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Liquid−Liquid and Vapor−Liquid−Liquid Equilibrium of the 4-Methyl-2-pentanone + 2-Butanol + Water System

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ABSTRACT: Liquid−liquid equilibrium (LLE) data have been measured for the ternary system 4-methyl-2 pentanone + 2-butanol + water at (283.15 and 333.15) K. Experimental results show a low influence of temperature on immiscibility zone size and shape. The NRTL and UNIQUAC models were applied to correlate the ternary system at (283.15 and 333.15) K, and 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, as well as the correlation obtained with these models. The prediction of the UNIFAC LL model has been obtained and compared with the previous results, to confirm the necessity to obtain experimental data in this type of system.

INTRODUCTION

To be able to design distillation columns appropriately is essential to have reliable information on the equilibrium of the systems involved. 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, partially miscible ternary mixtures would be highly desirable to have experimental vapor−liquid−liquid equilibrium (VLLE) 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 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. In this case, the necessity of experimental data already is more peremptory.

In this sense, previous studies[1,2] have demonstrated that the estimation of VLLE carried out using parameters obtained from VLE or LLE data did not always agree with the experimental data. In a previous work,[3] the 2-butanone + 2-butanol + water system has been focused on because of the extreme phase sensitivity of this system to temperature. Moreover, the estimation of VLLE of a partially miscible ternary mixture was studied using UNIQUAC[4] and NRTL[5] methods applying 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 vapor−liquid equilibrium (VLE) and liquid−liquid equilibrium (LLE) accurately. In conclusion, a good estimation of VLLE needs parameters correlated from experimental VLLE data.

So, this work continues this line with the study of the 4-methyl-2-pentanone + 2-butanol + water system, which involves one of the ketones more used in industry.

4-Methyl-2-pentanone (well-known as methyl isobutyl ketone or MIBK) is the third most important ketone used in industry, after acetone and 2-butanone (or methyl−ethyl ketone (MEK)). It is one of the most important products synthesized from acetone, through direct condensation. It is used as solvent in paints, protective coatings, adhesives, textile coatings, and leader finishing. 4-Methyl-2-pentanone is used also as a separation agent in the process to obtain metals from solutions of mixed metal salts, in the extraction and purification of antibiotics and other pharmaceuticals, in the manufacture of insecticides and other pesticides, in purifying stearic acid, in refining tall oil, and in extracting rosin from softwood. In some applications, it is used as solvent mixed with alcohols or other ketones.

No references were found about VLLE or LLE data of this partially miscible ternary system. However, the references of the constituent binary systems of both VLE and LLE data are relatively abundant. So, data were found in the literature for the 2-butanol + water system,[6−10] the 4-methyl-2-pentanone + water system,[11−13] and the 2-butanol + 4-methyl-2-pentanone system.[14]

This paper reports the results obtained for the vapor−liquid−liquid equilibrium at 101.3 kPa as well as the liquid−liquid equilibrium at (283.15 and 333.15) K, to study the influence of temperature, for the ternary 4-methyl-2-pentanone + 2-butanol + water system.

The results obtained have been analyzed by applying the thermodynamic models such as NRTL[5] and UNIQUAC[4] to correlate experimental data or the UNIFAC[15] model to predict them.

EXPERIMENTAL SECTION

Chemicals. 4-Methyl-2-pentanone ($w > 0.995$, assay GC) was purchased from Aldrich Ltd.; 2-butanol ($w = 0.99$, assay GC) was supplied from Fluka; and water was bidistilled. The reagents were

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

	ρ(298.15 K)/kg·m^{-3}		n_D(298.15 K)		T_b(101.3 kPa)/K		UNIQUAC parameters	
component	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]	r_i[b]	q_i[b]
4-methyl-2-pentanone (1)	796.01	796.40	1.3932	1.3933	388.87	389.15	4.5959	3.9520
2-butanol (2)	802.39	802.60	1.3947	1.3949	372.56	372.70	3.4535	3.0480
water (3)	997.03	997.04	1.3327	1.3325	373.15	373.15	0.9200	1.3997

[a] Ref 16. [b] Ref 17.

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 ($w < 0.0005$). Before measurements, the liquids were degassed and subsequently dried over molecular sieves (Union Carbide, type 4 Å, 1/16 in. pellets). 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 integrated on the equipment. The uncertainty in refractive index and density measurements is ± 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.[16,17] Appropriate precautions were taken when handling the reagents to avoid hydration.

Apparatus and Procedure. *For LLE Data.* The equipment used and the procedure for the determination of liquid−liquid data have been described in a previous work.[18] 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 × 2.55 μm capillary column (DB-MTBE, J & Scientific). The GC response peaks were treated with Chrom-Card software for Windows. Column, injector, and detector temperatures were (373, 443, and 403) 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.

For VLLE Data. To determine the vapor−liquid−liquid equilibrium data, a dynamic recirculating still equipped with a Cottrell circulation pump manufactured by Fischer Labor and Verfahrenstechnik (Labodest VLE 602/D) was used, whose detailed description can be found in a previous work.[19] This equipment has been modified according to indications of Gomis et al.,[20] 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 and sampling and analysis of both phases can be found in previous references.[1,19]The equilibrium temperature was measured with a digital Hart Scientific thermometer model 1502 A and a Pt 100 probe Hart Scientific, model 5622, calibrated at the ENAC-accredited Spanish Instituto Nacional de Técnica Aeroespacial. The accuracy was estimated to be ± 0.01 K. The pressure accuracy is ± 0.1 kPa. The manometer was calibrated using the vapor pressure of ultrapure water.

The compositions of the sampled liquid phases and vapor phase were determined as we have reported in the LLE data section analysis. The uncertainty in the mole fraction was usually less than 0.001.

Table 2. LLE Data for the 4-Methyl-2-pentanone (1) + 2-Butanol (2) + Water (3) System at Different Temperatures

	4-methyl-2-pentanone-rich phase/x_i^{I}		water-rich phase/x_i^{II}	
T/K	x_1	x_2	x_1	x_2
283.15	0.899	0.000	0.003	0.000
	0.839	0.045	0.004	0.004
	0.747	0.106	0.004	0.010
	0.655	0.164	0.002	0.014
	0.579	0.205	0.002	0.016
	0.476	0.253	0.002	0.020
	0.369	0.286	0.004	0.023
	0.223	0.313	0.003	0.028
	0.240	0.312	0.003	0.028
	0.162	0.314	0.003	0.031
	0.096	0.306	0.002	0.036
	0.054	0.295	0.002	0.042
	0.038	0.293	0.002	0.046
	0.000	0.271	0.000	0.068
333.15	0.917	0.000	0.001	0.000
	0.824	0.048	0.002	0.002
	0.711	0.128	0.001	0.004
	0.615	0.181	0.001	0.005
	0.552	0.227	0.001	0.007
	0.436	0.267	0.001	0.008
	0.349	0.312	0.001	0.011
	0.277	0.312	0.001	0.012
	0.211	0.324	0.001	0.014
	0.154	0.335	0.001	0.016
	0.092	0.335	0.000	0.020
	0.051	0.330	0.000	0.023
	0.000	0.330	0.000	0.024
	0.010	0.296	0.000	0.024

■ RESULTS AND DISCUSSION

Experimental Data. To observe the influence of the temperature on the mutual solubility of the ternary system 4-methyl-2-pentanone + 2-butanol + water, experimental LLE measurements were made for two different temperatures [(283.15 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.

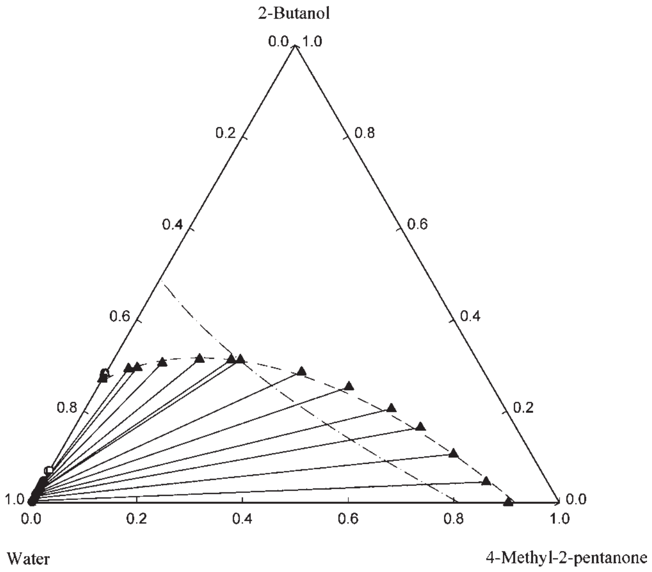

Figure 1. Liquid−liquid equilibrium of the 4-methyl-2-pentanone (1) + 2-butanol (2) + water (3) system at 283.15 K. Experimental data: ▲, 4-methyl-2-pentanone-rich phase; ●, aqueous-rich phase; —, experimental tie lines. Binary from Bozlag and Lamb:[7] Δ, 4-methyl-2-pentanone-rich phase; ○, aqueous-rich phase. Binary from Moriyoshi et al.:[8] ■, 4-methyl-2-pentanone-rich phase; □, aqueous-rich phase. Estimated using the UNIFAC model: — · —, binodal curve. Calculated using the UNIQUAC model, parameters Table 4: — — —, binodal curve.

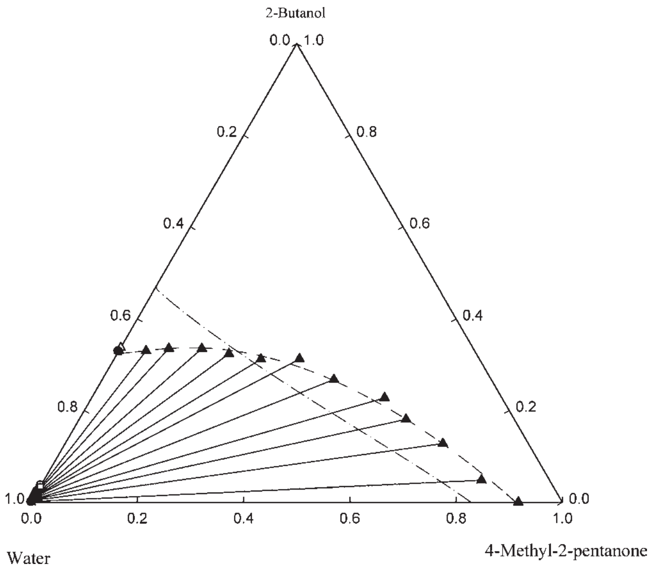

Figure 2. Liquid−liquid equilibrium of the 4-methyl-2-pentanone (1) + 2-butanol (2) + water (3) system at 333.15 K. Experimental data: ▲, 4-methyl-2-pentanone-rich phase; ●, aqueous-rich phase; —, experimental tie lines. Binary from Bozlag and Lamb:[7] Δ, 4-methyl-2-pentanone-rich phase; ○, aqueous-rich phase. Binary from Moriyoshi et al.:[8] ■, 4-methyl-2-pentanone-rich phase; □, aqueous-rich phase. Estimated using the UNIFAC model: — · —, binodal curve. Calculated using the UNIQUAC model, parameters Table 4: — — —, binodal curve.

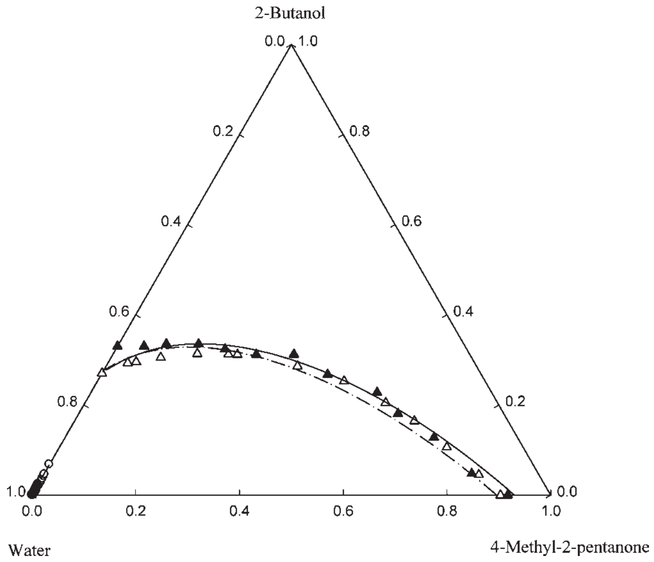

Figure 3. Influence of temperature on liquid−liquid equilibrium of the 4-methyl-2-pentanone (1) + 2-butanol (2) + water (3) system. Experimental data at 283.15 K: Δ, 4-methyl-2-pentanone-rich phase; ○, aqueous-rich phase. Experimental data at 333.15 K: ▲, 4-methyl-2-pentanone-rich phase; ●, aqueous-rich phase. Binodal curve calculated using the UNIQUAC model, parameters Table 5: —, at 283.15 K; — · —, at 333.15 K.

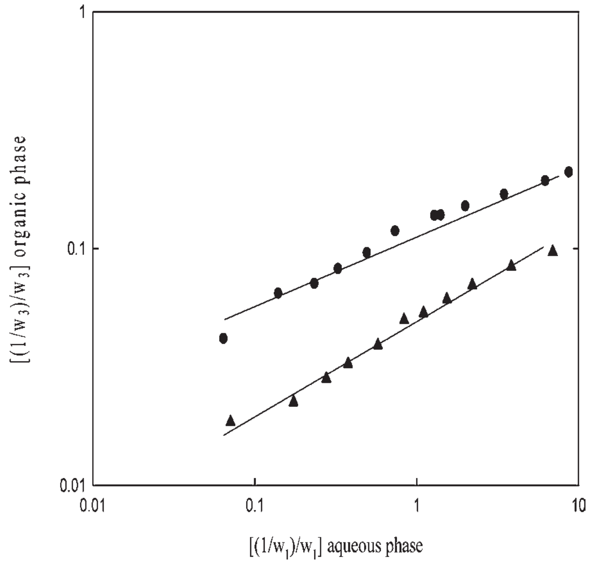

Figure 4. Othmer−Tobias plot of the 4-methyl-2-pentanone (1) + 2-butanol (2) + water (3) system. Experimental data: ▲, at 283.15 K; ●, at 333.15 K. Curve fit: solid lines.

In Figures 1 and 2, the data of liquid−liquid equilibrium of this system at (283.15 and 333.15) K, respectively, are shown. In these figures, a comparison with data of binary 2-butanol + water at the same conditions from the literature was performed successfully. It was impossible to do a similar checkout for binary 4-mathyl-2-pentanona because, to our knowledge, there are no data in the literature at similar conditions to those measured in this work. As can be seen in Figure 3, temperature has a low effect on the liquid−liquid equilibrium of this system, showing a reduced influence on the shape and size of the immiscibility zone.

The reliability of experimental results (tie-lines) can be ascertained by applying the Othmer–Tobias correlation[21]

$$\left[\frac{1-w_1}{w_1}\right]_{\text{organicphase}} = a\left[\frac{1-w_3}{w_3}\right]^{b}_{\text{aqueousphase}} \qquad (1)$$

were w_1 is the mass fraction of 4-methyl-2-pentanone; w_3 is the mass fraction of water; and a and b are constants in eq 1. Figure 4 shows the plot on logarithmic scale of $[(1 - w_1)/(w_1)]_{\text{organic phase}}$ against $[(1 - w_3)/(w_3)]_{\text{aqueous phase}}$ at both temperatures for the system under study. The linearity of these plots indicates the degree of consistency of related data. The parameters and the boundary of this correlation are given in Table 3.

Complete VLLE data of the ternary system 4-methyl-2-pentanone + 2-butanol + water at 101.3 kPa are listed in Table 4. The experimental ternary VLLE data were tested by the point-to-point L/W Wisniak[22] consistency test and were found to be thermodynamically consistent. All L/W values are between 0.98 and 1.01. The consistency of the ternary data was also checked with the Wisniak and Tamir[23] modification of the McDermot–Ellis[24] 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 experimental composition of the ternary azeotrope.

Actually, Figure 5 represents the projection on the ternary composition diagram of the intersection of the single liquid–liquid envelope with the VLE surface.[25] As can be seen in this figure, the water is partially miscible with 4-methyl-2-pentanone and 2-butanol, which are completely soluble with each other. This behavior is the same as that observed for LLE data at the temperatures studied (Figures 1 and 2).

The vapor phase is part inside and part outside of the binodal curve, which means that the vapor a few times forms a single liquid phase once it is condensed and, in most cases, once it is condensed forms a heterogeneous mixture.

The existence 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) was proved, which is shown in Figure 5 and Table 4.

Data Correlation. The NRTL[3] and UNIQUAC[4] models were used to correlate the experimental data for the ternary LLE systems discussed. These models are tested for each of the temperatures using the commercial program ChemCad data processing. To fit the UNIQUAC interaction parameters, the structural parameters (r_i and q_i) recommended by DECHEMA[17] were used for the pure components and are listed in Table 1. The nonrandomness parameter (α_{ij}) of the NRTL equation was fixed at 0.2 or 0.3, during the correlation process for the binary 4-methyl-2-pentanone + 2-butanol system, so the parameter value which gives the best results is given in Table 5. For the other binaries, the nonrandomness parameter (α_{ij}) of the NRTL equation given in Table 5 has been fixed by the commercial program ChemCad data processing and maintained in all cases. This solution has provided the best results along this work for the system of focus (Tables 5, 6, and 8), 4-methyl-2-pentanone + 2-butanol + water.

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 calculated mole fraction for each of the components over all the lie lines. The objective function (OF LLE) used for LLE data is

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

where M is the number of tie lines; x indicates the experimental mole fraction in the liquid phase; $\hat{x}$ is the calculated mole fraction in the liquid phase; and subscripts i, j, and k denote, respectively, the number of component, phase, and tie line.

Table 3. Parameters of Othmer–Tobias Correlation for the System 4-Methyl-2-pentanone (1) + 2-Butanol (2) + Water (3) at 101.3 kPa

T/K	a	b	R^2
283.15	723.27	3.0522	0.9737
333.15	1924.60	2.5130	0.9873

Table 4. Experimental Vapor–Liquid–Liquid Equilibrium Data of the System 4-Methyl-2-pentanone (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	0.314	0.000	0.032	0.000	0.358	360.4
2	0.027	0.296	0.001	0.022	0.040	0.324	360.2
3	0.058	0.316	0.001	0.019	0.072	0.298	360.0
4	0.090	0.310	0.001	0.016	0.100	0.277	359.8
5	0.131	0.313	0.002	0.018	0.124	0.254	359.8
6	0.198	0.307	0.002	0.012	0.152	0.223	359.7
7	0.264	0.299	0.003	0.010	0.176	0.200	359.7
8	0.400	0.263	0.002	0.007	0.217	0.160	359.7
9	0.531	0.204	0.003	0.005	0.242	0.118	359.9
10	0.600	0.163	0.005	0.004	0.266	0.096	360.1
11	0.697	0.102	0.002	0.002	0.296	0.063	360.4
12	0.767	0.038	0.004	0.001	0.322	0.025	360.7
BIN[a]	0.883	0.000	0.002	0.000	0.337	0.000	361.0
TER[b]	0.178	0.223	0.178	0.223	0.178	0.223	359.5

[a] Binary azeotrope. [b] Ternary azeotrope.

The root-mean-square deviation (rmsd) between the experimental and calculated data is also included in Table 5

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

In Table 5, it can be observed that both models were found to properly correlate the data, but the UNIQUAC model led, in general, to better results. In Figures 1 and 2 the experimental LLE data at (283.15 and 333.15) K have been plotted together with the binodal curves calculated using the UNIQUAC model. As can be seen, the result is good.

Although a good fit is obtained for each temperature, the parameters determined have no relation between them. Therefore, a simultaneous correlation of all the experimental LLE data for the two temperatures was carried out to obtain a unique set of parameters (global parameters), valid for the range of temperatures studied, increasing in this way their application. Nonetheless, the residuals obtained are higher. Table 6 lists the optimized interaction parameters for simultaneous correlation obtained using UNIQUAC and NRTL for the 4-methyl-2-pentanone + 2-butanol + water system. Finally, Figure 3 shows the boundary of these parameters, which can be used for any temperature in the range from (283.15 to 333.15) K.

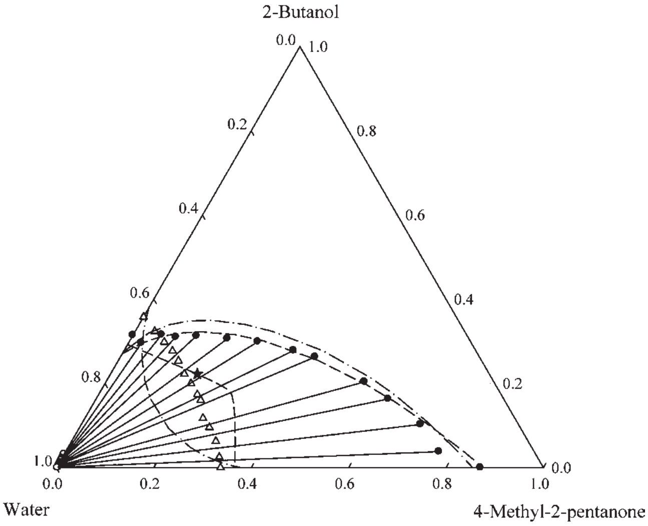

Figure 5. Comparison of the VLLE data for the 4-methyl-2-pentanone (1) + 2-butanol (2) + water (3) ternary system at 101.3 kPa. Experimental data: ●, 4-methyl-2-pentanone-rich phase; ○, aqueous-rich phase; Δ, the vapor phase; —, experimental tie lines; ★, ternary azeotrope (x_1 = 0.178, x_2 = 0.223). Calculated data: — — —, estimated with LLE parameters using the UNIQUAC model (Table 5); — · —, estimated with LLE parameters using the NRTL model (Table 5).

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 estimate the VLLE using parameters obtained from simple LLE experiments.

In this way, the VLLE of this system was estimated using the global LLE parameters obtained in Table 6.

The objective function for VLLE data is

$$\text{OF VLLE} = \sum_{k=1}^{M}\sum_{i=1}^{3}(y_{ik}-\hat{y}_{ik})^2 + \sum_{k=1}^{M}\sum_{j=1}^{3}\sum_{i=1}^{3}(x_{ijk}-\hat{x}_{ijk})^2 + \sum_{k=1}^{M}(T-\hat{T})^2 \tag{4}$$

were M is the number of tie lines; x indicates the experimental mole fraction in the liquid phase; $\hat{x}$ is the calculated mole fraction in the liquid phase; y indicates the experimental mole fraction in the vapor phase; the $\hat{y}$ calculates mole fraction in vapor phase; T is the experimental temperature; $\hat{T}$ is the calculated temperature for each tie line; and subscripts i, j, and k denote, respectively, the number of component, phase, and tie line.

The average absolute deviations (AADs) between experimental (α) and estimated (γ) values are shown in Table 7

$$\text{ADD} = \frac{\sum \text{ABS}(\alpha-\gamma)}{N} \tag{5}$$

where N is the number of experimental data.

In general, the estimation is relatively good, but as expected, the largest deviations are obtained in the approximation of the vapor phase because the parameters used have been acquired

Table 6. Global Binary Interaction Parameters (Temperature Independent) for the LLE of the 4-Methyl-2-pentanone (1) + 2-Butanol (2) + Water (3) System

	UNIQUAC parameters			NRTL parameters			
	A_{ij}	A_{ji}			A_{ij}	A_{ji}	
i-j	J·mol^{-1}	J·mol^{-1}	rmsd	α_{ij}	J·mol^{-1}	J·mol^{-1}	rmsd
1−2	1439.30	159.42	1.51	0.200	−3586.92	−2655.45	1.64
1−3	3122.47	2276.28		0.369	5386.98	8517.35	
2−3	−1429.29	4030.72		0.519	3259.83	9183.50	

Table 5. UNIQUAC and NRTL Binary Interaction Parameters for the LLE of System 4-Methyl-2-pentanone (1) + 2-Butanol (2) + Water (3)

		UNIQUAC parameters			NRTL parameters			
		A_{ij}	A_{ji}			A_{ij}	A_{ji}	
T/K	i−j	J·mol^{-1}	J·mol^{-1}	rmsd	α_{ij}	J·mol^{-1}	J·mol^{-1}	rmsd
283.15	1−2	482.70	681.86	0.56	0.200	−3837.43	6144.09	0.48
	1−3	3625.02	1011.74		0.369	5386.23	10286.33	
	2−3	−619.65	2142.93		0.519	3304.23	6783.14	
333.15	1−2	−1122.23	2462.93	0.56	0.200	−2953.86	−3500.86	0.98
	1−3	3660.73	1914.83		0.369	5968.66	10210.00	
	2−3	−1053.27	3406.46		0.519	3361.01	9583.76	

Table 7. Average Absolute Deviations between Experimental and Calculated Values for Different G^E Models for the 4-Methyl-2-pentanone (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]	0.018	0.008	0.001	0.005	0.069	0.053	1.97
UNIQUAC[a]/VLLE[c]	0.009	0.007	0.001	0.007	0.010	0.012	0.91
NRTL[a]/LLE[b]	0.012	0.021	0.012	0.004	0.042	0.033	2.50
NRTL[a]/VLLE[c]	0.010	0.007	0.004	0.001	0.019	0.014	0.60
UNIFAC[a]	0.024	0.044	0.001	0.002	0.032	0.005	0.85

[a] Estimated using Aspen HYSYS v2006. [b] With parameters of LLE determined in this work (Table 6). [c] With parameters of VLLE determined in this work (Table 8).

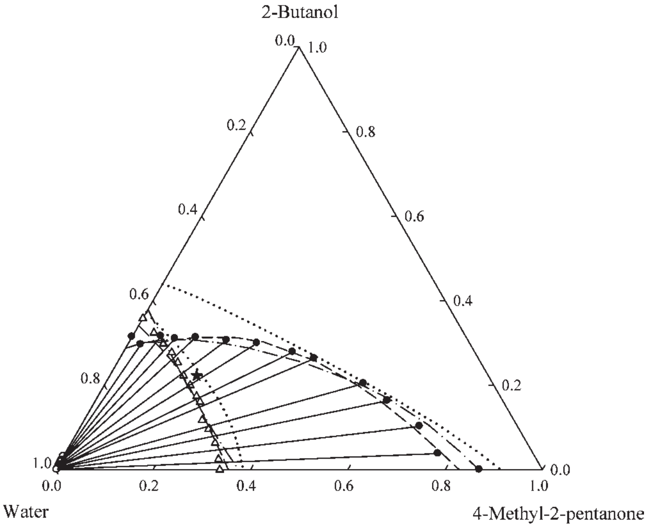

Figure 6. Comparison of the VLLE data for the 4-methyl-2-pentanone (1) + 2-butanol (2) + water (3) ternary system at 101.3 kPa. Experimental data: ●, 4-methyl-2-pentanone-rich phase; ○, aqueous-rich phase; Δ, the vapor phase; —, experimental tie lines; ★, ternary azeotrope ($x_1 = 0.178$, $x_2 = 0.223$). Calculated data: — — —, using the UNIQUAC model (parameters Table 8); — · —, using the NRTL model (parameters Table 8). Predicted data: · · · · · ·, using the UNIFAC LL prediction model.

with LLE data. This behavior can be seen in Figure 6, which shows that the results obtained from parameters estimated with LLE data do not always reproduce adequately the behavior of both phases. So, these results lead us to consider the necessity to obtain parameters correlated from experimental VLLE data to reproduce adequately the behavior of the system.

Finally, the experimental VLLE data were correlated using UNIQUAC and NRTL models (Aspen COMThermo v2006), to compare these results with the estimations or predictions that are usually applied in this type of systems. The parameters obtained are shown in Table 8, as well as the absolute average deviation in Table 7, reflecting that it is recommended to use parameters obtained from VLLE data. Both models are adequate to reproduce the behavior of the system, leading a better resulting UNIQUAC model as is reflected in the rmsd values in Table 8. Figure 6 shows that the correlation of VLLE data maintains a good fit of liquid phases and improves greatly the reproducibility of the vapor phase.

Table 8. UNIQUAC and NRTL Binary Interaction Parameters for the VLLE of the 4-Methyl-2-pentanone (1) + 2-Butanol (2) + Water (3) System

	UNIQUAC parameters				NRTL parameters		
	A_{ij}	A_{ji}			A_{ij}	A_{ji}	
i−*j*	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	rmsd	α_{ij}	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	rmsd
1−2	13309.13	−2923.98	1.24	0.200	−2441.24	1407.23	1.44
1−3	2191.04	2507.68		0.369	11171.35	5939.10	
2−3	2329.03	−321.63		0.519	9811.98	3550.32	

Table 9. UNIFAC R_k and Q_k Parameters[26]

sub group (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 10. UNIFAC Group Interaction Parameters[26]

m	n	a_{mn}/K	a_{nm}/K
CH_3, CH_2, CH	CH_3CO	472.6	66.56
CH_3, CH_2, CH	OH	644.6	328.2
CH_3, CH_2, CH	H_2O	1300.0	342.4
CH_3CO	OH	216.0	67.1
CH_3CO	H_2O	634.8	−171.8
OH	H_2O	28.73	−122.4

Data Prediction by the UNIFAC LL. The experimental LLE data were compared with those predicted by the UNIFAC LL[15] group contribution model. The interaction and structural parameters required for the implementation of the prediction method were taken from Magnussen et al.[26] and are summarized in Tables 9 and 10. The quality of the prediction can be observed in Figures 1 to 2 where the binodal curves predicted by UNIFAC LL have been included. In these figures, this estimation has been presented, calculated using the commercial program ChemCad data processing. As can be seen, the estimation is not realistic, demonstrating the necessity of the experimental determination of the LLE of the 4-methyl-2-pentanone + 2-butanol + water system to obtain good parameters and to be able to apply models such as UNIQUAC or NRTL with confidence.

The prediction of VLLE data by UNIFAC LL is obtained using Aspen HYSYS v2006 and is shown in Figure 6. As can be observed, the prediction in this case is better than for LLE, obtaining surprising results, because it is capable of reproducing better the vapor phase than the estimation with UNIQUAC or NRTL with LLE parameters. Anyway, the prediction of the shape and size of the immiscibility zone is not realistic.

■ CONCLUSIONS

Liquid−liquid equilibrium data of the ternary system composed of 4-methyl-2-pentanone + 2-butanol + water were measured at two different temperatures, (283.15 and 333.15) K. The reliability of experimental data has been checked by means of the Othmer−Tobias correlation. Temperature has a low effect on the liquid−liquid equilibrium of this system, showing a reduced influence on the shape and size of the immiscibility zone. Isobaric vapor−liquid−liquid equilibrium data were also measured for this ternary system at 101.3 kPa.

The LLE data were correlated using the NRTL and UNIQUAC models. Both models were found to properly correlate the data, but the UNIQUAC model led, in general, to better results.

A simultaneous correlation of all the experimental LLE data for the two temperatures was carried out to obtain a unique set of parameters (global parameters), valid for the range of temperatures studied, increasing in this way their application.

Estimation of VLLE of partially miscible ternary mixture was studied using the 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.

Finally, the experimental VLLE data were correlated using the UNIQUAC and NRTL models. This correlation maintains a good fit of liquids phases and improves greatly the reproducibility of the vapor phase.

The experimental LLE and VLLE data were compared with those predicted by the UNIFAC group contribution model. For LLE data, it seems that the prediction is not realistic, whereas for the VLLE data the UNIFAC model is capable of reproducing the vapor phase better than the estimation with UNIQUAC or NRTL with LLE parameters, but the prediction of the shape and size of the immiscibility zone is not adequate.

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■ REFERENCES

(1) 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.

(2) Gomis, V.; Pequenín, A.; Asensi, J. C. Isobaric vapor-liquid-liquid equilibrium and vapor-liquid equilibrium for the system water-ethanol-1,4-dimethylbenzene at 101.3 kPa. *Fluid Phase Equilib.* **2009**, *281*, 1–4.

(3) Lladosa, E.; Montón, J. B.; de la Torre, J.; Martínez, N. F. Liquid-liquid and vapour-liquid-liquid equilibrium of 2-butanone + 2-butanol + water system. *J. Chem. Eng. Data*, DOI: 10.1021/je1004643.

(4) 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.

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

(6) 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.

(7) 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.

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

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

(10) 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.

(11) Cho, T.; Ochi, K.; Kojima, K. Measurement of vapor-liquid equilibrium for systems with limited miscibility. *Fluid Phase Equilib.* **1983**, *11*, 137–152.

(12) Rawat., B. S.; Krishna, S. Isobaric vapor-liquid equilibria for the partially miscible system of water-methyl isobutyl ketone. *J. Chem. Eng. Data* **1984**, *29*, 403–406.

(13) Sever, L.; Lieto, J.; Boudehen, A.; Bousquet, J. A novel technique for rapid measurement of liquid-liquid-vapour equilibrium. *Chem. Eng. Sci.* **1998**, *53*, 2587–2594.

(14) Martínez, N. F.; Lladosa, E.; Burguet, M. C.; Montón, J. B.; Yazimon, M. Isobaric vapor-liquid equilibria for the binary systems 4-methyl-2-pentanone + 1-butanol and + 2-butanol at 20 and 101.3 kPa. *Fluid Phase Equilib.* **2009**, *277*, 49–54.

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

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

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

(18) 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.

(19) 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.

(20) 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.

(21) Othmer, D. F.; Tobias, P. E. Tie Line Correlation. *Ind. Eng. Chem.* **1942**, *34*, 693–696.

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

(23) 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.

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

(25) Walas, S. M. *Phase equilibria in chemical engineering*; Butterworth – Heinemann: Boston, 1984.

(26) Magnussen, T.; Rasmussen, P.; Fredenslund, A. J. Parametr Table for Prediction of Liquid-Liquid Equilibria. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 231–239.