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Liquid−Liquid Equilibrium of Diisopropyl Ether + Ethanol + Water System at Different Temperatures

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Diisopropyl ether (DIPE) could be a suitable gasoline additive. In this work, we report liquid−liquid equilibrium data for the ternary system isopropyl ether + ethanol + water at (298.15, 308.15, and 318.15) K. The parameters for the NRTL and UNIQUAC models were obtained by fitting the thermodynamic models to the experimental data. The predictive ability of the UNIFAC method was tested.

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1. Introduction

While MTBE has admirable blending characteristics, it has two problems. It is moderately soluble in water (a few percent) and it has a very distinct odor and taste that can be detected in water at very low concentrations. Because of the pollution of the groundwater sources, MTBE faces an uncertain future. Nonetheless the advances of clean-burning fuels must be maintained. DIPE (diisopropyl ether, 2-isopropoxyisopropane, or isopropyl ether) has emerged as possible replacement for MTBE because it has good antiknock properties and its solubility in water is low.

Thus, we have been focusing part of our research into the study of the thermodynamic behavior of this ether. In previous work,[1] we presented physical and equilibrium properties of the DIPE + isopropyl alcohol + water ternary system, and now we report liquid−liquid equilibrium data for the system DIPE + ethanol + water at (298.15, 308.15, and 318.15) K. As far as we know, no liquid−liquid equilibrium has previously been published for this ternary system.

The experimental data are correlated using the UNIQUAC and NRTL equations, and the energetic parameters of these models at each temperature are obtained. Finally, the UNIFAC method has been tested to predict the LLE data for the system studied.

2. Experimental Section

Materials. Water was purified using a Milli-Q Plus system. Diisopropyl ether and ethanol were supplied by Merck and have nominal purities >99.0 and >99.8 mass % respectively. Water contents of the DIPE and ethanol (determined with a Metrohm 737 KF coulometer) were (0.02 and 0.08) mass %, respectively. Purities, before mentioned, were verified with gas chromatography, and the chemicals were used without further purification.

The densities and refractive indices of pure substances were measured and compared with literature values[2] at 298.15 K and atmospheric pressure (Table 1). Densities were measured with an Anton Paar DMA 60/602 densimeter to within $\pm 10^{-2}$ g·cm^{-3}. Refractive indices were measured with an Atago RX-5000 refractometer with an uncertainty of $\pm 4 \times 10^{-5}$.

Table 1. Densities (ρ) and Refractive Indices (n_D) of the Pure Components at 298.15 K and Atmospheric Pressure

	ρ/g·cm^{-3}		n_D	
component	experimental	literature[2]	experimental	literature[2]
DIPE	0.718 45	0.718 54	1.365 12	1.3655
ethanol	0.785 22	0.784 93	1.359 20	1.359 41
water	0.997 04	0.997 04	1.332 50	1.332 50

Table 2. Experimental Tie Lines of the System DIPE (1) + Ethanol (2) + Water (3), Giving Compositions in Molar Fraction

organic phase		aqueous phase	
x_1	x_2	x_1	x_2
	T = 298.15 K		
0.9711	0.0000	0.0020	0.0000
0.9291	0.0358	0.0022	0.0479
0.9033	0.0599	0.0021	0.0660
0.8748	0.0817	0.0020	0.0789
0.8182	0.1280	0.0021	0.0998
0.6850	0.1937	0.0022	0.1431
0.5704	0.2720	0.0045	0.1590
0.4647	0.3333	0.0053	0.1749
0.3805	0.4137	0.0061	0.1953
	T = 308.15 K		
0.9846	0.0000	0.0016	0.0000
0.9477	0.0368	0.0017	0.0507
0.8161	0.1521	0.0014	0.1028
0.7198	0.2215	0.0020	0.1231
0.5980	0.3103	0.0020	0.1463
0.5581	0.3481	0.0029	0.1505
0.4093	0.4291	0.0027	0.1718
0.1996	0.4535	0.0070	0.2029
0.2509	0.4583	0.0084	0.2126
	T = 318.15 K		
0.9809	0.0000	0.0016	0.0000
0.9560	0.0307	0.0015	0.0496
0.8992	0.0847	0.0015	0.0743
0.8224	0.1467	0.0013	0.0935
0.7380	0.2194	0.0012	0.1135
0.6065	0.3160	0.0015	0.1384
0.4955	0.3930	0.0016	0.1553
0.3906	0.4288	0.0021	0.1711
0.3562	0.4261	0.0035	0.1807

Apparatus and Procedure. First, the solubility curves at (298.15, 308.15, and 318.15) K were determined by the cloud point method.[3] These curves were employed for calibrating the gas chromatograph using an internal standard calibration method; the technique is more fully explained elsewhere.[4] The chromatograph used was a

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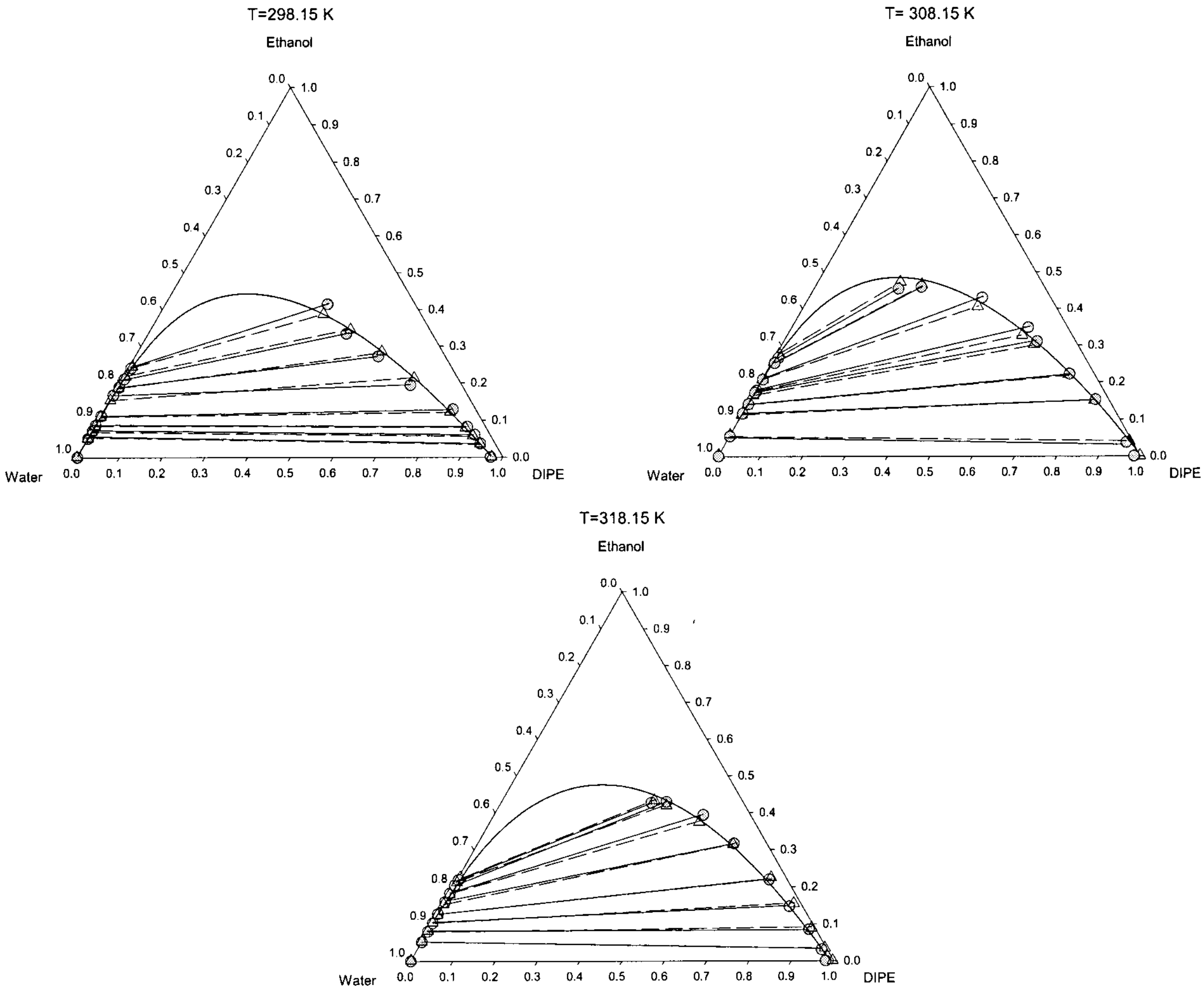

Figure 1. Experimental tie lines (—•) and the corresponding UNIQUAC correlation using the optimal value of the solute distribution ratio at infinite dilution (- - -▽) at different temperatures.

Hewlett-Packard 5890 Series II equipped with a TCD and a capillary column (HP5: 30 m × 0.32 mm × 0.25 mm). Helium was used as mobile phase, and the injection volume was 0.5 mL with a split ratio of 1:100. Separation was made up to 363.15 K under isothermal conditions. The greatest errors in the determination of mole fraction composition using the calibration curves were of ±0.004 and ±0.003 molar fraction in the aqueous and organic phases, respectively.

The tie line data were determined by analysis of the two layers of a heterogeneous mixture. A mixture with partial miscibility was placed inside an equilibrium cell, where it was agitated for 1 h in order to allow an intimate contact between the phases, and the thermodynamic equilibrium is finally achieved by letting the mixture rest for 5 h. The complete process was carried out at constant temperature using a thermostatic bath. When thermodynamic equilibrium was achieved, samples of both liquid phases were collected and analyzed by gas chromatography.

3. Results and Discussion

3.1. Experimental Data. The experimental tie line data for isopropyl ether + ethanol + water at the three temperatures are listed in Table 2.

3.2. Correlation. The NRTL[5] and UNIQUAC[6] equations were fitted to the experimental LLE data using the program developed by Sørensen.[7] The NRTL nonrandomness factor α was optimized at a 0.1 value. The UNIQUAC structural parameters *r* and *q* were taken from the literature.[8,9] The binary interaction parameters were determined, for both equations, by minimizing two objective functions. The first, F_a, does not require initial guesses of parameters, and after convergence uses the second function, F_b, to fit the experimental mole fraction compositions

$$F_a = \sum_k \sum_i \sum_j [(a^{I}_{ijk} - a^{II}_{ijk})/(a^{I}_{ijk} + a^{II}_{ijk})]^2 + Q \sum_n P_n^{\,2} \qquad (1)$$

$$F_b = \sum_k min \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2 + Q \sum P_n^{\,2} + \left[ln\left(\frac{\hat{\gamma}^{I}_{S\infty}}{\hat{\gamma}^{II}_{S\infty}}\beta_\infty\right)\right]^2 \qquad (2)$$

where x is the experimental mole fraction, $\hat{x}$ is the mole fraction of the calculated tie line considered, a is the activity, i are the components of the mixture, j are the phases, and k are the tie lines. Both functions include a penalization term to reduce the risks of multiple solutions associated with parameters of high value, in which Q is a constant and P_n are the adjustable parameters. F_b also includes a term to correctly fit experimental results when working with low solute concentrations, in which $\hat{\gamma}^{I}_{S\infty}$ and $\hat{\gamma}^{II}_{S\infty}$ represent the solute activity coefficients calculated at infinite dilution in both phases and β_∞ is the solute molar distribution ratio at infinite dilution.

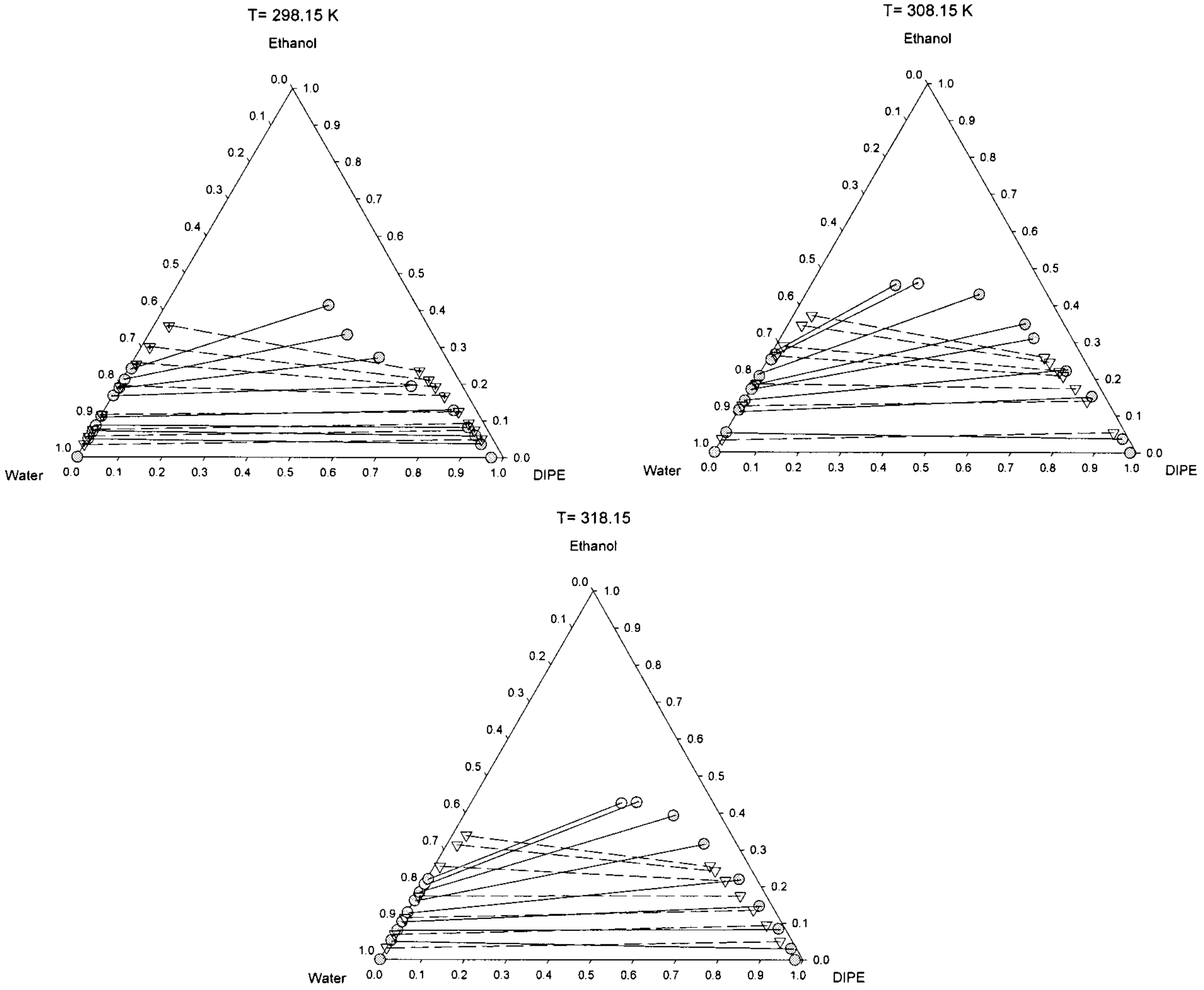

Figure 2. Experimental tie lines (—•) and predicted using the UNIFAC method (- - -▽) at different temperatures.

Table 3. LLE Data Correlation: Root Mean Square Deviations (rmsd, in %) for Each Model and Each Temperature, Defining or Not the Solute Distribution Ratio at Infinite Dilution β_∞

		rmsd					
model		T = 298.15 K		T = 308.15 K		T = 318.15 K	
UNIQUAC	β_∞		0.41		0.27		0.20
	$\Delta\beta$ (%)	9.61	8.82	19.55	3.23	14.66	5.18
	F (%)	0.8222	0.8070	0.6585	0.8637	0.5628	0.7746
NRTL	β_∞		0.36		0.18		0.13
(a = 0.1)	$\Delta\beta$ (%)	10.38	10.02	24.50	8.02	19.75	3.22
	F (%)	0.7126	0.9012	0.5813	1.0135	0.6015	0.6961

Structural Parameters for the UNIQUAC Equation

	DIPE[8]	ethanol[8]	water[9]
r	4.7421	2.1055	0.92
q	4.088	1.972	1.40

The quality of correlation is measured by the residual function F and by the mean error of the solute distribution ratio, $\Delta\beta$:

$$F = 100\left[\sum_k min \sum_i \sum_j \frac{(x_{ijk} - \hat{x}_{ijk})^2}{6M}\right]^{0.5} \tag{3}$$

$$\Delta\beta = 100\left[\sum_k \frac{((\beta_k - \hat{\beta}_k)/\beta_k)}{M}\right]^{0.5} \tag{4}$$

Correlation of the experimental data was made without defining a value to β_∞ and also using the optimal value for this parameter. In the latter case, the optimal β_∞ was found by trial and error with $\Delta\beta$ as optimality criterion. Table 3 lists the root-mean-square deviations found with both models NRTL ($\alpha = 0.1$) and UNIQUAC obtained for each temperature defining the β_∞ or not. The correlation defining β_∞ is the best fit of the experimental data.

Table 4 lists the NRTL and UNIQUAC parameters obtained for each temperature when using the optimal value of the β_∞. Figure 1 shows a comparison of experimental tie lines and those calculated with UNIQUAC for each temperature.

3.3. Prediction. The experimental data were compared with those predicted by UNIFAC method.[10] The interaction and structural parameters were taken from literature.[11] The quality of prediction is evaluated with the residual F

Table 4. LLE Data Correlation. Binary Interaction Parameters for NRTL ($\alpha = 0.1$) and UNIQUAC Equations for Each Temperature, Specifying the Optimal Value of the Solute Distribution Ratio at Infinite Dilution β_∞

		NRTL		UNIQUAC	
temp (K)		a_{ij}/J·mol^{-1}	a_{ji}/J·mol^{-1}	b_{ij}/J·mol^{-1}	b_{ji}/J·mol^{-1}
298.15	1−2	−14228.58	9191.13	−5001.37	3122.15
	1−3	−95.64	28158.69	5078.52	2303.98
	2−3	−12436.08	9558.61	−2122.81	−2772.39
308.15	1−2	14339.16	−7546.37	−9336.62	6516.68
	1−3	2655.24	27644.05	13161.89	3511.00
	2−3	−5399.44	9489.60	−2510.66	−5985.58
318.15	1−2	−29172.99	12855.94	−6970.29	1345.95
	1−3	6410.09	24476.42	9890.33	9361.56
	2−3	14203.64	2461.78	−3052.82	−4007.02

(Equation 3), this value was 11.9% at 298.15 K, 13.8% at 308.15 K, and 13.5% at 318.15 K. Figure 2 shows a comparison of the predicted and the experimental tie lines for each temperature.

4. Conclusions

Liquid−liquid equilibrium of the DIPE + ethanol + water system was measured at different temperatures. The LLE data were correlated using the NRTL and UNIQUAC activity models, without defining a value to the solute distribution ratio at infinite dilution and also using the optimal value to this parameter. As is frequently found in open literature, the correlation using the optimal β_∞ normally has a slightly larger value of the residual F than the correlation without defining β_∞, but the value of the residual $\Delta\beta$ is much smaller. Thus, this method of correlation was selected in this work.

In this way, from ternary data optimal binary parameters for the UNIQUAC and NRTL equations were found. The correlation with the UNIQUAC equation gives the best results, but also the NRTL equation with a value of the nonrandomness parameter optimized in $\alpha = 0.1$ fits the experimental data satisfactorily, the results being even better for 318.15 K temperature.

The LLE data predicted with the UNIFAC method gives slope tie lines opposite to those of the experimental data and the residual F value is too great, this method is undesirable for the LLE prediction of the DIPE + ethanol + water system.

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