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## Liquid–Liquid Phase Equilibrium of Methanol + Ethylbenzene + Isooctane + Ethanol System at 303 K<sup>1</sup>

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**Abstract**—The phase equilibrium data for methanol + ethanol + isooctane systems were obtained at 303.15 K. Data for methanol + ethylbenzene + isooctane system were taken from literature. The effect of ethanol addition on the system equilibrium was investigated at the same temperature. The distribution curves for ternary and quaternary system was analyzed. The experimental results for ternary systems were correlated with UNIQUAC and NRTL equations. For the ternary systems studied here, the NRTL equation is more accurate than the UNIQUAC. The equilibrium data for the three ternary systems were used to determine interactions parameters for the UNIQUAC equation. For the quaternary system, the experimental data can be fitted more accurately to UNIQUAC equation than by the UNIFAC method.

**Keywords:** data, liquid-liquid equilibria, ternary system, quaternary system

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### 1. INTRODUCTION

The possibility of using alcohols as motor fuel in gasoline blends has been considered from time to time for over seventy years [1]. The current energy shortage has generated renewed interest to the use of alcohols, particularly methanol, since it can be produced from coal [2] at costs which have been estimated to be roughly comparable to those for other coal-derived synthetic fuels [3]. In the past, the disadvantages associated with methanol gasoline blends such as phase separation, increased volatility, and corrosion problems, have always vastly outweighed any potential advantages. However, in today's climate of energy shortages and environmental awareness, this idea is being reevaluated. Experimental results suggesting that significant benefits in fuel economy, emissions, and performance are possible with methanol gasoline blends, have been published [4, 5]. These blends have also been found to have increased octane numbers compared to similar blends without methanol [6, 7]. However, one of the oxygenated compounds that is presently used more often in reformulated gasoline is ethanol [8]. Therefore, this is the reason for which we are studying the effect of the addition of ethanol on the liquid–liquid equilibrium (LLE) in methanol + ethylbenzene + isooctane ternary system.

Having this in mind, LLE measurements for  $\{w_1$  methanol +  $w_2$  ethylbenzene +  $w_3$  isooctane +

$w_4$  ethanol} and  $\{w_1$  methanol +  $w_2$  ethanol +  $w_3$  isooctane} systems, named throughout the text as  $\{w_1$  CH<sub>4</sub>O +  $w_2$  C<sub>8</sub>H<sub>10</sub> +  $w_3$  C<sub>8</sub>H<sub>18</sub> +  $w_4$  C<sub>2</sub>H<sub>6</sub>O} and  $\{w_1$  CH<sub>4</sub>O +  $w_2$  C<sub>2</sub>H<sub>6</sub>O +  $w_3$  C<sub>8</sub>H<sub>10</sub>} at  $T = (303.15 \pm 0.05)$  K and atmospheric pressure were performed. The respective Treybal [9] classification types for these systems are shown in Table 1.

The experimental data for the ternary systems studied here were correlated with the UNIQUAC [10] and NRTL [11] models.

All the pairs of the UNIQUAC interaction parameters obtained from the two partially miscible ternary subsystems included in the quaternary system were averaged and, after that, they were used to predict the quaternary LLE by this model. The original UNIFAC method was also used for this purpose [12].

A single work can be found in the literature regarding LLE data for this ternary system at 303 K [13] and

**Table 1.** Ternary and quaternary systems, including their Treybal's classification type,  $w_i$  denotes mass fraction of component  $i$

No.	Type	System
1	1	$w_1$ CH <sub>4</sub> O + $w_2$ C <sub>2</sub> H <sub>6</sub> O + $(1 - w_1 - w_2)$ C <sub>8</sub> H <sub>18</sub>
2	1	$w_1$ CH <sub>4</sub> O + $w_2$ C <sub>8</sub> H <sub>10</sub> + $w_3$ C <sub>8</sub> H <sub>18</sub> + $(1 - w_1 - w_2 - w_3)$ C <sub>2</sub> H <sub>6</sub> O

<sup>1</sup> The article is published in the original.

there is no reference in the literature about of LLE in the quaternary system studied in this work.

## 2. EXPERIMENTAL

### 2.1. Materials

Methanol (99.98% purity), ethanol (99.99% purity), isooctane (99.99% purity) and ethylbenzene (99.99% purity), all of analytical grade, were supplied by Merck. Methanol and ethanol were kept over 3 Å activated molecular sieves, to prevent water absorption. The purity of the chemicals was verified chromatographically using an HP 6890 gas chromatograph with a TCD detector and nitrogen as the carrier gas. The internal standard method was used. The mass fraction values have an uncertainty of  $\pm 0.0001$ . A typical value of the water content in the reagents and their mixtures was checked throughout the experiments. The largest found water content was 0.0002 mass fraction.

### 2.2. Methods

Ternary and quaternary equilibrium data were obtained by preparing mixtures of known overall mass composition within the heterogeneous region using a dual range Mettler Toledo AG245 balance with an accuracy of  $\pm 0.1/0.01$  mg. All mixtures were prepared in 16 mL sample vials (Agilent Technologies Inc., USA, HP 5183–4535) equipped with a screw cap and septum. The mixtures were stirred with a Teflon coated magnetic stirring bar for at least two days. These vials were filled up to  $\sim 90\%$  of their volumes, to maintain the vapor space at minimum. Then the vials were placed in a water bath jacket thermostatted at  $(303.15 \pm 0.05)$  K [14]. Uniformity of temperature within the vials was maintained by continuous agitation of the mixtures samples with the multipoint magnetic stirrer (SBS, model A-04, SBS Instruments S.A., Spain) placed under the water bath. After the phase equilibrium was reached, the stirring was turned off and liquid phases were allowed to settle for 24 h.

At the end of each experiment, samples were taken from both phases with hypodermic syringes and analyzed by means of gas chromatography. In order to prevent the contamination of the lower phase with the upper one during sampling, the needle of the syringe was introduced through the upper phase while its piston was pushed gently. The same procedure was adopted to remove the needle. The needle was dried with a soft paper tissue before the sample was introduced into the 2 mL analysis vial (HP 5182–0714) containing the compound used as the internal standard (acetone, Merck, chromatographic quality, with a mass fraction purity  $> 0.9999$ ).

A Hewlett Packard 6890 gas chromatograph with an automatic sample injector (Agilent G2613A) directly connected to a ChemStation (HP G2070AA) was used. Good separation of the five components was

obtained on a  $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{m}$  capillary column (HP-5 cross-linked 5% PH ME Siloxane, HP 19091J-413). The temperature program used was: initial temperature 303 K for 1 min, ramp  $5 \text{ K min}^{-1}$ , and final temperature 308 K and other ramp  $605 \text{ K min}^{-1}$  and final temperature 423 K for another one minute. The nitrogen carrier gas flow rate was electronically kept constant working with a split ratio of 20 : 1. The injector temperature was maintained at 453 K. The thermal conductivity detector temperature was 523 K. Three or four analyses were performed for each sample in order to obtain a mean mass fraction value with repeatability better than 1%.

To obtain overall mixtures for LLE studies we weighed the components with the lowest balance accuracy. For the four components, linear correlations always provided the best fit for chromatographic calibration curves. In order to obtain a calibration curve for each component by the internal standard method, a Mettler AG245 dual range balance with an accuracy of  $\pm 0.1/0.01$  mg was used to weigh the chemicals with the highest accuracy.

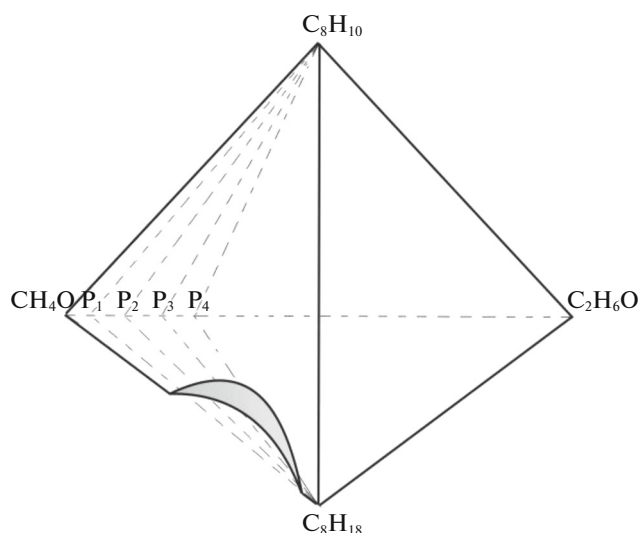
We prepare several ternary mixtures with well known mass fractions of the components to evaluate the uncertainty of the equilibrium mass fraction values. These mixtures were analyzed, and their concentrations determined chromatographically were compared with mass fractions by preparation. This comparison shows that the reported mass fraction values have an uncertainty of  $\pm 0.004$ .

To determine the quaternary binodal surface, the measurements were carried out at four different ethanol/ methanol ratios, which characterize four quaternary planes (named  $P_1$ ,  $P_2$ ,  $P_3$ , and  $P_4$  in Fig. 1). Figure 1 shows a schematic representation of  $\{w_1 \text{ CH}_4\text{O} + w_2 \text{ C}_8\text{H}_{10} + w_3 \text{ C}_8\text{H}_{18} + w_4 \text{ C}_2\text{H}_6\text{O}\}$  quaternary system. In this work, the initial mixtures (corresponding to the  $P_1$ ,  $P_2$ ,  $P_3$ , and  $P_4$  planes) were selected to determine tie lines within the whole heterogeneous region.

## 3. RESULTS AND DISCUSSION

Tables 2 lists the (liquid + liquid) equilibrium data for the ternary systems:  $\{w_1 \text{ CH}_4\text{O} + w_2 \text{ C}_2\text{H}_6\text{O} + w_3 \text{ C}_8\text{H}_{18}\}$  at  $T = (303.15 \pm 0.05)$  K.

Table 3 lists the (liquid + liquid) equilibrium data, expressed in mass fractions, for  $\{w_1 \text{ CH}_4\text{O} + w_2 \text{ C}_8\text{H}_{10} + w_3 \text{ C}_8\text{H}_{18} + w_4 \text{ C}_2\text{H}_6\text{O}\}$  quaternary system for each quaternary plane:  $P_1 = (0.9767 \text{ CH}_4\text{O} + 0.0233 \text{ C}_2\text{H}_6\text{O})$ ,  $P_2 = (0.9556 \text{ CH}_4\text{O} + 0.0444 \text{ C}_2\text{H}_6\text{O})$ ,  $P_3 = (0.9338 \text{ CH}_4\text{O} + 0.0662 \text{ C}_2\text{H}_6\text{O})$ , and  $P_4 = (0.9145 \text{ CH}_4\text{O} + 0.0855 \text{ C}_2\text{H}_6\text{O})$ . Experimental results reported in Tables 2, 3 satisfy the mass balance with a maximum deviation of 5 wt %. Figure 2 shows the LLE diagram for  $\{w_1 \text{ CH}_4\text{O} + w_2 \text{ C}_2\text{H}_6\text{O} + w_3 \text{ C}_8\text{H}_{18}\}$  ternary system at 303.15 K and  $\{w_1 \text{ CH}_4\text{O} + w_2 \text{ C}_8\text{H}_{10} + w_3 \text{ C}_8\text{H}_{18} + w_4 \text{ C}_2\text{H}_6\text{O}\}$  quaternary system

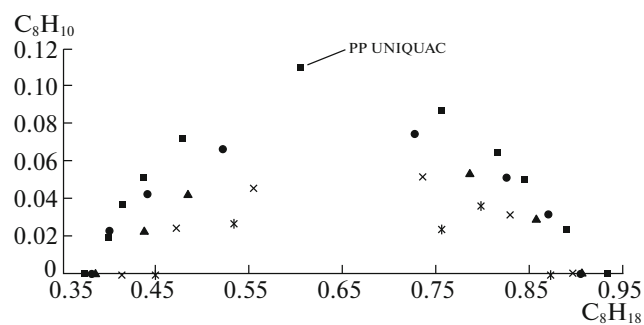


**Fig. 1.** Schematic representation of  $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_8\text{H}_{10} + w_3 \text{C}_8\text{H}_{18} + w_4 \text{C}_2\text{H}_6\text{O}\}$  quaternary system at  $T = 303.15 \text{ K}$ .  $P_1$ ,  $P_2$ ,  $P_3$ , and  $P_4$  are sectional planes for the determination of the binodal surface.

on ethanol free basis (the equilibrium data for quaternary system recalculated without ethanol) at 303.15 K.

Figure 3 shows distribution curves for ethylbenzene in the hydrocarbon-rich phase ( $w_2^{\text{II}}$ ) and methanol-rich phase ( $w_2^{\text{I}}$ ) for ternary system and quaternary system for  $P_1$ ,  $P_2$ ,  $P_3$ , and  $P_4$  on ethanol-free basis in the hydrocarbon-rich phase ( $w_2^{0\text{II}}$ ) and methanol-rich phase ( $w_2^{0\text{I}}$ ). As it can be seen in Fig. 4, the distribution curves for ethylbenzene are similar for ternary and quaternary systems.

Figure 4 shows the distribution coefficient for ethylbenzene  $m = \frac{w_2^{\text{I}}}{w_2^{\text{II}}}$  for ternary system and  $m = \frac{w_2^{0\text{I}}}{w_2^{0\text{II}}}$  for



**Fig. 2.** LLE diagram for the  $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_2\text{H}_6\text{O} + w_3 \text{C}_8\text{H}_{18}\}$  ternary system at 303.15 K.  $\blacksquare$ , Experimental data and  $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_8\text{H}_{10} + w_3 \text{C}_8\text{H}_{18} + w_4 \text{C}_2\text{H}_6\text{O}\}$  quaternary system on ethanol free basis at 303.15 K;  $\bullet$ , 2.33%  $\text{C}_2\text{H}_6\text{O}$ ;  $\blacktriangle$ , 4.44%  $\text{C}_2\text{H}_6\text{O}$ ;  $\times$ , 6.62%  $\text{C}_2\text{H}_6\text{O}$ ;  $*$ , 8.55%  $\text{C}_2\text{H}_6\text{O}$ .

quaternary system for  $P_1$ ,  $P_2$ ,  $P_3$ , and  $P_4$  on an ethanol basis. Experimental results show that the distribution coefficient for ethylbenzene is slightly higher for the quaternary system than the ternary one.

The LLE data for the ternary systems studied here were correlated by the UNIQUAC and NRTL activity coefficient models, using an iterative computer program developed by Sørensen [15]. The program minimizes the values of the following objective functions:

$$F_a = \sum_k \sum_i \left\{ \left( \frac{a_{ik}^{\text{I}} - a_{ik}^{\text{II}}}{a_{ik}^{\text{I}} + a_{ik}^{\text{II}}} \right)^2 + Q \sum_n P_n^2 \right\} \quad (1)$$

$$F_x = \sum_k \min \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2 + Q \sum_n P_n^2 \quad (2)$$

Here,  $a_{ik}^{\text{I,II}}$  are the activities obtained from the experimental concentrations, I and II are the phases,  $x_{ijk}$  and  $\hat{x}_{ijk}$  are the experimental mole fraction values of the liquid phase and of the calculated tie line lying

**Table 2.** Liquid–liquid equilibrium data of  $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_2\text{H}_6\text{O} + w_3 \text{C}_8\text{H}_{18}\}$  ternary system at  $T = (303.15 \pm 0.05) \text{ K}$ ;  $w_i$  denotes mass fraction of component  $i$

Global compositions			$w_i^{\text{I}}$			$w_i^{\text{II}}$		
$w_1 \text{CH}_4\text{O}$	$w_2 \text{C}_2\text{H}_6\text{O}$	$w_3 \text{C}_8\text{H}_{18}$	$w_1^{\text{I}} \text{CH}_4\text{O}$	$w_2^{\text{I}} \text{C}_2\text{H}_6\text{O}$	$w_3^{\text{I}} \text{C}_8\text{H}_{18}$	$w_1^{\text{II}} \text{CH}_4\text{O}$	$w_2^{\text{II}} \text{C}_2\text{H}_6\text{O}$	$w_3^{\text{II}} \text{C}_8\text{H}_{18}$
0.3834	0	0.6166	0.628	0	0.372	0.069	0	0.931
0.3195	0.0080	0.6725	0.601	0.017	0.382	0.074	0.000	0.926
0.3096	0.0240	0.6725	0.528	0.041	0.430	0.111	0.009	0.879
0.3157	0.0437	0.6406	0.430	0.059	0.511	0.134	0.020	0.846
PP <sup>a</sup>			0.251	0.049	0.699	0.251	0.049	0.699
PP <sup>b</sup>			0.266	0.046	0.688	0.266	0.046	0.688

<sup>a</sup> Estimated plait point by the UNIQUAC model.

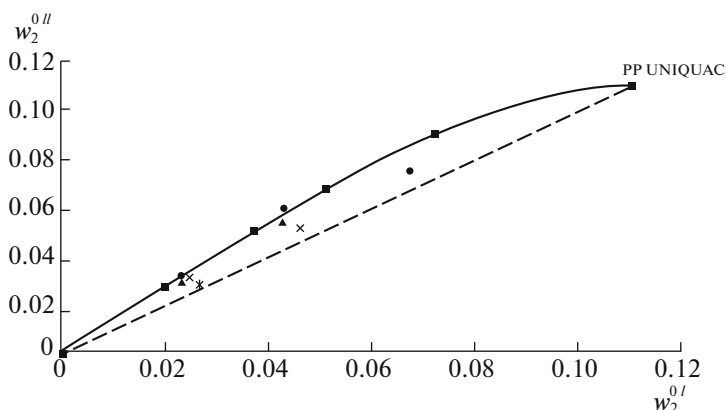
<sup>b</sup> Estimated plait point by the NRTL model.

**Table 3.** Liquid–liquid equilibrium data of  $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_8\text{H}_{10} + w_3 \text{C}_8\text{H}_{18} + w_4 \text{C}_2\text{H}_6\text{O}\}$  quaternary system at  $T = (303.15 \pm 0.05) \text{ K}$ ;  $w_i$  denotes mass fraction of component  $i$ 

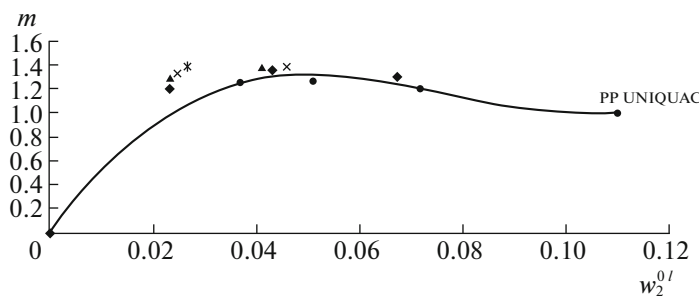
Global compositions				$w_i^I$				$w_i^{II}$			
$w_1$ CH <sub>4</sub> O	$w_2$ C <sub>8</sub> H <sub>10</sub>	$w_3$ C <sub>8</sub> H <sub>18</sub>	$w_4$ C <sub>2</sub> H <sub>6</sub> O	$w_1^I$ CH <sub>4</sub> O	$w_2^I$ C <sub>8</sub> H <sub>10</sub>	$w_3^I$ C <sub>8</sub> H <sub>18</sub>	$w_4^I$ C <sub>2</sub> H <sub>6</sub> O	$w_1^{II}$ CH <sub>4</sub> O	$w_2^{II}$ C <sub>8</sub> H <sub>10</sub>	$w_3^{II}$ C <sub>8</sub> H <sub>18</sub>	$w_4^{II}$ C <sub>2</sub> H <sub>6</sub> O
$P_1 = (0.9767 \text{CH}_4\text{O} + 0.0233 \text{C}_2\text{H}_6\text{O})$											
0.3439	0	0.6478	0.0082	0.606	0	0.379	0.015	0.095	0	0.903	0.003
0.3184	0.0277	0.6459	0.0079	0.564	0.023	0.399	0.014	0.098	0.032	0.868	0.003
0.2886	0.0478	0.6560	0.0076	0.505	0.043	0.439	0.013	0.121	0.052	0.824	0.004
0.3001	0.0710	0.6210	0.0079	0.402	0.067	0.520	0.010	0.195	0.075	0.725	0.005
$P_2 = (0.9556 \text{CH}_4\text{O} + 0.0444 \text{C}_2\text{H}_6\text{O})$											
0.3340	0	0.6505	0.0155	0.589	0	0.384	0.027	0.091	0	0.904	0.005
0.3189	0.0264	0.6397	0.0150	0.518	0.023	0.435	0.023	0.109	0.030	0.854	0.006
0.3025	0.0478	0.6348	0.0149	0.453	0.043	0.483	0.022	0.154	0.053	0.785	0.008
$P_3 = (0.9338 \text{CH}_4\text{O} + 0.0662 \text{C}_2\text{H}_6\text{O})$											
0.3165	0	0.6611	0.0224	0	0.037	0.412	0.037	0.098	0	0.894	0.008
0.2873	0.0283	0.6635	0.0210	0.025	0.033	0.469	0.033	0.131	0.031	0.827	0.011
0.2802	0.0486	0.6499	0.0212	0.046	0.028	0.552	0.028	0.199	0.051	0.734	0.016
$P_4 = (0.9145 \text{CH}_4\text{O} + 0.0855 \text{C}_2\text{H}_6\text{O})$											
0.3354	0	0.6333	0.0313	0.507	0	0.448	0.046	0.118	0	0.869	0.013
0.2842	0.0313	0.6575	0.0270	0.404	0.027	0.532	0.037	0.151	0.036	0.797	0.016

close to the considered experimental line, respectively, where  $i$  represents the components,  $j$  the phases, and  $k$  the tie lines.  $P_n$  and  $Q$  are the parameter and the constant values in the penalty term, respectively.

This penalty term was established to reduce the risk of multiple solutions associated with high parameter values. Table 4 shows the structural parameters of the pure components taken from the



**Fig. 3.** Distribution curve of ethylbenzene between isooctane phase and methanol phase for the  $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_8\text{H}_{10} + w_3 \text{C}_8\text{H}_{18} + w_4 \text{C}_2\text{H}_6\text{O}\}$  quaternary system at  $T = 303.15 \text{ K}$  with ethanol  $w_2^{II}$ ,  $w_2^I$  and without ethanol (on ethanol-free basis)  $w_2^{0II}$ ,  $w_2^{0I}$ . ■, Experimental ternary data; ●, 2.33% C<sub>2</sub>H<sub>6</sub>O; ×, 4.44% C<sub>2</sub>H<sub>6</sub>O; \*, 6.62% C<sub>2</sub>H<sub>6</sub>O; ▲, 8.55% C<sub>2</sub>H<sub>6</sub>O. Broken line: 45° diagonal.



**Fig. 4.** Distribution coefficient of ethylbenzene with ethanol  $\frac{w_2^I}{w_2^{II}}$  and without ethanol (on ethanol-free basis)  $\frac{w_2^{0I}}{w_2^{0II}}$  vs. mass fraction of ethylbenzene in the methanol phase on ethanol-free basis  $w_2^{0I}$  for the  $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_2\text{H}_6\text{O} + w_3 \text{C}_8\text{H}_{18} + w_4 \text{C}_8\text{H}_{10}\}$  quaternary system at  $T = 303.15 \text{ K}$ . ■, Experimental ternary data; •, 2.33%  $\text{C}_2\text{H}_6\text{O}$ ; ×, 4.44%  $\text{C}_2\text{H}_6\text{O}$ ; \*, 6.62%  $\text{C}_2\text{H}_6\text{O}$ ; ▲, 8.55%  $\text{C}_2\text{H}_6\text{O}$ .

literature [16] and the optimized binary interaction parameters of the UNIQUAC and NRTL models, for the ternary systems. The non-randomness parameter for the NRTL equation is also given.

Fitting quality, expressed by the r.m.s. deviation in mole fraction  $F$ , is given by the equation:

$$F = 100 \left\{ \sum_k \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2 / 2nM \right\}^{1/2}, \quad (3)$$

**Table 4.** Deviation  $F$  and  $\Delta m$  for UNIQUAC and NRTL optimized parameters of the UNIQUAC and NRTL equations, and non-randomness parameter ( $\alpha_{ij}$ ), for the system  $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_2\text{H}_6\text{O} + (1 - w_1 - w_2) \text{C}_8\text{H}_{18}\}$  at  $T = 303.15 \text{ K}^a$

$F$ , %	$\Delta m$ , %	$i, j$	$a_{ij}^b$	$a_{ji}^b$	$\alpha_{ij}$
UNIQUAC					
1.0	68.9	1.2	147.80	-184.92	
		1.3	-12.983	644.83	
		2.3	-74.649	155.37	
NRTL					
1.0	39.9	1.2	-2110.6	1713.3	0.4
		1.3	602.53	286.03	
		2.3	-376.04	-188.96	

<sup>a</sup> The following UNIQUAC structural parameters were used [16]: for  $\text{CH}_4\text{O}$ ,  $r = 1.4311$  and  $q = 1.4320$ ; for  $\text{C}_2\text{H}_6\text{O}$ ,  $r = 2.1055$  and  $q = 1.972$ ; for  $\text{C}_8\text{H}_{18}$ ,  $r = 5.8463$  and  $q = 5.0080$ .

<sup>b</sup>  $a_{ij} = (u_{ij} - u_{ji})/R$  for the UNIQUAC equation, where  $u_{ij}$  is the UNIQUAC binary interaction parameter,  $\text{J mol}^{-1}$ ;  $R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$ .  $a_{ij} = (g_{ij} - g_{ji})/R$  for the NRTL equation, where  $g_{ij}$  is the energy of interaction between an  $i$ - $j$  pair of molecules ( $\text{J mol}^{-1}$ ).

where  $n$  is the number of components in the system. The r.m.s. relative error in the solute distribution ratio  $\Delta m$  is given by the equation

$$\Delta m = 100 \sum_k \left[ \left\{ (m_k - \hat{m}_k / m_k)^2 \right\} / M \right]^{1/2}. \quad (4)$$

These deviation are listed in Table 4 for these two models. Here,  $x_{ijk}$  is the experimental mole fraction of the  $i$ th component in the  $j$ th phase on the  $k$ th tie line,  $\hat{x}_{ijk}$  is the corresponding calculated value, and  $m_k$  and  $\hat{m}_k$  are the experimental and calculated solute distribution ratios, respectively, given by  $\frac{w_2^I}{w_2^{II}}$ .

The UNIQUAC equation fitted to the experimental results is considerably more accurate than NRTL equation taking into account both overall errors,  $F$  and  $\Delta m$ , listed in Table 4.

Table 5 lists the deviation for the UNIFAC and UNIQUAC models of  $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_8\text{H}_{10} + w_3 \text{C}_8\text{H}_{18} + w_4 \text{C}_2\text{H}_6\text{O}\}$  quaternary system. The fit was poor in terms of  $\Delta m$  for UNIFAC model, due to the large relative error associated with the very low concentrations of ethylbenzene in both phases, while the goodness of fit in terms of  $F$  was satisfactory, particularly for the UNIQUAC model. Therefore, the UNIQUAC equation fitting for the experimental data is more accurate than the UNIFAC method for this quaternary system.

The average of all the binary interaction parameters, calculated from their respective ternary subsystems, was chosen in order to obtain a unique set of binary parameters suitable for prediction of the quaternary equilibrium data with the UNIQUAC model. They are reported in Table 6.

## 4. CONCLUSIONS

Liquid–liquid equilibrium in the  $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_2\text{H}_6\text{O} + w_3 \text{C}_8\text{H}_{18}\}$  ternary and in  $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_8\text{H}_{10} + w_3 \text{C}_8\text{H}_{18} + w_4 \text{C}_2\text{H}_6\text{O}\}$  quaternary systems were investigated at  $T = 303.15 \text{ K}$ .

The distribution curves for ethylbenzene are similar for ternary and quaternary systems, and the distribution coefficient for ethylbenzene is slightly higher in the quaternary system.

The experimental results lead to the conclusion that the addition of ethanol to the ternary system does not produce large changes in the distribution of the ethylbenzene.

The fitting of the experimental data to NRTL equations is considerably more accurate than UNIQUAC model taking into account both overall errors,  $F$  and  $\Delta m$ . These deviation also show that the UNIQUAC model is better than the NRTL one (see Table 4) for the ternary systems.

**Table 5.** Deviation  $F$  and  $\Delta m$  of  $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_8\text{H}_{10} + w_3 \text{C}_8\text{H}_{18} + w_4 \text{C}_2\text{H}_6\text{O}\}$  quaternary system at  $T = 303.15 \text{ K}$ <sup>a</sup>

Planes	$F, \%$	$\Delta m, \%$
UNIQUAC		
P <sub>1</sub>	12.9	47.2
P <sub>2</sub>	12.6	43.1
P <sub>3</sub>	15.4	51.4
P <sub>4</sub>	15.7	36.1
UNIQUAC		
P <sub>1</sub>	2.4	7.7
P <sub>2</sub>	2.2	4.2
P <sub>3</sub>	4.5	7.7
P <sub>4</sub>	4.5	10.9

<sup>a</sup> The values of  $\Delta m$  were calculated only for  $\text{C}_8\text{H}_{10}$ . The distribution coefficient for this compound is defined as  $m = \text{mass fraction of } \text{C}_8\text{H}_{10} \text{ in the II phase } (w_2^{\text{II}}) / \text{mass fraction of } \text{C}_8\text{H}_{10} \text{ in the I phase } (w_2^{\text{I}})$ .

**Table 6.** Average UNIQUAC interaction parameters for the prediction of the quaternary system

$i-j$	$a_{ij}$	$a_{ji}$
1–2	304.02	155.36
1–3	–16.2205	650.00
1–4	147.80	–184.92
2–3	239.60	16.651
2–4	476.570	–109.068
3–4	155.37	–74.649

The quaternary equilibrium was predicted by the UNIQUAC and UNIFAC models, showing that the fitting was poor in terms of  $\Delta m$  for UNIFAC model, due to the large relative error associated with the very low concentrations of ethylbenzene in both phases, while the fitting quality in terms of  $F$  was satisfactory, particularly for the UNIQUAC model. Therefore, fitting of the experimental data to UNIQUAC equation is more accurate than the UNIFAC method for this quaternary system.

## List of symbols

- $a$  activity obtained directly from the model by insertion of the experimental concentrations Eq. (1)
- $a_{ij}, a_{ji}$  parameters of the UNIQUAC and NRTL models
- $\alpha_{ij}$  non-randomness parameter for the NRTL equation
- $F$  r.m.s. deviation in mole fraction given by Eq. (3)
- $F_a, F_x$  objective function given by Eqs. (1) and (2).
- $m_k$  experimental solute distribution ratio Eq. (4)
- $\hat{m}_k$  calculated solute distribution ratio Eq. (4)
- $\Delta m$  r.m.s. relative error in the solute distribution ratio given by Eq. (4)
- $m$  ethylbenzene distribution coefficient for ternary  $\left(\frac{w_2^{\text{I}}}{w_2^{\text{II}}}\right)$  and quaternary  $\left(\frac{w_2^{0 \text{ I}}}{w_2^{0 \text{ II}}}\right)$  systems on ethanol – free basis
- $M$  number of tie lines, Eqs. (3) and (4)
- $n$  number of the components in the system (3) or (4)
- $P_i$  quaternary planes for the construction of the binodal surface
- $P_n$  parameter in the penalty term, Eqs. (1) and (2)
- $Q$  constant value in the penalty term, Eqs. (1) and (2)
- $w_i$  mass fraction of component  $i$
- $x_{ijk}$  experimental mole fraction of the  $i$ th component in the  $j$ th phase on the  $k$ th tie line, Eqs. (2) and (3)
- $\hat{x}_{ijk}$  calculated mole fraction of the  $i$ th component in the  $j$ th phase on the  $k$ th tie-line, Eqs. (2) and (3)
- $w_i^{\text{I}}$  mass fraction of the  $i$ th component in the methanol phase
- $w_i^{\text{II}}$  mass fraction of the  $i$ th component in the hydrocarbon phase
- Subscripts*
- $i$  lower index-denoting components (1–4)
- $j$  lower index-denoting phases (' or '')
- $k$  lower index denoting tie lines (1 to  $M$ )
- $\text{'}$  methanol phase
- $\text{''}$  hydrocarbon phase
- Superscripts*
- $0$  Concentration on ethanol-free basis

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