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Liquid−Liquid Equilibria of Water + Ethanol + Reformate at Different Temperatures

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The liquid−liquid equilibrium for the system water + ethanol + reformate was studied over the temperatures of (288.15, 298.15, 308.15, and 318.15) K. A typical reformate containing 5 mass % cyclohexane, 35 mass % isooctane, and 60 mass % xylene was used in this study. The results of this study showed that the addition of ethanol to a reformate + water mixture results in an increased water solubility in the organic phase. Raising the temperature will increase the solubility of ethanol in the organic phase and decrease the solubility of ethanol in the aqueous phase. The experimental data have been correlated using UNIQUAC and NRTL equations with average RMSDs of 0.168 and 0.287, respectively. The experimental results were used to estimate the interaction parameters between water, ethanol, and reformate for the UNIQUAC and NRTL equations as a function of temperature.

Introduction

The study of the liquid−liquid equilibria in multicomponent systems is of interest not only to provide necessary useful data but also to check the thermodynamic models for the treatment of these data. The addition of an oxygenate to gasoline improves its performance as antiknocking agents and by reducing carbon monoxide emissions.[1] However, the addition of an oxygenate to gasoline also may affect the mutual hydrocarbon−water solubility, resulting in either greater or less likelihood of an aqueous phase appearing in the gasoline tank or fuel line. To assess the effect of oxygenate addition on hydrocarbon−water mutual solubility, we have measured the liquid−liquid equilibrium phase diagram of the system water + ethanol + reformate from 288.15 to 318.15 K.

All the published data in this area deal with the binary and ternary systems, whereas no attention has been paid to multicomponent systems, despite the fact that data for multicomponent systems are valuable when designing separation protocols. The importance of oxygenated compounds such as ethers and alcohol started when they started being considered as antiknocking agents added to the gasoline because of their expected air pollution-reducing capabilities. The major problem associated with all gasoline-containing alcohol is their mutual hydrocarbons−water solubility. In the presence of water, a gasoline/alcohol mixture can separate into two phases: an alcohol-rich aqueous phase and a reformate-rich organic phase. A few liquid−liquid equilibrium data have been published for water + oxygenated compound + individual hydrocarbon and hardly any for multicomponent systems: water + oxygenated compound + reformate.[2]

Multicomponent systems are difficult to represent graphically. In many of the multicomponent systems of industrial importance the number of components is so large that they cannot be conveniently identified. In the case of a multicomponent mixture to be separated by a single solvent, simplification to a pseudoternary mixture and a single ternary diagram was presented previously.[3,4]

The objective of this work is to study the solubility of water in reformate/ethanol mixtures at several temperatures and to test the capability of the various equilibrium models to correlate these data. The typical reformate consists of three major hydrocarbon compounds (cyclohexane, 5 mass %; isooctane, 35 mass %; and xylene, 60 mass %) representing the main hydrocarbon groups in Kuwaiti reformate. The compositions were measured at (288.15, 298.15, 308.15, and 318.15) K and regressed by the (NRTL)[5] and the universal quasi-chemical (UNIQUAC) equations.[6]

Experimental Section

Chemicals. Water, ethanol, and isooctane were supplied by Fluka with a purity of 99.8%, 99.8%, and 99.5%, respectively. Cyclohexane and xylene were supplied by Scharlau with a purity of 99.7% and 99.5%, respectively. All the chemicals used in this study were used without further purification. No appreciable peaks of impurities were detected by chromatographic analysis.

Equilibrium Measurements. The mixture was placed in an equilibrium cell, whose volume was 60 mL, stirred with a Teflon-coated magnetic stirrer for 1 h, and kept for 4 h, enough for phase separation. The mixture was prepared by mixing an equal amount of water and reformate and then ethanol stepwise to cover almost the full range of the two-phase region. Samples were taken by a syringe from both the upper and lower layers. A series of

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Table 1. Experimental LLE Data for the System Water (1) + Ethanol (2) + Reformate Compounds (3)

aqueous phase					organic phase				
		x_3					x_3		
x_1	x_2	x_{cyclo}	x_{isooct}	x_{xylene}	x_1	x_2	x_{cyclo}	x_{isooct}	x_{xylene}
288.15 K									
1.0000	0.0000	0.0000	0.0000	0.0000	0.0019	0.0000	0.0637	0.3285	0.6059
0.9106	0.0894	0.0000	0.0000	0.0000	0.0025	0.0094	0.0622	0.3258	0.6003
0.7655	0.2345	0.0000	0.0000	0.0000	0.0038	0.0351	0.0616	0.3162	0.5833
0.6515	0.3476	0.0000	0.0000	0.0009	0.0060	0.0584	0.0598	0.3082	0.5676
0.5682	0.4256	0.0008	0.0027	0.0027	0.0082	0.0774	0.0590	0.2997	0.5557
0.4980	0.4809	0.0014	0.0050	0.0148	0.0107	0.0986	0.0568	0.2947	0.5393
0.4678	0.5059	0.0018	0.0068	0.0177	0.0120	0.1080	0.0562	0.2910	0.5328
0.4446	0.5246	0.0021	0.0085	0.0202	0.0134	0.1201	0.0551	0.2861	0.5253
298.15 K									
1.0000	0.0000	0.0000	0.0000	0.0000	0.0024	0.0000	0.0636	0.3284	0.6056
0.9125	0.0875	0.0000	0.0000	0.0000	0.0034	0.0135	0.0629	0.3237	0.5966
0.7660	0.2340	0.0000	0.0000	0.0000	0.0051	0.0463	0.0606	0.3120	0.5759
0.6512	0.3438	0.0000	0.0008	0.0042	0.0085	0.0764	0.0587	0.3023	0.5542
0.5651	0.4217	0.0000	0.0037	0.0095	0.0116	0.0992	0.0569	0.2937	0.5387
0.4951	0.4793	0.0017	0.0066	0.0173	0.0146	0.1236	0.0544	0.2853	0.5221
0.4655	0.5038	0.0020	0.0085	0.0201	0.0181	0.1479	0.0532	0.2758	0.5050
0.4424	0.5224	0.0023	0.0103	0.0226	0.0204	0.1681	0.0518	0.2685	0.4913
308.15 K									
1.0000	0.0000	0.0000	0.0000	0.0000	0.0045	0.0000	0.0635	0.3277	0.6043
0.9157	0.0843	0.0000	0.0000	0.0000	0.0053	0.0242	0.0627	0.3191	0.5886
0.7683	0.2306	0.0000	0.0000	0.0011	0.0073	0.0663	0.0594	0.3051	0.5619
0.6445	0.3485	0.0004	0.0011	0.0055	0.0128	0.1088	0.0550	0.2933	0.5301
0.5562	0.4283	0.0010	0.0032	0.0113	0.0181	0.1582	0.0532	0.2764	0.4942
0.4833	0.4901	0.0017	0.0068	0.0181	0.0256	0.2114	0.0485	0.2570	0.4575
0.4532	0.5141	0.0022	0.0092	0.0214	0.0312	0.2563	0.0447	0.2395	0.4283
0.4305	0.5309	0.0024	0.0116	0.0246	0.0461	0.3458	0.0386	0.2049	0.3646
318.15 K									
1.0000	0.0000	0.0000	0.0000	0.0000	0.0022	0.0000	0.0637	0.3284	0.6057
0.9183	0.0817	0.0000	0.0000	0.0000	0.0069	0.0228	0.0620	0.3194	0.5888
0.7696	0.2285	0.0002	0.0002	0.0015	0.0084	0.0696	0.0591	0.3041	0.5588
0.6446	0.3471	0.0005	0.0014	0.0064	0.0151	0.1148	0.0564	0.2892	0.5245
0.5592	0.4233	0.0011	0.0037	0.0127	0.0184	0.1425	0.0544	0.2811	0.5035
0.4831	0.4866	0.0020	0.0080	0.0203	0.0272	0.1918	0.0505	0.2615	0.4691
0.4519	0.5100	0.0025	0.0113	0.0244	0.0316	0.2260	0.0468	0.2473	0.4483
0.4295	0.5264	0.0026	0.0135	0.0280	0.0401	0.2611	0.0447	0.2325	0.4216

liquid−liquid equilibrium (LLE) measurements over a temperature range of (288.15 to 318.15) K were performed. The temperature was controlled within ±0.2 K.

The composition of equilibrated mixtures for the two layers were determined using a Chrompack CP 9700 gas chromatography configured with TCD. A HP Chrompack QS, with a 2-mm diameter and 2-m long column, was used to separate the components. The temperature program used to idealize the gas chromatography was held at 453.15 K for 2 min with a rising temperature rate of 50 K/min until 513.15 K for 9 min. The carrier gas (Helium, grade 5.6) flow rate was maintained at 30 mL/min. The injection temperature was 523.15 K and the detector temperature was 573.15 K.

For quantitative analysis, the system was calibrated using the respective chemicals (HPLC grade), mixed by weight to represent a typical reformate. A standard solution was prepared, which consists of equal weights of ethanol and the reformate. The GC was calibrated using 5−7 different concentrations of this standard solution, diluted in ethanol. Another standard solution of ethanol in water was prepared. The GC was accordingly calibrated. In each case the calibration curve produced was perfectly linear in the entire range of concentrations used in this study, and the linear fit was more than 99.5%.

Results and Discussion

Experimental Data. The measured equilibrium mole fractions are shown in Table 1.The experimental and the predicted tie lines for the system at (288.15, 298.15, 308.15, and 318.15) K are shown in Figures 1−4.

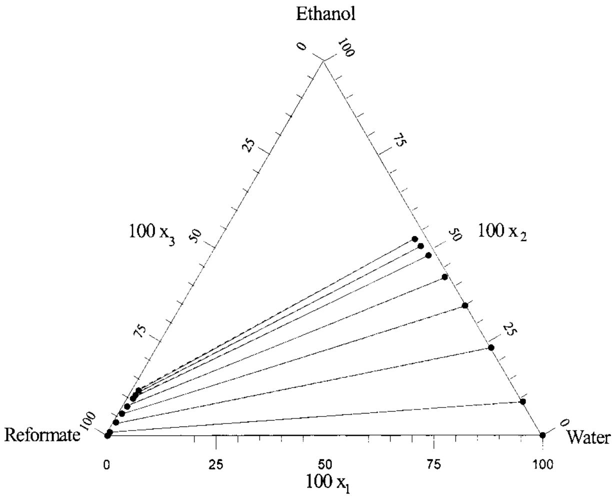

Figure 1.

Data Correlation. The experimental tie-line data were used to determine the optimum UNIQUAC and NRTL interaction parameters between water, ethanol, and reformate. The values of these parameters for the two equations are shown in Table 2. The UNIQUAC and NRTL equations were fitted to experimental data using an iterative compound computer program with the objective function developed by Sørensen.[7,8] The objective

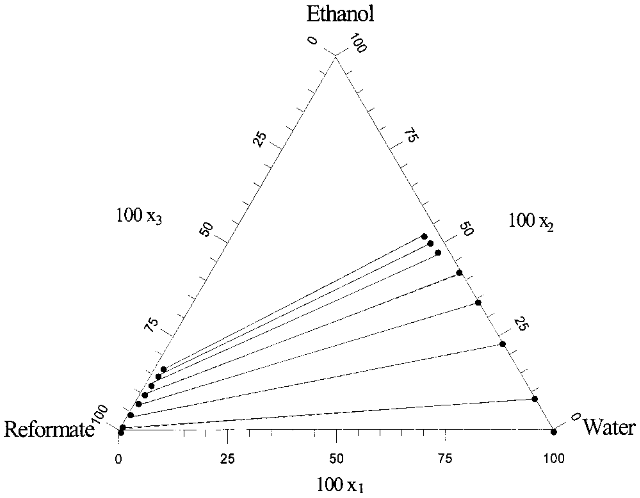

Figure 2.

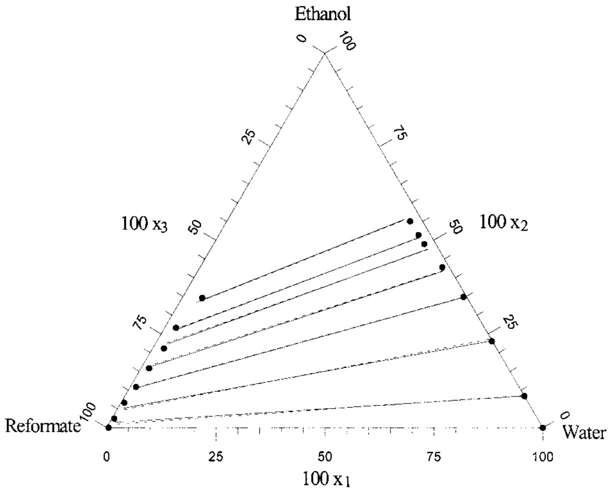

Figure 3.

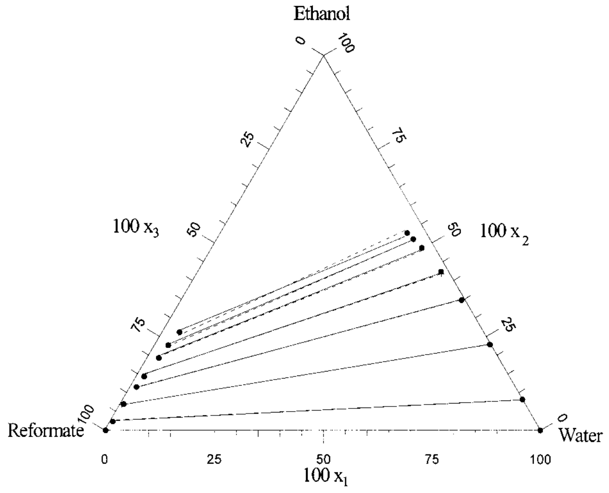

Figure 4.

Table 2. UNIQUAC and NRTL Interaction Parameters at Different Temperatures

		UNIQUAC		NRTL	
i	*j*	a_{ij} (K)	a_{ji} (K)	a_{ij} (K)	a_{ji} (K)
		$T = 288.15$ K			
water	ethanol	−170.04	10.66	−193.20	−350.01
water	reformate	851.45	491.55	1674.2	983.98
ethanol	reformate	419.81	−89.51	514.61	128.04
		$T = 298.15$ K			
water	ethanol	−203.72	−35.513	361.37	−491.46
water	reformate	321.2	848.34	1724.8	980.33
ethanol	reformate	−82.026	326.05	570.97	31.535
		$T = 308.15$ K			
water	ethanol	−942.05	49.152	−414.34	−375.68
water	reformate	−118.4	1464.2	1976.3	875.63
ethanol	reformate	−75.766	−188.37	527.78	−367.57
		$T = 318.15$ K			
water	ethanol	65.653	−29.94	1166.85	−708.67
water	reformate	1189.6	815.63	2183.5	1615.30
ethanol	reformate	−165.79	612.56	907.10	−151.93

Table 3. Optimum Interaction Parameters According to the Equation $a_{ij} = a^0_{ij} + a^1_{ij}(T/K - 273.15) + a^2_{ij}(T/K - 273.15)^2 + a^3_{ij}(T/K - 273.15)^3$

		UNIQUAC			
i	*j*	a^0_{ij}	a^1_{ij}	a^2_{ij}	a^3_{ij}
water	ethanol	−6801.607	862.555	−34.156	0.408
water	reformate	1722.156	−86.415	2.822	−0.027
ethanol	reformate	−459.151	103.540	−3.536	0.036
		a^0_{ji}	a^1_{ji}	a^2_{ji}	a^3_{ji}
water	ethanol	969.667	−117.935	4.336	−0.049
water	reformate	−2029.969	278.783	−9.619	0.101
ethanol	reformate	337.501	−46.947	1.597	−0.0166

		NRTL			
i	*j*	a^0_{ij}	a^1_{ij}	a^2_{ij}	a^3_{ij}
water	ethanol	−1300.653	135.022	−4.737	0.048
water	reformate	1079.072	−118.041	4.4912	−0.046
ethanol	reformate	994.324	0.923	−0.029	0.0005
		a^0_{ji}	a^1_{ji}	a^2_{ji}	a^3_{ji}
water	ethanol	1079.071	−118.041	4.491	−0.046
water	reformate	99.143	163.261	−5.405	0.058
ethanol	reformate	337.515	−46.947	1.597	−0.016

Table 4. UNIQUAC Structural (Volume and Area) Parameters

component	*r*	*q*
water	0.9200	1.4000
ethanol	2.1055	1.9720
reformate	4.9550	3.9297

function in this case was determined by minimizing the square of the difference between the mole fractions predicted by the respective method and these experimentally measured.

For the NRTL, a fixed value of the nonrandomness parameter, $\alpha = 0.2$, between each pair of components was found to be satisfactory. The resulting values of the interaction parameters between each pair of molecules were fitted as a function of temperature *T* using a third-order polynomial equation as follows:

$$a_{ij} = a^0_{ij} + a^1_{ij}(T/\mathrm{K} - 273.15) + a^2_{ij}(T/\mathrm{K} - 273.15)^2 + a^3_{ij}(T/\mathrm{K} - 273.15)^3 \quad (1)$$

where a_{ij} is the interaction parameter between molecules *i* and *j* and a^0_{ij}, a^1_{ij}, a^2_{ij}, and a^3_{ij} are the correlation constants between each two components in the system. The values of the correlation constants for the two equilibrium models are shown in Table 3.

The UNIQUAC structural parameter *r* and *q* listed in Table 4 were calculated from the group contribution data.[9] The corresponding values for reformate were calculated from the equivalent sum of the component constituting the reformate and their respective compositions.

The goodness of UNIQUAC and NRTL equations fit was measured by the root-mean-square deviation (RMSD) and the relative error in the solute distribution ratio ($\Delta\beta$) from

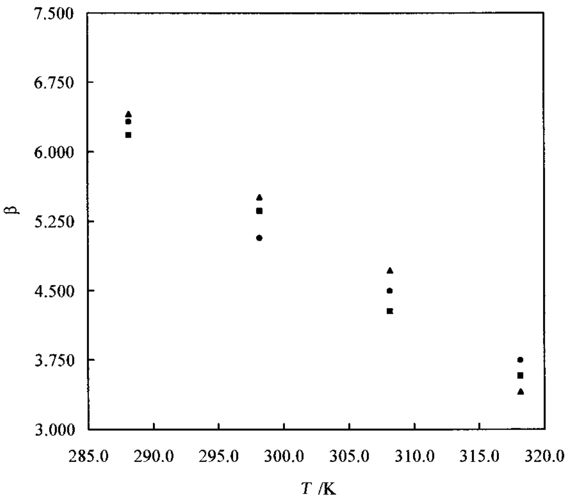

Figure 5.

the results of each model at a given temperature according to the following equations:

$$\mathrm{RMSD} = 100\{\Sigma_k[\Sigma_j\Sigma_i(x_{i,\mathrm{exp}} - x_{i,\,\mathrm{cal}})^2]/6n\}^{1/2} \qquad (2)$$

$$\Delta\beta = 100\{[\Sigma_k\{(\beta_{k,\mathrm{cal}} - \beta_{k,\mathrm{exp}})/\beta_{k,\mathrm{exp}}\}^2]/n\}^{1/2} \qquad (3)$$

where $x_{i,\mathrm{exp}}$ and $x_{i,\mathrm{cal}}$ are, respectively, the experimental and calculated mole fraction of component i, j in the extract or raffinate phase and $k = 1, 2, ..., n$ (tie lines), β_{exp} and β_{cal} are the experimental and calculated solute distribution, on a mole basis, of ethanol, respectively. The results of RMSD and $\Delta\beta$ values are reported in Table 5. These data may be compared with the results of Sørensen et al. for many data sets of different systems, which gave RMSDs ranging from 0.18 to 1.37 and $\Delta\beta$ ranging from 2.68 to 42.59.[10] These results show that UNIQUAC and NRTL equations fit our experimental data satisfactorily.

Table 5. RMSD Deviations of the LLE Data Correlated Using UNIQUAC and NRTL Equations

	UNIQUAC		NRTL	
T (K)	RMSD	$\Delta\beta$	RMSD	$\Delta\beta$
288.15	0.0894	5.9015	0.2287	7.3296
298.15	0.1731	5.4624	0.3161	4.8547
308.15	0.1460	4.6652	0.2555	6.2162
318.15	0.2621	3.0203	0.3466	3.3633

The ethanol distribution ratio can be predicted at different temperatures using UNIQUAC and NRTL equations. This ratio decreases as the temperature increases. The results are compared with experimental data as shown in Figure 5 and compared. In Figure 6, it is shown that as the ethanol increases in the reformate, the water content also increases in reformate.

These results agree with those results obtained for the system water + ethanol + 2,2,4-trimethylpentane.[2]

Conclusions

An experimental investigation of equilibrium behavior of liquid−liquid, water + ethanol + typical reformate, multicomponent system was carried out at temperatures of 288.15 to 308.15 K and at atmospheric pressure. It can be seen from Figure 5 that as the temperature increases, the solubility of ethanol increases in the organic phase, while the solubility of ethanol in the aqueous phase decreased. Rising temperature will increase the solubility of water in the reformate as more ethanol will be present in the reformate. A simplification of the homogeneous multicomponent mixture, to be separated by a single solvent, to a pseudoternary system is more useful. Both the UNIQUAC and the NRTL equations satisfactorily correlate the LLE experimental data. The calculation based on both UNIQUAC and NRTL equations give a good representation of the tie-line data for the system studied. However, according to RMSD, the values based on the

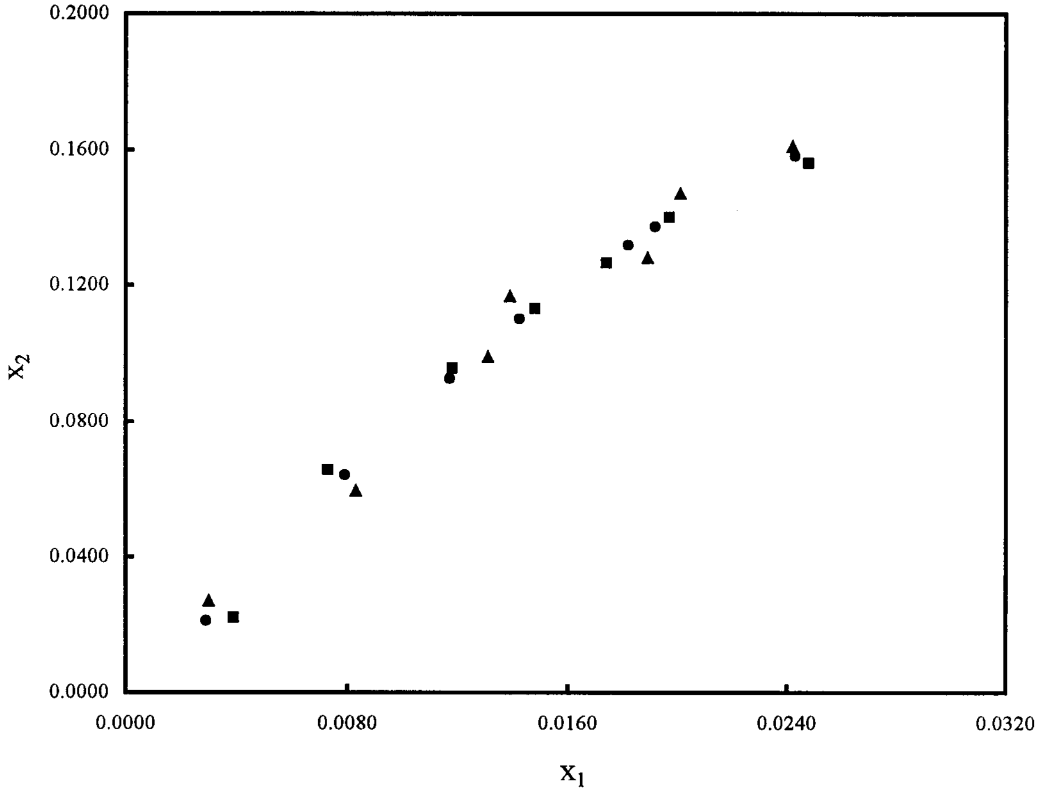

Figure 6.

UNIQUAC are found to be better than those based on the NRTL.

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