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Experimental Determination of Quaternary and Ternary Isobaric Vapor−Liquid−Liquid Equilibrium and Vapor−Liquid Equilibrium for the Systems Water−Ethanol−Hexane−Toluene and Water−Hexane−Toluene at 101.3 kPa

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ABSTRACT: Experimental isobaric vapor−liquid−liquid and vapor−liquid equilibrium (VLLE and VLE) data for the ternary system water (1)−hexane (2)−toluene (3) and the quaternary system water (1)−ethanol (2)−hexane (3)−toluene (4) were measured at 101.3 kPa. An all-glass, dynamic recirculating still equipped with an ultrasonic homogenizer was used to determine the VLLE. The results obtained show that the system does not present quaternary azeotropes. The point-by-point method by Wisniak for testing the thermodynamic consistency of isobaric measurements was used to test the equilibrium data.

INTRODUCTION

Water−ethanol−hydrocarbon systems are of great interest in the fuel industry. Ethanol is used to increase the octane levels of gasoline while also promoting more complete combustion, which reduces harmful exhaust pipe emissions. However, small amounts of water in the blend can lead to incorrect motor operation. For this reason, ethanol must be dehydrated prior to blending with gasoline. This process is carried out by different techniques, adsorption and azeotropic distillation being one of the most commonly used. We showed recently in previous works[1] that it is possible to obtain a “dry” mixture of ethanol + hydrocarbon by heterogeneous azeotropic distillation. The ethanol + hydrocarbon mixture so obtained may be employed directly as gasoline. The feasibility of dehydrating ethanol to obtain a hydrocarbon−ethanol mixture by using one or a mixture of the many hydrocarbons present in gasoline has been studied in previous works.[2,3] Nowadays, we are working with other mixtures of the hydrocarbons present in gasoline, studying the behavior and properties of different kinds of hydrocarbons, alkanes, cycloalkanes, aromatics, etc., and their influence on the behavior of the global mixture. In this work, hexane and toluene were selected, and experimental isobaric vapor−liquid (VLE) and vapor−liquid−liquid equilibrium (VLLE) data for the quaternary system water + ethanol + hexane + toluene at atmospheric pressure have been obtained.

EXPERIMENTAL SECTION

Chemicals Used. All the reagents were “for analysis” grade and acquired from Merck. The purity of ethanol, hexane, and toluene was higher than 0.99 mass fraction, so no further purification was needed. The internal standard used for gas chromatography was 2-propanol. The water content (mass %) was determined by the Karl Fischer titration method and for hexane, toluene, ethanol, and 2-propanol was around $100\,w = 0.006$, 0.003, 0.04, and 0.07, respectively. The water used was purified using a Milli Q-Plus system.

Apparatus and Procedures. An all-glass, dynamic recirculating still equipped with an ultrasonic homogenizer (Braun Labsonic P) coupled to a boiling flask was used to determine the VLLE data. This commercially available apparatus (Labodest model 602) is assembled in Germany by Fischer Labor and Verfahrenstechnik and has been modified by Gomis et al.[4] The application of ultrasound to the boiling flask causes emulsification of the two liquid phases throughout the still and thus prevents the fluctuations in temperature and flow rate characteristic of two liquid phase systems.[5] Visual observation confirmed that the emulsified state was maintained everywhere throughout the apparatus during operation. For VLE determinations, the apparatus was used without further modification since it permits good mixing and separation of the vapor and liquid phases once they achieve equilibrium. The experimental procedure described in previous studies was followed.[2,4,6] Accordingly, only essential parts are reproduced here.

A Pt-100 sensor was employed to measure the equilibrium temperatures. The probe was connected to a Presys thermometer (model ST-501), with an uncertainty of 0.01 K according to the calibration certificate (scale ITS 90[7]). A Fischer M101 control system was used to measure and control the pressure, as well as the heating power. The pressure in the still was 101.3 kPa, measured and controlled to an accuracy of 0.1 kPa. To check that the apparatus operated properly, the boiling point of water was measured and compared with its value in the bibliography.

Sampling was carried out in three different ways:

(a) Gaseous samples were injected into the GC via a UW type six-port valve from Valco Instruments Co. The connecting tube walls were superheated with a resistance tape controlled by a potentiometer to ensure the vapor to remain unsaturated and avoid condensation.

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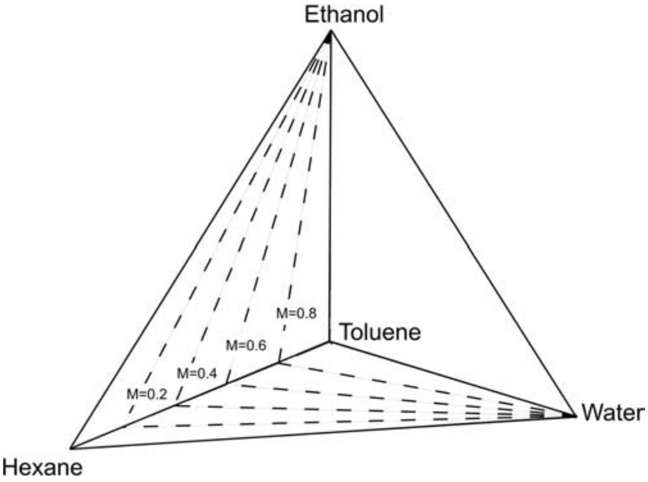

Figure 1. Tetrahedral representation. Sectional planes.

Table 1. Vapor−Liquid−Liquid Equilibrium Data (Mole Fraction) for the Water (1) + Hexane (3) + Toluene (4) Ternary System at 101.3 kPa

aqueous		organic		vapor		T_b
x_3	x_4	x_3	x_4	y_3	y_4	K
<0.0002	0.00002	0.733	0.266	0.692	0.071	338.65
<0.0002	0.00009	0.505	0.493	0.592	0.128	341.80
<0.0002	0.00009	0.261	0.735	0.477	0.186	344.92
<0.0002	0.0001	0.086	0.908	0.340	0.265	351.65

(b) For sampling of the liquid phase in the heterogeneous region, a small amount of the liquid coming from the separation chamber of the instrument was diverted to a tube by a solenoid valve. The tube was placed in a thermostatic bath at a temperature equal to the boiling point of the mixture. In this way, the dispersed liquid phases enter the tube and separate into two layers at their respective bubble points. A sample was taken from each layer and placed in a vial along with a small amount of 2-propanol as internal standard. Between equilibrium determinations, the drops of sample remaining in the feed line to the tube were flushed out using vacuum and external heating.

(c) For the homogeneous region, samples were withdrawn from the liquid coming from the separator chamber using a syringe and put into a vial along with a small amount of internal standard.

All analytical work was carried out by gas chromatography in a Shimadzu GC-14A coupled to a personal computer employing Shimadzu Labsolution GC-Solution software. Component separation was achieved in a 2 m × 3 mm column packed with Porapak Q 80/100. The oven temperature was 473.15 K. The helium flow rate was 50 mL/min.

Detection was carried out by various techniques, which depended upon the composition of the samples: thermal conductivity detection (TCD) for organic and aqueous samples (analysis for water, ethanol, hexane, and toluene) and flame ionization detection (FID) for aqueous samples (analysis for ethanol, hexane, and toluene). The temperature of the detector was 493.15 K, and the current intensity on the TCD was 100 mA. The water in the organic phase was also determined by the Karl Fischer titration method.

Table 2. .Vapor−Liquid−Liquid Equilibrium Data (Mole Fraction) for the Water (1) + Ethanol (2) + Hexane (3) + Toluene (4) Quaternary System at 101.3 kPa

	aqueous				organic				vapor				T_b
M^a	x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4	K
0.2	0.847	0.149	0.0011	0.0020	0.0044	0.051	0.693	0.251	0.170	0.186	0.593	0.051	332.67
	0.712	0.283	0.0023	0.0034	0.0045	0.061	0.718	0.217	0.157	0.225	0.573	0.046	332.39
	0.603	0.379	0.0085	0.0093	0.010	0.099	0.670	0.222	0.151	0.234	0.571	0.044	332.16
	0.527	0.443	0.017	0.014	0.014	0.128	0.662	0.196	0.149	0.240	0.566	0.045	331.82
	0.452	0.498	0.030	0.020	0.025	0.165	0.632	0.178	0.139	0.254	0.567	0.040	331.80
	0.362	0.527	0.077	0.034	0.054	0.271	0.532	0.143	0.130	0.264	0.570	0.036	331.68
0.4	0.753	0.243	0.0009	0.0036	0.016	0.085	0.521	0.378	0.175	0.240	0.497	0.088	334.88
	0.642	0.339	0.0063	0.013	0.016	0.127	0.457	0.400	0.171	0.256	0.487	0.086	334.71
	0.556	0.405	0.015	0.025	0.029	0.168	0.444	0.359	0.166	0.264	0.487	0.084	334.65
	0.465	0.467	0.028	0.040	0.054	0.221	0.411	0.314	0.162	0.271	0.487	0.080	334.49
	0.358	0.502	0.068	0.072	0.106	0.322	0.321	0.251	0.157	0.275	0.492	0.076	334.25
0.6	0.856	0.142	0.0002	0.0014	0.014	0.069	0.276	0.641	0.223	0.240	0.394	0.143	338.51
	0.744	0.247	0.0017	0.0067	0.030	0.121	0.269	0.581	0.205	0.274	0.382	0.139	338.28
	0.662	0.319	0.003	0.016	0.037	0.171	0.250	0.542	0.203	0.285	0.376	0.137	337.98
	0.570	0.382	0.009	0.039	0.069	0.237	0.186	0.508	0.197	0.294	0.378	0.131	337.94
	0.494	0.425	0.019	0.062	0.095	0.281	0.184	0.441	0.189	0.298	0.381	0.132	337.97
0.8	0.866	0.132	<0.0002	0.0016	0.019	0.092	0.133	0.755	0.268	0.291	0.229	0.211	343.35
	0.790	0.202	0.0011	0.0063	0.043	0.157	0.109	0.690	0.252	0.317	0.227	0.205	342.74
	0.680	0.294	0.003	0.023	0.070	0.227	0.078	0.624	0.245	0.333	0.224	0.198	342.50
	0.576	0.364	0.006	0.055	0.121	0.290	0.068	0.521	0.239	0.338	0.230	0.194	342.34
	0.472	0.410	0.013	0.104	0.203	0.349	0.046	0.402	0.241	0.344	0.218	0.197	342.52

[a] $M = x_4/(x_3 + x_4)$ in the initial mixture.

Table 3. Vapor−Liquid Equilibrium Data (Mole Fraction) for the Water (1) + Ethanol (2) + Hexane (3) + Toluene (4) Quaternary System at 101.3 kPa

	liquid				vapor				T_b
M^a	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4	K
0.2	0.204	0.540	0.198	0.058	0.120	0.273	0.573	0.034	331.71
	0.174	0.654	0.130	0.042	0.100	0.308	0.561	0.031	332.55
	0.170	0.772	0.042	0.016	0.101	0.457	0.422	0.020	338.16
	0.289	0.667	0.030	0.014	0.131	0.373	0.474	0.022	336.28
	0.081	0.437	0.379	0.103	0.099	0.297	0.569	0.036	332.24
	0.059	0.617	0.253	0.071	0.059	0.351	0.557	0.034	333.34
	0.040	0.762	0.151	0.047	0.033	0.420	0.516	0.031	335.28
	0.064	0.859	0.055	0.022	0.048	0.561	0.367	0.024	340.65
0.4	0.054	0.479	0.268	0.199	0.080	0.358	0.493	0.070	335.57
	0.041	0.630	0.186	0.144	0.046	0.406	0.477	0.070	336.51
	0.048	0.751	0.108	0.092	0.043	0.456	0.437	0.064	337.89
	0.035	0.875	0.046	0.044	0.028	0.595	0.332	0.046	341.38
	0.143	0.521	0.192	0.143	0.124	0.312	0.494	0.071	334.50
	0.167	0.624	0.116	0.093	0.113	0.336	0.483	0.067	335.17
	0.216	0.726	0.025	0.033	0.137	0.499	0.309	0.056	341.35
	0.322	0.621	0.028	0.029	0.155	0.392	0.398	0.055	338.41
0.6	0.069	0.425	0.186	0.321	0.114	0.380	0.387	0.120	338.50
	0.067	0.579	0.124	0.230	0.083	0.431	0.369	0.117	339.55
	0.062	0.707	0.081	0.150	0.061	0.495	0.339	0.106	340.35
	0.167	0.652	0.061	0.120	0.128	0.407	0.360	0.106	338.85
	0.206	0.493	0.111	0.189	0.164	0.325	0.395	0.116	337.35
	0.304	0.516	0.064	0.116	0.170	0.314	0.402	0.114	337.09
	0.381	0.519	0.036	0.064	0.170	0.320	0.405	0.106	337.41
	0.280	0.652	0.022	0.047	0.161	0.442	0.316	0.082	340.60
	0.196	0.742	0.019	0.043	0.139	0.585	0.220	0.056	345.40
	0.094	0.867	0.010	0.030	0.082	0.796	0.095	0.027	349.54
0.8	0.067	0.406	0.092	0.435	0.142	0.445	0.233	0.181	342.85
	0.071	0.537	0.069	0.324	0.114	0.486	0.229	0.172	343.45
	0.059	0.699	0.040	0.203	0.073	0.576	0.193	0.159	344.18
	0.045	0.855	0.017	0.084	0.046	0.712	0.139	0.103	346.45
	0.190	0.468	0.061	0.280	0.202	0.381	0.240	0.177	341.80
	0.190	0.622	0.028	0.160	0.169	0.459	0.213	0.159	342.80
	0.197	0.724	0.010	0.069	0.160	0.577	0.150	0.113	345.32
	0.357	0.572	0.007	0.064	0.215	0.448	0.192	0.146	343.41
	0.335	0.473	0.026	0.166	0.221	0.352	0.249	0.177	341.50

[a] $M = x_4/(x_3 + x_4)$ in the initial mixture.

An internal standard was used to obtain quantitative results from the analysis of the liquid phases. For this reason, 2-propanol, which is completely miscible in water, ethanol, hexane, and toluene, was also added to the sample vials. Moreover, addition of the standard prevents phase splitting when the temperature is adjusted after separation of the phases.

The percent uncertainty (uncertainty · 100/measurand) of the mole fraction measurements is 2 % if the mole fractions are greater than 0.01. For water in the organic phase and organic compounds in the aqueous phase, when the mole fractions are lower than 0.01, the percent uncertainty increases until it reaches approximately 20 % for a 0.00002 mole fraction of toluene and 0.0002 mole fraction of hexane, the lowest mole fraction encountered.

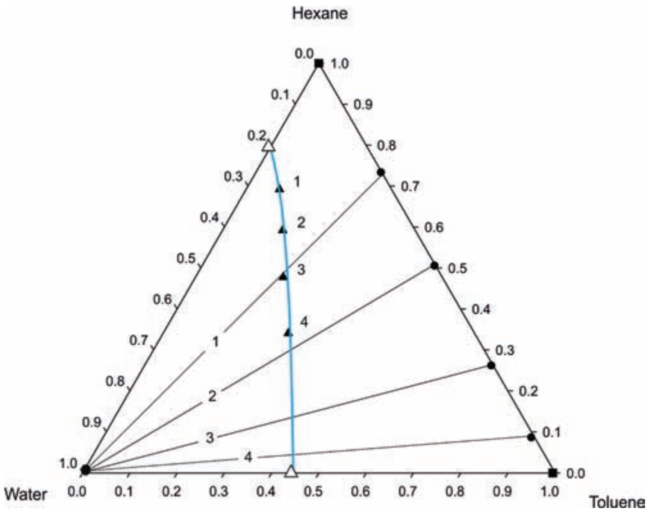

Figure 2. VLLE (mole fraction) diagram for the water (1) + hexane (3) + toluene (4) ternary system at 101.3 kPa: ●, liquid phase, from this work; ▲, vapor phase, from this work; —, tie line; ■, liquid phase, data from Gomis et al.;[6,8] △, vapor phase, data from Gomis et al.[6,8]

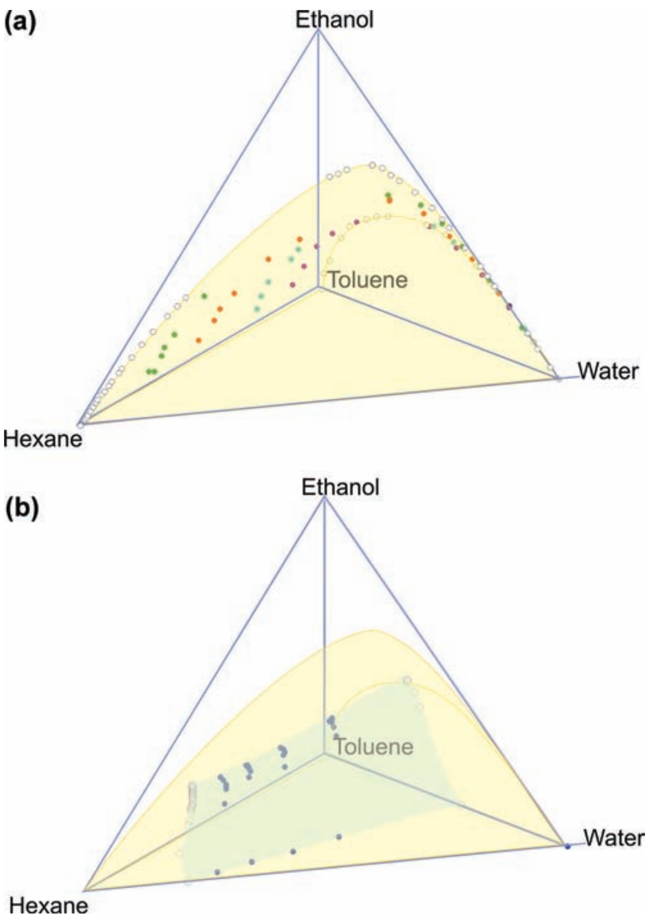

Figure 3. (a) VLLE data (mole fraction) for the quaternary system water (1)−ethanol (2)−hexane (3)−toluene (4) at 101.3 kPa, liquid phase: ●, data from this work; ○, data from Gomis et al.[6,8] (b) VLLE data (mole fraction) for the quaternary system water (1)−ethanol (2)−hexane (3)−toluene (4) at 101.3 kPa, vapor phase: ●, data from this work; ○, data from Gomis et al.[6,8]

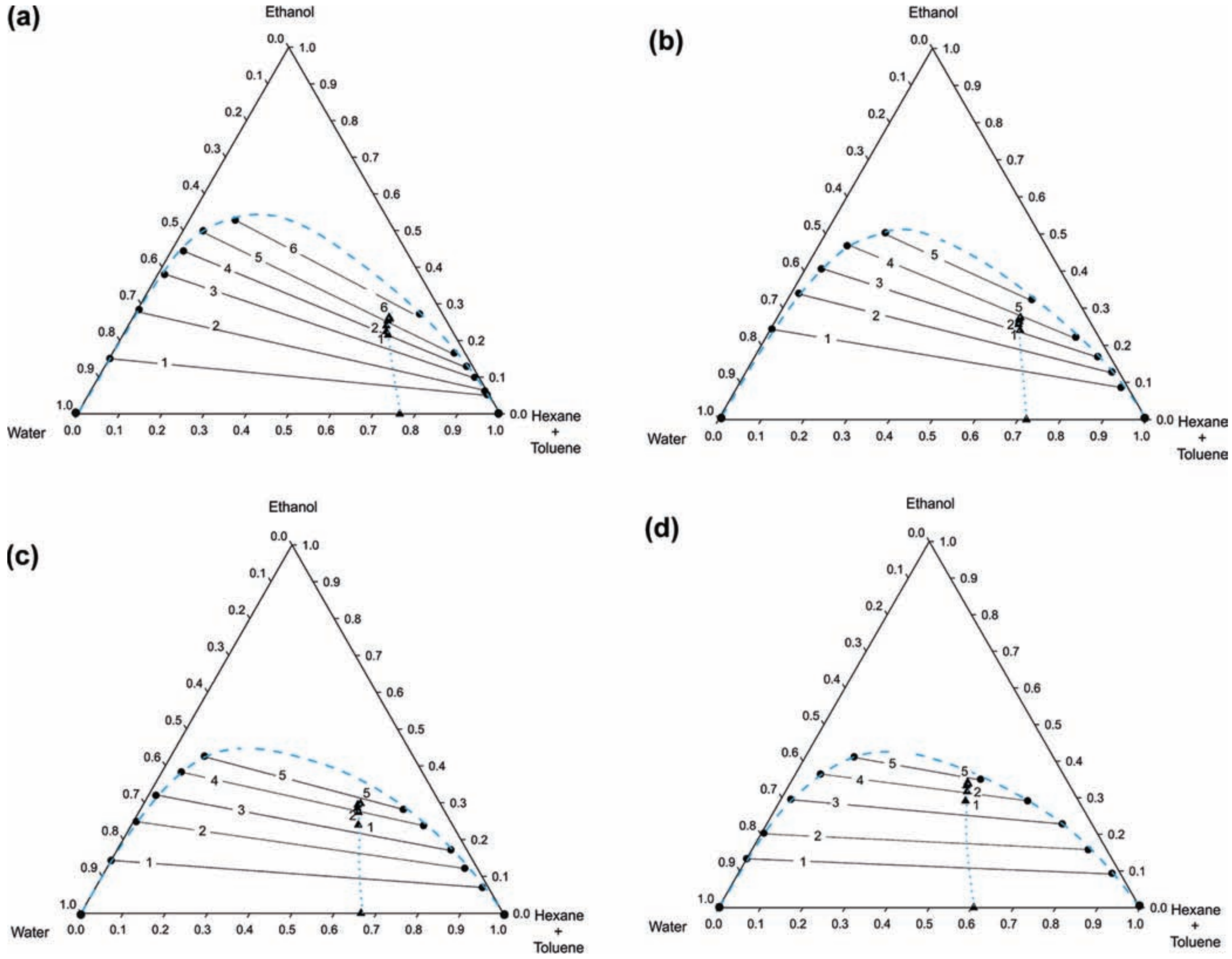

Figure 4. (a) Pseudoternary VLLE (mole fraction) representations for the system water (1) + ethanol (2) + hexane (3) + toluene (4) quaternary system at 101.3 kPa, $M = 0.2$: ●, liquid phase; ▲, vapor phase; —, tie line. (b) Pseudoternary VLLE (mole fraction) representations for the system water (1) + ethanol (2) + hexane (3) + toluene (4) quaternary system at 101.3 kPa, $M = 0.4$: ●, liquid phase; ▲, vapor phase; —, tie line. (c) Pseudoternary VLLE (mole fraction) representations for the system water (1) + ethanol (2) + hexane (3) + toluene (4) quaternary system at 101.3 kPa, $M = 0.6$: ●, liquid phase; ▲, vapor phase; —, tie line. (d) Pseudoternary VLLE (mole fraction) representations for the system water (1) + ethanol (2) + hexane (3) + toluene (4) quaternary system at 101.3 kPa, $M = 0.8$: ●, liquid phase; ▲, vapor phase; —, tie line.

With a view to obtaining experimental data for the entire region comprising quaternary mixtures (the region in which the liquid mixtures are heterogeneous at the bubble point as well as the one in which they are homogeneous), the liquid mixtures introduced in the vapor—liquid equilibrium apparatus at the start of every experiment were chosen to more or less lie in the planes shown in the tetrahedral diagram in Figure 1. All the points in a given plane represent mixtures of equal molarity, which is defined as $x_4/(x_3 + x_4)$, where x_3 and x_4 are the molar fractions of hexane and toluene, respectively.

■ RESULTS AND DISCUSSION

The experimental isobaric VLLE data for the ternary system water (1)—hexane (2)—toluene (3) and the quaternary system water (1)—ethanol (2)—hexane (3)—toluene (4) at 101.3 kPa are reported in Tables 1 and 2, respectively. VLE data for the homogeneous region of the quaternary system are shown in Table 3. The bubble point (T_b/K) and composition (mole fraction) of the liquid phases (x_i) and the vapor phases (y_i) are recorded in these tables.

Figure 2 shows the isobaric vapor—liquid—liquid equilibrium data for the ternary system. It also includes the binary heterogeneous azeotropes determined by Gomis et al.[6] and Gomis et al.[8] Tie lines connecting conjugate liquid phases, the vapor line, and the nonisothermal binodal curve are also shown. Numbers indicate the correspondence between equilibrium liquid and vapor phases. As can be seen, all the vapor phase composition points lie above the tie lines connecting their corresponding equilibrium liquid phases. This confirms that a ternary heterogeneous azeotrope is not present in this ternary system.

Figure 3 shows the isobaric vapor—liquid—liquid equilibrium data for the quaternary system. It also shows the equilibrium data determined by Gomis et al.[6] and Gomis et al.[8] for those ternary systems comprising a pair of partially miscible compounds. The points plotted in Figure 3a represent the liquid phases; they define the bubble-point-temperature solubility surface. This surface (shaded in Figure 3a) envelopes the region in which

Table 4. Antoine Equation Parameters[a] for the Pure Substances

compound	A	B	C	temperature range/K
water[11]	7.196	1730.630	−39.724	273.15 to 373.15
ethanol[11]	7.237	1592.864	−46.966	293.15 to 366.15
hexane[12]	6.035	1189.640	−46.870	243.15 to 443.15
toluene[11]	7.196	1730.630	−39.724	246.15 to 384.15

[a] Antoine Equation: $\log(P) = A - B/(T + C)$, with P in kPa and T in K.

the liquid mixtures are heterogeneous at the bubble point temperature. It occupies most of the tetrahedron as a result of the high immiscibility of organic compounds 3 and 4 in water. The points plotted in Figure 3b represent the compositions of the vapor phases in equilibrium with the heterogeneous liquid mixtures. They also define a surface the area of which has been shaded using a dark color. This surface is completely inside the heterogeneous liquid mixture region.

Figure 4 shows, for every sectional plane of the tetrahedron, pseudoternary representations of the tie lines connecting the conjugate liquid phases and the vapor phases in equilibrium with the liquid phases. An evolution in the shape of the heterogeneous region can be observed. The area of this region decreases since the plane of ternary water−ethanol−hexane becomes closer to that of water−ethanol−toluene. Regarding the tie lines, the ones closer to the ternary water−ethanol−hexane have a higher slope, and this slope is decreasing near the ternary water−ethanol−toluene. This confirms that the higher quantity of aromatic hydrocarbons the mixture has, the more horizontal are the tie lines and the smaller is the heterogeneous region.

PRO-VLE 2.0[9] was used to apply the Wisniak thermodynamic consistency test[10] to the equilibrium data of the ternary system. To apply this test to mixtures of more components, a program developed by Pequenín et al.[3] was utilized, where activity coefficients were obtained following the procedure explained in PRO-VLE 2.0.[9,10] The test did not reveal any significant inconsistency in the data. Vapor pressures for the four components were calculated using the Antoine equation, with parameters A_i, B_i, and C_i taken from the literature[11,12] and shown in Table 4.

With respect to the azeotropic points, the system at 101.3 kPa has two heterogeneous binary azeotropes (water−hexane and water−toluene), three homogeneous binary azeotropes (water−ethanol, ethanol−hexane, and ethanol−toluene), one homogeneous ternary azeotrope (water−ethanol−toluene), and one heterogeneous ternary azeotrope (water−ethanol−hexane). All of these have been determined previously.[6,8] The VLLE data for the quaternary mixtures show that the equilibrium vapor phases occur away from the corresponding tie lines that connect the liquid phases and always on the side favoring mixtures richer in hexane. This confirms that a quaternary heterogeneous azeotrope is not present either and consequently the minimum boiling temperature of the system corresponds to that of the ternary azeotrope of the system water−ethanol−hexane.

The shape and size of the solubility surface of the system and the liquid−liquid equilibrium lines vary smoothly from the ternary water−ethanol−toluene system with a smaller heterogeneous region and horizontal tie lines toward the ternary system water−ethanol−hexane with a greater heterogeneous region and lower boiling temperatures. In the quaternary system, there is no new distillation node with respect to the ternary systems and as a result the distillation regions of the residue curve map are not different from those of the ternary systems water−ethanol−hexane or water−ethanol−toluene. Because these systems can be used in azeotropic distillation to dehydrate ethanol, the quaternary system can also be used, and its behavior will be similar to that of the ternary systems provided the mixture hexane + toluene is treated as a pseudocomponent.

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