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LIQUID–LIQUID EQUILIBRIA OF TERNARY AND QUATERNARY SYSTEMS INCLUDING 2,2,4-TRIMETHYLPENTANE, BENZENE, ETHANOL, AND WATER AT 303.15 K

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ABSTRACT

Tie-line data for ternary systems including ethanol (C_2H_6O), water (H_2O), benzene (C_6H_6), and 2,2,4-trimethylpentane (C_8H_{18}) were investigated. Phase diagrams of $\{w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_6H_6\}$ and $\{w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_8H_{18}\}$ ternary systems were obtained at 303.15K, while $\{w_1H_2O + w_2C_8H_{18} + (1 - w_1 - w_2)C_6H_6\}$ ternary system was taken from literature. A quaternary system containing these four compounds $\{w_1C_2H_6O + w_2C_6H_6 + w_3C_8H_{18} + (1 - w_1 - w_2 - w_3)H_2O\}$ was also studied at the same temperature. From our experimental results, we can conclude that this quaternary system presents a very low water tolerance. Small quantities of water from ambient humidity or infiltration into storage tanks could produce phase separation with a considerable loss of C_2H_6O

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drawn into the aqueous phase. On the other hand, the results also show that the aqueous phase contains a higher concentration of C_6H_6 compared to C_8H_{18}. The ternary experimental results were correlated with the NRTL and UNIQUAC equations, and predicted with the UNIFAC group contribution method. The three models lead to accurate results according to the two overall errors. In order to predict the equilibrium data for the quaternary system the UNIFAC method was used. This method predicts the binodal surface, satisfactorily although its prediction of the ethanol distribution ratio is rather poor.

Key Words: Phase equilibria; Quaternary system; Ternary systems; Gasohol; Ethanol

INTRODUCTION

There has been increasing demands for the use of oxygenates to produce lead free gasolines in recent years. Ethers and alcohols are used as gasoline additives to provide antiknock quality and to help reduce harmful combustion emissions. Methyl *tert*-butyl ether (MTBE) is currently the primary oxygenated compound being used in reformulated gasolines. However, over the past few years there has been a growing concern about contamination of groundwater by MTBE, due to leaking storage tanks and pipelines. Therefore, it is very important to have some other oxygenates, in order to use them as alternative gasoline additives (1).

Light alkanols such as methanol and ethanol are some of the promising compounds that could produce lead free gasolines (2). However, the use of these alkanols in gasoline blends can raise phase separation problems in the presence of water (arising from ambient humidity and/or infiltration in storage tanks), depending on the unfavorable distribution factor between the aqueous and the hydrocarbon phases.

To determine the possibility of using ethanol as a gasoline additive, phase diagrams studies need to be performed at room temperature and atmospheric pressure to guarantee that there is no phase separation. In this work we used ethanol, a synthetic gasoline (represented by a mixture of an aromatic and an aliphatic hydrocarbon—benzene and 2,2,4-trimethyl pentane, respectively), and water.

Liquid–liquid equilibrium (LLE) measurements were performed for a quaternary system at 303.15 K and atmospheric pressure and its corresponding ternary subsystems in similar conditions. Ternary and quaternary systems are

Table 1. Ternary and Quaternary Systems, Including Their Treybal's Classification Type

No.	Type	System
1	1	$w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_6H_6$
2	1	$w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_8H_{18}$
3	1	$w_1C_2H_6O + w_2C_6H_6 + w_3C_8H_{18} + (1 - w_1 - w_2 - w_3)H_2O$

w_i being the mass fraction of component i.

shown in Table 1, where in their respective types in the Treybal's (3) classification are also included.

Additionally, the experimental results were compared with those estimated by means of the UNIFAC group contribution method (4) using the LLE interaction parameters reported by Magnussen et al. (5). They were also correlated with the NRTL (6) and UNIQUAC (7) models fitted to the experimental results for all ternary mixtures. For the quaternary mixture only the UNIFAC method was used.

EXPERIMENTAL

Ethanol chromatographic quality (C_2H_6O) and benzene p.a. (C_6H_6) were supplied by Merck (Darmstadt, Germany), and 2,2,4-trimethylpentane (also called isooctane) p.a. (C_8H_{18}) by Fluka Chemie AG (Buchs, Switzerland). The purity of the chemicals was verified chromatographically, their mass fractions found always to be >0.998, and were used without further purification. Water (H_2O) was bidistilled in an all-glass apparatus.

Before obtaining the LLE results for the quaternary system, the two partially miscible ternary systems included in Table 1 were studied, while the $\{w_1H_2O + w_2C_8H_{18} + (1 - w_1 - w_2)C_6H_6\}$ ternary one was taken from literature (8). On the other hand, the $\{w_1C_2H_6O + w_2C_8H_{18} + (1 - w_1 - w_2)C_6H_6\}$ ternary system was found to be completely miscible. Ternary equilibrium data were obtained by preparing mixtures of known overall mass composition within the heterogeneous region, using a dual range Mettler Toledo (Switzerland) AG245 balance with a precision of ± 0.1 mg/0.01 mg. All mixtures were prepared simultaneously introducing each one in 16 mL screw sample vials (Agilent Technologies Inc., USA, HP 5183-4535) equipped with cap, septa, and a Teflon coated magnetic bar to provide an intense stirring for at least seven days. A water bath thermostatized at (303.15 ± 0.05)K was connected in series with a set of two acrylic boxes having each six holes with O'ring seals where the sample vials were

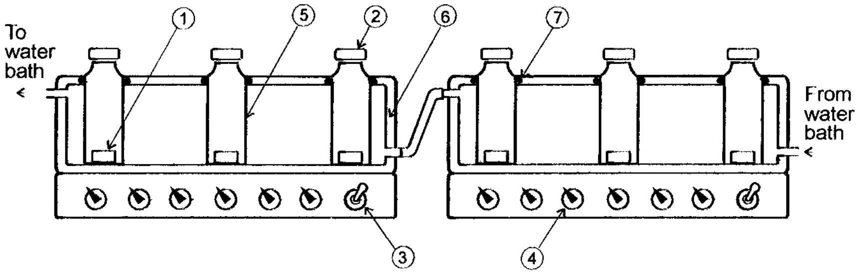

Figure 1. Line drawing of the experimental device. 1, Teflon coated magnetic bar; 2, screw caps with PTFE/white silicone septa; 3, power switch; 4, speed controls; 5, 16 mL screw sample vials (HP 5183-4535); 6, acrylic box (wall thickness: 10 mm); 7, O'ring seals.

inserted. Uniformity of temperature within the vials was maintained by continuous agitation of the mixture samples with a multipoint magnetically coupled stirrer (SBS, model A-04, SBS Instruments S.A., Spain) placed under the boxes. Figure 1 shows a line drawing of the experimental device. After phase-equilibrium was reached, the magnetic stirrers were turned off and both liquid phases were allowed to settle for 24 hr.

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 hypodermic 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.

A Hewlett Packard 6890 gas chromatograph directly connected to a ChemStation (Hewlett-Packard, USA, HP G2070AA) was used, and the internal standard method was applied to obtain quantitative results. Acetone (C_3H_6O) (Merck, p.a.) with a purity in mass fraction >0.999 (GC) was the standard compound used for this purpose. Good separation of the four components was obtained on a $30\,\mathrm{m} \times 0.25\,\mathrm{mm} \times 0.5\,\mu\mathrm{m}$ capillary column (INNOWax, cross-linked polyethylene glycol, Agilent Technologies Inc., USA, HP 19091N-233). The temperature program was as follows: initial temperature 343K for 2 min, ramp $15\mathrm{K\,min}^{-1}$, and final temperature 373K for another two minutes. The nitrogen carrier gas flow rate was electronically kept constant working with a split ratio 20:1 and the injector fitted at 453K. Detection was carried out by a thermal conductivity detector at 523K. Three or four analyses were performed for each sample in order to obtain a mean mass fraction value with a repeatability better than 1%.

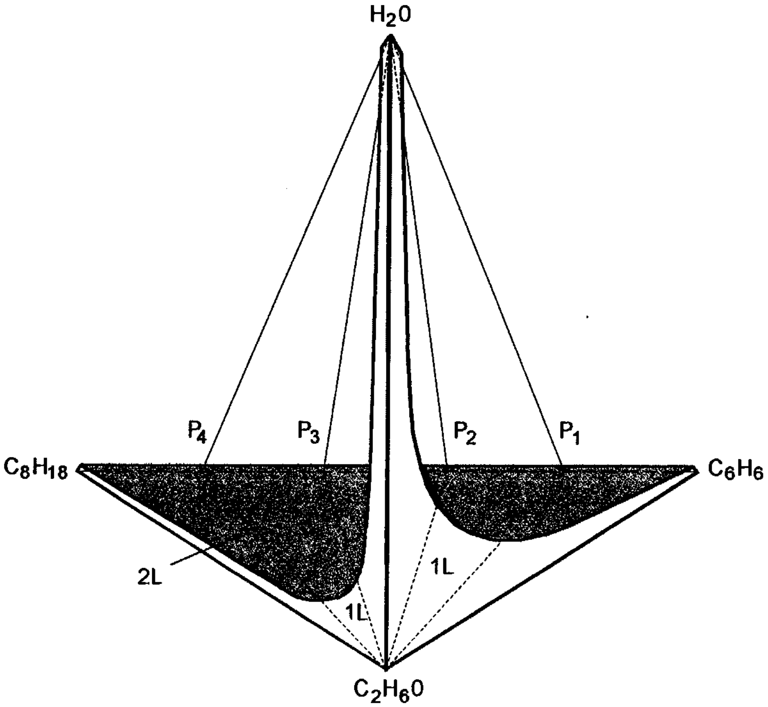

Figure 2. Schematic representation of the $\{w_1C_2H_6O + w_2C_6H_6 + w_3C_8H_{18} + (1 - w_1 - w_2 - w_3)H_2O\}$ quaternary system at 303.15K. P_1, P_2, P_3, and P_4 are sectional planes for the determination of the binodal surface. Dashed region: binodal surface.

Only after all ternary equilibrium data were determined experimentally, the quaternary binodal surface could be characterized fully. For this purpose, the LLE were determined on four quaternary planes (named P_1, P_2, P_3, and P_4) as can be seen in Fig. 2, which shows a schematic representation of the quaternary system $\{w_1C_2H_6O + w_2C_6H_6 + w_3C_8H_{18} + (1 - w_1 - w_2 - w_3)H_2O\}$. The equilibrium data for this system were obtained with the same procedure used for the ternary ones.

RESULTS AND DISCUSSION

Tables 2 and 3 list the equilibrium compositions for the ternary systems: $\{w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_6H_6\}$ and $\{w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_8H_{18}\}$ at (303.15 ± 0.05)K. Figures 3 and 4 show the corresponding

Table 2. Liquid–Liquid Equilibrium Data for the $\{w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_6H_6\}$ System at 303.15 K

Global Composition			Aqueous Phase			Benzene Phase		
w_1H_2O	$w_2C_2H_6O$	$(1 - w_1 - w_2)C_6H_6$	w_1H_2O	$w_2C_2H_6O$	$(1 - w_1 - w_2)C_6H_6$	w_1H_2O	$w_2C_2H_6O$	$(1 - w_1 - w_2)C_6H_6$
0.1329	0.3419	0.5252	0.231	0.520	0.250	0.0409	0.245	0.714
0.1730	0.3168	0.5103	0.351	0.517	0.133	0.0238	0.185	0.792
0.2139	0.2910	0.4951	0.441	0.487	0.0717	0.0172	0.152	0.830
0.2569	0.2482	0.4950	0.527	0.435	0.0380	0.0124	0.118	0.869
0.2968	0.2141	0.4891	0.601	0.382	0.0167	0.0074	0.0886	0.904
0.3489	0.1813	0.4698	0.661	0.331	0.0077	0.0053	0.0649	0.930
0.4043	0.1212	0.4745	0.761	0.236	0.0036	0.0024	0.0332	0.964
0.4316	0.0886	0.4798	0.822	0.178	n.d.[a]	0.0017	0.0208	0.977
0.4740	0.0391	0.4868	0.906	0.0906	0.0034	0.0023	0.0084	0.989
0.5140	0.0000	0.4860	1.000	0.0000	n.d.[a]	0.0014	0.0000	0.999
PP[b]			0.114	0.440	0.446	0.114	0.440	0.446

[a] n.d.: not detectable.

[b] Estimated plait point (PP) by Othmer and Tobias' method. Parameters of Eq. (1) : $m = 0.9174$, $b = 0.8036$. Linear correlation coefficient $= 0.9900$.

Table 3. Liquid–Liquid Equilibrium Data for the $\{w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_8H_{18}\}$ System at 303.15 K

Global Composition			Aqueous Phase			Isooctane Phase		
W_1H_2O	$w_2C_2H_6O$	$(1 - w_1 - w_2)C_8H_{18}$	w_1H_2O	$w_2C_2H_6O$	$(1 - w_1 - w_2)C_8H_{18}$	w_1H_2O	$w_2C_2H_6O$	$(1 - w_1 - w_2)C_8H_{18}$
0.0510	0.3703	0.5786	0.113	0.747	0.140	0.0075	0.0898	0.903
0.1012	0.3615	0.5373	0.217	0.737	0.0460	0.0052	0.0458	0.949
0.1535	0.3451	0.5014	0.304	0.678	0.0175	0.0053	0.0325	0.962
0.1891	0.3265	0.4844	0.363	0.628	0.0090	0.0050	0.0259	0.969
0.2539	0.2948	0.4514	0.455	0.545	n.d.[a]	0.0047	0.0192	0.976
0.2866	0.2708	0.4426	0.504	0.496	n.d.[a]	0.0046	0.0165	0.979
0.3277	0.2504	0.4219	0.558	0.442	n.d.[a]	0.0052	0.0132	0.982
0.3754	0.1914	0.4332	0.650	0.350	n.d.[a]	0.0048	0.0103	0.985
0.4115	0.1451	0.4435	0.725	0.275	n.d.[a]	0.0055	0.0074	0.987
0.4448	0.0968	0.4584	0.805	0.195	n.d.[a]	0.0069	0.0044	0.989
0.4699	0.0487	0.4814	0.894	0.106	n.d.[a]	0.0069	0.0023	0.991
0.5040	0.0000	0.4960	1.000	0.000	n.d.[a]	0.0056	0.0000	0.994
PP[b]			0.018	0.281	0.701	0.018	0.281	0.701

[a] n.d.: not detectable.

[b] Estimated plait point (PP) by Othmer and Tobias' method. Parameters of Eq. (1): $m = 1.3633$, $b = 2.2576$. Linear correlation coefficient $= 0.9929$.

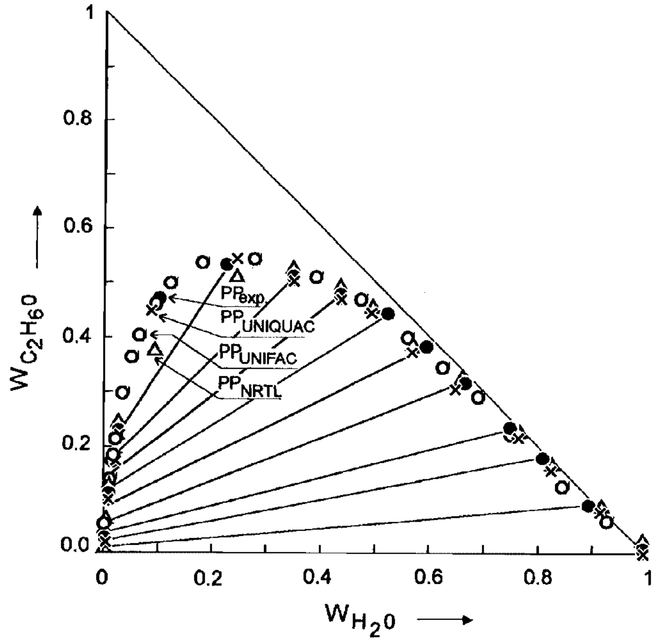

Figure 3. Liquid–liquid equilibria of the $\{w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_6H_6\}$ system at 303.15 K. –●–, Experimental; ×, UNIQUAC equation; △, NRTL equation; ○ UNIFAC prediction. PP, plait point.

LLE diagrams. Data predicted by the UNIFAC method and correlated by the NRTL and UNIQUAC equations are also shown.

For the ternary systems (numbers 1 and 2, in Table 1), the tie-lines are correlated satisfactorily by the method of Othmer and Tobias (9). The empirical equation,

$$\log\{(1 - w_{11})/w_{11}\} = m \times \log\{(1 - w_{33})/w_{33}\} + b \qquad (1)$$

can represent all the tie-line data with adequate precision. Here w_{11} and w_{33} are the mass fractions of the components 1 and 3 in the raffinate (phase 1) and extract (phase 2) phases, respectively, and m and b are parameters. The values of these parameters together with the linear correlation coefficients are given as footnotes in Tables 2 and 3.

The LLE data were fitted with the NRTL and UNIQUAC equations using a computer program developed by Sørensen (10). A penalty term was included in both objective functions (in terms of activity and mole fraction) to reduce the risk of multiple solutions associated with high parameter values. Table 4 shows the

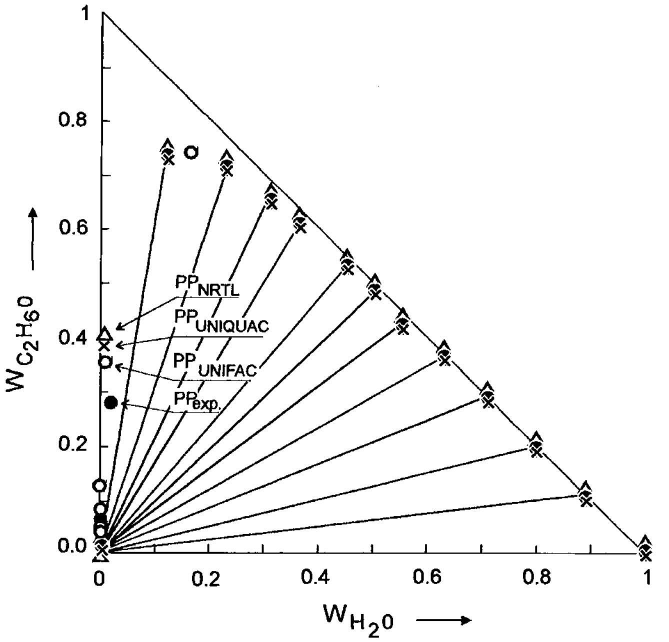

Figure 4. Liquid–liquid equilibria of the $\{w_1 H_2O + w_2 C_2H_6O + (1 - w_1 - w_2) C_8H_{18}\}$ system at 303.15 K. –●–, Experimental; ×, UNIQUAC equation; △, NRTL equation; ○, UNIFAC prediction. PP, plait point.

UNIQUAC structural parameters for the pure components taken from literature (11), the optimized non-randomness parameter for the NRTL equation, α_{ij}, and the optimized binary interaction parameters for both models and for each system.

Goodness of fit, as measured by the rms deviation in mole fraction

$$F = 100\left\{\sum_k \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2 / 6M\right\}^{1/2} \tag{2}$$

and by the rms relative error in the solute distribution ratio

$$\Delta m = 100 \sum_k \left\{\left[(m_k - \hat{m}_k)/m_k\right]^2 / M\right\}^{1/2} \tag{3}$$

is also indicated in Table 4. Here x_{ijk} is the experimental mole fraction of the *i*th component in the *j*th phase on the *k*th tie-line and $\hat{x}_{ijk}$ is the corresponding

Table 4. Residuals F and Δm, Optimized Parameters of the UNIQUAC and NRTL Equations for the Systems: No. 1, $\{w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_6H_6\}$ and No. 2, $\{w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_8H_{18}\}$, at 303.15 K

System No.	F (%)	Δm (%)	i–j	a_{ij}	a_{ji}	α_{ij}
UNIQUAC						
1	0.69	28.0	1–2	270.12	−237.60	
			1–3	226.45	1286.0	
			2–3	48.188	79.234	
2	0.37	7.3	1–2	−573.92	676.35	
			1–3	698.05	476.48	
			2–3	−38.877	289.57	
NRTL						
1	0.64	18.0	1–2	−814.31	−424.35	0.1
			1–3	2600.1	322.28	
			2–3	−909.83	202.20	
2	0.53	15.5	1–2	−513.55	197.58	0.2
			1–3	2172.2	508.08	
			2–3	580.76	83.301	
UNIQUAC structural parameters						
Component	r	q				
H_2O	0.9200	1.400				
C_2H_6O	2.1055	1.9720				
C_6H_6	3.1878	2.400				
C_8H_{18}	5.8463	5.008				

$a_{ij} = (g_{ij} - g_{jj})/R(K)$ for the NRTL equation, where g_{ij} is the energy of interaction between an i–j pair of molecules (J mol^{-1}). $a_{ij} = (u_{ij} - u_{jj})/R(K)$ for the UNIQUAC equation, where u_{ij} is the UNIQUAC binary interaction parameter (J mol^{-1}). R = Universal gas constant (J mol^{-1} K^{-1}).

calculated value. M is the number of tie-lines. m_k and $\hat{m}_k$ are the experimental and calculated solute distribution ratio, respectively.

The fit was fairly poor in terms of Δm due to the large relative error associated with the very low concentrations of some compounds in both phases, particularly for the UNIQUAC equation applied to the $\{w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_6H_6\}$ ternary system. On the other hand, the goodness of fit in terms of F was satisfactory, as can be seen in Table 4.

The LLE data of the ternary systems were also predicted using the UNIFAC group contribution method by means of a computer program named LLECAL, using the group interaction parameters obtained by Magnussen et al. (5) from LLE data, which are listed in Table 5. This method allows calculation of the activity coefficients of the three components of both phases. Figures 3 and 4 show that for the two ternary systems included in Table 1, the UNIFAC method predicts an immiscible region similar to the experimentally observed, which is close to those correlated with the NRTL and UNIQUAC equations.

On the other hand, the NRTL equation fitted to the experimental data using an iterative computing program, was more accurate than UNIQUAC for the $\{w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_6H_6\}$ ternary system, but the opposite occurred for the $\{w_1H_2O + w_2C_2H_6O + (1 - w_1 - w_2)C_8H_{18}\}$ ternary system (see both overall errors: F and Δm, listed in Table 4).

Table 6 lists equilibrium data for the $\{w_1C_2H_6O + w_2C_6H_6 + w_3C_8H_{18} + (1 - w_1 - w_2 - w_3)H_2O\}$ quaternary system, concerning the planes $P_1 = \{0.196\ C_8H_{18} + 0.804\ C_6H_6\}$, $P_2 = \{0.400\ C_8H_{18} + 0.600\ C_6H_6\}$, $P_3 = \{0.596\ C_8H_{18} + 0.404\ C_6H_6\}$, and $P_4 = \{0.804\ C_8H_{18} + 0.196\ C_6H_6\}$, expressed in mass fraction, which were used for the determination of the binodal surface. Since the compositions of the four components were determined individually, the sum of the mass fractions for each phase in Table 6 is not precisely equal to one. The same consideration is applicable to Tables 2 and 3 for ternary systems. In this work, the orientations of the P_1, P_2, P_3, and P_4 planes were selected taking into account that gasoline is represented by a mixture of aromatic and saturated hydrocarbons, although this leads to tie-lines that are almost parallel to these planes.

Table 5. UNIFAC Interaction Parameters

Main Group	CH_2	ACH	OH	H_2O
1 CH_2	0	−114.8	644.6	1300.0
3 ACH	156.5	0	703.9	859.4
5 OH	328.2	−9.210	0	28.73
8 H_2O	342.4	372.8	−122.4	0

Table 6. Quaternary Equilibrium Data for the $\{w_1C_2H_6O + w_2C_6H_6 + w_3C_8H_{18} + (1 - w_1 - w_2 - w_3)H_2O\}$ system at (303.15 ± 0.05) K

Global Composition				Aqueous Phase				Organic Phase			
w_1 C_2H_6O	w_2 C_6H_6	w_3 C_8H_{18}	$(1-w_1-w_2-w_3)$ H_2O	w_1 C_2H_6O	w_2 C_6H_6	w_3 C_8H_{18}	$(1-w_1-w_2-w_3)$ H_2O	w_1 C_2H_6O	w_2 C_6H_6	w_3 C_8H_{18}	$(1-w_1-w_2-w_3)$ H_2O
P_1 (0.196 C_8H_{18} + 0.804 C_6H_6, mass fraction)											
0.3647	0.4170	0.1017	0.1166	0.507	0.268	0.0420	0.183	0.212	0.603	0.159	0.0262
0.3544	0.3955	0.0965	0.1536	0.546	0.177	0.0184	0.258	0.156	0.653	0.177	0.0140
0.3425	0.3628	0.0885	0.2062	0.540	0.103	0.0052	0.351	0.127	0.677	0.185	0.0109
0.3385	0.3611	0.0881	0.2124	0.539	0.0955	0.0044	0.362	0.122	0.682	0.187	0.0097
0.2941	0.3728	0.0909	0.2422	0.507	0.0490	n.d.[a]	0.444	0.0977	0.708	0.186	0.0080
0.2700	0.3513	0.0857	0.2929	0.464	0.0199	n.d.[a]	0.516	0.0769	0.729	0.188	0.0056
0.2251	0.3593	0.0876	0.3279	0.398	0.0086	n.d.[a]	0.594	0.0567	0.749	0.191	0.0038
0.1918	0.3582	0.0874	0.3626	0.344	n.d.[a]	n.d.[a]	0.656	0.0434	0.762	0.191	0.0033
0.1424	0.3592	0.0876	0.4108	0.265	n.d.[a]	n.d.[a]	0.735	0.0266	0.778	0.192	0.0036
0.0948	0.3632	0.0886	0.4534	0.189	n.d.[a]	n.d.[a]	0.811	0.0133	0.786	0.198	0.0023
0.0478	0.3732	0.0910	0.4880	0.107	n.d.[a]	n.d.[a]	0.893	0.0062	0.797	0.194	0.0024
0.0000	0.3980	0.0971	0.5049	0.000	n.d.[a]	n.d.[a]	1.000	0.0000	0.803	0.195	0.0021
P_2 (0.400 C_8H_{18} + 0.600 C_6H_6, mass fraction)											
0.3636	0.3309	0.2204	0.0851	0.500	0.261	0.117	0.122	0.177	0.465	0.342	0.0149
0.3597	0.3097	0.2063	0.1244	0.580	0.168	0.0480	0.204	0.114	0.506	0.373	0.0068
0.3549	0.2919	0.1944	0.1588	0.587	0.122	0.0265	0.264	0.0997	0.518	0.375	0.0069
0.3393	0.2801	0.1866	0.1939	0.580	0.0836	0.0111	0.325	0.0836	0.537	0.374	0.0054
0.3027	0.2747	0.1830	0.2397	0.543	0.0389	n.d.[a]	0.418	0.0647	0.549	0.383	0.0042
0.2660	0.2625	0.1749	0.2966	0.472	0.0131	n.d.[a]	0.515	0.0492	0.564	0.381	0.0057
0.2246	0.2622	0.1747	0.3385	0.432	n.d.[a]	n.d.[a]	0.568	0.0381	0.584	0.375	0.0028
0.1913	0.2591	0.1726	0.3771	0.368	n.d.[a]	n.d.[a]	0.632	0.0282	0.596	0.373	0.0026
0.1268	0.2771	0.1846	0.4115	0.286	n.d.[a]	n.d.[a]	0.714	0.0149	0.608	0.375	0.0021
0.0991	0.2649	0.1764	0.4597	0.242	n.d.[a]	n.d.[a]	0.758	0.0104	0.609	0.378	0.0034

0.0480	0.2796	0.1862	0.4862	0.126	n.d.[a]	n.d.[a]	0.874	0.0047	0.618	0.375	0.0018
0.0000	0.2917	0.1943	0.5140	0.000	n.d.[a]	n.d.[a]	1.000	0.0000	0.629	0.369	0.0022
P_3 (0.596 C_8H_{18} + 0.404 C_6H_6, mass fraction)											
0.3781	0.2172	0.3208	0.0839	0.586	0.163	0.122	0.129	0.117	0.336	0.540	0.0069
0.3624	0.2065	0.3049	0.1263	0.623	0.103	0.0465	0.228	0.0779	0.363	0.554	0.0048
0.3645	0.1970	0.2909	0.1475	0.623	0.0891	0.0326	0.255	0.0694	0.374	0.553	0.0038
0.3339	0.1883	0.2781	0.1997	0.586	0.0466	0.0102	0.357	0.0540	0.391	0.551	0.0037
0.2998	0.1844	0.2723	0.2435	0.533	0.0257	n.d.[a]	0.441	0.0446	0.407	0.546	0.0032
0.2695	0.1737	0.2566	0.3002	0.466	0.0099	n.d.[a]	0.524	0.0354	0.415	0.546	0.0034
0.2332	0.1723	0.2544	0.3400	0.408	0.0056	n.d.[a]	0.587	0.0283	0.427	0.542	0.0027
0.1955	0.1773	0.2618	0.3655	0.363	n.d.[a]	n.d.[a]	0.637	0.0214	0.431	0.545	0.0024
0.1333	0.1778	0.2625	0.4265	0.249	n.d.[a]	n.d.[a]	0.751	0.0124	0.441	0.544	0.0025
0.0989	0.1813	0.2678	0.4520	0.197	n.d.[a]	n.d.[a]	0.803	0.0084	0.450	0.539	0.0024
0.0485	0.1889	0.2790	0.4836	0.110	n.d.[a]	n.d.[a]	0.890	0.0038	0.451	0.543	0.0025
0.0000	0.1989	0.2937	0.5074	0.000	n.d.[a]	n.d.[a]	1.000	0.0000	0.441	0.556	0.0027
P_4 (0.804 C_8H_{18} + 0.196 C_6H_6, mass fraction)											
0.3769	0.1057	0.4332	0.0842	0.684	0.0635	0.0966	0.156	0.0876	0.170	0.738	0.0050
0.3548	0.1019	0.4175	0.1258	0.678	0.0400	0.0407	0.242	0.0567	0.186	0.753	0.0045
0.3599	0.0960	0.3932	0.1510	0.662	0.0310	0.0278	0.279	0.0495	0.188	0.759	0.0038
0.3370	0.0905	0.3709	0.2016	0.608	0.0161	0.0107	0.365	0.0384	0.202	0.755	0.0037
0.3066	0.0903	0.3701	0.2330	0.564	0.0103	0.0040	0.422	0.0290	0.223	0.744	0.0034
0.2700	0.0859	0.3518	0.2923	0.477	0.0054	n.d.[a]	0.518	0.0244	0.217	0.756	0.0026
0.2269	0.0854	0.3501	0.3375	0.410	n.d.[a]	n.d.[a]	0.590	0.0183	0.222	0.757	0.0029
0.1916	0.0845	0.3462	0.3777	0.366	n.d.[a]	n.d.[a]	0.634	0.0143	0.227	0.756	0.0026
0.1420	0.0896	0.3671	0.4014	0.266	n.d.[a]	n.d.[a]	0.734	0.0108	0.236	0.750	0.0030
0.0995	0.0877	0.3594	0.4534	0.191	n.d.[a]	n.d.[a]	0.809	0.0061	0.238	0.753	0.0030
0.0498	0.0898	0.3681	0.4923	0.121	n.d.[a]	n.d.[a]	0.879	0.0031	0.242	0.752	0.0029
0.0000	0.0989	0.4050	0.4961	0.000	n.d.[a]	n.d.[a]	1.000	0.0000	0.250	0.747	0.0027

[a] n.d.: not detectable.

Table 7. Residuals F and Δm of the UNIFAC Equation for the Quaternary: $\{w_1C_2H_6O + w_2C_6H_6 + w_3C_8H_{18} + (1 - w_1 - w_2 - w_3)H_2O\}$ System at 303.15 K[a]

Plane	F (%)[b]	Δm (%)[b]
P_1	2.99	10.5
P_2	2.97	7.8
P_3	2.83	5.4
P_4	2.38	5.0

[a] The values of Δm were calculated only for C_2H_6O. The distribution coefficient for this compound is defined as m = mass fraction of C_2H_6O in the organic phase/mass fraction of C_2H_6O in the aqueous phase.

[b] Calculated with Eqs. (2) and (3).

The water compositions in the organic phase represent the water tolerance for this quaternary system. These values are very small, ranging from 0.0021 to 0.0262 for P_1, 0.0018 to 0.0149 for P_2, 0.0024 to 0.0069 for P_3, and 0.0026 to 0.0050 for P_4, always expressed in mass fraction (see Table 6). These values are higher than those obtained for a similar quaternary system studied previously at the same temperature (8), which included methanol instead of ethanol. This difference is very important for a quaternary system used as a gasohol, because a higher water tolerance reduces the possibility of a phase separation in the storage tanks.

The results also show that when a phase separation does occur, a large fraction of C_2H_6O is drawn into the aqueous phase. On the other hand, the greater solubility of C_6H_6 as compared to C_8H_{18} in the aqueous phase is evident due to the higher solubility of C_6H_6 in C_2H_6O. A similar behavior was observed for methanol in the $\{w_1CH_4O + w_2C_6H_6 + w_3C_8H_{18} + (1 - w_1 - w_2 - w_3)H_2O\}$ quaternary system (8).

The quaternary equilibrium data was only predicted by the UNIFAC group contribution method using the same computer program as for the ternary systems. The UNIFAC method fitted very well to the binodal surface for the quaternary system, but it was relatively poor for the prediction of the ethanol distribution ratio, as can be seen in Table 7.

CONCLUSIONS

From our experimental results we can conclude that the quaternary system $\{w_1C_2H_6O + w_2C_6H_6 + w_3C_8H_{18} + (1 - w_1 - w_2 - w_3)H_2O\}$ presents a very low water tolerance, but higher than that observed for a similar quaternary system including methanol. Small quantities of water from ambient humidity or infiltration into storage tanks could produce phase separation with a considerable loss of C_2H_6O drawn into the aqueous phase. This would leave gasoline with a lower oxygen content than that required by the Environmental Protection Agency (EPA) regulations (2.0 mass% of oxygen in reformulated gasolines) (12) if a large quantity of water is available.

On the other hand, the UNIFAC group contribution method was adequate for the prediction of the binodal surface of this quaternary system, but only led to qualitative results for the equilibrium data. However, its predictions were satisfactory for both ternary systems included in Table 1 (see Figs. 3 and 4).

From the analysis of these figures, and of Table 4, we conclude that the UNIFAC, NRTL, and UNIQUAC methods can represent adequately the equilibrium data of both ternary systems included in Table 1.

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