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Liquid−Liquid Equilibrium for the Water + Diethyl Carbonate + Ethanol System at Different Temperatures

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ABSTRACT: Liquid−liquid equilibrium (LLE) and tie lines were measured for the ternary system water + diethyl carbonate + ethanol between 296.15 and 338.15 K and at atmospheric pressure. Thermodynamic consistencies of the experimental data were verified by Othmer and Tobias correlation. The liquid−liquid equilibrium results were correlated with the NRTL and UNIQUAC coefficient models and the reliability of these models was tested by comparison with experimental results. New UNIQUAC and NRTL binary interaction parameters are reported.
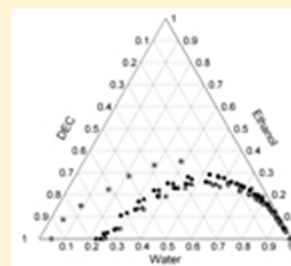
INTRODUCTION

Oxygenated compounds like ethanol, methyl *tert*-butyl ether (MTBE), and diethyl carbonate (DEC) may be used as fuel additive, because they increase the octane number, improve gasoline performance and reduce emissions of CO and NOx.[1] The DEC has a high oxygen content (40.7%) compared with other additives, such as MTBE (18.2%) and ethanol (34.8%), and compared with dimethyl carbonate (DMC) it has a higher energy content, lower vapor pressure, and better distribution into gasoline in comparison to water.[2] Additionally, it is considered an environmentally benign chemical because of its low toxicity, low bioaccumulation, and fast biodegradability.[1]

The study of the viability of some of the techniques used to separate DEC from the ethanol + water + DEC ternary system
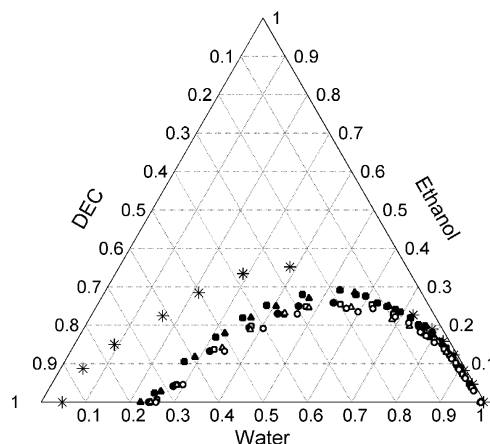
Figure 2. Ternary liquid−liquid equilibrium of ELL of water (1) + DEC (2) + ethanol (3). Experimental binodal curve: ■, 296.15 K; ▲, 303.15 K; ●, 318.15 K; □, 323.15 K; △, 333.15 K; ○, 338.15 K. Reported binodal curve (*) at 298.15 K.[11]

is limited by the lack of data on the thermodynamic behavior of systems containing DEC, water and ethanol, such as compositions of each of the compounds in the two liquid phases that may be obtained with these three components. It has been reported the liquid−liquid equilibrium (LLE) data of similar systems such as DMC + methanol + water from 283 to 333 K;[3] water, 2-propanol, and DMC with isooctane or toluene or heptane at 298.15 K;[4] nonane + DMC + methanol and decane + DMC + methanol at 298.15 K;[5] quaternary liquid−liquid equilibrium for fuel additive systems containing DEC or 1,1-dimethylethyl methyl ether at 298.15 K;[6] ternary and quaternary mixtures of DEC and DMC with water, 1-butanol, and hexane,[7] with ethanol and heptane,[8] and with toluene, methanol, and ethanol,[9] at 298.15 K; other reported
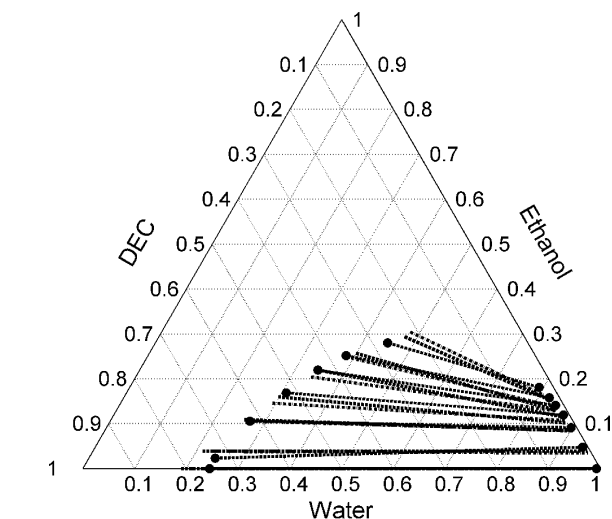
Figure 1. Ternary liquid−liquid equilibrium of water (1) + DEC (2) + ethanol (3) at 296.15 K. Experimental binodal curve (●—) experimental tie lines, correlated data by: --, NRTL; ···, UNIQUAC models.

Table 1. UNIQUAC Binary and Ternary Interaction Parameters Reported in the Literature for the Water (1) + DEC (2) + Ethanol (3) System

T	$i-j$	model	A_{ij}	A_{ji}	ref
K			K	K	
351.73−396.02	3−2	modified UNIQUAC	39.99	314.36	11
		extended UNIQUAC	52.62	314.13	11
298.15	3−1	modified UNIQUAC	212.17	−46.98	11
		extended UNIQUAC	157.12	37.08	11
298.15	1−2	modified UNIQUAC	248.21	1177.6	11
		extended UNIQUAC	273.66	961.41	11
298.15	1−2	UNIQUAC	461.53	245.06	16

T	$i-j-k$	model	A_{ikj}	A_{kji}	A_{ijk}	ref
K			K	K	K	
298.15	1−3−2	modified UNIQUAC	0.1186	0.1954	−0.0024	6
		extended UNIQUAC	1.4540	−0.6851	17.185	

Table 2. Experimental (Liquid + Liquid) Equilibrium Data of the Water (1) + DEC (2) + Ethanol (3) System

T	aqueous phase		organic phase		T	aqueous phase		organic phase	
K	x_1	x_2	x_1	x_2	K	x_1	x_2	x_1	x_2
296.15	0.9415	0.0107	0.2439	0.7330		$u(x_1^{\text{I}}) = 0.0060\ u(x_1^{\text{II}}) = 0.0036$			
	0.8976	0.0111	0.2697	0.6243	323.15	0.9524	0.0098	0.2818	0.6723
	0.8688	0.0117	0.3090	0.5221		0.9133	0.0133	0.3218	0.5409
	0.8426	0.0161	0.3442	0.4363		0.8840	0.0142	0.3743	0.4270
	0.8223	0.0197	0.3828	0.3652		0.8608	0.0175	0.4333	0.3374
	0.7912	0.0276	0.4488	0.2710		0.8400	0.0216	0.4724	0.2786
	0.9925	0.0075	0.2134	0.7866		0.8052	0.0313	0.5468	0.1981
	$u(x_1^{\text{I}}) = 0.0098\ u(x_1^{\text{II}}) = 0.0026$					0.9917	0.0083	0.2578	0.7422
303.15	0.9461	0.0098	0.2556	0.7161		$u(x_1^{\text{I}}) = 0.0098\ u(x_1^{\text{II}}) = 0.0022$			
	0.9003	0.0121	0.2879	0.5946	333.15	0.9607	0.0093	0.2833	0.6720
	0.8724	0.0141	0.3244	0.4958		0.9217	0.0121	0.3380	0.5210
	0.8507	0.0162	0.3632	0.4161		0.8962	0.0147	0.3770	0.4342
	0.8292	0.0197	0.4049	0.3448		0.8689	0.0176	0.4332	0.3351
	0.7983	0.0283	0.4686	0.2603		0.8492	0.0212	0.4804	0.2732
	0.9904	0.0096	0.2241	0.7759		0.8163	0.0264	0.5753	0.1777
	$u(x_1^{\text{I}}) = 0.0018\ u(x_1^{\text{II}}) = 0.0008$					0.9918	0.0082	0.2464	0.7536
318.15	0.9511	0.0103	0.2771	0.6814		$u(x_1^{\text{I}}) = 0.0098\ u(x_1^{\text{II}}) = 0.0022$			
	0.9089	0.0129	0.3137	0.5537	338.15	0.9600	0.0105	0.2968	0.6573
	0.8883	0.0146	0.3718	0.4345		0.9254	0.0121	0.3468	0.5201
	0.8582	0.0174	0.4181	0.3513		0.9000	0.0151	0.4046	0.4035
	0.8383	0.0205	0.4549	0.2951		0.8685	0.0183	0.4624	0.3076
	0.8014	0.0319	0.5296	0.2114		0.8116	0.0511	0.5657	0.1899
	0.9913	0.0087	0.2426	0.7574		0.8088	0.0358	0.5967	0.1676
						0.9532	0.0468	0.4545	0.7416
						$u(x_1^{\text{I}}) = 0.0203\ u(x_1^{\text{II}}) = 0.0136$			

**Table 3. Constants of the Othmer−Tobias Correlation (A and B) and Regression Coefficients (R^2), for the Ternary System Water (1) + DEC (2) + Ethanol (3)**

T	A	B	R^2
K			
296.15	0.8551	0.1579	0.8773
303.15	0.8305	0.1063	0.9212
318.15	0.8291	0.0047	0.9389
323.15	0.8474	−0.0158	0.929
333.15	0.8119	−0.0784	0.9565
338.15	0.795	−0.105	0.969

Table 4. Volume Parameters (r) and Surface Area Parameters (q)

component	r	q	ref
Water	0.92	1.40	17
DEC	4.41	3.90	18
Ethanol	2.11	1.97	19

systems are water + ethanol + DEC + 2,2,4-trimethylpentane or n-heptane and water + DMC + n-heptane + toluene at 298.15.[10] It was reported that the LLE is of type I and that the modified and extend UNIQUAC equations correlate the quaternary system.[11]
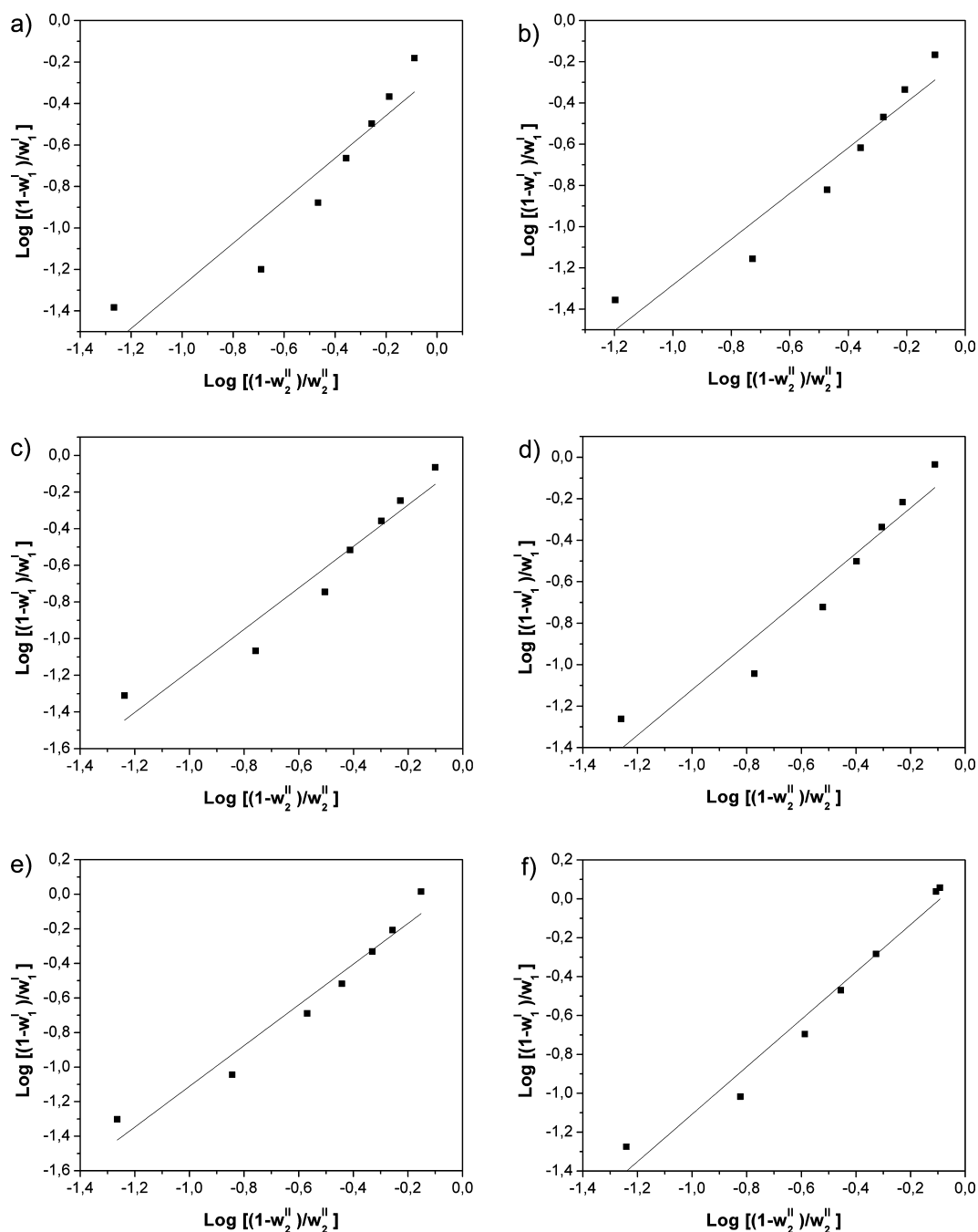
Figure 3. Othmer–Tobias plot of the water (1) + DEC (2) + ethanol (3) system at (a) 296.15 K, (b) 303.15 K, (c) 318.15 K, (d) 323.15 K, (e) 333.15 K, (f) 338.15 K.

UNIQUAC binary interaction parameters for ethanol, water and DEC have been reported at 298.15 and between 351.73 and 396.02 K, Table 1.

In this work, LLE data for systems containing water + DEC + ethanol were measured at atmospheric pressure and at 296.15 K, 306.15 K, 316.15 K, and 323.15 K. The LLE data were correlated with NRTL and the UNIQUAC models. New UNIQUAC and NRTL binary interaction parameter for the ternary system were determined.

■ EXPERIMENTAL SECTION

Chemicals. Commercial products were used as received. Diethyl carbonate (anhydrous) was supplied by Aldrich and ethanol

by Beaker with a nominal minimum mass composition of 99% and 99.7%, respectively. Distilled water was used in all experiments.

Equilibrium Measurements. The experimental binodal curve for the ternary system was built by the cloud-point method.[12] A binary heterogeneous mixture of known composition of diethyl carbonate and water was prepared with weighted amounts of each compound, using an electronic balance with an accurate to 0.0001 g, and the mixture was stirred in a glass cell (8 mL) that was placed in a temperature-controlled water bath. The other component, ethanol, was added by an automated microburet (Dosimat) with an accuracy of 0.005 mL until a cloud point was reached.

To establish tie lines, ternary mixtures were prepared and loaded into the glass cell placed in a temperature-controlled

Table 5. Optimized UNIQUAC and NRTL Binary Interaction Parameters for the Water (1) + DEC (2) + Ethanol (3) System

| T | ij | UNIQUAC parameters | | | NRTL parameters | | | |
| | | A_{12} | A_{21} | rmsd | α | A_{12} | A_{21} | rmsd |
K		J/mol	J/mol	%		J/mol	J/mol	%
296.15	1−2	1229.11	2248.78	0.0284	0.20	13966.29	332.63	0.0272
	1−3	536.71	1033.37		0.30	2942.71	1660.67	
	2−3	4212.45	−762.66		0.20	6920.04	−774.71	
303.15	1−2	1260.70	2256.99	0.0112	0.20	13982.92	271.29	0.0228
	1−3	391.35	883.71		0.30	2959.30	1677.30	
	2−3	4062.80	−912.31		0.20	6753.76	−791.34	
318.15	1−2	1270.31	2177.76	0.0119	0.20	14650.38	−470.20	0.0298
	1−3	782.40	661.30		0.30	4789.04	911.90	
	2−3	4046.17	−928.94		0.20	6558.37	−33.13	
323.15	1−2	1327.53	2229.77	0.0218	0.20	14765.51	−549.26	0.0199
	1−3	−960.62	3504.34		0.30	3243.23	3149.49	
	2−3	4029.54	−945.54		0.20	6724.66	133.11	
333.15	1−2	1343.12	2145.45	0.0107	0.20	15139.23	−866.07	0.0240
	1−3	1624.42	19.34		0.30	6447.77	−230.58	
	2−3	4446.24	−1047.82		0.20	4417.35	1105.79	
338.15	1−2	1273.53	2400.82	0.0353	0.20	15300.02	−381.21	0.0273
	1−3	2222.55	−963.31		0.30	3327.17	2202.92	
	2−3	5380.78	−1735.27		0.20	8608.30	−1751.44	

water bath. The mixture was stirred for 2.5 h by a magnetic stirrer and then allowed to settle for 3 h in order to separate the two liquid phases; similar results were obtained when the mixture was stirred 24 h, and it was allowed to settle for 36 h. After equilibration, each of the liquid phases was sampled by a syringe and then analyzed by a gas chromatograph (Agilent technologies 5975c VL MSD) equipped with a thermal conductivity detector (TCD) for performing the quantitative analysis of water, DEC and ethanol. The capillary column used was a megabore DB-Wax (30 m × 0.320 mm × 0.50 μm film thickness). The temperature of the detectors was 250 °C. After 1 min at 40 °C, the oven temperature was programmed to reach 70 °C at 20 °C/min, then to reach 120 °C at 30 °C/min, keeping this temperature for 1 min. The injection port temperature was held at 225 °C. Helium was the carrier gas with a column flow rate of 2 mL/min and a split ratio of 100:1. Each sample (1.0 μL) was measured three times and the mean value of the mass of each component was determined from a calibration curve prepared by mass percent.

■ RESULTS AND DISCUSSION

Experimental Data. The liquid−liquid equilibrium (LLE) data of the ternary system water (1) + DEC (2) + ethanol (3) at 296.15 K, 303.15 K, 318.15 K, 323.15 K, 333.15 K, and 338.15 K and at atmospheric pressure are presented in Table 3. All concentrations are expressed in mole fraction. As an example, in Figure 1 the tie lines have been plotted at 296.15 K including the experimental and correlated data by NRTL and UNIQUAC equations and in Figure 2 the experimental data of the binodal curves at all temperatures tested are shown. From Figure 2, it is also observed that under our hands it was not possible to reproduce the reported data for the ternary system water (1) + DEC (2) + ethanol (3) at 298.15 K.[11]

The system presents a type I liquid−liquid phase behavior, having one pair of components partially miscible (water + DEC), and two pairs of components completely miscible (water + ethanol and ethanol + DEC). At the temperature range evaluated, two phase regions were observed. The size of

the two phase regions decreased with an increase in temperature, but this effect is quite small.

The reliability of the experimental tie-lines was verified by applying the Othmer−Tobias correlation[13]

$$\log \frac{1 - w_2^{\mathrm{I}}}{w_2^{\mathrm{I}}} = a + b\left(\log \frac{1 - w_1^{\mathrm{II}}}{w_1^{\mathrm{II}}}\right) \tag{1}$$

where w_2^{I} is the mass fraction of DEC in the organic phase and w_1^{II} is the mass fraction of water in the aqueous phase. Table 3 gives the constants (A and B) values and the regression coefficients (R^2) of the experimental data correlation given in Figure 3. The linearity of the plots denotes a high degree of consistency of the experimental data.

Correlation Data. The UNIQUAC[14] and NRTL[15] models were used to correlate the experimental results. The six binary interaction parameters (A_{ij} and A_{ji}) for the ternary system were determined with the objective function (OF) given in eq 2.[12] This equation minimizes the differences between the experimental and calculated distribution coefficients. Experimental data correlation was carried out separately at each temperature using ASPEN PLUS V7.1 and the Britt-Luecke optimization algorithm. The structural parameters for the UNIQUAC model, r and q, were taken from literature, see Table 4. The nonrandomness parameter (α_{ij}) of the NRTL model was varied between 0.2 and 0.47 as recommended. The optimized UNIQUAC and NRTL binary interaction parameters are show in Table 5.

$$\mathrm{OF} = \sum_n^k \frac{\left[\sum_3^i \frac{(K_{i,\exp} - K_{i,\mathrm{calcd}})}{K_{i,\exp}}\right]^2}{n} \tag{2}$$

Where i = components; k = 1, 2, 3, ..., n tie lines, $K_{i,\exp}$ is the experimental distribution coefficient for the i component, and $K_{i,\mathrm{calcd}}$ is the calculated distribution coefficient for the i component. The quality of the correlations were evaluated by the magnitude of the root-mean-square deviation (rmsd)

obtained from the difference between the experimental and calculated mass fraction eq 3

$$rmsd\% = 100*\left[\sum_n^k \left[\frac{\sum_3^i \sum_2^j (x_{i,\exp} - x_{i,\text{cal}})_j^2}{6n}\right]\right]^{1/2}$$

(3)

where i = components, j = phases, and k = tie lines.

Visual comparison of experimental tie line data with calculated UNIQUAC and NRTL values were also plotted in Figure 1. The calculation based on UNIQUAC and NRTL models provide a good representation of the tie line data for the system studied from both qualitative and quantitative perspective.

CONCLUSIONS

LLE data for the ternary system water + DEC + ethanol were measured at several temperatures and at atmospheric pressure. The reliability of experimentally measured tie-line data of each temperature was confirmed by the Othmer−Tobias correlation. The ELL data were correlated using UNIQUAC and NRTL activity coefficient models. The correlation with UNIQUAC and NRTL equations fits the experimental data satisfactorily.

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Notes
The authors declare no competing financial interest.

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