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Articles

Liquid−Liquid Equilibria for the System Water + Ethanol + Ethyl *tert*-Butyl Ether

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The liquid−liquid equilibrium (LLE) for the system water + ethanol + ethyl *tert*-butyl ether (ETBE) has been studied in the temperature range of (288.15 to 308.15) K. The NRTL equation and UNIQUAC method were used to regress the experimental data. The UNIFAC method was used to predict the phase equilibrium in the system using the interaction parameters determined from experimental data between groups CH_2, CH_2O, OH, and H_2O. The UNIQUAC and NRTL equations fit the experimental data with a root mean square deviation of 0.36% for each, while the UNIFAC method predicted the results with a root mean square deviation of 0.65%.

Introduction

In recent years there have been increasing demands to use oxygenates to produce lead free gasolines. The low-blending Reid vapor pressure "RVP" and high octane number of ethyl *tert*-butyl ether (ETBE) makes study of this system quite attractive. ETBE derived from renewable ethanol and isobutylene has emerged as a promising new oxygenate. The removing of ethanol from the product is important. Water has been used as a solvent for this purpose. This system has not been previously investigated at any temperature. In this work liquid−liquid equilibrium (LLE) data for this system were carried out and correlated with the NRTL (Renon and Prausnitz, 1968), the universal quasi-chemical model (UNIQUAC) (Abrams and Prausnitz, 1975), and the universal function-group activity coefficient method (UNIFAC) (Fredenslund et al., 1977). The UNIFAC method depends on the optimized interaction parameters between each pair of main groups present in the system, whereas the NRTL and the UNIQUAC models depend on the optimized interaction parameters between the compounds in the system. The experimental results were obtained at (288.15, 298.15, 303.15, and 308.15) K and regressed by the NRTL and UNIQUAC models and the UNIFAC method.

Experimental Section

Chemicals. ETBE and ethanol supplied by Sigma Aldrich (Madrid, Spain) were HPLC grade, and their nominal purities were determined by GC and are shown 99.5% for each. HPLC reagent grade water from Fluka was used. The GC has shown purity of more than 99.95%. The chemicals were used without further purification. Some properties of the chemicals used are given in Table 1.

Apparatus and Procedure. The equilibrium runs were performed in a 60 cm^3 extraction cell surrounded by a water jacket. The jacket was thermostatically controlled using a controller mounted on a Haake K15 water bath fitted with a Haake DC1 thermostat. The temperature range for this thermostat was (253.15 to 373.15 K) with a controller accuracy of ±0.2 K. The cell constituents were prepared by mixing equal masses of water, ETBE, and different amounts of ethanol, stirred for not less than 2 h, and allowed to settle for not less than 4 h. Samples were taken by a syringe from the upper and lower mixtures. The mixtures of water and organic phase were analyzed on a Chrompack CP900 gas chromatograph configured with a thermal conductivity detector (TCD), Porpack Q of 2 mm diameter, and 2 m long column. The temperature program used was 150 °C for 2 min with an increasing rate of 30 °C/min until 240 °C for 5 min. The carrier gas (helium, grade 5.6) flow rate was maintained at 30 mL/min. The system was calibrated using preproposed standard mixtures of the components used in respective experiments. The accuracy of weighing was ±0.0001 g. The standard accuracy and reproducibility in the composition for all the components were found to be ±0.1% to ±0.3%, respectively.

Models and Predictions

Computation of the LLE phase compositions start with a material balance on the system

$$x_i^{F} = x_i^{II}\theta + x_i^{I}(1 - \theta) \qquad (i = 1, 2, ..., N) \tag{1}$$

$$(\gamma_i x_i)^{I} = (x_i \gamma_i)^{II} \tag{2}$$

where θ is the fraction extracted. The values, of x_i^F, x_i^{II}, and x_i^I are the mole fractions of component i in the feed, the extract, and the raffinate phases, respectively.

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Table 1. Physical Data for the Chemicals Used

item	water		ethanol		ETBE	
	expt	ref	expt	ref	expt	ref
density/(g/mL at 20 °C)	1.0000	0.9982[a]	0.7876	0.7893[a]	0.7422	0.7403[b]
boiling point/°C	100.0	100.0	79.0	78.5	72.9	73.1
refractive index at 20 °C	1.3341	1.3330[a]	1.3610	1.3611[a]	1.3756	1.3794[a]
GC purity measured/%	99.95		99.5		99.5	

[a] Values at 20 °C from *Handbook of Chemisrtry and Physics* (1973). [b] Values at 20 °C from Newton (1957).

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

aqueous phase		organic phase	
x_1	x_2	x_1	x_2
$T = 288.15$ K			
0.9972	0.0000	0.0099	0.0000
0.9563	0.0396	0.0221	0.0587
0.9458	0.0405	0.0354	0.0670
0.9299	0.0657	0.0580	0.0812
0.8947	0.0997	0.1098	0.1574
0.8641	0.1269	0.2005	0.2384
0.8168	0.1656	0.3432	0.3030
$T = 298.15$ K			
0.9947	0.0000	0.0150	0.0000
0.9721	0.0259	0.0483	0.0444
0.9564	0.0409	0.0716	0.0629
0.9495	0.0504	0.0597	0.0738
0.9105	0.0893	0.1186	0.1623
0.8666	0.1248	0.2109	0.2520
0.8168	0.1656	0.3433	0.3029
$T = 303.15$ K			
0.9912	0.0000	0.0183	0.0000
0.9701	0.0278	0.0476	0.0324
0.9431	0.0541	0.0625	0.0763
0.9057	0.0941	0.1229	0.1652
0.8597	0.1309	0.2220	0.2577
0.8256	0.1588	0.3031	0.2998
0.8128	0.1636	0.3393	0.3031
$T = 308.15$ K			
0.9908	0.0000	0.0131	0.0000
0.9594	0.0385	0.0665	0.0907
0.9346	0.0623	0.0777	0.1051
0.8975	0.0897	0.1377	0.1849
0.8660	0.1249	0.2237	0.2599
0.8250	0.1591	0.3096	0.3026
0.8170	0.1644	0.3497	0.3108

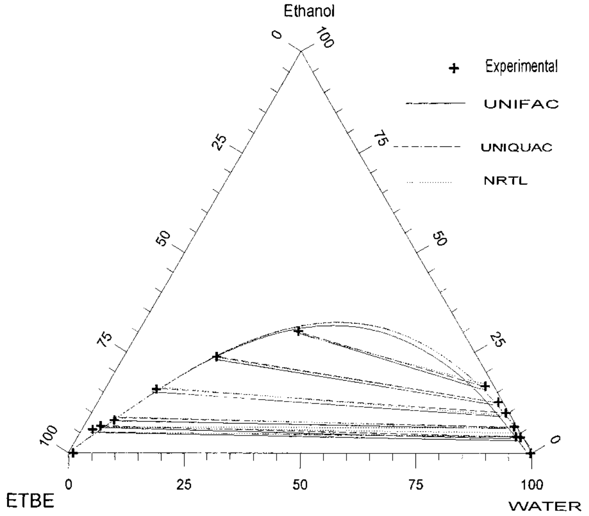

Figure 1. Equilibrium compositions of the water/ethanol/ETBE system at 288 K.

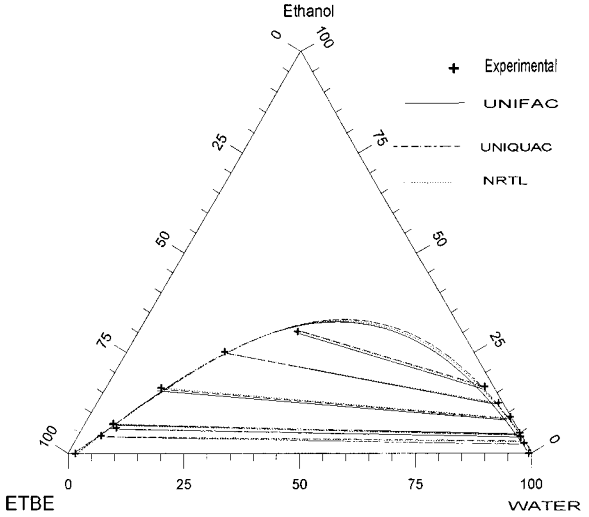

Figure 2. Equilibrium compositions of the water/ethanol/ETBE system at 298 K.

The procedure involves estimation for θ and x_i^{I} and successive iteration until eq 1 is satisfied; the γ_i^{I} and γ_i^{II} are calculated next, using the composition just obtained from the equilibrium model, i.e., NRTL, UNIQUAC, or UNIFAC. The interaction parameters between water, ethanol, and ETBE are used to estimate the activity coefficients from NRTL and UNIQUAC, whereas the interaction parameters between H_2O, (CH_3, CH_2, C), CH_2O, and OH were used to predict the activity coefficients by UNIFAC.

Results and Discussion

Experimental LLE data for this system are shown in Table 2. The experimental and predicted tie lines and the biondal curves for the system at temperatures (288.15, 298.15. 303.15, and 308.15) K are shown in Figures 1−4. These measurements were used to calculate the optimum UNIFAC interaction parameters between the main groups of H_2O, (CH_3, CH_2, C), OH, and CH_2O. They were also used to determine the optimum UNIQUAC and NRTL interaction parameters between water, ethanol, and ETBE. The NRTL and UNIQUAC equations were fitted to experimental data using an iterative compound computer program with the objective functions developed by (Sørensen, 1980; Sørensen and Arlt, 1980). The interaction parameters in the UNIFAC method were optimized using the same objective functions.

The resulting values of the interaction parameters between each pair of the UNIFAC, UNIQUAC, and NRTL groups (or molecules) were fitted linearly with the temperature according to the following equation.

$$a_{ij} = a^{\circ}_{ij} + b_{ij}((T/\mathrm{K}) - 273.15) \qquad (3)$$

where a_{ij} is the interaction parameter between groups (or molecules) i and j, T is the temperature in kelvin, and a°_{ij}, b_{ij} are the correlation constants between each two groups or components in the system. The values of these constants

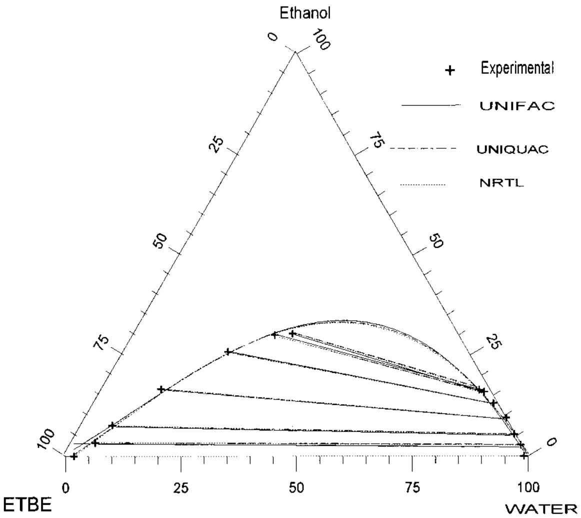

Figure 3. Equilibrium compositions of the water/ethanol/ETBE system at 303 K.

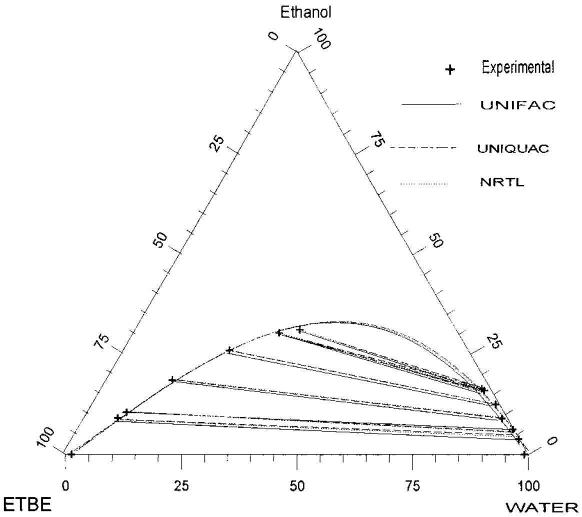

Figure 4. Equilibrium compositions of the water/ethanol/ETBE system at 308 K.

Table 3. Optimum Interaction Parameters According to the Equation $a_{ij} = a°_{ij} + b_{ij}((T/\mathrm{K}) - 273.15)$

i	j	$a°_{ij}$/K	b_{ij}	$a°_{ji}$/K	b_{ji}
		UNIFAC			
CH_3,CH_2,C	CH_2O	−59.62	−1.15	−740.70	−0.43
CH_3,CH_2,C	OH	66.70	−0.70	1153.40	5.55
CH_3,CH_2,C	H_2O	2332.60	1.97	392.57	−1.98
CH_2O	OH	−1825.90	29.51	74.11	44.40
CH_2O	H_2O	1605.00	0.78	412.00	−0.98
OH	H_2O	357.10	−8.00	889.80	5.52
		UNIQUAC			
water	ethanol	−579.00	15.69	356.10	11.65
water	ETBE	117.89	2.08	1055.90	−11.97
ethanol	ETBE	−146.64	−2.30	422.20	1.66
		NRTL			
water	ethanol	1610.10	−44.17	1354.70	45.69
water	ETBE	1785.54	8.96	495.68	0.92
ethanol	ETBE	1267.52	−51.33	−2198.04	93.62

Table 4. Root Mean Square Deviation[a] (%) Values for the Studied Model

T/K	NRTL	UNIQUAC	UNIFAC	UNIFAC[b]
288.15	0.48	0.37	0.89	5.73
298.15	0.31	0.36	0.65	1.69
303.15	0.27	0.29	0.41	7.09
308.15	0.39	0.41	0.67	5.75
av	0.36	0.36	0.65	4.56

[a] RMSD = $\{\sum_k[\sum_j(\sum_i(x_{i,\mathrm{exptl}} - x_{i,\mathrm{calcd}})^2)]/6n\}^{1/2}$. [b] Sandler (1994).

for the three methods are shown in Table 3. The NRTL model was fitted with fixed values of α for each pair of compounds. The optimization results were judged by calculating the corresponding root mean square deviation values. A fixed a value of α = 0.2 between each pair of compounds was found to be satisfactory.

The root mean square deviation are calculated from the difference between the experimental data and the predictions of each model at each temperature according to the following formula:

$$\mathrm{RMSD} =\{\sum_k[\sum_j(\sum_i(x_{i,\mathrm{exp}} - x_{i,\mathrm{calcd}})^2)]/6n\}^{1/2} \qquad (4)$$

where i is water or ethanol, j is the extract or raffinate phase, and k = 1, 2, ..., n (tie lines).

The NRTL, UNIQUAC models gave an average root mean square deviation value of 0.36%. The UNIFAC method had satisfactorily correlated the experimental data with root mean square deviation values of 0.65%. As UNIFAC interaction parameters are determined between the main groups of the system, they have the advantage of being appropriate to be used with any other system containing the same groups. Therefore, the UNIFAC interaction parameters generated from this work can be extended to similar systems. Equilibria data predicted by the UNIFAC method using the optimized interaction parameters in this work were compared with those obtained from the literature (Sandler, 1994). The predictions that correspond to the optimized parameters were noticeably better than those published previously. The comparison is shown in Table 4.

Conclusions

LLE data for the system water + ethanol + ETBE was studied in the temperature range of (288.15 to 308.15) K. The data were regressed using NRTL, UNIQUAC, and UNIFAC. The optimized interaction parameters were used respectively to predict the phase equilibrium at the same conditions. This gave a root mean square deviation of almost 0.36% for both NRTL and UNIQUAC. On the other hand UNIFAC gave a root mean square deviation of 0.65%.

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