable to have experimental vapor−liquid−liquid data, since in this case, the data available in the literature are scarce and in most cases there is no prior information. Furthermore, estimation or simulation of the vapor−liquid−liquid equilibrium (VLLE) with commercial simulation software is defective; obtaining results that do not correspond with reality and therefore its use for the design should be done with great caution.

The 2-butanone + 2-butanol + water ternary system is a partially miscible mixture which has great interest because 2-butanone is the third most important ketone after acetone and cyclohexanone. It is used as a solvent in paints, dyes, and pharmaceutical and refining industries. 2-Butanone is used also as an important raw material for organic synthesis industry, as an intermediate in the perfumery industry, and for catalytic production.[1,2]

Currently, 2-butanone is commercially produced by dehydrogenation of 2-butanol, and this, in turn, is obtained by hydration of 2-butene.[1] In this manufacturing process, the 2-butanone + 2-butanol + water ternary mixture is obtained, which is studied in this work.

No references were found about VLLE data of this partially miscible ternary system, and only two references about liquid−liquid equilibrium (LLE) data at various temperatures[3,4] were found. However, the references of the constituent binary systems of both vapor−liquid equilibrium (VLE) and LLE data are relatively abundant. So, data were found in the literature for the 2-butanol−water system,[4−8] 2-butanone−water system,[9−15] and 2-butanol−2-butanone system.[16−19]

In a previous paper,[20] we report a study of the VLLE data of the di-*n*-propyl ether + *n*-propyl alcohol + water ternary system which describes the problems associated with the experimental determination and the theoretical estimation of such equilibrium data based on parameters of thermodynamic models obtained from VLE or LLE data.

This paper reports the results obtained for the ternary system 2-butanone + 2-butanol + water, so the VLLE at 101.3 kPa and the LLE at four different temperatures.

The results obtained have been analyzed by applying thermodynamic models such as the nonrandom two-liquid (NRTL)[21] and universal quasichemical activity coefficient (UNIQUAC)[22] or the universal functional activity coefficient (UNIFAC)[23] model to predict them.

EXPERIMENTAL SECTION

Chemicals. 2-Butanone (w > 99.7 %, assay GC) was purchased from Aldrich Ltd.; 2-butanol (w = 99.0 %, assay GC) was supplied from Fluka, and water was bidistilled. The reagents were used without further purification after chromatography failed to show any significant impurities. The water content, determined using a Karl Fischer volumetric automatic titrator (Metrohm, 701 KF Titrino), was small in all chemicals (w < 0.05 %). Before measurements, the liquids were degassed and subsequently dried over molecular sieves (Union Carbide, type 4 Å, 1/16 in. pellets).

Received: May 4, 2010
Accepted: February 1, 2011
Published: February 24, 2011

dx.doi.org/10.1021/je1004643 | *J. Chem. Eng. Data* 2011, 56, 1755–1761

Table 1. Density ρ, Refractive Index n_D, and Normal Boiling Point T_b of Pure Components

component	ρ (298.15 K)/kg·m^{-3}		n_D (298.15 K)		T_b (101.3 kPa)/K		UNIQUAC parameters	
	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]	r_i[b]	q_i[b]
2-butanone (1)	799.62	800.02	1.3761	1.3764	352.68	352.79	3.2479	2.8759
2-butanol (2)	802.35	802.60	1.3951	1.3949	372.56	372.70	3.4535	3.0480
water (3)	997.00	997.04	1.3332	1.3325	373.15	373.15	0.9200	1.3997

[a] Ref 24. [b] Ref 25.

The refractive indices of the pure components were measured at 298.15 K using an Abbe refractometer Atago 3T, and the densities were measured at 298.15 K using an Anton Paar DMA 58 densimeter. Temperature was controlled to ± 0.01 K with a thermostatted bath. The uncertainly in refractive index and density measurements are ± 0.0002 and ± 0.01 kg·m^{-3}, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those given in the literature.[24,25] Appropriate precautions were taken when handling the reagents to avoid hydration.

Apparatus and Procedure. *LLE Data.* The equipment used and the procedure for the determination of liquid−liquid data have been described in a previous work.[26] The composition of the sampled liquid phases was determined using a CE Instruments GC 8000 Top gas chromatograph equipped with a thermal conductivity detector (TCD), using a 30 m, 0.454 mm inner diameter (i.d.) capillary column (DB-MTBE, J & Scientific). The GC response peaks were treated with Chrom-Card software for Windows. Column, injector, and detector temperatures were (343, 473, and 373) K, respectively. Very good peak separation was achieved under these conditions, and calibration analyses were carried out to convert the peak area ratio to the mass composition of the sample. To obtain homogeneous mixtures of the standard, 0.5 mL of ethanol has been added to the calibration vials.

Additionally, for this system, experimental points close to the plate point or plate points have been determined (at low temperatures there are two independent immiscibility zones) by the cloud-point method.[26] In this method, initially, known amounts of the three components were weighted, with a global composition close to the plate point, into a thermostatted equilibrium cell with sealed heated vials. The temperature of the cell was fixed at 313.15 K at which the mixture became homogeneous. Then, we slowly added known quantities of adequate component (usually, 2-butanol or water) until the mixture became slightly cloudy. So, the end point was determining by observing the transition from a homogeneous to a heterogeneous solution. The phase changes were detected visually using a direct oblique light.

The temperature in the equilibrium cell was controlled within ± 0.01 K using a HC5 Julabo thermostat with water as thermostatting liquid, and weighing was carried out with an uncertainty of 0.0001 g.

As it can be seen in Figure 2, the cloud-point corroborates the existence of two independent immiscibility zones.

VLLE Data. To determine the VLLE data it has been used a dynamic recirculating still equipped with a Cottrell circulation pump manufactured by Fischer Labor and Verfahrenstechnik (model Labodest VLE 602/D), whose detailed description can be found in a previous work,[27] modified according to indications of Gomis et al.,[11] by coupling an ultrasonic homogenizer to the boiling flask that ensures a good dispersion of partly miscible liquid phases. Detailed description of the modified equipment and the experimental procedure, sampling and analysis of both phases, can be found in previous references.[20,27]

The composition of the sampled liquid phases and vapor phase were determined using a CE Instruments GC 8000 Top gas chromatograph after calibration with gravimetrically prepared standard solutions. A thermal conductivity detector (TCD), using a 30 m, 0.454 mm i. d. capillary column (DB-MTBE, J & Scientific), was used to determine the compositions of the different phases. The GC response peaks were treated with Chrom-Card for Windows. The same gas chromatograph and conditions than LLE were used to determine the composition of the sampled liquids and vapor phases. Very good peak separation was achieved under these conditions, and calibration analyses were used to convert the peak area ratio to the mass composition of the sample. The uncertainty in the mole fraction was usually less than 0.001.

■ RESULTS AND DISCUSSION

Experimental LLE Data. To observe the influence of the temperature on the mutual solubility of the ternary system 2-butanone + 2-butanol + water, experimental measurements were made for four different temperatures (293.25, 313.15, 323.15, and 333.15) K, determining the composition of both phases in equilibrium (ends of the tie lines). Table 2 shows the experimental data obtained, where the subscript I represents the organic rich phase and II the aqueous rich phase. All concentrations are expressed in mole fractions.

Figures 1 to 4 are the data of LLE of this system at different temperatures. As it can be seen, temperature has a great influence on the LLE of this system; the solubility clearly decreases with increasing temperature (increasing the area of immiscibility). Moreover, at (293.15 and 313.15) K there are two different areas of immiscibility. At (323.15 and 333.15) K the system shows a single immiscibility zone characterized by two partially miscible binary systems (type II of Treybal classification[28]). In Figures 1, 2, and 4 the experimental data obtained by Altsybeeva[3] at the same temperatures have been included.

Moreover, it has been included a table (Table 3) where it is compared the values of aqueous solubility for binary subsystems with the literature data. As can be seen in Table 3, the experimental data of the binary subsystems are in good agreement with the literature data.

LLE Data Correlation. It has been attempted to correlate the experimental data together with the literature data at the same conditions, both binary[5,6,14,15] and ternary data,[3] using the NRTL[21] and UNIQUAC[22] models (Appendix) for each of the temperatures tested using the commercial program Chem-Cad data processing, with uneven results. With the equilibrium data corresponding to (293.15 and 313.15) K (Figures 1 and 2) was not possible to obtain an acceptable correlation because the program cannot correlate two independent immiscibility zones. However, at (323.15 and 333.15) K good correlations were obtained as shown in Table 4.

To fit the UNIQUAC interaction parameters, the structural parameters (r_i and q_i) recommended by DECHEMA[25] were used for the pure components, and they are listed in Table 1.

Table 2. LLE Data for the 2-Butanone (1) + 2-Butanol (2) + Water (3) System at Different Temperatures

T/K	2-butanone-rich phase/x_i^{I}		water-rich phase/x_i^{II}	
	x_1	x_2	x_1	x_2
293.15	0.649	0.000	0.082	0.000
	0.538	0.026	0.090	0.003
	0.482	0.036	0.091	0.006
	0.409	0.051	0.095	0.012
	0.315	0.053	0.108	0.019
	0.303	0.052	0.110	0.020
	0.014	0.236	0.005	0.066
	0.000	0.298	0.000	0.056
313.15	0.633	0.000	0.061	0.000
	0.545	0.029	0.064	0.002
	0.505	0.041	0.063	0.004
	0.462	0.055	0.062	0.008
	0.409	0.068	0.063	0.010
	0.404	0.071	0.062	0.011
	0.329	0.087	0.062	0.016
	0.264	0.096	0.062	0.022
	0.209	0.096	0.064	0.028
	0.164	0.096	0.069	0.039
	0.063	0.167	0.025	0.058
	0.059	0.180	0.021	0.056
	0.048	0.221	0.013	0.050
	0.040	0.243	0.010	0.048
	0.017	0.296	0.003	0.044
	0.000	0.335	0.000	0.042
323.15	0.612	0.000	0.056	0.000
	0.549	0.028	0.054	0.002
	0.512	0.040	0.059	0.005
	0.469	0.054	0.053	0.007
	0.416	0.071	0.053	0.009
	0.412	0.075	0.054	0.010
	0.345	0.088	0.052	0.013
	0.290	0.104	0.050	0.017
	0.245	0.112	0.050	0.021
	0.204	0.120	0.047	0.026
	0.146	0.134	0.041	0.034
	0.128	0.141	0.039	0.038
	0.096	0.167	0.027	0.042
	0.074	0.198	0.019	0.041
	0.070	0.209	0.017	0.042
	0.053	0.235	0.012	0.041
	0.042	0.255	0.008	0.041
	0.018	0.300	0.003	0.039
	0.000	0.336	0.000	0.042
333.15	0.623	0.000	0.050	0.000
	0.541	0.029	0.051	0.003
	0.505	0.039	0.050	0.004
	0.420	0.070	0.048	0.008
	0.413	0.073	0.049	0.008
	0.355	0.092	0.046	0.012
	0.306	0.110	0.044	0.016
	0.263	0.121	0.043	0.018
	0.227	0.133	0.040	0.022
	0.169	0.154	0.035	0.028
	0.147	0.162	0.031	0.030
	0.109	0.186	0.023	0.035
	0.080	0.214	0.017	0.037
	0.074	0.222	0.015	0.037
	0.056	0.249	0.011	0.038
	0.045	0.265	0.008	0.037
	0.019	0.305	0.003	0.037
	0.000	0.335	0.000	0.037

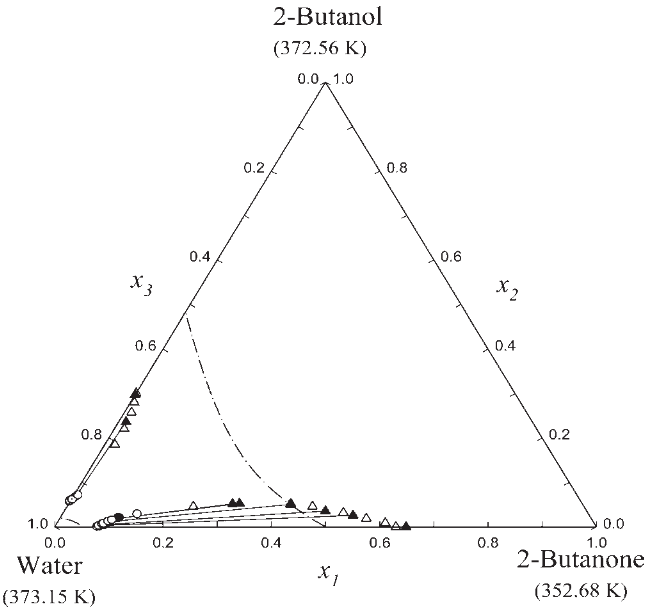

Figure 1. LLE of the 2-butanone (1) + 2-butanol (2) + water (3) system at 293.15 K. Experimental data: ▲, 2-butanone rich phase; ●, aqueous rich phase; —, experimental tie lines. References: △, 2-butanone rich phase from ref 3; ○, aqueous rich phase from ref 3. Estimated using the UNIFAC model: — · —, binodal curve.

The nonrandomness parameter (α_{ij}) of the NRTL equation was fixed at values between 0.2 and 0.3 during the calculations, and the best results, achieved with $\alpha_{ij} = 0.3$, are given in Table 4.

There are two effective binary interaction parameters for a binary subsystem. Therefore, six effective binary interaction parameters are required for a ternary system. The corresponding sets of binary interaction parameters were determined by minimizing the differences between the experimental and the calculated mole fraction for each of the components over all of the lie lines. The objective function (OF) used is:

$$\mathrm{OF} = \sum_{k=1}^{M} \sum_{j=1}^{2} \sum_{i=1}^{3} (x_{ijk} - \hat{x}_{ijk})^2 \qquad (1)$$

where M is the number of tie lines, x indicates the experimental mole fraction, $\hat{x}$ the calculated mole fraction, and subscripts i, j, and k denote, respectively, the number of components, phases, and tie lines.

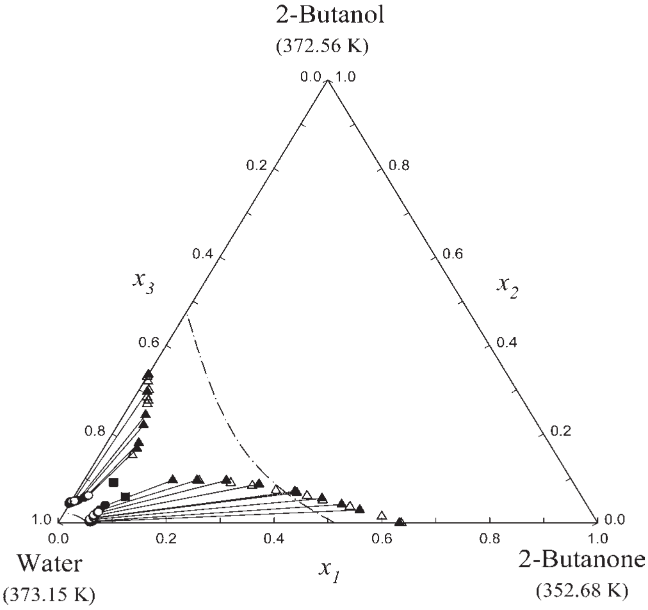

Figure 2. LLE of the 2-butanone (1) + 2-butanol (2) + water (3) system at 313.15 K. Experimental data: ▲, 2-butanone rich phase; ●, aqueous rich phase; —, experimental tie lines; ■, experimental cloud point. References: △, 2-butanone rich phase from ref 3; ○, aqueous rich phase from ref 3. Estimated using the UNIFAC model: — · —, binodal curve.

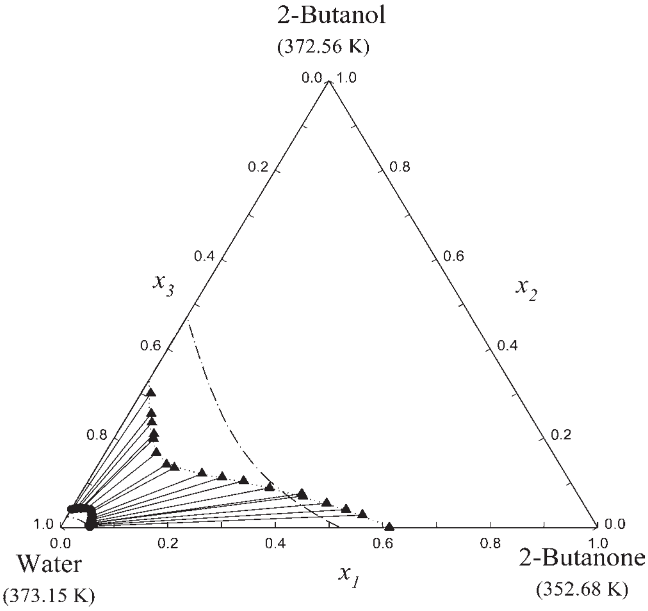

Figure 3. LLE of the 2-butanone (1) + 2-butanol (2) + water (3) system at 323.15 K. Experimental data: ▲, 2-butanone rich phase; ●, aqueous rich phase; —, experimental tie lines. Estimated using the UNIFAC model: — · —, binodal curve. Calculated using the UNIQUAC model: · · ·, binodal curve.

The root-mean-square deviation (rmsd) between the experimental and the calculated data is also included in Table 4:

$$\text{rmsd} = 100\cdot\left(\sum_{k=1}^{M}\sum_{j=1}^{2}\sum_{i=1}^{3}\frac{(x_{ijk}-\hat{x}_{ijk})^2}{6M}\right)^{1/2} \qquad (2)$$

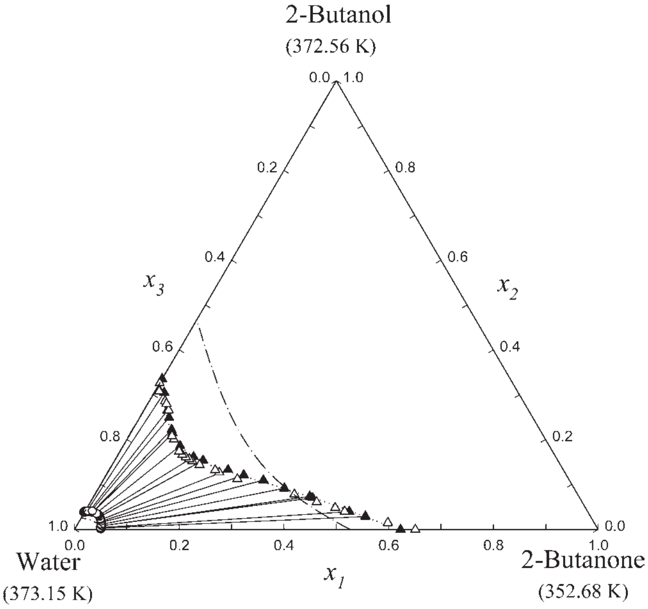

Figure 4. LLE of the 2-butanone (1) + 2-butanol (2) + water (3) system at 333.15 K. Experimental data: ▲, 2-butanone rich phase; ●, aqueous rich phase; —, experimental tie lines. References: △, 2-butanone rich phase from ref 3; ○, aqueous rich phase from ref 3. Estimated using the UNIFAC model: — · —, binodal curve. Calculated using the UNIQUAC model: · · ·, binodal curve.

Table 3. Comparison of the Binary Subsystems of LLE Data for the 2-Butanone (1) + 2-Butanol (2) + Water (3) System at Different Temperatures

	2-butanone-rich phase/x_i^{I}		water-rich phase/x_i^{II}		
T/K	x_1	x_2	x_1	x_2	ref
293.15	0.649	0.000	0.082	0.000	exptl.
	0.661	0.000	0.093	0.000	9
	0.000	0.298	0.000	0.056	exptl.
	0.000	0.304	0.000	0.058	5
	0.000	0.299	0.000	0.058	6
313.15	0.633	0.000	0.061	0.000	exptl.
	0.636	0.000	0.059	0.000	3
	0.000	0.335	0.000	0.042	exptl.
	0.000	0.340	0.000	0.042	5
	0.000	0.332	0.000	0.041	6
323.15	0.612	0.000	0.056	0.000	exptl.
	0.628	0.000	0.061	0.000	14
	0.000	0.336	0.000	0.042	exptl.
	0.000	0.342	0.000	0.038	5
	0.000	0.335	0.000	0.035	6
333.15	0.623	0.000	0.050	0.000	exptl.
	0.645	0.000	0.046	0.000	15
	0.000	0.335	0.000	0.037	exptl.
	0.000	0.337	0.000	0.036	5
	0.000	0.329	0.000	0.034	6

In Table 4, it can be observed that both models were found to properly correlate the data, but UNIQUAC model led to better results. In Figures 3 and 4 the experimental data at (323.15 and 333.15) K together with the binodal curves calculated using the

Table 4. UNIQUAC and NRTL Binary Interaction Parameters for the System 2-Butanone (1) + 2-Butanol (2) + Water (3)

		UNIQUAC parameters			NRTL parameters			
T/K	$i-j$	$A_{ij}/\mathrm{J\cdot mol^{-1}}$	$A_{ji}/\mathrm{J\cdot mol^{-1}}$	rmsd	α_{ij}	$A_{ij}/\mathrm{J\cdot mol^{-1}}$	$A_{ji}/\mathrm{J\cdot mol^{-1}}$	rmsd
323.15	1−2	−209.34	1826.96	0.45	0.3	−2006.64	5771.32	1.08
	1−3	1875.69	679.33		0.3	1206.92	7628.50	
	2−3	−658.24	2625.88		0.3	−2014.44	11454.05	
333.15	1−2	−49.82	1067.90	0.42	0.3	−2756.97	5539.99	1.18
	1−3	2277.64	465.76		0.3	1231.35	7912.83	
	2−3	−804.23	2901.16		0.3	−2023.81	11691.92	

Table 5. UNIFAC R_k and Q_k Parameters[29]

subgroup (k)	main group no.	R_k	Q_k
CH_3	1	0.9011	0.848
CH_2	1	0.6744	0.540
CH_3CO	10	1.6724	1.448
CH	11	0.4469	0.228
OH	5	1.0000	1.200
H_2O	7	0.9200	1.400

Table 6. UNIFAC Group Interaction Parameters[29]

M	N	a_{mn}/K	a_{nm}/K
CH_3,CH_2,CH	CH_3CO	476.4	26.76
CH_3,CH_2,CH	OH	986.5	156.4
CH_3,CH_2,CH	H_2O	1318.0	300.0
CH_3CO	OH	164.5	84.0
CH_3CO	H_2O	472.5	−195.4
OH	H_2O	353.5	−229.1

Table 7. Experimental VLLE Data of the System 2-Butanone (1) + 2-Butanol (2) + Water (3) at 101. 3 kPa

	organic-rich phase, x_i^{I}		aqueous-rich phase, x_i^{II}		vapor phase, y_i		
	x_1	x_2	x_1	x_2	y_1	y_2	T/K
1	0.000	0.324	0.000	0.037	0.000	0.388	360.46
2	0.029	0.273	0.006	0.038	0.098	0.332	358.81
3	0.053	0.244	0.010	0.037	0.184	0.281	357.31
4	0.064	0.224	0.012	0.035	0.224	0.255	356.39
5	0.080	0.204	0.016	0.034	0.265	0.229	355.66
6	0.127	0.176	0.024	0.030	0.375	0.167	353.44
7	0.183	0.147	0.032	0.023	0.443	0.128	352.02
8	0.228	0.132	0.039	0.021	0.502	0.094	350.80
9	0.341	0.093	0.042	0.011	0.555	0.062	349.24
10	0.415	0.066	0.045	0.007	0.597	0.035	348.16
11	0.493	0.044	0.049	0.003	0.621	0.020	347.52
BIN	0.617	0.000	0.054	0.000	0.649	0.000	346.68

UNIQUAC model have been plotted. As can be seen the result is good.

LLE Data Prediction by UNIFAC. The experimental LLE data were compared with those predicted by the UNIFAC[23] group contribution model. The interaction and structural parameters required for the implementation of the prediction method were taken from Hanse et al.,[29] and they are summarized in Tables 5 and 6. The quality of the prediction can be observed in Figures 1 to 4 where it has been included the binodal curves predicted by UNIFAC. As shown in Figures 1 to 4 the liquid compositions predicted by the UNIFAC method cannot adequately fit the experimental data.

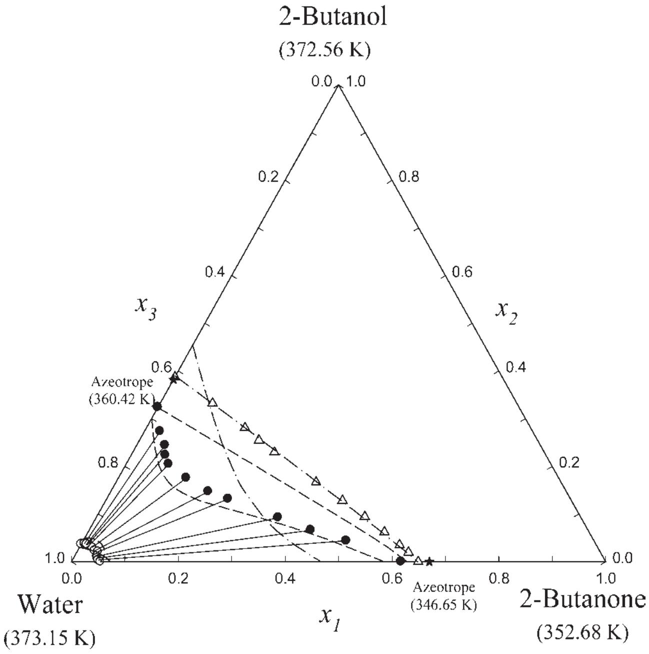

Figure 5. Comparison of the VLLE data for the 2-butanone (1) + 2-butanol (2) + water (3) ternary system at 101.3 kPa. Experimental data: ●, the 2-butanone rich phase; ○, the aqueous rich phase; △, the vapor phase; —, experimental tie lines. Binary azeotropes references: ★, 2-butanone−water azeotropic data;[33] 2-butanol−water azeotropic data.[34] Calculated data: − − −, estimated with LLE parameters using UNIQUAC model. Predicted data: − · −, using UNIFAC prediction model.

Experimental VLLE Data. Complete VLLE data of the ternary system 2-butanone + 2-butanol + water system at 101.3 kPa are listed in Table 7. The experimental ternary VLLE data were tested by the point-to-point L/W Wisniak[30] consistency test (consistent data ratio values $0.92 < L/W < 1.10$) and were found to be thermodynamically consistent. All L/W values are between 0.99 and 1.00. The test did not reveal any significant inconsistency in the data. The consistency of the ternary data was also checked with the Wisniak and Tamir[31] modification of the McDermot−Ellis[32] test ($D < D_{\max}$ at all data points).

Figure 5 shows the ternary diagram of the VLLE equilibrium of this system including the experimental tie lines, the binodal curve, the vapor-phase composition of the experimental data, and the binary azeotropes from the literature.[33,34]

Table 8. Average Absolute Deviations Between Experimental and Calculated Values for Different G^E Models for the 2-Butanone (1) + 2-Butanol (2) + Water (3) System

	aqueous phase		organic phase		vapor phase		
	AAD x_1	AAD x_2	AAD x_1	AAD x_2	AAD y_1	AAD y_2	AAD T
UNIQUAC[a]/LLE[b]	0.013	0.012	0.008	0.005	0.012	0.027	1.66
NRTL[a]/LLE[b]	0.020	0.019	0.018	0.012	0.023	0.028	2.83
UNIFAC[a]	0.006	0.005	0.042	0.060	0.0133	0.0076	0.20

[a] Estimated using Aspen HYSYS v2006. [b] With parameters of LLE at 333.15 K determined in this work (Table 4).

Actually, Figure 5 represents the projection on the ternary composition diagram of the intersection of the single liquid−liquid envelope with the VLE surface.[35] As can be seen in this figure, the water is partially miscible with 2-butanone and 2-butanol, which are completely soluble each other. This behavior is the same that observed for LLE data at temperatures above 323.15 K (Figures 3 and 4).

The vapor phase is outside the binodal curve which means that the vapor forms a single liquid phase when once it is condensed. It was proved the nonexistence of a ternary azeotrope using a distillation column (Fischer SPALTROHR column HMS-500, controlled by Fischer system D301-C with a high equivalent a hundred theoretical trays). In all cases, it was obtained as overhead product the 2-butanone−water binary azeotrope,[34] which is the lowest boiling point of the two binary azeotropes.[33,34]

Estimation of VLLE from LLE Binary Interaction Parameters. Beyond determining experimental VLLE data, one objective of this work would be to study the possibility of using thermodynamic models such as NRTL and UNIQUAC to predict the VLLE using parameters obtained from simple LLE experiments.

The VLLE of this system has been estimated using the LLE parameters obtained at 333.15 K (Table 3). The average absolute deviations (AAD) between experimental and estimated values are shown in Table 8.

In general, the estimation is pretty good, but as expected, the largest deviations are obtained by estimating the vapor phase because the parameters used come from LLE data. This behavior can be seen in Figure 5, in which the experimental data together with the data estimated with the best model, in this case the UNIQUAC model, are represented.

VLLE Data Prediction by UNIFAC. The experimental VLLE data of this system were predicted by the UNIFAC method using the Aspen Hysys v.2006 simulation software. The quality of the prediction can be evaluated with AAD between experimental and calculated values of the composition of both liquid phases and vapor phase, which are shown in Table 8. Surprisingly, this model predicts very well the boiling temperature and vapor composition but fails in the prediction of the two liquid phases; especially the phase rich in 2-butanone, as can also be seen in Figure 5.

CONCLUSIONS

LLE data of the ternary system composed of 2-butanone + 2-butanol + water were measured at different temperatures of (298.15 to 333.15) K. Temperature has a great effect on the size of the immiscibility region for this ternary system. The LLE data were correlated using the NRTL and UNIQUAC models. The correlation with UNIQUAC equation gives the best results, but also the NRTL equation with a value of the nonrandomness parameter $\alpha = 0.3$ fits the experimental data satisfactorily.

Isobaric VLLE data were also measured for this ternary system at 101.3 kPa. Estimation of VLLE of partially miscible ternary mixture was studied using UNIQUAC and NRTL methods using the parameters obtained in the LLE data correlation. The results obtained did not always reproduce adequately the behavior of both phases. It is well-known that it is difficult to find a set of parameters which can simultaneously correlate both VLE and LLE accurately. In conclusion, a good estimation of VLLE needs parameters correlated from experimental VLLE data.

In general, the UNIFAC prediction model is not very suitable to predict this type of system.

APPENDIX

NRTL Equation and Related Parameters.

$$\ln \gamma_i = \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{N} G_{ki} x_k} + \sum_{j=1}^{N} \frac{x_j G_{ij}}{\sum_{k=1}^{N} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{i=1}^{N} x_i \tau_{ij} G_{ij}}{\sum_{k=1}^{N} G_{kj} x_k} \right) \tag{A.1}$$

where:

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{A_{ji}}{RT} \tag{A.2}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{A.3}$$

UNIQUAC Equation and Related Parameters.

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{C}} + \ln \gamma_i^{\mathrm{R}} \tag{A.4}$$

$$\ln \gamma_i^{\mathrm{C}} = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{N} x_j l_j \tag{A.5}$$

$$\ln \gamma_i^{\mathrm{R}} = -q_i \ln \sum_{j=1}^{N} \theta_j \tau_{ji} + q_i - q_i \sum_{j=1}^{N} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{N} \theta_k \tau_{kj}} \tag{A.6}$$

where:

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \tag{A.7}$$

$$\tau_{ij} = \exp\left(-\frac{u_{ji} - u_{ii}}{RT} \right) = \exp\left(\frac{A_{ij}}{RT} \right) \tag{A.8}$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{N} q_j x_j} \tag{A.9}$$

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^{N} r_j x_j} \tag{A.10}$$

$$r_i = \frac{V_{wi}}{1.517 \cdot 10^{-2}} \tag{A.11}$$

$$q_i = \frac{A_{wi}}{2.5 \cdot 10^{8}} \tag{A.12}$$

■ AUTHOR INFORMATION

Corresponding Author

*Juan B. Montón. Tel.: +34 96 35 44317, juan.b.monton@uv.es. Fax: +37 963544898.

Funding Sources

Financial support from the Ministerio de Ciencia e Innovación of Spain, through project No. CTQ2007-61400/PPQ, the FEDER European Program, and the Conselleria de Cultura, Educació i Esport (Generalitat Valenciana) of Valencia (Spain) are gratefully acknowledged.

■ ACKNOWLEDGMENT

The authors are grateful to Prof. M. Cruz Burguet for her continuous dedication in our research group and valuable discussions.

■ REFERENCES

(1) Zhenhua, L.; Wenzhou, H.; Hao, M. A.; Kai, Q. Development and commercial application of methyl-ethyl ketone production technology. *Chin. J. Chem. Eng.* **2006**, *14*, 676–684.

(2) Neier, W.; Streklke, G. *Ullmann's Encyclopedia of Industrial Chemistry*, Version 3.6 (CD-ROM); Wiley-VCH, Verlag GmbH & Co.: Weinheim, Germany, 2002.

(3) Altsybeeva, A. I. Phase equilibrium in the ternary system of sec-butyl alcohol-methyl ethyl ketone-water. *Russ. J. Phys. Chem.* **1964**, *38*, 851–853.

(4) Kovach, J. W.; Seider, W. D. Vapor-liquid and liquid-liquid equilibria for the system sec-butyl alcohol-di-sec.butyl ether-water. *J. Chem. Eng. Data* **1988**, *33*, 16–20.

(5) Bozdag, O.; Lamb, J. A. Dependence of the mutual solubilities of (2-butanol + water) upon pressure and temperature. *J. Chem. Thermodyn.* **1983**, *15*, 165–171.

(6) Moriyoshi, T.; Kaneshina, S.; Aihara, K.; Yabumoto, K. Mutual solubility of 2-butanol + water under high pressure. *J. Chem. Thermodyn.* **1975**, *7*, 537–545.

(7) Altsybeeva, A. I. Phase equilibria and the thermodynamic properties of the system sec-butyl alcohol-water. *Russ. J. Phys. Chem.* **1964**, *38*, 676–679.

(8) Escobedo-Alvarado, G. N.; Sandler, S. I. Vapor-liquid equilibrium of two aqueous systems that exhibit liquid-liquid phase separation. *J. Chem. Eng. Data* **1999**, *44*, 319–322.

(9) Ferino, I.; Marongiu, B.; Solinas, V.; Torrazza, S. Thermodynamic properties of aqueous non-electrolyte mixtures. II. Excess enthalpies and liquid-liquid equilibrium of 2-alkanone + water mixtures. *Thermochim. Acta* **1983**, *70*, 149–161.

(10) Stephenson, R. M. Mutual solubilities: water-ketones, water-ehers, and water-gasoline-alcohols. *J. Chem. Eng. Data* **1992**, *37*, 80–95.

(11) Gomis, V. R.; Ruiz, F.; Asensi, J. C. The application of ultrasound in the determination of isobaric vapour-liquid-liquid equilibria data. *Fluid Phase Equilib.* **2000**, *172*, 245–259.

(12) Lencka, M.; Wichterle, I. Vapor-liquid equilibrium in the 2-butanone-water system at 101.325 kPa. *Fluid Phase Equilib.* **1984**, *18*, 245–252.

(13) Moon, H. M.; Ochi, K.; Kojima, K. Vapor-liquid equilibria for the ethyl methyl ketone + water system with limited miscibility. *J. Chem. Eng. Data* **1995**, *40*, 469–471.

(14) Campbell, A. N.; Kartzmark, E. M.; Falconer, W. E. The system: nicotine-methylethyl ketone-water. *Can. J. Chem.* **1958**, *36*, 1475–1486.

(15) Krupatkin, I. L.; Vorobeva, L. D.; Maskhuliya, V. P.; Veselova, M. B. Undersuchung der flüssing-flüssig-gleichgewicht in den systemen wasser-furfural-rhodanide und wasser-methylethyl ketone-rhodanide. *Zh. Obshch. Khim.* **1975**, *45*, 985–990.

(16) Miller, K. J.; Huang, H. Vapor-liquid equilibrium for binary systems 2-butanone with 2-butanol, 1-pentanol, and isoamyl alcohol. *J. Chem. Eng. Data* **1972**, *17*, 77–78.

(17) Di Cave, S.; Chianese, A.; Prantera, A. Vapor-liquid equilibrium of the system methylethylketone-sec-butyl alcohol. *J. Chem. Eng. Data* **1978**, *23*, 279–281.

(18) Tanaka, H.; Muramatsu, T.; Kato, M. Isobaric vapor-liquid equilibria for three binary systems of 2-butanone with 3-methyl-1-butanol, 1-butanol, or 2-butanol. *J. Chem. Eng. Data* **1992**, *37*, 164–166.

(19) Garriga, R.; Martinez, S.; Perez, P.; Gracia, M. Vapor pressures at several temperatures, and excess functions at T = 298.15 K of (butanone + 2-butanol). *J. Chem. Thermodyn.* **1999**, *31*, 117–127.

(20) Lladosa, E.; Montón, J. B.; Burguet, M. C.; de la Torre, J. Isobaric (vapour + liquid + liquid) equilibrium data for (di-n-propyl ether + n-propyl alcohol + water) and (diisopropyl ether + isopropyl alcohol + water) systems at 100 kPa. *J. Chem. Thermodyn.* **2008**, *40*, 867–873.

(21) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *1*, 135–144.

(22) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *1*, 116–128.

(23) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. *AIChE J.* **1975**, *21*, 1086–1099.

(24) *TRC Thermodynamic Tables. Non-Hydrocarbons*; Thermodynamics Research Center, NIST/TRC Table Database, WinTable: Gaithersburg, MD, 2004.

(25) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Frankfurt, Germany, 1977.

(26) Cháfer, A.; Lladosa, E.; de la Torre, J.; Burguet, M. C. Study of liquid-liquid equilibrium of the systems isobutyl acetate + acetic acid + water and isobutyl alcohol + acetic acid + water at different temperatures. *Fluid Phase Equilib.* **2008**, *271*, 76–81.

(27) Lladosa, E.; Montón, J. B.; Burguet, M. C. Phase equilibrium for the systems diisopropyl ether, isopropyl alcohol, + 2,2,4-trimethylpentane and n-heptane. *Fluid Phase Equilib.* **2010**, *289*, 135–139.

(28) Treybal, R. E. *Liquid extraction*; McGraw-Hill: New York, 1963.

(29) Hanse, H. K.; Rasmussen, P.; Fredenslund, A.; Schiller, M.; Gmehling, J. Vapor-liquid equilibria by UNIFAC group contribution. 5. Revision and extension. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352–2355.

(30) Wisniak, J. A new test for the thermodynamic consistency of vapor-liquid equilibrium. *Ind. Eng. Chem. Res.* **1993**, *32*, 1531–1533.

(31) Wisniak, J.; Tamir, A. Vapor-liquid equilibriums in the ternary systems water-formic acid-acetic acid and water-acetic acid-propionic acid. *J. Chem. Eng. Data* **1977**, *22*, 253–260.

(32) McDermott, C.; Ellis, S. R. M. A multicomponent consistency test. *Chem. Eng. Sci.* **1965**, *20*, 293–296.

(33) Tanaka, T. Attempting the prediction of an azeotrope and its x-y curve on the basis of the molecular parameters. *Fluid Phase Equilib.* **1985**, *24*, 187–203.

(34) Iwakabe, K.; Kosuge, H. Isobaric vapor-liquid-liquid equilibria with a newly developed still. *Fluid Phase Equilib.* **2001**, *192*, 171–186.

(35) Walas, S. M. *Phase equilibria in chemical engineering*; Butterworth-Heinemann; Boston, 1984.